

INFLUENCE OF ULTRASONIC CAVITATION TREATMENT ON FRAGMENTATION AND DE-AGGLOMERATION OF PRIMARY INTERMETALLICS AND OXIDES FORMED IN Al ALLOYS

by

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Influence of ultrasonic cavitation treatment on
fragmentation and de-agglomeration of primary
intermetallics and oxides formed in Al alloys

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*Dedicated to my grandmother
Ms. Tulu Rani Das
for always being an inspiration*

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Abstract

The utilisation of ultrasound in material processing, whether it is machining, welding, cleaning, mixing, disintegration, degassing, atomisation, emulsification, crystallisation and/or for accelerating diffusion in solid and liquid phases, has always mesmerised the scientific community with the remarkable effects that it produces during its application in fields ranging from automotive, aerospace, military, construction to even medical (therapeutics) and food sector. One such prevalent and industrially accepted processing technique is ultrasonic melt treatment (UST) which aids in improving the mechanical properties of metals and alloys by influencing their final microstructure. UST effectively promotes grain refinement by utilising the phenomena of acoustic cavitation that leads to fragmentation/de-agglomeration of solid phases, such as primary intermetallics and oxides, formed during solidification of as-cast alloys. Knowledge of the governing mechanisms associated with fragmentation and de-agglomeration of solid phases is prerequisite and instrumental for upscaling of UST in order to realise its substantial economical and sustainability benefits.

At present, there is a dearth of fundamental understanding of the process mechanism by which these solid phases found typically within the metallic melts fragment/de-agglomerate and gets refined during UST. Moreover, the output and yield of UST is primarily dependent on the optimisation of operating parameters such as sonication frequency, treatment time, amplitude and processing conditions i.e. temperature, residence time within plus the extent of the cavitation zone. Huge efforts have been made to systematically comprehend and characterise in real-time the in-situ cavitation dynamics occurring during ultrasonic processing of liquid metals through the use of advanced synchrotron X-ray facilities. Nonetheless, the use of such approach is frequently afflicted by complications associated with the opacity and handling of liquid metals, spatial and temporal resolution limitations and narrow field of view available for capturing and recording the multi-phase interactions during a continuously growing solid phase during imaging. To overcome these non-negligible restraints, use of transparent liquid systems becomes necessary to decode the fragmentation and de-agglomeration process of intermetallics and oxides. Over the years, water has been recognised as a suitable analogue to mimic molten aluminium showing similar acoustic cavitation behaviour under ultrasonic excitation.

This dissertation presents a novel approach that aims to investigate the interaction dynamics of cavitating bubbles with the fixed and floating Al_3Zr primary intermetallics and oxides such as

silica and magnesia in water medium at room temperature conditions. In this work, we have attempted to elucidate in detail the mechanisms of ultrasound-induced fragmentation and de-agglomeration of primary and secondary solid phases. Prior to conducting such studies, depth sensing indentation experiments were performed to measure and evaluate the mechanical properties of such intermetallic crystals that served as a tool for understanding the complexity of the overall process. Results disclosed that sono-fragmentation of intermetallics is primarily governed by the propagating shock waves emanating from inertial cavitation cloud collapses. Intermetallic fracture then occurs via low cycle fatigue loading, followed by catastrophic brittle failure. In contrast, de-agglomeration of oxide clusters is primarily governed by the sono-capillary effect and facilitated by the cavitation bubble activity and induced-acoustic streaming leading to its breakage and erosion. Having recognised the crucial role of shock waves in fragmentation of intermetallic crystals, we also explored the detailed characteristic of acoustic emissions produced during ultrasonic cavitation in water and liquid aluminium by using state-of-the-art advanced cavitation sensors calibrated from kHz to MHz broadband frequency range. The results obtained from these fundamental work motivated us to carry out pilot-scale experiments to assess the acoustic cavitation response in a continuous melt flow system by implementing UST in a conventional direct-chill casting setup. The casting trials demonstrated the positive impact of cavitation melt treatment on the grain refinement characteristics of end cast billet/ingots. The promising results from both fundamental and real-scale experiments are currently being utilised to develop numerical simulation tools to improve the output and yield of UST.

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“Let us be grateful to people who make us happy; they are the charming gardeners who make our souls blossom.” – Marcel Proust

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- **A. Priyadarshi**, M. Khavari, T. Subroto, P. Prentice, K. Pericleous, D. Eskin, J. Durodola, I. Tzanakis, *Mechanisms of ultrasonic de-agglomeration of oxides through in-situ high-speed observations and acoustic measurements*, Ultrason. Sonochem. 79 (2021) 105792.
- M. Khavari, **A. Priyadarshi**, A. Hurrell, K. Pericleous, D. Eskin, I. Tzanakis, *Characterization of shock waves in power ultrasound*, J. Fluid Mech. 915 (2021) R3.
- M. Khavari, **A. Priyadarshi**, T. Subroto, C. Beckwith, K. Pericleous, D.G. Eskin, I. Tzanakis, *Scale up design study on process vessel dimensions for ultrasonic processing of water and liquid aluminium*, Ultrason. Sonochem. 76 (2021) 105647.

Conference proceedings

- **A. Priyadarshi**, T. Subroto, M. Conte, K. Pericleous, D. Eskin, P. Prentice, I. Tzanakis, *Nanoindentation and Cavitation-Induced Fragmentation Study of Primary Al_3Zr Intermetallics Formed in Al Alloys*, in: Light Met. 2020, Springer, 2020: pp. 168-173.
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Papers under review

- **A. Priyadarshi**, T. Subroto, J. Nohava, S. Pavel, M. Conte, K. Pericleous, D. Eskin, I. Tzanakis, *Investigation of mechanical properties of Al₃Zr intermetallics at room and elevated temperatures using nanoindentation*, under review in Intermetallics.
- M. Khavari, **A. Priyadarshi**, J. Morton, K. Porfyrakis, K. Pericleous, D. Eskin, P. Prentice, I. Tzanakis, *Cavitation-Induced Shock Wave Behaviour in Different Liquids*, under review in Ultrasonics Sonochemistry.

Declaration

I hereby declare that this thesis titled “**Influence of ultrasonic cavitation treatment on fragmentation and de-agglomeration of primary intermetallics and oxides formed in Al alloys**” has been prepared by me under the direct supervision of Prof. Iakovos Tzanakis, Prof. Dmitry Eskin and Prof. John Durodola as a part of my study for the award of Doctor of Philosophy degree at Oxford Brookes University, Oxford, England. I have not submitted this thesis previously for the award of any degree or diploma at any other institution.

Signature



Date: 11 May 2022

Certificate

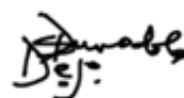
This is to certify that Mr. Abhinav Priyadarshi has done his research under my supervision and complied with all the requirements for the submission of this Doctor of Philosophy thesis to Oxford Brookes University, Oxford, England.



Prof. Iakovos Tzanakis



Prof. Dmitry Eskin



Prof. John Durodola

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List of symbols

P_{abs}	absolute pressure
λ	acoustic wavelength of sound wave
T_a	acoustic period
f	acoustic frequency
P_{∞}	ambient pressure
P_a	acoustic pressure amplitude
I_a	acoustic intensity
A_s	amplitude of ultrasound/sonotrode-tip
S_a	average surface roughness
D_{avg}	average fragment size
R_a	bubble equilibrium size
P_b	bubble pressure
ΔH	change in enthalpy
ΔV	change in specific molar volume
ΔS_v	change in entropy of fusion
C	Constant
S	contact stiffness
A_c	contact area
h_c	contact depth
a	contact radius
θ	crevice included angle
R_{cr}	critical bubble radius
R_c	critical size of nucleus
K_{Ic}	critical stress intensity factor
t_{frag}	crystal fragmentation time
ρ	density of the liquid medium
d_p	diameter of solute particle
d_s	diameter of sonotrode
D	diffusion coefficient of solute
W	distributed load

E_{eff}	effective elastic modulus
E_i	elastic modulus of indenter
E	elastic modulus of specimen
W_e	elastic indentation work
α_c	empirical constant of indenter
c_1	empirical constant
c_2	empirical constant
h_f	final indentation depth
Q	first moment of area
k	fitting constant
m_k	fitting constant
σ	fracture stress
K_c	fracture toughness
f_N	fragment number density
δ	free end deflection
g	function
f_0	fundamental/driving frequency
γ	gas specific heat ratio
χ	Gibbs-Thomson coefficient
D_o	grain size
Q	grain growth restriction factor
v	growth rate of S/L interface
H	hardness
H_v	height of vessel/container/tank/cuvette
P_h	hydrostatic pressure
β	indenter constant
P_d	indenter load
h	indenter displacement
φ	indenter half angle
n	integer
m	integer
α	interfacial contact angle
$\sigma_{S/L}$	interfacial surface tension

L_f	latent heat of fusion
L	length of vessel/container/tank/cuvette
L_C	length of crystal
c	length of indentation crack
V_L	liquid molecular volume
v_i	liquid jet velocity
y	longitudinal direction from the horn tip
ε	material dependent constant
$P_{\max}$	maximum acoustic/shock pressure
$\delta_{\max}$	maximum deflection
h_m	maximum indentation depth
P_m	maximum indentation load
$\tau_{\max}$	maximum shear stress
T_m	melting point
T_m^∞	melting temperature of planer interface
I	moment of inertia
f_m	natural frequency of oscillating bubble
ΔT	nucleation undercooling
N	number of acoustic cycles
N_i	number of indentation cycles
N_v	particle number density
f_{peak}	peak frequency
T_m^r	phase transition melting temperature
W_p	plastic indentation work
ν	Poisson's ratio of specimen
ν_i	Poisson's ratio of indenter
a_c	Pre-existing crack length
P_v	pressure at constant volume
r	radial distance
r_s	radius of circular horn
r_p	radius of curvature of concave particle
R_o	resonance size of bubble
P_{RMS}	root mean square pressure

h_s	sink-in depth
P_{sw}	shock wave pressure amplitude
u_{sw}	shock wave velocity
C_p	specific heat at constant pressure
C_v	specific heat at constant volume
c_s	speed of sound
σ_s	surface tension of liquid
T	temperature of melt
t	time
T_c	thickness of crystal
W_t	total indentation work
X	transverse direction from the horn tip
F	transverse shear force
v_s	velocity of reciprocating horn
V	voltage
P_w	water-hammer pressure
W_c	width of crystal
W_v	width of vessel/container/tank/cuvette

List of abbreviations

UST	Ultrasonic Melt Treatment
DSI	Depth Sensing Indentation
DC	Direct Chill
MMC	Metal Matrix Composite
O&P	Oliver and Pharr
D&N	Doerner and Nix
LEM	Lawn Evans Marshall
DIW	De-ionised Water
VDC	Voltage DC
FFT	Fast Fourier Transform
MCT	Multicycle Indentation Testing
IMC	Intermetallic Compounds
RT	Room Temperature
HT	High Temperature
CSM	Continuous Stiffness Measurement
ISE	Indentation Size Effect
FPS	Frames per Second
USP	Ultrasonic Processing
LIB	Laser Induced Bubble
FOH	Fibre Optic Hydrophone
NH	Needle Hydrophone
PIV	Particle Image Velocimetry
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
DAQ	Data Acquisition
μ B	Microbubble
AW	Acoustic Wave
SW	Shock Wave
USE	Ultrasonic Capillary Effect
BCAST	Brunel Centre for Advanced Solidification Technology

BRU	Brunel University London
GLA	University of Glasgow
GRE	University of Greenwich
PA	Precision Acoustics

Chapter 1

Introduction

1.1 Research background

In the present era of manufacturing metallic materials, we cannot stay away from the fact that design predicates the performance of any product or component. However, designing relies heavily on the available material databases and failure criteria and thus the product's performance can only be revised through alloying or process development. One of the areas where the minds of whole metallurgical fraternity has been focussed for decades is towards the development of either new materials or enhancing the properties of existing materials by utilising different advanced processing techniques. The choice of the technique is however a subject of ongoing debate on use of green energy sources, which requires the process to be economically viable and environment friendly with minimum energy consumption. Motivated by the present demand of circular economy, the scientists and engineers are opting for processes that include recovery and refining of secondary metals (recycle and reuse) instead of using primary metals, which currently poses a biggest challenge for the metal industry. Improvement in mechanical properties of metals and alloys is another big challenge and is of paramount importance for a range of engineering applications including aerospace, automotive, military and construction.

The structural framework of any engineering material is indirectly correlated to the configuration of its internal components. The genesis of metal's internal structural on an atomic level is recognised through the periodic arrangements of atoms relative to one another that gives rise to crystal/lattice structures. Metals and alloys exhibit different crystal structures depending on the thermomechanical conditions and composition, but in general the lattices are mostly arranged in four ways i.e., face-centred cubic (fcc), body-centred cubic (bcc), hexagonal closed pack (hcp) and tetragonal. Zooming out from an atomic level, the subsequent structure is realised on a microscopic level. In this case, the atomic configurations of many such lattices act as key components of the microstructure, which ultimately determines the material properties. The analysis of the microstructure reveals the important constituents that control the material properties to a large extent and are described through the presence of grains, primary and secondary phases, their shapes and size distributions. Apart from this,

inconsistencies in the form of point defects such as voids and pores, dislocations, grain boundaries and interfaces are also the important microstructural characteristics that often govern the resultant properties of the material.

Improvement in mechanical strength of a metallic material is primarily influenced by the microstructural parameters. In general, there are four practical ways to strengthen a metallic material during and after casting, these include: (a) strain or work hardening (for example, shot peening, forging, rolling, drawing etc.), (b) grain refinement (for example, special additions, rapid solidification, severe plastic deformation, vibration etc.), (c) solid solution strengthening (for example carburising, nitriding etc.), and (d) strengthening by particle precipitation (for example, ageing or dispersion hardening). The common strengthening method during casting is the grain refinement process, which not only improves the microstructure but also increases the hardness, toughness of the metal/alloys and reduces defects and porosity in the material. While these techniques independently play their role in strengthening of metallic materials, during casting process, the grain size reduction is the main mechanism that work through heterogeneous nucleation of either indigenous (oxides, intermetallics) or specially added and activated (wetting) substrates/particles (borides, carbides in aluminium). The use of inoculants, for example TiB_2 in case of aluminium (Al) alloys has proven to be an excellent grain refiner for structural refinement, although they have a very low mixing efficiency (about 1-2%) that results in agglomeration of particles in the structure during solidification. The addition of this refiner to Zr containing Al alloys used in aerospace such as 2xxx and 7xxx series, however significantly decreases the grain refinement efficiency through a phenomenon commonly referred as 'Zr poisoning'. Moreover, the use of such grain refiners in the alloy production process is expensive and their production is environmentally unfriendly. Researchers are, therefore, coming up with alternative methods of grain refinement during casting that involve the application of external forces in the form of shearing/vibration/stirring without the use of expensive grain refiners. Some of these techniques can be broadly classified into mechanical shearing, ultrasonic cavitation and electromagnetic stirring. The refinement achieved using such techniques relies on the processing of secondary phase particles/dendrites within the melt.

Secondary phase particles can be further classified as (a) precipitates (formed through solution/age hardening during thermomechanical processing (TMP)), (b) inclusions (impurities typically of size greater than $5\text{ }\mu\text{m}$ formed during the manufacturing process, such as oxides from the slag), (c) dispersoids (thermodynamically stable phase particles with sizes in the range of $0.1\text{--}1\text{ }\mu\text{m}$ that precipitate during TMP and does not dissolve during tempering/solution heat

treatment), and (d) constituent particles and inclusions. The present work involves the use of certain constituent particles and inclusions. Al_3Zr is one of the most common primary phases (also forms dispersoids upon precipitation from the solid solution) in 2xxx and 7xxx Al alloys. The size of the primary intermetallic phases can be refined and controlled during casting of metals/alloys by applying aforementioned different external treatment fields that can break the formed intermetallic crystals/dendrites during solidification and reduce the particle size to achieve effective grain refinement of alloys.

One such external field grain refinement technique is the use of ultrasound to treat liquid metals during their solidification, widely known as ultrasonic melt treatment (UST). UST (as will be discussed in the next chapter in detail) has shown great potential to not only reduce the amount of expensive grain refiners but also significantly improve the properties of metallic materials and structural integrity of as-cast Al alloys [1,2] by promoting particle dispersion strengthening in the alloy melt during casting. The introduction of ultrasonic waves within the molten metal result in formation and growth of bubbles (referred to as acoustic cavitation) that mechanically interact with the secondary solid particles causing multiplication of dispersoids/inclusions through breakage (fragmentation), de-agglomeration and dispersion of grain refining particles or formed intermetallics/oxide clusters. This in turn expedites heterogeneous grain nucleation and refinement (as cavitation-induced homogeneous nucleation is considered irrelevant to real solidification).

The core focus of this work deals with high-speed optical imaging of cavitation activity and its interaction with intermetallic crystals and oxide aggregates during UST. Therefore, an in-depth understanding of the fragmentation and de-agglomeration process can be further utilised to maximise the UST effect, where the emerging data from these studies can be fed into numerical models in order to upscale and optimise the UST process.

The findings presented in this thesis serve as a stepping stone towards understanding the crystal refinement process under the influence of ultrasound at a very fundamental level that opens a new direction of research for scientists and engineers to unravel and conquer. The national/international significance of such research is justified and reflected by keeping in mind the worldwide demand of metals in industries.

1.2 Global significance

The majority of the aforementioned strengthening methods of metallic materials, except the work/strain and precipitation/dispersion hardening technique, derives from the melting and casting processes using different alloying systems representing the most common industrial practice next to post processing of as-cast materials. Moreover, almost 97% of all the metallic components that are manufactured worldwide conforms to development that is mediated by involving at least a metal melting and solidification stage, which is of prime importance in realising the microstructural features emerging from their casting. If we see the latest trends, the worldwide market for metal casting in 2020 was valued close to \$315020 million and is further expected to reach \$323820 by the end of 2026 resulting in compound annual growth rate (CAGR) of almost 0.4% [3]. Although the UK was traditionally the frontrunner in metallurgical research, the Materials International Review consortium [4] in 2008 underlined the impending decline in this area. Consequently, the Engineering Physical Sciences and Research Council (EPSRC) took the initiative of forming Manufacturing Centres and Hubs, such as LiME based in Brunel University London, which focussed on the development of material science and processing activities in light metals.

The most important structural metal material next to iron is aluminium, which is one of the most valuable industrial raw material owing to its durability, lightweight, and versatility and is the proposed material in this research. Presently, the key leading players within the aluminium industry at a global scale are Aluminium Corporation of China (CHALCO) followed by Russia's UC RUSAL, the UK-Australian Rio Tinto and US based Alcoa Corporation. The worldwide market forecast for aluminium casting has been anticipated to rise from the present value of \$70.4 billion (2021) up to \$100.5 billion by 2026 with CAGR of almost 7.4% [5]. This expected market capitalisation in Al casting can be ascribed mainly to the growing demand of aluminium in industrial infrastructure, construction and transportation sector. However, the ongoing Ukraine-Russia crisis may have profound effect on Al production on a global scale in the long term due to closure of RUSAL's alumina refineries in Siberia and the imposed international sanctions.

This PhD project that is also adjunct to the EPSRC project UltraMelt2 (2018-2021) aims to build upon previous research work and expertise in experimental studies inherited by the earlier research within the EPSRC UltraMelt (2013-2016) and UltraCast (2015-2017) projects.

1.3 Project goals

The goal of this project is driven by the technological need to optimise and upscale the UST that requires effective distribution of nucleating substrate; but it is nevertheless fundamental, aimed at the development of understanding the underlying governing mechanisms involving breakage and dispersion of intermetallics and inclusion (oxides) during ultrasonic treatment of liquid aluminium using advanced in-situ characterisation techniques. This project also sheds some light to reflect upon the following important questions:

1. What are the governing mechanisms of fragmentation and de-agglomeration that will feed numerical models and define the important parameters for UST optimisation i.e., residence/processing time of the particles within the cavitation zone
2. What is the optimum vessel dimension used for treating liquid Al that leads to the condition of resonance using a single ultrasound source?

The insightful information and new knowledge gained as well as implementation of the developed experimental techniques can further become available for application in other research and technology fields, namely ultrasonic processing of powders (additive manufacturing, pharmaceuticals, nanotechnology), ultrasound-assisted crystallization (pharmaceuticals), processing of mixtures and suspensions (food, paint, fuel, coating). The findings of this research are disseminated and exploited to create an academic impact and scope for generating new research proposals that addresses such needs.

1.4 Project objectives

To determine the fundamental mechanism of fragmentation and de-agglomeration of solid phases and optimum parameters related to residence time (particle processing period) and resonance length of the treatment vessel for continuous melt treatment relevant to industrial applications, this project endeavours to develop a quantified experimental description of the ultrasonic melt processing, with a particular focus on the interaction between cavitating bubble structures and solid phases typically present in the melt. The objectives of this research project are as follows (in order):

1. Obtain unique nano-hardness data and mechanical properties (elastic modulus, fracture toughness) for extracted primary Al_3Zr intermetallic crystals using state-of-the-art high temperature nanoindentation technique in a range of temperatures up to 700°C.

2. Reveal and quantify through in situ acoustic pressure measurements, and high-speed imaging experiments, the mechanism of solid particle fragmentation.
3. Acoustically characterise the cavitation-induced shock response in terms of associated frequency and pressure fields generated by ultrasound.
4. Determine spatial and temporal distribution mapping of intermetallic fragmentation and their erosion characteristics when subjected to ultrasonic cavitation.
5. Reveal the ultrasonic de-agglomeration and dispersion mechanism and quantify the process based on acoustic pressure measurements.
6. Perform acoustic characterisation of water and Al to quantify the importance of container dimension (resonance lengths) during ultrasonic treatment of liquids and to measure and record the acoustic pressure profiles inside the cavitation induced environment of liquid Al and de-ionised water (used as analogue to Al).
7. Conduct up scaling UST studies through pilot-scale experiments in real case industrial system scenario involving DC casting of Al alloy melts by optimising melt flow management using strategically positioned baffles in the launder.

1.5 Novel contribution to knowledge

This research addresses and underpins some of the most important and novel contribution made in relation to the above objectives. These includes:

1. Determination of the intermetallic properties at elevated temperatures for the first time.
2. Elucidation of the cavitation-induced fragmentation mechanism of fixed and floating intermetallics under the influence of single (laser induced) bubble collapse and bubble cloud collapse (ultrasound) for the first time.
3. Elucidation of the cavitation-induced de-agglomeration mechanism of metal oxides for the first time.
4. Investigation on the effect of the resonance length of treatment vessel that plays an important role for the amplification of the bulk pressure field of the ultrasonically treated liquid metal environment.

The determination of resonance length of the treatment vessel will further help us to develop suitable and efficient launder system for direct-chill (DC) or continuous casting (CC) processes with strategically placed baffles at a distance that induce the maximum ultrasonic treatment

effect within the melt through achieved resonance conditions, and more efficiently promoting structure refinement of the end-cast product. The data obtained from the evaluation of mechanical properties of intermetallics and governing fragmentation/de-agglomeration mechanism will be used to develop advance numerical model and simulation tools and/or feed the existing models that could closely predict the grain refinement effect in various metal alloy systems subjected to UST. Potential success will subsequently allow the aluminium industry to adopt this novel design for treating large melt volumes through continuous UST in the melt flow and producing high strength alloys in a green environment.

1.6 Thesis outline

A great care has been taken in writing this dissertation by developing a coherent flow of topics, which are inter-related, and follow a logical order that can be easily understood by the scientific readers in a best possible way. This dissertation primarily explores the influence of ultrasound and associated physical effects in the form of acoustic cavitation and bubble dynamics on the fragmentation and de-agglomeration mechanism of solid particles.

The next chapter (Chapter 2) of the thesis uncovers the entire literature review on topics, which will help the readers to understand the important concepts and experimental results and discussion outlined in subsequent chapters. Chapter 2 starts with some basic overview on the grain refinement of Al alloys and significance of cast structure in influencing the mechanical properties. This chapter also sheds some light on the fundamentals of ultrasonic treatment along with its brief historical background with special focus on acoustic pressure, streaming, factors affecting cavitation activity and acoustic emission spectrum. To gain insight into the structural refinement capabilities of UST, this chapter discusses and takes into account the principal mechanisms, through which the grain refinement in light alloy melts transpires. Three vital mechanisms, i.e. cavitation aided nucleation, activation of substrate, and cavitation assisted fragmentation, have also been delineated. Finally, this chapter ends with brief discussion on intermetallic mechanical properties and the vital role it plays in governing the optimal UST conditions followed by some basics on depth sensing indentation (DSI) technique using which these properties such as hardness, elastic modulus and fracture toughness can be determined.

Following Chapters 3-8 are fully experimental and the content is structured in such a way that encompasses all-important segments of this fundamental work. All these chapters includes a

short introduction on the topic, experimental setup and methodology, results and discussion and conclusion. Chapter 3 starts with the intermetallic extraction process and then focuses on determining the mechanical properties, i.e. elastic modulus, hardness, fracture toughness and fatigue measurements of single and polycrystalline primary Al_3Zr intermetallics chemically extracted from the Al alloy matrix, measured using DSI from room temperature up to temperatures of molten Al alloys (700°C). Chapter 4 focuses on determination of the fragmentation mechanism of a fixed primary intermetallic crystal under controlled cavitation conditions (single and cloud of bubbles) in water at room temperature conditions. The sono-fragmentation process has been captured in-situ using advanced high-speed camera with sequences recorded at frame rates of up to 1 Mfps (million frames per second) and the fragmentation response been acoustically characterised and analysed using analytical calculations. The results confirm that cavitation-induced shock waves are predominantly responsible for fragmentation of intermetallics. The next Chapter 5 specifically talks about characterisation of the shock wave fronts emanating from ultrasonic source in terms of acoustic pressure field mapping and frequency spectrum that is responsible for fragmentation of intermetallics. Spatial maps obtained by collating individual shock wave pressures highlight the effect of pressure shielding with increasing input power, attributed to a cloud of bubbles surrounding the probe. Chapter 6 provides more statistical information on fixed intermetallic breakage by determining the spatial and temporal mapping of the fragmentation process. The work also includes determination of fracture and erosion mechanism for free-floating crystals under the action of ultrasonic cavitation. Chapter 7 is dedicated to the de-agglomeration and dispersion mechanism of oxide aggregates (silica and magnesia) when subjected to ultrasonic cavitation in water at ambient temperature conditions. The cavitation-induced de-agglomeration sequence has been captured and acoustically characterised using high-speed camera synchronised to cavitation sensors.

Chapter 8 deals with the scale-up study involving quantification of required container dimensions leading to resonance, which plays a crucial role in amplifying acoustic pressure amplitude during ultrasonic cavitation in liquid Al and water (used as analogue to Al) and professes its importance in determining the efficiency and scaling up of UST. Finally, the last Chapter 9 summarises the important findings from the aforementioned studies followed by the potential future work identified in Chapters 3-8.

In addition to resonance length determination, another important factor that influences the microstructure to a great extent is the estimation of residence time of the treated melt within

the cavitation zone during UST in a DC casting launder assisted with strategically placed baffles that results in a more uniform distribution of refining particles. This work is however beyond the realm of this PhD project but has been added as a separate section in the Appendix A3 of this thesis to reflect upon the path of moving from fundamental studies conducted in relation to understanding of grain refinement mechanisms to its application in actual melt processing environment. This section addresses this aspect using a multiphysics modelling and pilot-scale testing for determining effects of UST and optimisation of its efficiency through proper flow management. The positive effects of partitions with and without UST on the grain refinement of an AA6XXX aluminium alloy containing Zr is also demonstrated.

1.7 Collaborative research support

Since the work presented in this thesis is adjunct to the EPSRC UltraMelt2 project as mentioned earlier in Section 1.2, some parts of the current study derive from the research work that has been done in collaboration with the project partners involving Brunel University London (BRU), University of Glasgow (GLA) and University of Greenwich (GRE). Therefore, it is important to delineate for the readers beforehand the specific contributions made by the author of this thesis and other team members who helped in shaping and concluding the overall significance of this research based on project goals (Section 1.3), objectives (Section 1.4) and novel contribution (Section 1.5). The following are the segments of the experimental investigation in Chapters 3-8 that has been jointly performed as group work:

1. Intermetallic crystal extraction from the Al alloy matrix and polycrystalline intermetallic specimen preparation described in Chapter 3 is a joint effort conducted in collaboration with the group of Prof. Dmitry G Eskin at Brunel Centre for Advanced Solidification Technology (BCAST) in Brunel University London. BRU team assisted with preparation, cutting and chemical etching of the alloy. The author of this thesis contributed to this segment by preparing single crystal intermetallic specimens from the extracted Al_3Zr and analysing their microstructure.
2. Laser induced bubble and shock wave imaging experimental setup described in Chapter 4 and 5 is a combined effort undertaken in collaboration with the group of Dr. Paul Prentice at CavLab in GLA. The GLA team assisted with laser operation, optical alignment, and electronic connections. The author of this thesis contributed by

- identifying and adjusting the camera settings for high-speed filming, preparing and mounting of the crystal within the experimental setup, and capturing the measurements.
3. Deconvolution code of voltage data and image processing for wavelength estimation of shock wave described in Chapter 5 are done in collaboration with Research Fellow Dr. Mohammad Khavari of OBU and Precision Acoustics (PA). Dr. Khavari assisted with preparation of MATLAB code used for FFT of the raw data and image processing algorithm for wavelength estimation. The author of this thesis contributed to this part of the study by designing the experimental methodology, performing acoustic measurements, analysing and discussing the obtained results.
 4. Ultrasonic treatment of liquid Al for determining vessel's resonance length and microstructure experiments shown in Chapter 8 has been carried out in collaboration with the group of Prof. Dmitry G Eskin at BRU (BCAST). The BRU team supported with alloy melting and treatment, microstructure sample preparation and analysis. The author of this thesis contributed to these experiments by assisting with the identifying resources, designing the experimental methodology for acoustic measurements, analysing and discussing the recorded data.
 5. Pilot scale DC casting upscaling DC experiments, numerical modelling of the acoustic pressure field and residence time estimation presented in Appendix A3 is a collaborative work between BRU, GRE and Constellium.

Chapter 2

Literature review

2.1 Grain refinement of aluminium cast alloys

Aluminium (Al) being the most abundant metal takes up almost 8% of Earth's crust. The unique cocktail of properties exhibited by Al and its alloys makes it highly versatile, economically viable, and most attractive metallic material for use in multipurpose applications. It is used in wide range of engineering sectors such as automotive, aerospace, military, marine, packaging, construction owing to excellent electrical conductivity, corrosion resistance, non-magnetic properties, high strength to weight ratio and ductile characteristics. Since pure Al is relatively soft, it is mostly produced in an alloy form by combining materials such as copper (Cu), manganese (Mn), silicon (Si), magnesium (Mg), zinc (Zn), and other elements like titanium (Ti), zirconium (Zr), iron (Fe) etc., which results in improvement of their mechanical properties. Aluminium alloys are conveniently divided into two main categories: wrought and casting (foundary) alloys. Most of the aluminium alloys, whether casting or wrought alloys, are heat treatable depending on their phase solubilities, which include solution heat treatment, quenching and precipitation/age hardening. Some wrought alloy compositions alternatively bank on work hardening (usually a combination of mechanical reduction and annealing process). However, not all alloys are age hardenable and are, therefore, utilised only in as-cast, annealed or worked conditions. Producing Al alloys with enhanced physical properties using processes other than post-processing of wrought alloys is through melting and solidification of Al cast alloys, which is the subject of interest in this dissertation.

Generally, Al casting alloys have same alloying elements to those of wrought Al alloys, strengthened through similar mechanism (except strain hardening) and are therefore classified into heat treatable and non-heat treatable categories. The key difference between them comes from the fact that casting alloys often contain large percentages of alloying elements, far more than those found in wrought alloys. Silicon, for example, accounts for the major alloying element that is literally responsible for process performance of casting alloys. Casting Al alloys offer distinct advantages that may or may not be provided completely by wrought alloys. Casting alloys offer design and shape flexibility during casting. Casting alloys, however, have

lower strength than wrought alloys because of the casting defects and greater heterogeneity of the structure that are not easily eradicable.

For most of the manufacturers, innovative designers and industrial users, high quality and high performing materials are extremely desirable. Castability is one of the important properties, which indicates that the solidifying metal maintains high fluidity in molten state, has reduced shrinkage porosity and is not susceptible to hot cracking. Obtaining a high quality (free of defects and uniform in structure) billet or ingot assures the high quality of wrought products from it (plates, sheets, extrusions, forgings). With the increase in demand for superior mechanical properties of Al alloys, several techniques were employed to attain billet and ingots of high quality [6]. Among such techniques, filtration, degassing and grain refinement of Al alloys have been considered as key means for achieving remarkable effects on increasing Al products' mechanical performance. As much as filtration and degassing are essential in ensuring high-quality cast alloy products by removing solid and gaseous impurities, respectively, grain refinement is also vital for enhancing the mechanical properties of the Al alloys during and after casting process. To simultaneously improve the quality of casting (defect free) and increase the strength and plasticity of the metallic product, grain structure refinement becomes a preferable means of material processing.

Grain refinement upon casting leads to a more uniform structure, finer constituent particles, reduced porosity, improved ductility and reduced residual stresses. When compared with other strengthening techniques such as work hardening and precipitation hardening, grain refinement stand out as it can simultaneously reduce the tendency of forming columnar grains (promoting equiaxed structure) inducing strengthening and toughening of the material while suppressing the defects arising from casting i.e. porosity and segregation. For example, degradation of mechanical properties in plate-like deformed products has been found to be related to the as-cast grain structure that has not been adequately and uniformly refined [7] resulting in lower formability, elongation to fracture and yield strength of the alloy [8]. In addition, a coarse grain structure might lead to formation of various type of surface defects in extruded or rolled alloys [9]. Additionally, hot cracking may develop in the centre of round billets and sometimes in the shell zone of flat ingots if the grain structure is not fine and equiaxed [10]. Therefore, an equiaxed grain structure can allow one to achieve increased casting speed during direct-chill casting thereby diminishing the occurrence of hot crack to form. Grain refinement also lead to various other benefits that include homogenous distribution of the constituent phases, inducing microporosity at a fine scale, improved feeding for eliminating shrinkage porosity, increased

fatigue life [11]. Thus, majority of aluminium alloys with better mechanical properties are presently grain refined [12].

Grain refinement is achieved during casting process. The methods of achieving grain-refined structure can be classified into 3 broader categories, i.e. rapid solidification, vibration and stirring, and adding a grain refiner/inoculant during solidification. Each of these approaches has its own benefits and limitations along with suitable conditions of their usage. Of all, inoculation is the most commonly practised approach of grain refinement in the aluminium industry. However, the popularity of this method also brings various undesirable side effects in the form of particle agglomeration, formation of local defects and impurities. Also, there are still some open-ended questions in relation to the establishment of key variables (nucleation potency of inoculants, particle distribution and their number density, and growth rate/restrictions) that limit the fundamental comprehension of these techniques [13]. Thus, external field grain refinement methods that are free of such limitations, which inoculation cultivates, has attracted lot of research interest since past few decades. These physically grain refining methods involve introduction of an external energy source into the liquid or semi-solid metals and alloys at a particular frequency and intensity. In literature, such kind of liquid metal processing and casting has been distinguished and termed as dynamic solidification. The present work focusses on the cavitation stimulated grain structure refinement technique falling under the broader umbrella of vibration and stirring.

Vibration and stirring methods applied during casting have been extensively utilised for grain refinement of Al alloys. Under the stirring approach, various techniques were developed such as electromagnetic stirring, bubble mixing and mechanical stirring [14–16]. Vibration approach primarily involves ultrasonic and mechanical oscillations [17,18]. What makes these external force vibration techniques so unique and efficient is that these processes are capable to refine Al alloys even in the absence of inoculants/grain refiners like TiB_2 . The present need of eco-friendly, economical coupled with high performance and efficient melt processing technology has pushed ultrasonic vibration at the forefront of casting and solidification research on grain refinement. The following sections will be shed some light on the fundamentals of ultrasonic melt processing.

2.2 Ultrasonic melt treatment

The idea of treating metals by introducing high frequency (ultrasonic) vibrations in the range of 17-25 kHz into its molten state with the intention of improving the material strength is not something new and has been in use since 1950's. Some of the early most noteworthy reviews on the use of ultrasound in treating solidifying liquid melts has been made by Hiedemann [19], Eskin [20], Flynn [21], Seemann et al. [22], Abramov [23] and Campbell [2]. Sokolov [24] is recognised to be a pioneer when it comes to treating metals with ultrasound. He was the first person known to have applied ultrasonic treatment in solidifying metals like aluminium and zinc using the piezoceramic transducer operating at frequencies in the range of 600-4500 kHz. A plethora of studies on various metals such as copper, tin and a wide range of other foundry alloys and composites were performed under the influence of ultrasonic fields of varying intensities and frequencies in 1930-40's [25–28]. The experimental evidence suggested that application of ultrasound led to substantial refinement in the grain structure of the solidifying metal (alloy) via the phenomenon of ultrasonic or acoustic cavitation. Cavitation is the formation of highly energetic bubbly clouds due to alternating variations in the ultrasonic pressure field (see section 2.2.1) in the bulk liquid from a sonotrode attached to a high frequency ultrasonic transducer (Fig. 2.1). This induced cavitation and associated acoustic streaming (see section 2.2.3) offers a range of beneficial effects in the melt such as degassing, cluster breakup leading to heterogeneous nucleation, particle dispersion, accelerated diffusion, activation and improved wetting of inclusions which ultimately results in enhanced properties of the solidified product in terms of grain refinement and de-agglomeration of reinforcing particles [1,2]. However, understanding the dynamic effects of solidification in liquid metals has been limited in relation to the operating mechanisms that drives the refinement process.

The present-day demand in solidification research is mainly focussed on the advancement of traditional casting technologies such as direct chill (DC), shape or continuous casting into a high standard, energy-efficient, cost-effective and eco-friendly melt processing tool that can be applied to a range of conventional and complex metallic alloy systems. Ultrasound-induced cavitation melt treatment (UST) is one such green alternative means that embraces the efforts of discovering novel methods to produce lightweight and high strength materials in a feasible, inexpensive, pollution-free environment, and can also be potentially integrated with emerging fields like additive manufacturing and production of nanocomposite materials. Ultrasonic treatment in metals such as liquid aluminium has added a significant value to the manufacturing

industry through its environmental-friendly nature of degassing, i.e. without any need of polluting gases such as Cl, F and Ar. This not only eliminates the process of fluxing or gas-assisted degassing but also reduces the demand for expensive grain refinement additives such as Ti and B. Before we delve deep into the ultrasonic processing mechanisms in metallic melts, let us develop some foundation on the phenomena of acoustic cavitation in liquids and associated fundamentals that would be useful in understanding the research work reported in this thesis.

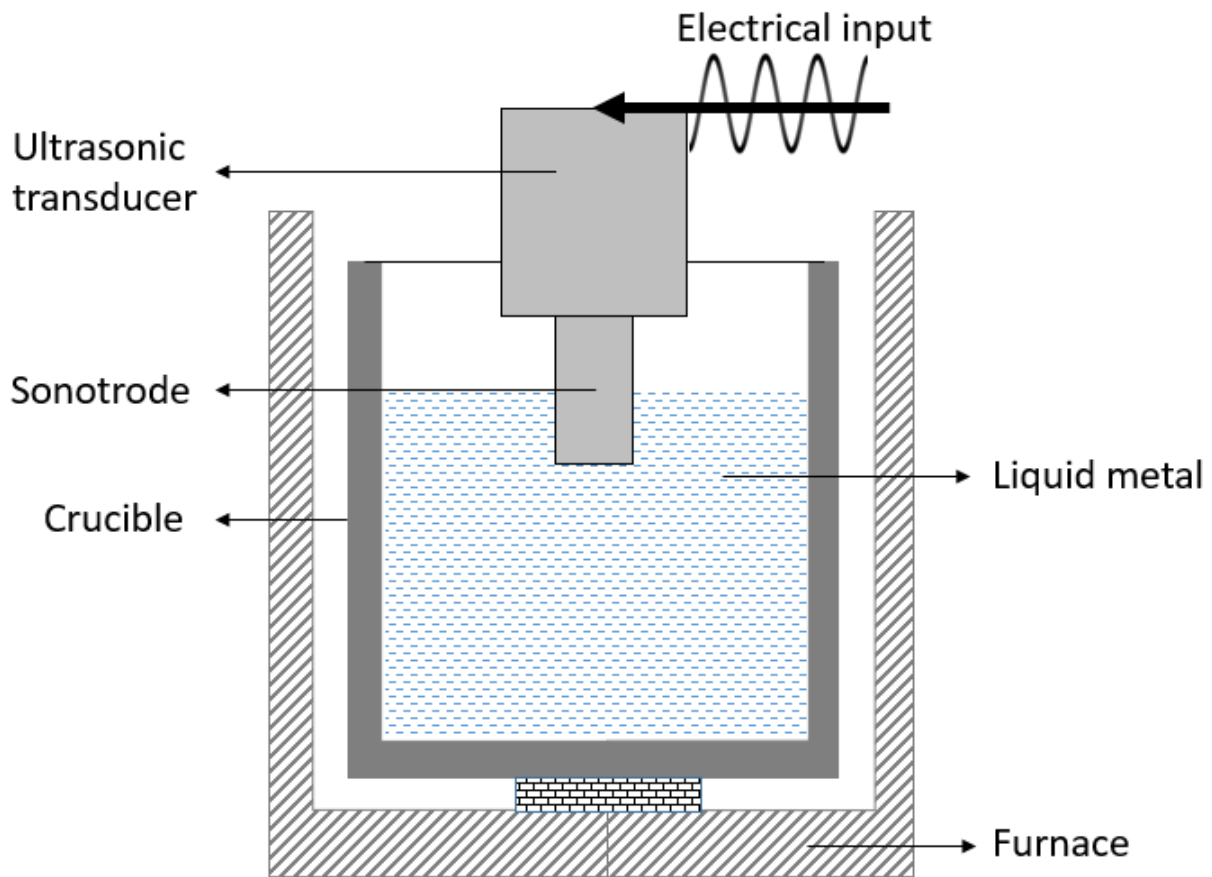


Fig. 2.1 Schematic representation of ultrasound-induced cavitation melt treatment technology. Adapted from [1].

Prior to understanding the ultrasonic (acoustic) cavitation process in detail, it is vital to understand the phenomena of cavitation in general. The word ‘cavitation’ is derived from the Latin word called ‘cavus’, which means ‘hollow’ in English. Cavitation is defined as the phenomena of the formation of vapour/gas cavities (bubbles) as a result of pressure difference within the surrounding fluid. In case of vapour cavitation, the formation of cavities occurs when the pressure in the medium suddenly drops below the vapour pressure of the liquid while in gaseous cavitation (typical for liquid metals) pre-existing bubbles grow under sufficient

pressure drop (typically less than that of required for vapour cavitation). The drop in pressure is caused by pushing the liquid quicker than it can react, leaving behind an area of low pressure often as an air or vapour bubble in case of water. The cavitation process consists of three distinct stages i.e., nucleation, growth and collapse (implosion).

Nucleation or creation of bubble can occur via three different mechanisms [29]; first and most common mechanism is the nucleation at solid surfaces such as container walls especially in the crevices or particles within the liquid with pre-existing air pockets (see Fig. 2.2a). The second mechanism of nucleation is through the presence of gas bubble nuclei within the liquid medium and the third mechanism of nucleation is the fragmentation (proliferation) of pre-existing active cavitation bubbles into multiple daughter bubbles which then act as new nuclei for further formation of bubbles. In vaporous cavitation, nucleation occurs from the tensile stresses that rupture the liquid leading to formation of vapour pockets. Whereas in gaseous cavitation, the nucleation transpires from the presence of both gas bubble nuclei and crevices/cracks on the solid surface (typical in case of liquid aluminium caused by the adsorption of hydrogen (H_2) gas within the melt). Then comes the growth stage, which occurs in two ways; first one is through the bubble coalescence and the other one is the diffusion of gas into bubbles (during rarefaction cycle, the bubbly cell wall becomes thinner while bubbly surface increases in size facilitating entrainment of gas from the bulk liquid) allowing them to grow further from their equilibrium size. The third and final stage is the collapse, which can be catastrophic and violent when the pressure in the nearby region increases producing side effects such as light emission and damage to nearby solid surfaces. The collapse process is based on the instability of the spherical bubble (resonance size or Minnaert bubble size, see more below and in section 8.3.1 of Chapter 8) when it is exposed to inertial forces or when it is in the vicinity of solid walls and/or free surfaces. The nearby surfaces change the pressure field in the surrounding forcing the bubble to lose its initial shape by folding on itself leading to implosion. Folding occurs as the upper section of the bubble (north pole) accelerates downwards towards the bottom wall (south pole) piercing it forming a liquid microjet by pushing part of the gas/vapour content (see Fig. 2.2b). When this liquid jet impacts the other end of the wall, shock waves bands are emitted [30].

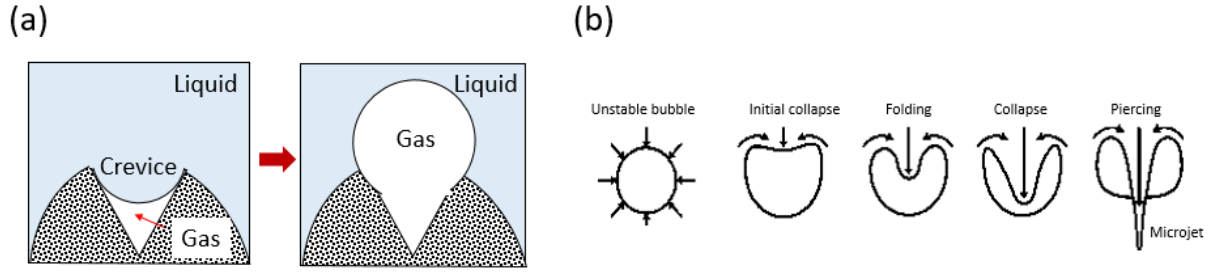


Fig. 2.2 (a) Bubble nucleation mechanism from a crevice. Adapted from [29]. (b) Schematic drawing of a bubble implosion process leading to emission of microjet. Adapted from [31].

Cavitation can be classified in terms of the mode through which it evolves, these are acoustic cavitation, hydrodynamic cavitation, optic/light cavitation and particle cavitation. In this thesis, we shall be focussing strictly on the acoustic cavitation due to its application in liquid metals.

2.2.1 Acoustic cavitation

The irradiation of high-energy acoustic (sound) waves into liquids induces pressure fluctuations resulting in the formation (rarefaction cycle) and subsequent collapse (compression cycle) of cavities or bubbles. The length of one complete pressure oscillation indicates the wavelength (λ) of the propagating wave. The time taken for one complete cycle of the wave is referred to as an acoustic period (T_a). The corresponding frequency (f) of the oscillations occurring per unit time (seconds) is defined as $f = 1/T_a$. The speed of the sound wave is obtained from the wavelength of the pressure oscillations and the frequency of acoustic cycle as $c_s = f \times \lambda$. The intensity of alternating high (compression) and low (rarefaction) instantaneous pressure field that drives the growth and collapse of bubbles depends on the frequency of the propagating wave. A sound wave with oscillating frequencies above the human audible range (>20 kHz) is termed as ultrasonic wave. During the rarefaction phase of the ultrasonic wave, the local pressure becomes negative if the acoustic pressure is more than the ambient pressure ($P_\infty = 101.325$ kPa). It should be noted that this pressure magnitude maybe much less depending on the amount of gas nuclei inside the liquid. This net pressure causes the liquid part to expand [32]. Thus, under negative pressure the dissolved gases cause nucleation of tiny bubbles (voids) within the medium that grows until the bubble wall pressure exceeds the overall pressure in the liquid. When these bubbles reach a certain volume/size (the so called resonance size) beyond which they cannot absorb any further acoustic energy, they become unstable and undergo violent implosions during the compression phase [33]. This cyclic

phenomenon of bubble nucleation, growth and subsequent implosions occurring under the presence of a uniform ultrasonic wave is termed as acoustic cavitation. Fig. 2.3 depicts the schematic representation of acoustic cavitation induced by the ultrasonic wave. These imploding bubbles generate very high-pressure pulses (up to 1 GPa) and temperatures (up to 5000 K) with cooling rates of more than 10^{10} K/s in the nearby-localised region and this process also creates numerous smaller cavitation bubbles causing a series of events of bubble reproduction [34–36]. The violent implosions also lead to high-speed liquid jets and shock waves travelling at almost 100 m/s or more and 4000 m/s, respectively, causing degradation/erosion of nearby solid surfaces [37–40].

Bubbles that simply pulsate non-linearly over the mean equilibrium dimension with a continuous period of sound field constitute stable cavitation. Whereas, bubbles which grow to almost double their equilibrium size (R_a) undergoing violent collapses in less than one acoustic cycle are referred to as transient or inertial cavitation. Transient bubbles often produce smaller microbubbles in a chain reaction upon intense implosions. Imaging studies have confirmed that bubble breakdown takes place either with the initial implosion or during the first rebound collapse. Thus, the stable and transient cavitation differ in both violent collapse and oscillating time scale. The inertial cavitation is mostly accountable for powerful outcomes such as fragmentation, erosion, sonoluminescence and emulsification effects. Moreover, plenty of industrial and medical practices involve the use of transient cavitation conditions, which includes food and chemical processing, wastewater treatment, ultrasonic cleaning, lithotripsy, liposuction, cancer cell treatment and drug delivery [18,41–48] as well as in liquid metal processing [49]. On the other hand, stable cavitation, though less remarkable, produces essential and useful side reactions such as microstreaming and surface wave modulations in fluids with bubbles pulsating for much longer durations [50,51]. Stable cavitation can be used for cleaning surfaces/parts [52], where these bubbles gently scrub the surface avoiding their damage/erosion or can be used in nanomaterial synthesis [53] by opening the bulk pristine materials apart. With the intention of benefiting from the effects of acoustic cavitation to promote a particular processing application, it is imperative to recognize the factors that affect the cavitation threshold, and activity and acoustic behaviour in liquids (see section 2.2.4).

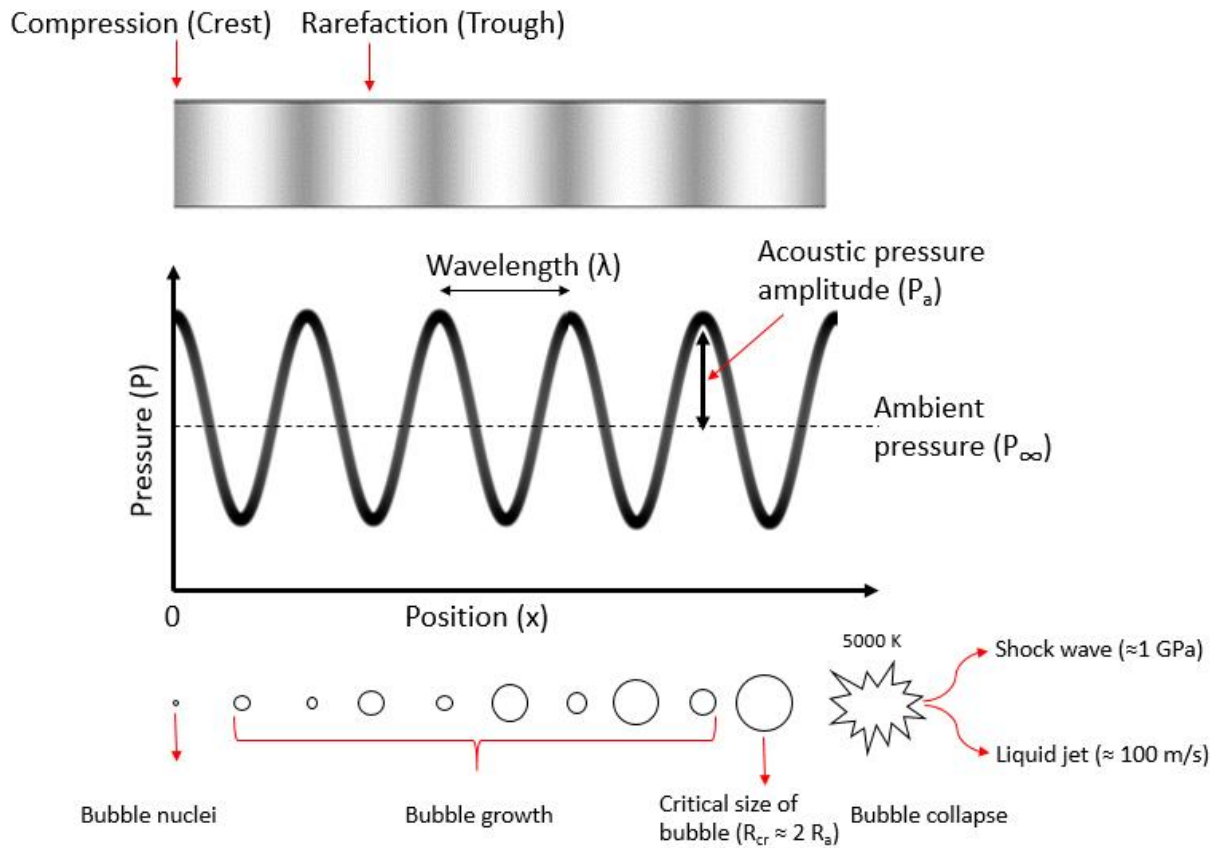


Fig. 2.3 Graphic representation of acoustic cavitation phenomenon induced by ultrasonic waves. Adapted from [54].

Frenkel [55] and Harvey et al. [56] provided noteworthy contribution in understanding the phenomena of cavitation in liquids. It was proposed that the nuclei needed for causing cavitation in liquids is characterised by the small and stable gas pockets that subsist in the crevices and cavities of the solid surfaces and particles. The presence of these minute gas nuclei essentially lowers the cavitation threshold much below the liquid tensile strength, so called Blake's threshold (see section 2.2.2). Nolting and Neppiras [57] scientifically interpreted the bubble pulsation based on its resonance size. It was found that cavitation bubble smaller than the resonance (bubble pulsating at its natural frequency) radius would grow and collapse rapidly within the pressure wave cycle. Whereas, the bubble with size greater than the resonance radius does not undergo implosion and rather stably pulsates close to its size. The population density of the cavitation bubbles is usually described by the term cavitation index, which is the product of the number of bubbles formed in the unit volume and the maximum volume of a single bubble. As this index approaches 1, the number of bubbles formed per unit volume becomes maximum almost substituting the liquid phase. This leads to a quick reduction

in the transfer of ultrasonic energy into the liquid phase which is also termed as cavitation shielding [58,59].

Theoretical estimation of the ultrasound induced acoustic pressure amplitude (P_a) for a plane sinusoidal wave can be expressed in terms of acoustic intensity [60]. This intensity (I_a) is described as the average energy flow rate per unit area perpendicular to the propagation direction and is specified in W/m^2 using the following equation:

$$I_a = \frac{P_a^2}{2\rho c_s} \quad (2.1)$$

where, ρ denotes the density of the surrounding (liquid) medium. With the surge in the acoustic intensity, the pressure amplitude also rises. Thus for a constant input power of the ultrasound, the acoustic pressure increases with the decrease in the area of the ultrasonic sonotrode (horn) tip. The acoustic pressure spatial distribution ($P_a(y)$) along the axis-symmetrical position away from the vibrating circular horn irradiating an ultrasonic wave in the surrounding medium is mathematically expressed as [60]:

$$P_a(y) = 2\rho c_s v_s \left| \sin \left(\frac{\pi}{\lambda} \left(\sqrt{y^2 + r_s^2} - y \right) \right) \right| \quad (2.2)$$

Here, v_s represents the velocity of the reciprocating horn, y denotes the distance away from the horn tip along its symmetrical axis, and r_s corresponds to the radius of the circular horn and λ corresponds to the acoustic resonant wavelength amplitude. With the formation of cavitation bubbles under the action of ultrasound, the speed of sound and the density of the surrounding medium change. In general, the occurrence of cavitation bubbles leads to a decrease in the velocity of sound and the density of the liquid medium. Therefore, the pressure amplitude reduces with the formation of bubbles beneath the sonotrode tip. The decrease in the acoustic pressure has actually been experimentally recognised below the horn tip in [61].

Accurate determination of acoustic pressure and spectral characteristics produced from ultrasonic transducers is often carried out using hydrophones [62] in low temperature liquids like water or cavitometers [18] in high temperature liquid metals. Precise measurement of the ultrasound-induced pressure is plausible if the frequency response (sensitivity) of the hydrophone is stable across the operating bandwidth of generated acoustic signal. The commonly used approach for estimating the pressure amplitude is by dividing the output signal (voltage) captured from the hydrophone with its sensitivity at the working frequency (f_0) [63,64]. Nevertheless, this conventional technique becomes problematic with acoustic

waveforms that contain substantial amounts of energy in the harmonic frequency range ($n f_0$, where n is an integer) arising from the nonlinear wave propagation. If the calibrated frequency response of the hydrophone is not stable, particularly over the working range of the broadband frequency, the acoustic pressure amplitude can be obtained by deconvoluting the measured waveform using the inverse Fourier transfer of the hydrophone sensitivity. As per the International Electrotechnical Commission (IEC) standard, the hydrophone bandwidth must be more than 8 times the operating frequency in order to have measurement inaccuracies below 5% [63]. When this kind of bandwidth is unattainable, then deconvolution should be applied to the signal with a large measurement uncertainty owing to restricted bandwidth of the hydrophone [63]. More details on the deconvolution technique used for the determination of acoustics pressure measurements in ultrasonicated liquid is provided in the Appendix.

2.2.2 Cavitation threshold

In order to understand the cavitation threshold in a multibubble liquid environment produced by the ultrasound, it is important to understand the dynamics of a simpler system of single bubble. Within the ultrasonic field, considering a single bubble in isolation trapped at the antinodal location of the induced standing wave field, the bubble can stably pulsate with respect to its equilibrium size when the acoustic pressure amplitude is below the threshold value needed for generating shape instability and bubble repulsion from the antinodal location within the acoustic field. For acoustic frequencies close to 20 kHz, the cavitation inception in various liquids occurs when the pressure amplitude exceeds the threshold limit, e.g. 0.06-0.1 MPa for deionised water [51], 6.3 MPa for glycerol [65] and 0.7 MPa for some liquid metals [1]. Once the induced pressure goes beyond the cavitation threshold value, violent collapse is triggered. Similarly, in case of multibubble system, as the acoustic pressure within the ultrasonic field reaches the critical pressure, the bubbles/bubbly clouds become unstable and collapses. It is important to note here that threshold pressure amplitude required for violent implosion of bubble can often be different than the one needed for its nucleation. Blake [66] identified a critical size (radius) that provided clear distinction between the quasistatic stable bubbles and cavitating bubbles when the average acoustic pressure reduced below the liquid's vapour pressure. For example, It has been reported that for a bubble with equilibrium radius of 37 nm, the critical radius is close to 64 nm at a driving frequency of 0.75 MHz [67]. The onset of the quasistatic evolution leading to formation and growth of bubble in liquids can be indicated by the classical Blake threshold.

In order for the bubbles to collapse, they need to overcome the Blake threshold pressure. The Blake threshold pressure is defined as the peak acoustic pressure during the rarefaction phase when the bubble size reaches the critical Blake radius (about 2 times the equilibrium radius [68]). The formed bubble becomes highly unstable and collapses violently behaving like an inertial cavity. The intensity of the sound wave that results in occurrence of the first cavitation event upon increase in the input power is called as cavitation initiation threshold or just cavitation (Blake) threshold. This threshold is affected by the type and the characteristics of dissolved gas content in the liquid. The container and sound field geometry also influence this cavitation threshold. The higher the driving frequency, the higher the threshold will be, and it undergoes cavitation hysteresis with the decrease in the input acoustic power. The critical cavitation threshold also brings about distinction between the stable and inertial (transient) cavitation condition.

When the liquid is subjected to negative pressure field developed during the rarefaction phase of the acoustic wave cycle and the distance amongst the vibrating molecules surpasses the critical distance required to confine the liquid together, vapour cavities (voids) form within the medium. If this distance for water medium were of the order of $0.1\text{ }\mu\text{m}$, the resulting pressure threshold would be in the range of GPa [69]. Thus, it is difficult to initiate cavitation from the sonotrode in gas-free water, the only active/prominent sites would be the voids. Once the cavitation establishes, the produced shock waves can easily reach pressures in the GPa range and further facilitating the multiplication of bubbles in the liquid. However, this assumption is only valid for pure water. In reality, the threshold required for causing cavitation in liquid is much lower owing to the existence of various weak gas spots. These weak spots can be in the form of dissolved gases, microparticles or nuclei for cavitation that are responsible for lowering the liquid tensile strength. Depending upon the size distribution of these weak spots, the portion of bubbles behaving in stable or transient manner will vary based on the acoustic parameters. Cavitation threshold can be calculated by measuring the sound spectrum and its intensity. Upon further surge in acoustic pressure amplitude, the cavitation regime becomes fully established with formation of numerous microbubbles that also control the fluid kinetics (acoustic spectrum) in the bulk liquid [70].

2.2.3 Acoustic streaming

In 1884, Lord Rayleigh [71] was first to define the phenomenon of acoustic streaming which was later reviewed by several researchers [72–75]. It refers to the stable vortical flow that is produced from the propagation of acoustic waves and momentum loss required to overcome

the liquid viscosity. It occurs in both non-homogeneous sound fields and near boundary interfaces through acoustic energy scattering mechanism. The dissipation of this energy flux induces variations in momentum flux that causes streaming motions within the medium. The measure of the streaming force and velocity depends on the properties of the liquid and configuration of the external boundary field.

The application of ultrasound in liquids generates acoustic streaming resulting from the attenuation of ultrasonic waves in the surrounding medium [76]. The streaming velocity is a direct function of the ultrasound intensity, surface area of radiating source, liquid's attenuation coefficient, and an inverse function of the bulk viscosity and sound velocity within the medium as well as the bubble fraction and bubbly clouds [77]. The streaming flow velocity may be of the order of $\mu\text{m/s}$ under slow streaming conditions and can reach up to the order of cm/s or more in case of fast streaming [74]. The intensity and the corresponding velocity of the streaming generated from the ultrasonic source are always less than the driving velocity of the radiating surface (horn tip) irrespective of its amplitude [2]. Acoustic streaming can be mainly distinguished either as the Eckart streaming or as the Rayleigh streaming. The Eckart streaming is an effect of unbalanced radiation pressure that causes acceleration of fluid flowing in the direction of attenuating acoustic wave propagation. The Rayleigh streaming is a result of vortex-like fluid flow propagation occurring due to the viscous stress generated close to the boundary layer. This type of streaming is also called microstreaming if its length scale near to a cavitation bubble is smaller than the acoustic wavelength. The phenomenon of liquid flows induced from the acoustic cavitation is very complex. Intensification of the Eckart streaming results from the strong attenuation of ultrasound caused by cavitation bubbles. The movement of bubbles is governed through both the primary and secondary Bjerknes forces, whereas the movement of liquid is controlled by drag forces produced from bubbles. Ultrasound induced streaming is mostly observed in (i) bulk liquid streaming, (ii) streaming constrained by rigid walls, (iii) minuscule vortices developed near a viscous boundary layer. From the context of this thesis, acoustic streaming in bulk of the fluid is highlighted in detail.

With the propagation of ultrasonic signal, part of its acoustic energy is absorbed within the medium. The rate of absorption is proportional to the square of the introduced ultrasonic frequency. The energy absorption causes the amplitude of ultrasonic wave to dissipate in the liquid leading to decrease in the acoustic pressure with distances away from the source. The acoustic energy loss gives rise to steady momentum flux thereby generating primary cavitation jet along the direction of wave propagation. If the liquid jet formation occurs within the rigid

walls of a small container, vorticity will naturally be induced producing fluid circulation on either or both side of the jet (Fig. 2.4). The ultrasonic transducer will produce near field effect due to finite size of the horn, which will vary quickly with increasing distance, steadily becoming uniform at distances higher than the horn size [60]. With further increase in the distance from the source, the streaming field will ultimately diminish because of geometrical spreading.

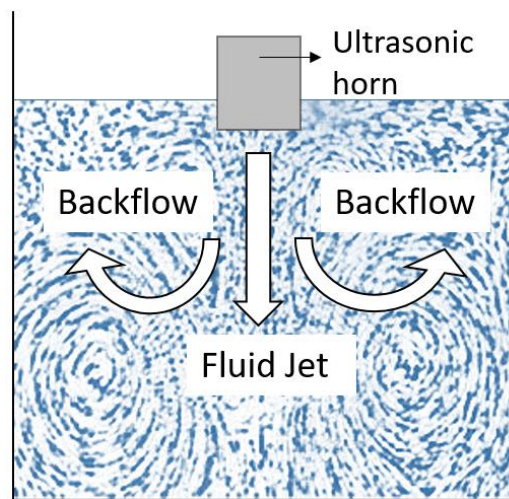


Fig. 2.4 Acoustic streaming field generated by an ultrasonic horn showing primary cavitation jet and recirculating back flow. Adapted from [78].

With the high enough ultrasonic intensity suitable to generate cavitation using sonotrodes or commercial horns, acoustic streaming goes hand-in-hand with ultrasonic cavitation. This system becomes highly complex considering the involvement of both linear and nonlinear interactions between cavitating microbubbles and associated microstreaming at a smaller scale in addition to the occurrence of large scale acoustic streaming. Substantial amount of power is lost from the ultrasonic waves responsible for the formation of cavitation bubbles as they absorb and scatter the propagating waves.

The use of acoustic streaming encompasses all non-invasive intervention applications in medicine and industry. Some of these uses include medical diagnosis of cysts, drug delivery, convective transport mechanism microfluidic channels [79,80]. The recent and trending application of acoustic streaming phenomenon includes generation of enhanced thermal convection and efficient mixing [81–83]. The application of ultrasound induced streaming has also been utilized in molten metals with an aim to advance the stirring and metal crystallisation [18,84].

2.2.4 Factors affecting cavitation activity

Some of the physical parameters that govern the acoustic behaviour in liquids are briefly discussed below:

(a) Acoustic Frequency: There is strong dependence of the cavitation threshold on the driving frequency of the sound field. Bubbles that are oscillating with a frequency higher than the resonance frequency will only cavitate. With the increase in acoustic frequency, the size of cavitating bubbles reduces. Fig. 2.5 represents the typical variation of threshold intensity measured in aerated and degassed water at room temperature as a function of acoustic frequency. Beyond 100 kHz, the threshold value for vapour bubbles rises drastically, which indicates that cavitation can be generated pragmatically under a specific frequency range only.

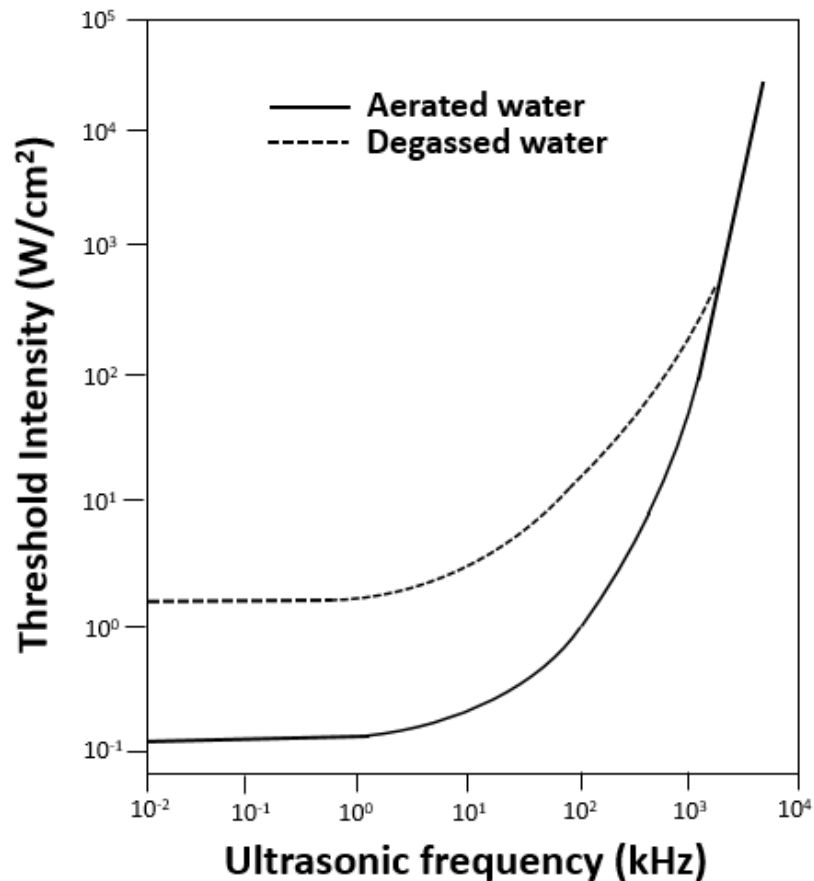


Fig. 2.5 Variation in cavitation threshold intensity as a function of ultrasonic frequency in aerated and degassed water. Adapter from [85].

(b) Acoustic Intensity: A higher intensity will result in a larger acoustic pressure amplitude produced from moving and violently imploding cavitation bubbles. With further increase in

the pressure (oscillating) amplitude, even the tiniest bubbles are likely to expand and become unstable, thereby contributing towards the cavitation activity. Therefore, with the increased intensity, cavitation activity also increases through the rise in the number of bubbles and their maximum size. In general, a larger acoustic intensity leads to the increased bubble growth. At higher intensities, the bubble growth could be exceedingly large, preventing its collapse in the next rarefaction phase owing to short time remaining for collapse. Moreover, formation of large bubble cloud beneath the tip of a sonotrode may reduce the transmission of sound wave into the system. An extensive rise in the ultrasonic intensity might also cause damage to a radiating horn due to cavitation erosion. Thus, a suitable power for generating acoustic cavitation exists and may be system dependent.

(c) External Pressure: The higher the external pressure, the greater the pressure resulting from violent bubble implosions. A higher static pressure within the liquid medium can give rise to the increased acoustic impedance of cavitating liquid owing to the induced resonance. This enhanced impedance could generate large acoustic power that is transmitted to the liquid through the ultrasonic transducer.

(d) Nature of dissolved gases: The evolution of cavitation bubbles within the sonicated medium mostly originates from the ubiquitous nuclei that could be in the form of vapour and/or gas micro-inhomogeneities on solid surface. As the ultrasonic wave propagates, each bubble that develops from the nucleus during the rarefaction phase of the acoustic cycle gets infused with the gas dissolved in the liquid through rectified and convective diffusion [86]. Increase of ultrasonic intensity will generate greater number of cavitation bubbles across a larger number of nuclei causing the effective liquid domain (responsible for infusing the dissolved gas into the bubbles) to become smaller. Thus, the amount of gas diffused into the cavitation bubbles is expected to decrease thereby lowering their equilibrium size. Cavitation in liquids can become more and more difficult if the liquid is degassed reducing the available nuclei for bubble formation. It should be noted that the amount of gas/vapour diffused into the bubble is dependent on the acoustic pressure. Moreover, cavitation threshold is strongly dependent on the concentration of impurities/gases present within the liquid in addition to the crevices on the walls of the container/vessel. With the increase in gas concentration, the cavitation threshold becomes smaller. For example, the cavitation threshold pressure in case of degassed water is close to 80 atm while the threshold reduces to 1 atm for air-saturated water [87]. This clearly indicates that the cavitation bubbles consist of both gas (air) and water vapour.

The temperature and pressure generated during the collapse phase of the cavitation bubbles is further dictated by the specific heat ratio ($\gamma = C_p/C_v$) of gas within the cavity. Since the specific heat ratio in case of a monoatomic gas is highest, therefore it is recommended to degas the bubble through the solution prior to ultrasonic irradiation as the gas pressure will cushion the cavitation collapses and produce non-inertial cavitation resulting in less pressure and temperature. Other factors that affect the temperature of imploding bubbles and their count include thermal conductivity and solubility limit in water. Gas with a high specific heat ratio and small thermal conductivity would lead to higher temperatures during bubble implosions. On the other hand a highly soluble gas would result in the increase of number of cavitation bubbles.

(e) Physical properties of the cavitating liquid: Every liquid has a unique set of characteristics making the choice of the cavitating medium a crucial factor during suitable ultrasonic treatment conditions [88]. Some of the important fluid properties are liquid viscosity, surface tension, density and vapour pressure. Cavitation (bubble growth and collapse) is predominantly favoured and pronounced when a liquid with high surface tension, low viscosity and low vapour pressure is chosen [89]. Thus, a sensible selection of fluid properties is essential for expediting the cavitation process. Aerated or tap water, in general, is considered as one of the most common and suitable media for inducing cavitation. On the other hand, de-ionised/degassed water, for instance, is difficult to cavitate owing to the high surface tension and large tensile strength that suppresses the nucleation of bubbles as a result of lesser impurities. However, bubbles that do nucleate and grow collapse violently producing significantly larger energy than tap (aerated) water under the same processing conditions.

(f) Bulk liquid temperature: The physical properties of liquids may also vary with the change in temperature. To achieve best cavitation results during ultrasonic treatment, it is crucial to use low liquid temperatures [90]. Reducing the liquid temperature causes the vapour pressure to decrease, thereby intensifying the cavitation intensity within the medium. If ultrasonic treatment is applied to the liquid with a higher bulk temperature, any bubble that is formed in the liquid would be filled almost immediately with the gases present in the liquid. The severity of these gas filled bubble collapses during the compression phase will lessen and rather a cushioning effect would be produced, causing temperature and pressure magnitude to drop significantly.

2.2.5 Acoustic emission spectrum

One of the primary objectives in the field of cavitation research is the experimental characterisation and theoretical analysis of ultrasonic emissions generated from an acoustic source. Use of high power ultrasound has been identified long back as an important tool in sonochemistry and sonoprocessing of several physical, chemical and biological systems [91–93]. Regardless of the deployment of ultrasonics in wide range of applications [18,94–97], studies related to basic understanding of cavitation characterisation is rather limited. Substantial understanding and awareness of the ultrasonic cavitation will be crucial in scaling up such processes from research laboratory to industrial unit [98], characterisation of ultrasonic activity is thus expected to aid in optimising many of the ultrasound assisted applications [99,100].

Methods used to characterise the cavitation activity in a confined space range from optical methods such as high-speed photography to the measurement of direct effects such as surface erosion, fragmentation and de-agglomeration [18,100–103]. Other approaches to characterise the cavitation activity and threshold levels include sono-capillary effect [104], and electrochemical nature of cavitation collapses [105,106]. However, in most of the above cases there is significant disturbance to the acoustic emissions resulting from the dramatically fluctuating multi-bubble cavitating domain. This bubbly regime produces complex interactions with other oscillating bubble cloud fields leading to non-linear acoustic behaviour that makes the observation and modelling of cavitation activity challenging [107]. However, with the use of appropriate cavitation measuring devices, acoustic field characterisation of the broadband emissions induced from pulsating microbubbles is possible. Real-time monitoring of cavitation emissions, method involving acoustic field spectrum identification has proven to be effective. It has been observed that in a sonicated environment, formed bubbles can behave as the source of secondary induced acoustic field with its emission spectrum containing plenty of data associated to the cavitation dynamics [108,109]. Research related to the detection of low frequency acoustic emissions for characterising the cavitation field in ultrasonic cleaning baths and other such commercial devices that function on the same modality have already been reported [110,111]. Earlier attempts have also been made to study the cavitation activity by measuring the ultrasonic emissions produced from the broadband noise [88]. However, having an in-depth understanding of the cavitation noise spectrum is still a subject of further research.

The experimental study on the measurement of cavitation signal dates back to 1977 when Bocquet and Ricq [112] were looking for an apparatus that could allow them to study the

natural and permanent subglacial cavities formed under the glaciers by the help of water-collection tunnels. Later in 1989, Young [113] and Leighton [114] provided the first insights into the acoustic emission generated from transient and stable cavitation bubbles. Acoustically induced cavitation noise spectrum typically comprises of several peaks that are closely associated with the driving frequency field (f_0). Some of these peaks belong to the harmonics (nf_0), subharmonics (f_0/n) and ultraharmonics (n/mf_0) where n and m are integers and n/m is non-interger. Typical features of acoustic cavitation signals are shown in Fig. 2.6 and has been described separately below:

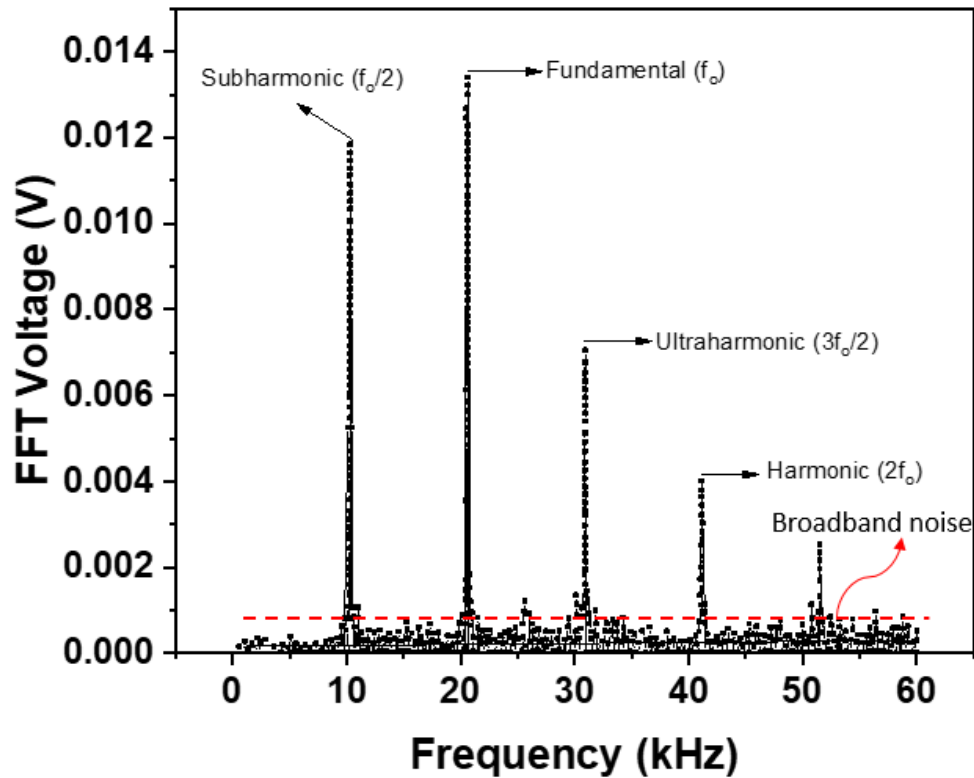


Fig. 2.6 Deconvoluted spectrum of acoustic cavitation noise obtained from a typical hydrophone system. Adapted from [115].

- (a) Driving frequency: It refers to the main fundamental frequency peak, which is generated by the driving acoustic field and is accompanied with linearly cavitating bubble emissions [114].
- (b) Harmonic frequency: It denotes the integer multiple of the fundamental driving frequency which is a consequence of nonlinear bubble oscillations [113], acoustic emissions generated from the ultrasonic transducer and probably nonlinear acoustic wave propagation from the source within the medium.

(c) Subharmonic frequency: These frequencies are the fraction or integer submultiple of the driving frequency component and are identified as the criterion of cavitation inception [113]. They possibly emerge when the bubbles with size equivalent to twice or more of the resonance size are excited and/or the formed bubble reaches the critical size in more than one acoustic cycles before collapsing [116,117]. The appearance of subharmonic frequency peaks in the acoustic spectrum also corresponds to the propagation of periodic shock waves [118].

(d) Ultraharmonic frequency: This represents the non-integral fraction of the fundamental frequency and are commonly associated with cavitation events as produced by those of subharmonic signals.

(e) Broadband noise: This represents the elevated noise floor of the spectrum expanding across all frequency ranges continuously from the chaotic oscillations of bubbles and shock waves emitted by high energy and violent cavity collapses of varying size [113].

Acoustic spectrum generated at low intensities comprises only the fundamental frequency. With gradual increase in the intensity, however lower than the transient cavitation threshold limit, larger bubbles tend to oscillate in a nonlinear fashion. Moreover, at such intensities the emission spectra contain the fundamental and harmonic frequency peaks with notable 2nd order harmonics. In cases of stable oscillating bubbles, the subharmonic emissions are rather weak compared to the inertial cavitation field. At low intensities, the shape distortion of bubble surface is not significant. Due to this weak coupling between the bubble and liquid, the emissions are difficult to be accurately sensed by the sensors/hydrophones. Detection of broadband noise signal allows for the computation of energy resulting from the transient bubble collapses [119]. Several studies have revealed that this energy magnitude can be linked to various physical effects like ultrasonic cleaning [120], erosion [121], fragmentation [122]. For capturing the broadband/noise signals, the measurement probe should have a provision of high frequency response and narrow spatial sensitivity, which can be recognised at regions where the ultrasonic wave propagation distance is restricted to only few centimetres owing to acoustic attenuation [119]. Neppiras [119] also believed that ultrasonic source operating at low (kHz) frequencies would generate cavitation noise across high (MHz) frequency spectral range, thus investigating frequencies up to few MHz should be relevant in characterising the acoustic spectrum.

Having covered the fundamentals of ultrasonic processing and acoustic characterisation, we now turn our attention back to UST, wherein we discuss the important mechanisms through which the structure/grain refinement transpires in alloy melts under the action of ultrasound.

2.3 Structure refinement mechanism via UST

The ultrasonic processing of commercial alloys was pioneered in 1936 by Seemann et al. [25,26], who confirmed substantial refinement of the grain structure and improved mechanical properties in the basic duralumin cast ingot. Further investigation on treating solidifying alloy of Al-4% Cu, Al-12% Si and Al-0.5% Mn was reported by Bradfield [123] where it was found that using 26 kHz of ultrasound frequency in the melt leads to very refined grain structure. UST has also been practiced on number of commercial Al foundry alloys i.e. hypereutectic and hypoeutectic alloys such as Al-Si where it was observed that the refinement not only occurs for the grain structure but also the intermetallic and primary crystals under the influence of acoustic cavitation [124]. In late 1930-40s, Schmid et al. [27,28] observed that the ultrasonic intensity greatly affects the structural refinement capabilities of the alloy, i.e. higher the intensity, greater will be the grain refining effect. It was then speculated that refinement in alloy melts happens through the fragmentation of formed crystals caused by the viscous friction between liquid and the solid interface.

To gain insight on the underlying mechanism of the observed phenomena, researchers started investigating the ultrasound effect on transparent organic liquids that show similar crystal morphological characteristics and could act as an analogue for molten metals. With the advent of high-speed motion cameras aided by high intensity lamps and laser illumination, direct imaging of the cavitation process became possible during 1950's and 60's [125–128]. Several studies related to observation of crystal nucleation and growth, solidifications and their response to ultrasound were performed in the 1950-70s using liquids such as camphene, naphthalene, salol, timol, ammonium chloride, piperine and Succinonitrile (SCN) [129–131]. Significant understanding of the crystallization and solidification behaviour caused by ultrasonic oscillations and induced cavitation was developed through these experiments. A group of researchers then professed the notion that ultrasonic treatment of alloy melts leads to the development of solid nuclei particles [132–134]. Danilov et al. [134] especially endorsed the idea of the influence of ultrasound induced acoustic cavitation on heterogeneous nucleation phenomena caused by the activation of impurities acting as substrate particles. Further, using transparent liquid analogues, Kapustin [130,135] reported and confirmed that nucleation of

crystallization sites upon ultrasonication was amplified by the treatment intensity and the amount of undercooling (driving force for nucleation). The formation of nuclei was also observed even in case of pure liquids signifying that different nucleation mechanism other than substrate activation must have occurred. It was hypothesised that ultrasound induced cavitation and streaming effect results in increased friction between solid and liquid phases reducing the surface tension effect and associated critical size of the nuclei [27,136].

Ultrasound induced controlled solidification is fundamentally governed by the acoustic cavitation and streaming effects as illustrated in Fig. 2.7 [1,137–140]. The growth and collapse of cavitation bubbles helps in promoting dendrite/crystal fragmentation and producing heterogeneous nucleation sites. Nucleation and growth of a grain on top of an active substrate/inclusion becomes easier when the activation energy needed for nucleation is decreased, which is further facilitated when the ultrasonic field reaches to its critical intensity [129]. The emission of microjets from cavitation bubble collapses near the substrate surface improves wettability of heterogeneous nucleation sites. However, it is important to note here that the operational mechanism during structural refinement of metals and alloys could change depending upon the temperature of the melt. For example, activation of substrate usually happens above the liquidus temperature of the alloy, nucleation occurs just below the liquidus, while the fragmentation of crystals and dendrites happen well below the liquidus. In principle, the fragmentation of dendritic arms and formed primary crystals occur when the strength of shock wave front and high speed microjets emitted from the bubble implosion exceeds the critical fracture stress [103,137]. The grain refinement of as-cast alloy results from the combined effect of cavitation assisted heterogeneous nucleation and fragmentation of dendritic crystals. The phenomenon of quasi-steady liquid metal flow induces the acoustic streaming effect. The flow is either caused by the ultrasonic horn displacement generating differential pressure zones in the bulk liquid or through the pulsating cavitation bubble [1,137]. The streaming effect causes (a) blending of molten metal and formed second phase crystals, (b) distribution of dendritic grains, and (c) fragmentation of primary intermetallics. Overall, this leads to modification in microstructural uniformity of the solidified alloy. Usually, during the ultrasonic treatment of the solidifying liquid metal (i.e. below liquidus), the three zones i.e. the slurry melt, mushy melt and as-cast ingot coexist. It should be noted that the presence of dendrites and oxides within the slurry zone is a result of the induced acoustic streaming within the melt that pushes solid particles/dendrites from the mushy zone to the slurry melt region (indicated by straight and curved black arrows in Fig. 2.7).

The major application of UST is associated with the microstructural refinement of the as-cast billet/ingot in DC castings. UST is typically performed in the liquid phase where the slurry zone is formed below (although could also be performed during solidification as shown in the left image of Fig. 2.7). There are several postulated mechanisms in the literature by means of which the refinement occurs, most of them established on the theoretical estimates without direct experimental proofs. In general, two theories are mostly considered to explain the refinement process through ultrasonic treatment. The first theory is based on the formation of a solid phase owing to induced supercooling caused by the bubble collapse in the liquid metals (so called homogeneous nucleation). Second theory takes into account cavitation-aided activation and wetting of substrate, which signifies the heterogeneous nucleation. Other than these two conventional theories, another alternative theory considers that the formed crystals fragment and subsequently disperse off within the melt to act as nuclei (cavitation-assisted fragmentation). The principal mechanisms by which the grain refinement essentially occurs in ultrasonically treated melts has been briefly discussed below.

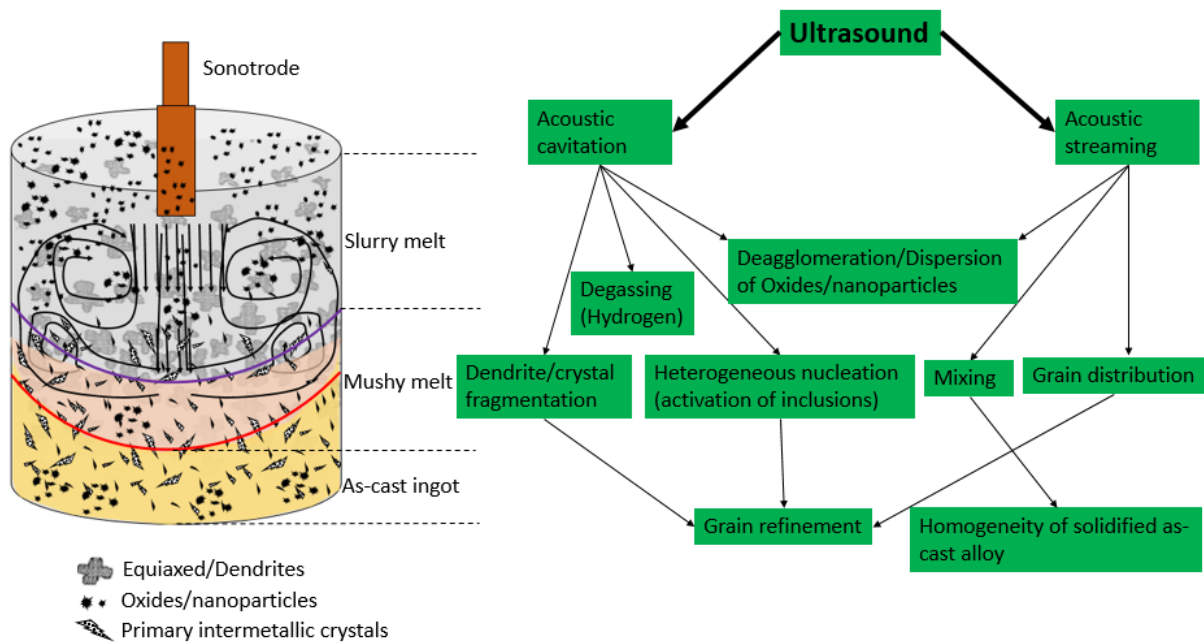


Fig. 2.7 Graphical illustration of dominant mechanism occurring during ultrasound-induced solidification of an alloy for manufacturing of alloys and metal matrix composites/nanocomposites. Adapted from [141].

2.3.1 Cavitation aided nucleation

A cavitating bubble can assist in nucleation of a stable solid phase (nucleus) as a result of induced supercooling by altering the equilibrium conditions through localised high-pressure (in orders of GPa) regions generated upon collapse [129]. The subsistence of the formed

nucleus is dependent on the temperature and flow conditions of the melt. Although this mechanism is theoretically established in case of homogeneous nucleation settings, a much more realistic mechanism is the heterogeneous nucleation befalling close to liquidus temperature. Nucleation, in actuality transpires largely over a foreign substrate. The presence of a solid phase within the liquid metal or when the melt is in contact with the mould/crucible or oxide particle, the nucleation process is enhanced upon the decrease of activation energy. This phenomenon is termed as heterogeneous nucleation. It is the process in which an embryo is formed over the active substrate and its critical size (radius, R_c) is attained with lesser atoms as would have been needed to form a spherical nucleus instead. This can happen in two ways:

1. The nucleus can be approximated as a spherical cap if the interfacial energy between the nucleus and substrate is less than that of between melt and substrate (see Fig. 2.8a). This alters the link between the volume and radius of the formed embryo and the nucleus in the form of cap develops into critical size at lower undercooling (ΔT) than that of a spherical embryo (Fig. 2.8b).
2. For heterogeneous nucleation to occur, the size of the nucleus (spherical cap) should essentially be a crystalline monolayer phase onto the substrate. The condition requires that the adsorption of a layer of atoms from the liquid metal occurs over the substrate in such as pattern over which the solid phase can grow. For this to take place, the adsorption sites should closely match the sites of an atomic layer of the solid phase. In addition to this, the substrate's surface should also be atomically flat across the region having adequate size such that a patch of a critical size can be formed.

The molten metal in this case can maintain any temperature that is above the nucleation temperature. However, when ultrasonic vibrations are introduced within the melt, the induced cavitation can initiate the nucleation process even when the liquid is in superheated (metastable) state. The occurrence of cavitation is supposed to affect the melting temperature as a result of pressure change during bubble collapse.

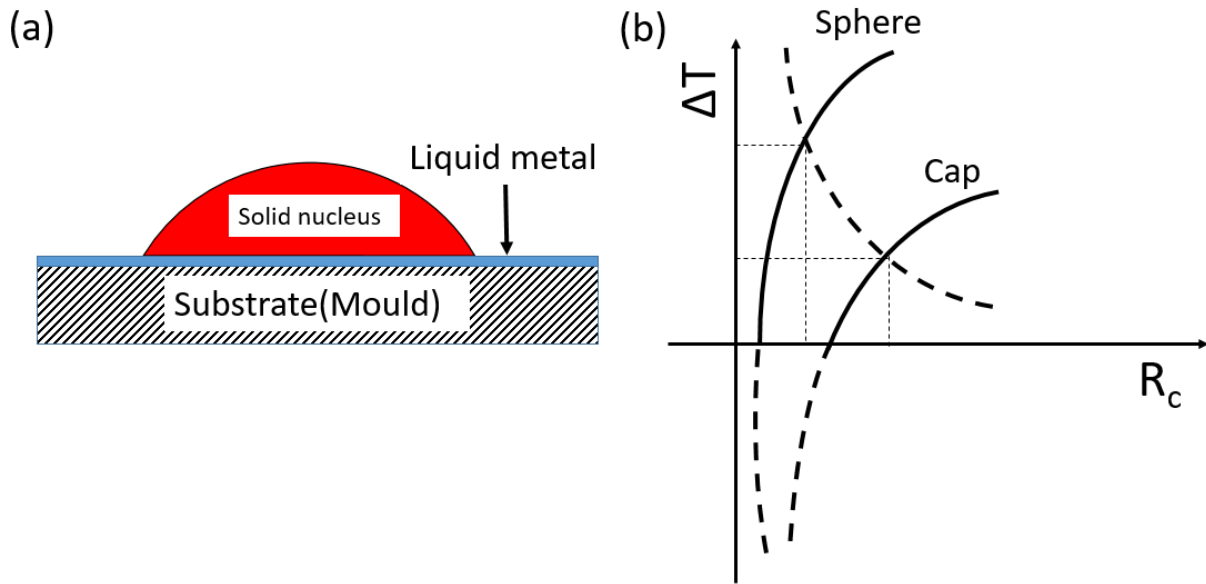


Fig. 2.8 (a) Model of cap shaped nucleus in case of heterogeneous nucleation, (b) undercooling as a function of nucleus size for formation of stable spherical and cap shaped embryo. Adapted from [142].

Increase in the number of potent nucleation sites through activation of substrate (see section 2.3.2) particles was initially reported during 1930-40s by Danilov et al. [133,134]. It was found that the cavitation occurring at the phase boundary is responsible for improved wetting, reduced surface tension and enhanced heterogeneous nucleation on existing inert inclusions like intermetallics, oxides and carbides. Cavitation-aided nucleation can be explicated using three different mechanisms:

(a) Pressure induced increase in the melting point: The melting point (T_m) of a material is the temperature during which both solid and liquid phase exists in equilibrium. For a pure bulk material, the melting point is often distinct and varies with the change in pressure, the relationship of which is given by the commonly known as Clapeyron effect. This typical effect can be deduced from the thermodynamic principles giving rise to the so-called Clausius-Clapeyron expression [143]:

$$\frac{dP_v}{dT} = \frac{\Delta H}{T_m \Delta V} \quad (2.3)$$

where, dP_v/dT denotes to the gradient of coexistence pressure-temperature curve of the alloy melt, ΔH and ΔV corresponds to the change in enthalpy and specific volume at the phase transition point. The Clapeyron effect i.e. dT/dP_v can be evaluated from the knowledge of T_m , ΔV and ΔH . Nevertheless, the dependence of melting temperature on pressure can have high calculation uncertainties due to the experimental limitations in determining the change in

specific molar volumes of the two phases (ΔV). Although, the Clapeyron effect is known and well recognised in area of solidification research, in most cases it is presumed to be negligible and is often not of much interest in the solidification of metals and alloys. In case of SCN, however, the Clapeyron effect is much larger than most of the metals (almost 25-200 times per unit of supercooling) [144].

The occurrence of cavitation in a liquid that is undercooled can result in nucleation of solid phases, though the change in pressure maybe too small for direct nucleation of solid. The intense ultrasonic field can induce negative pressures of the order of a few tens of atmospheric pressure that eventually leads to formation of cavitation bubble (gaseous cavitation), which upon collapse produces extremely large pressures up to a few GPa at a localised region with positive pressure transients. The surge in pressure increases the melting temperature of the alloy resulting in large undercooling promoting either homogeneous nucleation or heterogeneous nucleation if a potent substrate is present nearby [129,145]. Hunt and Jackson [129] showed that the change in the melting temperature upon bubble implosion can shoot up to tens of degrees reaching about $0.2T_m$. Table 2.1 shows the increase in the melting point with the change in pressure for a commercially pure Al.

Table 2.1 Effect of pressure change on the melting temperature of pure Al. Taken from [1].

P_v (MPa)	0.1	500	1000	2000	4000
T_m (°C)	660.5	690	720	780	830

It is important to note here that the solid phase evolution in metastable liquids depends on its nucleation and growth kinetics with large supercooling. One of the ways to model such Solid (S)-Liquid (L) phase transition occurrences is through Gibbs-Thomson effect that influences the dynamics of solid/crystal formation on an active substrate. The variation in the temperature of the S/L interface is explained by the Gibbs-Thomson interfacial condition. The phase transition melting temperature (T_m^r) at the interface largely depends on the curvature of the formed solid phase, which increase for concave particles inside the crevice (see Fig. 2.9) with respect to melting temperature of planer interface (T_m^∞). Therefore, the increase in the melting point of the S/L interface with negative curvature, r_p in case of concave particle can be expressed by the Gibbs-Thomson relation [146]:

$$T_m^r = T_m^\infty - \frac{2\mathcal{X}}{r_p} \quad (2.4)$$

where, $\mathcal{X}$ denotes the Gibbs-Thomson coefficient calculated based on the melt-particle interfacial surface tension ($\sigma_{S/L}$) that depends on the S/L interfacial contact angle (α), liquid molecular volume (V_L) and latent heat of fusion (L_f), given by $T_m^\infty \sigma_{S/L} V_L / L_f$.

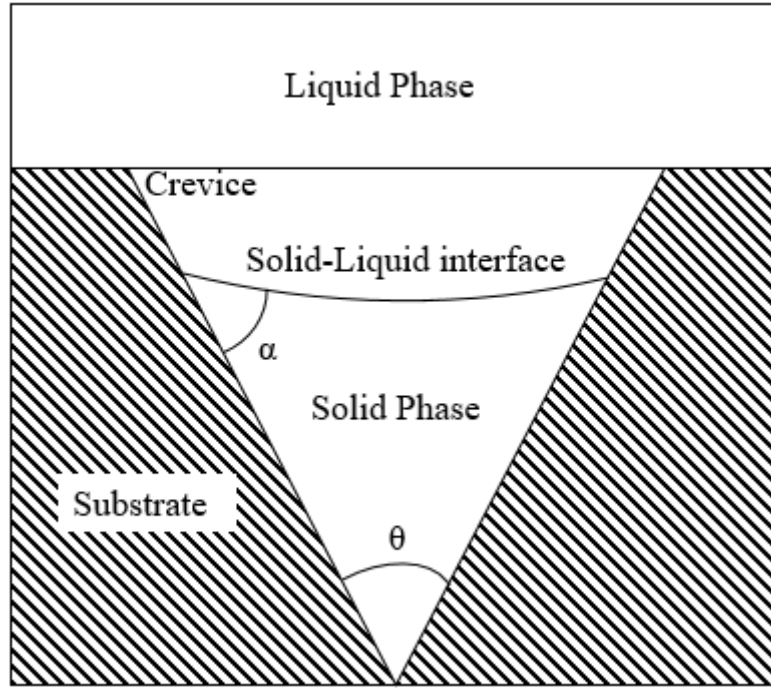


Fig. 2.9 Schematic representation of concave solid phase with contact angle α inside a crack or crevice with included angle θ at the surface of solid substrate. Adapted from [1].

(b) Particle wetting: The word ‘wetting’ is usually used to define the process of making a contact of the liquid with a solid surface. The physical phenomena of wetting can also be described in terms of surface free energy at the solid interface between the interacting phases, which evolves from the intermolecular cohesive forces. Based on the classic theory of heterogeneous nucleation, the influence of heterogeneity in promoting or suppressing the formation of solid phase over a substrate is explained in the language of wetting. The degree to which a substrate can be wetted is dependent on the contact angle (α) of the formed nucleus. The smaller is this angle, stronger is the wetting of the surface (spreading) thus lowering the change in free energy (less barrier to nucleation). The effectiveness of the heterogeneities in lowering the thermodynamic nucleation barrier can be affected by a range of microscopic properties of both the nucleus and substrate in terms of surface roughness, adsorption, crystal structure and the lattice misfit. For a surface to act as an active nucleation site, a good

crystallographic match of the substrate and the metal nuclei is necessary, which lowers the undercooling required for nucleation and increases the nucleation rate. In case of cavitation, the microjets produced from bubble collapses and the associated microstreaming effect pushes and recirculate (bringing fresh melt) the surrounding liquid towards the suspended substrate thereby promoting wetting of non-metallic inclusions within the melt that further escalate the rate of nucleation [147]. On the contrary, the wettability of the solid surfaces can also have large influence on the formation, growth and collapse of cavitation bubbles. Zhu et al. [148] recently reported that hydrophobicity (non-wetting) of the substrate surface can intensify the bubble implosion process, while the hydrophilicity (wetting) of the surface has only slight effect on the collapsing event.

When the liquid metal is ultrasonically processed above the liquidus temperature, the grain refinement occurs from the augmented nucleation sites over wet insoluble non-metallic inclusions [149]. The effect of improved wetting of non-metallic impurities under sonication has been found to be apparent in case of oxide containing MMCs [150]. The enhancement of heterogeneous nucleation under the influence of ultrasound can therefore be ascribed to the forced wetting (activation) of indigenous substrates in the form of inclusions, impurities and mould walls. The mechanism of substrate activation with the help of ultrasound has been discussed in detail in Section 2.3.2.

(c) Adiabatic bubble growth: The quick adiabatic expansion of formed cavitation bubble causes undercooling of the melt at the bubble-liquid interface thus augmenting nucleation events [151]. The formed cavitation bubbles during the rarefaction phase of oscillations tend to engross heat from the surrounding melt leading to localised supercooling occurring at bubble surfaces making it a potent region for nucleation. It is likely that these conditions would help in generating more heterogeneous nucleating sites during solidification which is presumed to be correlated with so-called “activation of inclusions” (see Section 2.3.2) [1,124]. However, this theoretical mechanism offered very little undercooling of the melt (not exceeding 1 K) as compared to the mechanism of pressure induced melt undercooling and has been rejected long ago.

Observation to liquid metal transparent analogues confirmed that nucleation is essentially assisted by ultrasound-induced cavitation [124]. Following the advancement in high-speed imaging technology, observation of the cavitation interaction dynamics with a solidifying phase became even more explicit. Ultrasound controlled solidification of Camphene showed

that refinement principally occurs by the combination of both nucleating solid phase and dendritic fragmentation caused by the pulsating bubbles [152]. Chow et al. [153] reported the dynamic nucleation in a 15% water sucrose solution that resulted in the immediate formation of ice nuclei and subsequent growth into equiaxed crystal after exposure to ultrasonic pulse generated from a transducer operating at 20 kHz.

2.3.2 Activation of substrates

Solidification process in actual metallic melts essentially takes place heterogeneously on existing nucleating substrates, which are either externally added (grain refining agents) or present within the melt as an indigenous impurity/inclusions. In any metallic alloys such as aluminium or magnesium, the impurities can be in the form of non-metallic compounds, oxides, carbides that can act as effective grain nucleating sites. Activation of substrates in true sense refers to the wettability of the particles and formation of metallised surface layers, leading to nucleation. UST provides a useful approach for substrate activation by converting hydrophobic inclusions into potent solidification sites [124]. Any kind of micro- and sub-micron inclusions within the melt that is compatible with the solidifying phase, is likely to behave as active nucleant. This compatibility of the substrate can arise due to similar crystallographic structure or existence of adsorbed solid phase on the surface of the nucleating substrate. To ensure the stability of the nucleation site, it is important that the adsorbed solid phase is stable above the liquidus temperature of the alloy. The presence of surface discontinuities in the form of cracks/fissures within the solid phase can further promote nucleation through the capillary effect where the actual melting temperature is much larger than the liquidus temperature under equilibrium conditions. Nevertheless, due to the presence of gases within the surface of microcracks, the melt flow is restricted within such inclusions, thus inhibiting the wetting of substrates during solidification.

Enhanced wetting can activate these inclusions through sono-capillary effect [104,124]. Sono-capillary or ultrasonic capillary effect is a phenomena that occurs when a liquid is subjected to ultrasonic irradiation in the vicinity of the narrow capillaries, voids, and pores, which causes the liquid to rise and penetrate into these narrow channels. This effect has recently been visualised at a micro scale through synchrotron observations of the instantaneous filling of micro-capillary channel/groove of size of the order of few hundred microns in molten Al-10wt% Cu alloy [104]. However, the observational validation related to intermetallics and crystal matrix nucleation on oxides facilitated by acoustic cavitation is still very limited. Wang

et al. [137,147] recently demonstrated the nucleation of primary intermetallic crystals on existing oxide inclusions using both in-situ (X-ray synchrotron) and ex-situ (TEM/SEM) observations in ultrasonically treated Al alloys.

The introduction of ultrasonic oscillations within the melt at intensities greater than the threshold causes the formation of bubbles near the crack opening. The violent collapse of the formed bubbles after pulsating for a while within the cavitating field generates high energy pressure pulses and liquid jets, which pushes the melt into the cavities through the mechanism of sono-capillary effect followed by solidification [104]. The emitted pressures upon cavitation collapses can range from 0.3 – 46 MPa in the localised region of the cavity, which is sufficient for filling of the capillary openings with sizes in submicron range. Simultaneously, the substrate also gets rid of the gaseous phase and other surface contamination that allows for easier access for the melt flow within the capillaries. Thus, the cavitation induced activation and local changes in the equilibrium solidification conditions cause the solidified portion inside the capillary to remain solid at temperatures equivalent to the surrounding liquid making it a perfect site for heterogeneous nucleation to occur. This substrate activation mechanism for nucleation should ideally be the same for other inclusions like oxides, intermetallics or any such non-metallic solidifying phases. Through nucleation, activation of impurities may also cause refinement of primary phases upon solidification. Eskin and Eskin [1] reported that ingots produced upon ultrasonic treatment of the high-strength Al alloy melt leads to increase in the number of active nuclei (evaluated based on the number of grains) by several orders of magnitude when compared to the one without the cavitation treatment. Figure 2.10 shows the effect of UST on the number of nuclei activation sites in the DC cast ingot of a high strength Al-Zr-Mg-Cu alloy in dependence on the billet diameter. It can be seen that ultrasonic treatment of small ingots with a diameter in the range of 60 – 70 mm causes substrate activation with nuclei density reaching up to 10^9 cm^{-3} compared to 10^3 cm^{-3} without treatment. For middle (200 – 300 mm) and large (800 – 900 mm) size ingots, the nuclei density difference between the treated and untreated ingot reduces by 10^4 cm^{-3} and 10^3 cm^{-3} , respectively. As the billet size increases, the difference between the nuclei density in treated and untreated alloy decreases though the difference is still significant.

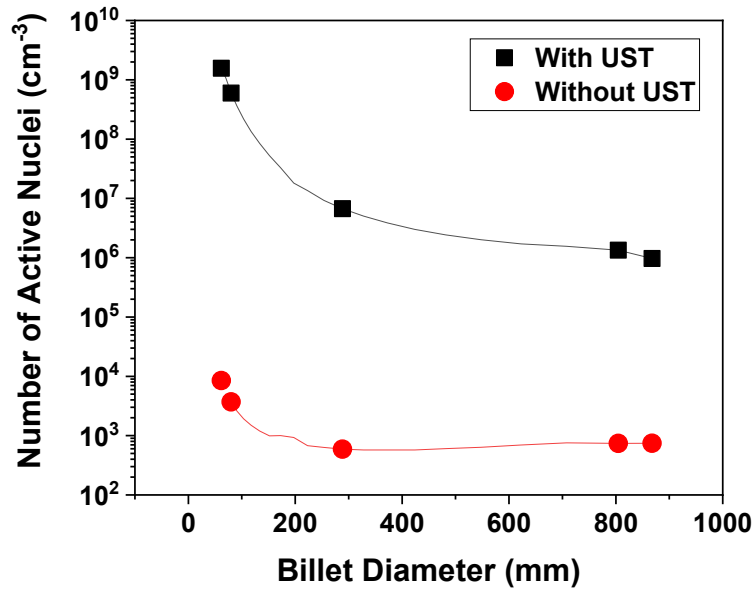


Fig. 2.10 Number of active solid inclusions formed during casting of Al-Zn-Mg-Cu-Zr alloys with and without UST. Adapted from [1].

Current viewpoint on grain refinement includes the theory of growth restriction, with the grain size dependent on two factors; (a) heterogeneous nucleation substrate activation through constitutional supercooling (positive temperature gradient resulting in supercooled region of liquid ahead of the solidification front) induced by solute segregation within the melt, and (b) grain growth restriction owing to latent heat discharge from the adjacent grain and solute segregation occurring near the S/L interface. This theory can be adopted for the cavitation-driven grain refinement where the grain size D_o depends on the process parameters as [154]:

$$D_o = 5.6 \left(\frac{D\Delta T}{vQ} \right) + \frac{1}{\sqrt[3]{g(A_s)N_v}} \quad (2.5)$$

where, D denotes the diffusion coefficient of solute present within the melt, ΔT refers to the nucleation undercooling, v refers to the growth rate of the S/L interface, and Q is the restricting factor for grain growth, A_s is the amplitude of ultrasound and N_v specifies the particle number density. StJohn et al. [154] applied this approach to account for cavitation induced grain refinement in magnesium alloys and found that the introduction of ultrasonic waves led to drastic rise in the number of nucleation sites following the substrate activation mechanism discussed above.

2.3.3 Cavitation-assisted fragmentation

The phenomenon of solid phase fragmentation has been widely recognised as a key mechanism for grain refinement in metallic alloys by several researchers [2,23,152,155,156]. Implosion of cavitation bubbles in liquid metal can induce dendrite/crystal breakage and the resulting fragments can further act as potent substrates for nucleation of new grains. Early works by Chvorinov [156] indicated that the solidifying dendrites near the S/L phase interface (semi-solid region) were displaced from the advancing solidification front through generated convection currents and the broken crystals were transported into the bulk liquid, possibly acting as active substrate for grain growth as long as they do not re-melt. Balandin [155] supported this observation and suggested that the inactive inert solid particles could become potent nucleation sites. As soon as the solid phase is detached from the solidification front, adsorbed nuclei present on the crystal surface are dispersed within the bulk liquid causing crystal to melt thus leaving only the active inclusion for further grain nucleation. Nevertheless, these notions did not explain the mechanism of solid crystal (dendrite) fragmentation and/or detachment from the solidification front. Previous evidence has suggested the dendrite breakage induced by the convective flow field as a more likely mechanism for dendrite/crystal separation. This physical rupture of the solid phase has been attributed to melt embrittlement, mechanical deformation and development of high angle interfaces [2,157]. The convective forced flow (acoustic streaming) can transport liquid metal from the bulk to the supercooled region leading to partial re-melting of loosely bounded crystals. The investigation of solid phase fragmentation conducted on microscopic level under cavitation confirms the crystal separation triggered by re-melting of dendritic root. The reasons for this re-melting can be associated with capillary, solute or thermal reactions. Solute atoms segregation at the solid/liquid interface affects the growth rate kinetics of crystal evolution and coarsening, which in turn produces necking and solute build-up at the dendrite roots caused by both the convective flow close to interdendritic region and solute rejection [158–161]. Accumulation of the solute produces localised constitutional superheating and finally melting of solid phase present nearby. Changes in the equilibrium solidification conditions in addition to capillary-based effects increases the solubility of solutes as compared to the bulk areas. Transport of dendritic fragments to the phase transition region and away into the bulk of liquid metal seems to be promoted by the forced convective flow. This kind of breakage is specifically valid for elongated dendrites, which are exposed to varying flow field that expedites the re-melting process and induces fatigue like fracture [137].

Figure 2.11 shows the schematic image of dendrite/crystal breakup caused by the impact force resulting from bubble collapse. Wang et al. [103] was first to actually observe fragmentation of various intermetallic crystal formed in Al alloys by pulsating and collapsing bubbles in water subjected to ultrasonic cavitation using in-situ high-speed imaging technique. It was shown that crystals tend to undergo fatigue type fracture before fragmentation when subjected to power ultrasound. However, detailed fragmentation study of these primary crystals under controlled cavitation environment has not been conducted yet. Other than ultrasonic cavitation, induced acoustic streaming can also be helpful in transfer of cavitating bubbles closer to the growing crystal/dendrite to stimulate its continuous fragmentation response and further transport of fragments into the bulk liquid metal.

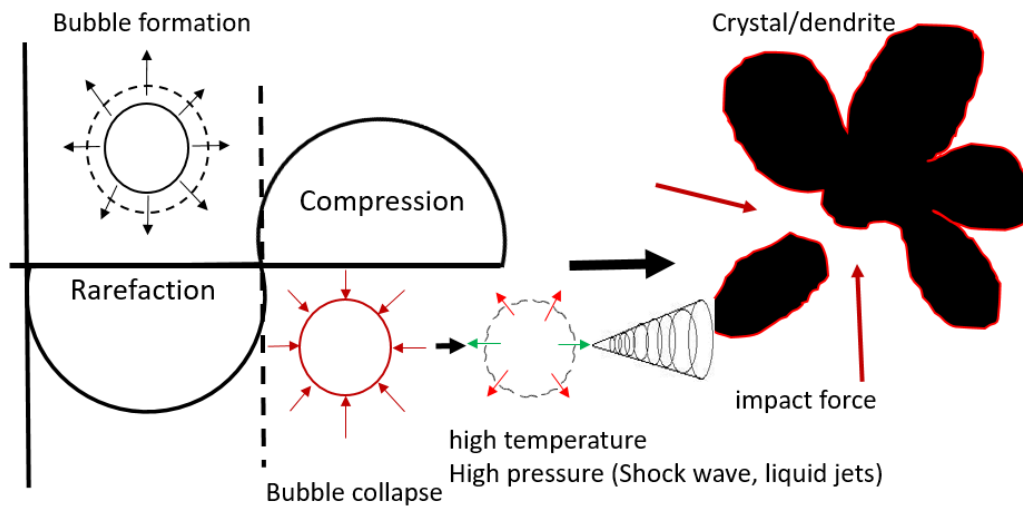


Fig. 2.11 Schematic illustration of the mechanism of cavitation-assisted fragmentation of dendrites/intermetallic crystals caused by the impact force arising from emitted shock waves and liquid jets upon bubble collapse. Adapted from [162].

For understanding the influence of intermetallic crystals on grain refinement in Al solidifying melt, it is important to study the heterogeneous nucleation of grains during solidification process as a whole. As discussed previously in Section 2.3.1, the typical analysis assumes the formation of a cap shaped nuclei on a flat solute particle (see Fig. 2.8a). The threshold energy for nucleation is reduced when the contact angle between nucleus curvature and liquid metal is smaller. If an active adsorbed layer exists on such particles (with zero contact angle) then these would act as perfect seeds for nucleation of Al grains (with no energy barrier). It doesn't necessarily mean that grain nucleation would occur on each of those particles. The formed nucleus would grow laterally until the curvature reaches maximum size with hemispherical interface. Further growth can occur with the reduction of the melt interface curvature. In such

case, if the diameter of the solute particle (d_p) is smaller than the critical size of the nucleus, then free growth of the nucleus would cease. The free growth would occur with larger undercooling when the critical size is reduced and size of the solute substrate becomes equal to the critical size of the formed nucleus. Plenty of research have revealed that grain size is dependent on the nucleation potential, nuclei density and growth restriction parameter of the solutes [163–165]. The size of the solute particles (d_p) effects the grain size determination from the free growth model perspective as [166,167]:

$$\Delta T = \frac{4\sigma_{S/L}}{\Delta S_v d_p} \quad (2.6)$$

Here, ΔT signifies the melt undercooling and ΔS_v represents the entropy for fusion. It should be noted here that the critical condition for free growth is not hugely altered by the wetting efficacy of the solute particle. The grain nucleation initiates first on a largest substrate with minimum undercooling and then based on the particle size and number density, there is equivalent spread in the critical undercooling values for further grain nucleation [166]. Thus for a given particle size distribution, grain initiation is only predicated on the maximum ΔT and is independent of time.

Zirconium (Zr), titanium (Ti) and vanadium (V) have been identified as peritectic forming elements that have potential of producing grain refinement in various Al alloys [168,169]. Significant grain refinement was observed in peritectic Al alloys with the inoculation by primary intermetallic crystals and growth limiting factor of such solutes [169–171]. For a hypereutectic Al-Si alloy containing more than 12% of Si, primary crystals act as a major structural constituent. These crystals generally nucleate and grow in the liquid as discrete particles. With the continuous growth of the primary crystals to a definite size, the particles get carried away by the convective flows. After a certain period, these crystals may come together and form agglomerates or clusters. Agglomeration of these crystals can affect the deformation behaviour of the as-cast product due to their hard and brittle nature (for example, primary Si in Al-Si alloys) resulting in stress concentration at the edges. However, primary particles (other than Si) can also work as a grain refiner (as long as they are fragmented into tiny particles) leading to improvement in the mechanical properties such as elastic modulus, wear and thermal resistance, thermal expansion coefficient of the alloy system under consideration. The properties that the final cast product will possess will depend on the extent of grain and crystal refinement. Wang et al. [171] performed the crystallographic study of the effect of Zr in grain refinement of Al cast alloy and reported that primary Al_3Zr intermetallics crystals act as perfect

heterogeneous nucleation sites for α -Al grains. However, the role of Zr in Al alloys is somewhat contentious. On one hand, Zr forms primary Al_3Zr at peritectic compositions and on the other, the grain refining capability of Al_3Zr is also moderate and these intermetallics usually tend to be bigger in size when compared to the typical exogenous inoculant such as TiB_2 particles, which is detrimental for the mechanical properties of the alloy [169–171]. Efficient refinement of these primary crystals can produce significant grain refinement by increasing the number density of fragmented particles. Earlier investigations have indicated that UST considerably helps in the refining of primary crystals such as $\text{Al}_3(\text{Zr,Ti})$, Al_3Ti and Al_3Zr that facilitate heterogeneous nucleation of Al, through their fragmentation via ultrasonic cavitation and streaming [147,172–176].

Now in order to comprehend and numerically model the fragmentation/refinement mechanism of the intermetallic crystals inside the solidifying melt caused by the acoustic cavitation, mechanical properties of intermetallics (e.g. elastic moduli, yield stress, impact/fracture toughness) are vital inputs. These properties can also have a generic value and can be utilised for other applications such as alloy development. Manoylov et al. [177] modelled the break-up of nano-particle clusters in Al- and Mg-based metal matrix nano-composites. It was observed that the Stoke drag force caused by stirring was not enough to breakdown the crystals and the break-up force was dependent on the selection of adhesion model. In principle, the implosion of cavitation bubbles which is triggered by high velocity pulses during the UST can lead to disintegration of the crystals/agglomerates. The model also predicted that the small particle clusters were relatively easier to de-agglomerate. Considerable amount of research work have been conducted to obtain the properties of intermetallics such as Al_3Zr and Al_3Ti using different theoretical and experimental approaches [178–181]. Nakamura et al. [178] measured the elastic constants of Al_3Ti and Al_3Zr single crystal using the velocity of ultrasonic waves through a pulse echo method. Values of elastic/shear modulus and Poisson's ratio were then evaluated for polycrystalline Al_3Ti and Al_3Zr intermetallics using stiffness and compliance constants of single crystals. However, till now there has been no study conducted to directly measure the mechanical properties of the extracted single crystal of Al based intermetallics using depth sensation indentation (DSI) system. Apparently, to extract the mechanical properties of the intermetallics of nano size dimensions and at elevated temperatures is not that simple. Nevertheless, using state-of-the art high temperature nanoindentation technique, these properties can be accurately determined. The capability of depth sensing indentation techniques goes beyond the conventional micro and macro indentation systems for determining hardness.

Various material properties can be quantified using a load-displacement curve. These include, indentation hardness, elastic and shear moduli, yield stress/residual stress, fracture toughness, strain hardening component, elastic and plastic energies of the sample material. Numerous research work have been undertaken to accurately determine the mechanical properties such as hardness and elastic modulus [182–187]. The below section will discuss mechanical properties of primary intermetallic crystals and the fundamentals of the measuring technique, which will be used later in Chapter 3.

2.4 Mechanical properties of intermetallics

Properties of as-cast alloys are affected by the presence of primary intermetallics. The mechanical properties of ultrasonically treated hypereutectic alloys is usually linked to the shape, size and number distribution of the fragmented intermetallic crystals. Intermetallics of large size typically tend to reduce the tensile strength, ductility and toughness of the castings as they are brittle in nature and could acts as stress concentration points [188]. It has been reported that alloy such as Al-Ni and Al-Fe are not workable without the refinement of intermetallic crystals [189]. Nevertheless, refinement of these formed crystals can allow the fragments to serve as reinforcing particles to produce MMCs [149]. The determination of mechanical characteristics of these primary crystals can potentially be helpful in outlining the best treatment conditions and operating parameters that can expedite the fragmentation/de-agglomeration process in actual melts.

Intermetallic compounds can be either a primary or if formed after the Al solid solution through eutectic reactions referred to as secondary phases formed in either binary or complex order metallic systems. The physical nature of these compounds attract attention owing to two primary reasons:

- (a) Lot of these intermetallic compounds hold desirable mechanical properties.
- (b) These crystals themselves are sometimes considered as primary materials for structural and elevated temperature applications.

The theoretical physical properties of these intermetallic compounds are inherently determined on the basis of interatomic forces present within the material. The magnitude of these forces is defined in terms of elastic modulus. Typically, 5-10% of the elastic modulus is taken as the

theoretical strength for a defect free crystal as a basic approximation [190]. Nonetheless, in reality these crystals exhibit much lesser strength and mostly fail through fracture or yielding much below their theoretical strength. The early failure of crystals is driven by the presence of defects/imperfections within the structure. It is well-known that the extensive fluctuations in the real strength of a solid phase alloy can be realised through variation in crystal's fine structure. Gilman [191] suggested that in order to increase the strength of the alloy at least by a degree or so, it is imperative to involve solid interstitial phases such as carbides, borides or nitrides, which exhibit high modulus value and offers large resistance to the movement of dislocations. However, due to their brittle behaviour, their use is rather limited in structural applications.

Although, numerous experimental and modelling studies have been conducted for interpreting mechanical behaviour of several metallic alloy systems containing a wide range of intermetallic compounds, knowledge on mechanical properties of intermetallic itself are comparatively less and is confined mostly to first principle methods for some Al based compounds owing to experimental limitations [179,180,192–195]. The search and need for thermally stable, oxidation resistant and lightweight materials has directed researchers towards the exploration of Al based trialuminides intermetallics of type Al_3X with a tetragonal lattice structure. Here X can be group IV-A elements such as Zr, Ti, Hf which form binary Al compounds that crystallise with ordered structures based on tetragonal lattices ($\text{D}_{022}/\text{D}_{023}$).

Al_3Zr have attracted lot of attention and extensively studied in recent years as reinforcing materials in Al based composite materials and Al-Zr binary alloys owing to its exceptional properties in terms of low density (4.1 g/cm^3), higher melting point (1580°C), high hardness, elastic modulus ($\sim 200 \text{ GPa}$) and high resistance to corrosion [196–200]. Nevertheless, intermetallics like this and most other trialuminide compounds are brittle in nature. The plausible reason for the brittle behaviour of Al_3Zr is their non-cubic D_{023} crystal structure. With regard to its poor ductility, the fracture toughness turns out to be a suitable parameter for its characterization. Although Al_3Zr crystallises mainly with a D_{023} tetragonal crystal structure, it can also develop as metastable L_{12} cubic structure through either precipitation process during solidification of supersaturated Al solid solution [201] or mechanical alloying process [202]. The L_{12} metastable Al_3Zr when heated, it converts into stable D_{023} state. It is understood that the elastic behaviour of single crystal compounds are rarely isotropic in nature and the formation of microcracks and defects within the material is a result of elastic anisotropy [203]. Determination of elastic constant (defined as the index of materials' elasticity, which derives

from stress-strain behaviour in an anisotropic medium) is a very important parameter to characterise the physical properties of intermetallic compounds. Knowing the elastic response of a material not only provides information regarding anisotropy but also provides indication of the crystal dynamics on mechanical properties such as ductility, brittleness, hardness, etc. Often when the measurement of properties of such compounds are not attainable using experimental means, theoretical simulation methods become very handy and effective to predict their properties. Thus, lot of research has been performed in determining the elastic anisotropic properties including elastic, bulk, shear modulus by applying first principle energy calculations based on the density functional theory [179,195,204–208]. Nakamura and Kimura [178] experimentally measured the elastic stiffness constants from the ultrasonic wave velocities for different crystal orientation (plane). For a symmetric tetragonal structures $D0_{22}$ and $D0_{23}$, the stiffness matrix contains a total of six non-zero independent elastic stiffness constants (C_{11} , C_{12} , C_{13} , C_{33} , C_{44} and C_{66}). In tetragonal systems, constants C_{11} and C_{33} mean the compressibility of the crystal structure along the three axes and generally corresponds to the interatomic bonding forces and the average distance between the atoms. Constant C_{44} signifies the ability of the material to resist shear in (1 0 0) and (0 1 0) plane, whereas C_{66} indicates the ability to resist in (0 0 1) plane [178,207]. The elastic constants such as Young's, shear and bulk modulus and Poisson's ratio was also found to be direction and plane dependent. Like for example, for Al_3Zr single crystals, the elastic modulus was found to be highest in $\langle 1\ 1\ 0 \rangle$ direction with atoms arranged in a closest packed manner. The theoretically calculated Young's, shear and bulk in different crystal directions can be found elsewhere [207]. Table 2.2 shows the list of mechanical properties for the Al_3Zr intermetallic compound at room temperature available in literature and obtained using different experimental and theoretical approaches. Note, the modulus values shown in this table from the first-principles method has been estimated by the Voigt-Reuss-Hill (VRH) approximation. In this thesis, we haven't focussed on the anisotropy nature of properties i.e., the effect of crystal plane/direction on the mechanical properties and is out of scope for the present research work.

Table 2.2 Mechanical properties of the Al₃Zr intermetallic measured using theoretical and experimental techniques.

Technique	Elastic modulus (GPa)	Shear modulus (GPa)	Bulk modulus (GPa)	Poisson's ratio	Hardness (GPa)	Fracture toughness (MPa√m)
Ultrasonic acoustic wave	205* [209] 201.8* [178] 196* [210]	90 [211] 85.1 [178]	95.4 [211] 102.2 [178]	0.141* [211] 0.185* [178]	--	--
First principles method	167.2 [#] [212] 197.6* [179] 197.2* [181] 215.3 [@] [204] 201.3 [@] [180]	65.3 [212] 84 [181] 83.2 [179]	100.7 [181] 105.3 [179] 100.05 [204] 101.5 [212]	0.17* [181] 0.233 [#] [213]	18.45 [207]	0.85 [180]
Microhardness indentation	--	--	--	--	7.631 [214] 4.2-7.4 [215]	

* D0₂₃

[#] L1₂

[@] D0₂₃, C1₁

One of the techniques to assess the mechanical properties of such materials at smaller length scales is nanoindentation that involves continuous capturing of applied load and the resulting probe displacement upon indentation. DSI is mainly utilised to obtain hardness, elastic modulus, and fracture toughness of the material subjected to indentation under varying temperature conditions. The technique of nanoindentation was first established in early 1980's laying out the ability to continuously record and sense the mechanical load (P_d) and the indenter displacement (h) from the surface throughout the loading and unloading phase [216]. The appeal of this technique essentially originates from the point that the nanomechanical properties can be directly measured using the P_d - h curve without involving any analysis of the indentation impression. This technique also allows for accurate measurement of material's properties, especially in cases of alloys that contain various secondary phases. Unlike micro indentation, the smaller indent size can further enable determination of properties of intermetallic phases.

In the last 40 years, significant amount of effort has been laid on the foundation for the analysis of the depth sensing indentation data. One of the most simple and well-known method of

analysis and interpretation of the P_d - h curve was given by Oliver and Pharr (O&P) [217]. However, since a decade or so, a number of improvements in the O&P method have been made in terms of precision and its application domain. This analysis was designed to quantify the elastic modulus and hardness of the elasto-plastic material using the load–displacement data applicable to different axisymmetric indenter (Berkovich and sphere) with the assumption that deformation during loading of the indenter is both elastic as well as plastic and while unloading is purely elastic in nature. Figure 2.12 shows a typical nanoindentation load-displacement curve data set obtained using a sharp Berkovich indenter. To obtain the accurate values of elastic modulus and hardness from this P_d - h curve, it is foremost important to know certain parameters that can be measured experimentally. The three most essential parameters are the maximum load P_m , the corresponding maximum displacement h_m and the contact stiffness of unloading curve $S = dP_d/dh$. The final depth (h_f), i.e. the permanent depth of penetration, is also one of the key parameter to be known.

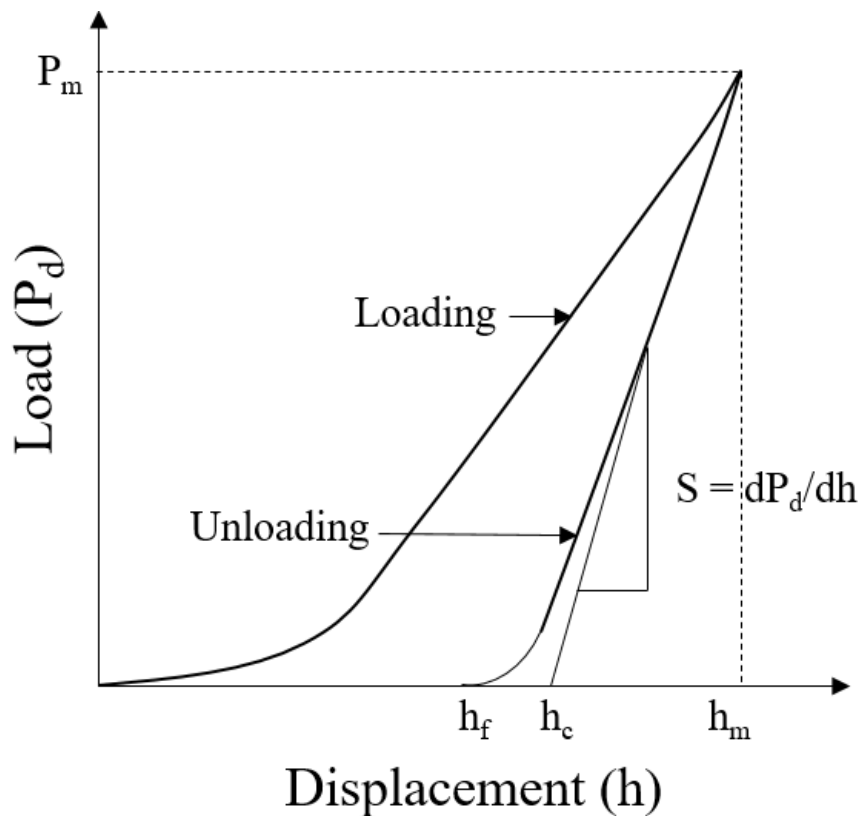


Fig. 2.12 Schematic of load-displacement curve obtained from DSI experiment indicating loading, unloading and compliance curves with maximum load, P_m , maximum penetration depth, h_m , residual/final impression depth, h_f , slope of the unloading curve, dP_d/dh , which allow elastic modulus and hardness of the specimen to be evaluated.

The O&P method is basically an extension to the model proposed by Doerner and Nix (D&N) [182]. The model takes into consideration that flat punch ballpark figure cannot be applied to behaviour of the unloading curve. As per the D&N model, the unloading curve is assumed to be linear as a result of the constant contact area upon the withdrawal of the indenter. However, further research has suggested that the unloading curve are usually curved and can be very well estimated using a power law function [217]:

$$P_d = k(h - h_f)^{m_k} \quad (2.7)$$

Here, k and m_k denotes the fitting constant depending on the indenter tip shape [217]. The value of m varies between 1.2 and 1.6 and does not include any integral value as explained using ‘effective indenter shape’ [218].

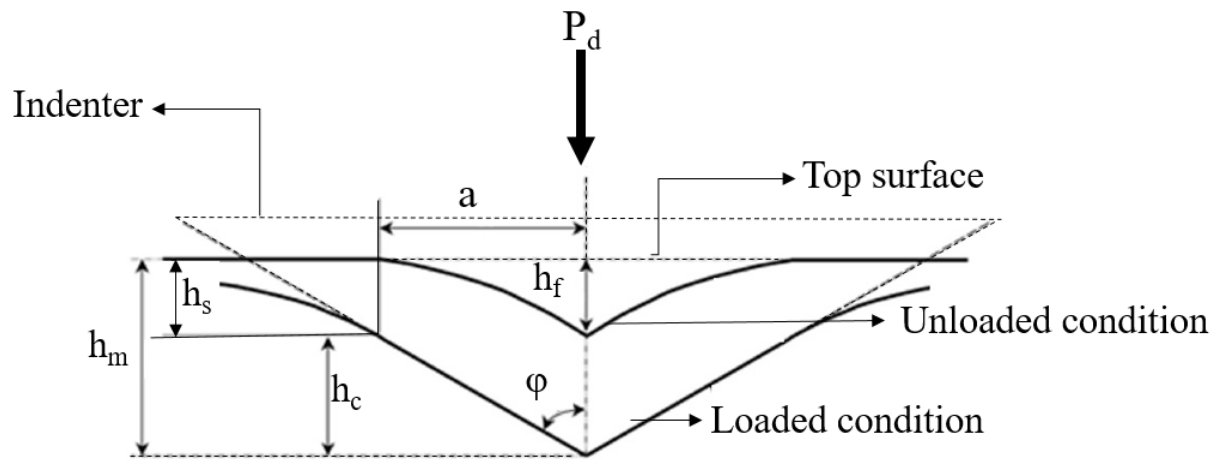


Fig. 2.13 Schematic image showing the cross-section of indentation at maximum loaded condition and after complete unloading.

The process of determining elastic modulus and hardness can be explained using Fig. 2.13 based on an assumption that the conical indenter with same depth to area relationship i.e. $\phi = 70.3^\circ$ is a best model for a sharp Berkovich indenter and its performance. Another major assumption says that the model based on indentation using a flat elastic half space (rigid punches) can be pre-eminently used to define the sinking of the contact periphery [219–223]. The application of this model is however limited by the fact that the material does not take into consideration the effect of pile-up occurring at the contact periphery which usually happens in elastic plastic materials. Considering that the pile up is negligible, the magnitude of sink-in depth, h_s can be expressed as [185]:

$$h_s = \varepsilon \frac{P_m}{S} \quad (2.8)$$

where the constant ε is material dependent based on indenter geometry. For some indenters like conical punch, the value of ε is 0.72, for spherical punch (paraboloid) it is about 0.75 and 1 for flat punch [219]. As a standard for the model analysis, ε is taken as 0.75 and constant m_k is 1.5 deduced from empirical findings and through best approximation of the unloading curves. The contact depth (h_c) can be expressed using the sink-in depth equation as follows [185]:

$$h_c = h_m - h_s \quad (2.9)$$

$$h_c = h_m - \varepsilon \frac{P_m}{S} \quad (2.10)$$

Assuming that the projected area of the indenter is at a contact depth h_c from the top surface is denoted by an area function (indenter shape function), $g(h_c)$, the corresponding contact area A_c is given by [224]:

$$A_c = \pi h_c^2 \tan^2 \varphi \quad (2.11)$$

This shape function has to be prudently standardised so as to avoid any kind of deviations that may arise from the non-ideal geometry of the indenter. Rounding of the tip is quite an evident cause as the rubbing action while the indenter penetrates into the sample can lead to severe deviations in the shape function. Indentation hardness can be computed based on the contact area calculations using the following expression [185]:

$$H = \frac{P_m}{A_c} \quad (2.12)$$

It is to be noted that the above expression of indentation hardness is measured from the area of contact under the loading conditions and can be reasonably different than the hardness measured using residual impression analysis. Hardness measured using contact area measurement will be only valid if there is substantial elastic recovery during unloading. This recovery is nevertheless significant for materials with lower values of E/H [225]. Elastic modulus measurements can be obtained from the relation of contact area and unloading stiffness (S) given by [226]:

$$S = \beta \frac{2}{\sqrt{\pi}} E_{eff} \sqrt{A_c} \quad (2.13)$$

where the effective elastic modulus (E_{eff}) can be expressed as:

$$\frac{1}{E_{eff}} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i} \quad (2.14)$$

Here ν and ν_i denotes the Poisson's ratio of specimen and the indenter, respectively, E_{eff} takes into consideration that the elastic displacements occur in both the specimen (E) and the indenter (E_i) with respective elastic constants. It is to be noted that Eq. 2.13 is a generic relationship that can be applied to any axisymmetric indenter [217,227]. Even though the above Eq. 2.14 was established for the elastic based contact initially [217], it has been found out that this expression can also be applied to the elastic-plastic based contact in the very same way [227]. Moreover, any kind of changes in the axisymmetric indenter geometry, pile-up or sink-in does not have any effect on it. The dimensionless term β was initially taken as 1 for determining the hardness and modulus values to account for variations in stiffness value owing to lack of symmetry in axial direction for pyramidal indenters. Nevertheless, it was later recognized that value of β can considerably vary from 1 during indentation of an elastic half-space using axisymmetric rigid conical indenter [228].

Quantification of fracture toughness in the case of materials with small-scale volumes has been undertaken by applying various approaches. However, use of indentation based technique involving sharp three-sided pyramid indenters has been widely employed owing to relatively easier testing and difficulties arising from sample preparation [229–233]. This technique of determining fracture toughness takes into consideration the crack length originating from sharp indentation tip impression at a given specific load. Depending upon the geometrical configuration of the indenter and the nature of crack, i.e., lateral, radial, cone, median or half-penny, an appropriate model for calculating fracture toughness can be chosen [234,235]. The mathematical expression for interpretation of indentation fracture toughness (K_c) is typically of the form [234,235]:

$$K_c = \frac{P_m}{c^{3/2}} \prod \left(\frac{E}{H}, \nu, \phi, \frac{c}{a} \right) \quad (2.15)$$

Here, c denotes the length of crack, and a is the distance measured from the centre point of indentation to one of the corners of contact (contact size). Thus, in order to estimate the fracture toughness, it is essential to have information regarding elastic properties of the intermetallic compound, generated crack lengths and the geometry of the indenter involved. In case of large cracks where $c/a \gg 1$, the above equation can be further simplified leading to the expression of the classic Law-Evans-Marshall (LEM) model [229,230]:

$$K_c = \alpha_c \sqrt{\frac{E}{H} \frac{P_m}{c^{3/2}}} \quad (2.16)$$

where, α_c is the LEM empirical constant depending upon geometry of the indenter. The value of α is usually taken as ~ 0.032 for a cube corner type indenter and ~ 0.016 for Berkovich- and Vickers-type pyramid sharp indenters which is experimentally deduced by analysing number of brittle materials. A cube corner-type indenter is usually chosen as it helps in considerably reducing the crack threshold limit. Schematic representation of a typical indentation produced by a cube corner-type indenter is shown in Fig. 2.14.

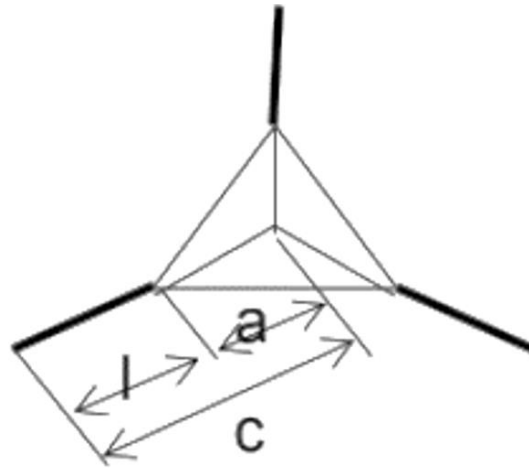


Fig. 2.14 Schematic image showing a typical indentation mark obtained from cube corner indenter (black line shows the generated cracks of length, c around the indentation corners).

To summarise, in this chapter, we gained the fundamental knowledge associated with the UST process for grain refinement of aluminium cast alloys. We also looked at the basics of acoustic cavitation, cavitation threshold, factors affecting cavitation activity and acoustic emission characterisation that helped us to understand the established structural refinement mechanisms, i.e. cavitation aided nucleation, activation of substrates and cavitation assisted fragmentation/de-agglomeration. However, the underlying mechanism related to structural refinement obtained through breakage/disintegration of solid phases such as intermetallics and secondary phases like oxides, where the fragmented solid phase act as potent nucleating sites for Al grain growth, has not yet been adequately addressed in the literature and is still under scrutiny. We further learned that in order to analyse and model the breakage of solid phases such as intermetallics in liquid aluminium environment, their mechanical properties such as elastic modulus, hardness and fracture toughness are crucial parameters to understand the fracture behaviour under the cavitation action. Nevertheless, these properties especially at

elevated temperatures are missing from the literature database. Thus, the subsequent chapters will focus on closing these existing fundamental knowledge gaps related to determination of mechanical properties of Al_3Zr intermetallics (Chapter 3) and observation and evaluation of the cavitation-induced fragmentation and de-agglomeration process within a transparent liquid analogue to molten aluminium using an in-situ advanced high-speed optical photography technique and state-of-the-art cavitation sensors (Chapter 4, 6 and 7) before moving to application of UST and determining its effectiveness in scaling up the refinement process of Al melts during casting (Chapter 8 and Appendix A3).

Chapter 3

Mechanical properties of primary intermetallic crystals[§]

Having developed a basic knowledge of ultrasonic treatment process, acoustic cavitation fundamentals and its application in liquid metal processing, we now delve deeper into the experimental research sections (Chapter 3 to 8) targeting to achieve holistic understanding of governing grain refinement mechanisms during ultrasonic melt treatment process. However, before we study the intermetallic fragmentation process, it is imperative to evaluate the mechanical properties of the primary Al_3Zr intermetallics which allows for accurate assessment of fracture behaviour under cavitation action through analytical means.

*This chapter specifically deals with the measurement of mechanical properties at ambient and elevated temperature conditions using nano-indentation experiments. In this study, we employed single and polycrystalline intermetallic specimens that were produced after chemically extracting the intermetallics from an Al-3 wt% Zr alloy matrix. The properties such as elastic modulus, hardness and fracture toughness were determined under quasistatic loading conditions using a geometrically fixed Berkovich nano-diamond and cube corner indenter, respectively at room temperature. The specimens were further subjected to multicycle indentation testing (MCT) using Vickers indenter to understand the fatigue response of intermetallics at high load low cycle setting. The mechanical properties of intermetallic specimen has also been investigated as a function of operating temperature using high temperature nanoindentation technique. The results show that Al_3Zr intermetallics are highly brittle in nature with high elastic modulus, hardness and low fracture toughness close to that of quartz at ambient temperatures similar to the values obtained from first principle calculations. The properties were found to be slightly dependent on intermetallic orientation, where polycrystalline sample showed higher elastic modulus than single crystal specimens. MCT experiments revealed that contact pressure of more 7 GPa is needed to fracture the crystal under dynamic loading conditions. **This is the first ever study that attempts to accurately measure the properties of intermetallic up to 700°C using high temperature nano-indentation.** Elevated temperature measurements indicated that intermetallics had high creep resistance at low and intermediate temperatures but exhibited high plastic deformation close to melting point of pure aluminium.*

[§] Some text extracts taken from published article ‘A. Priyadarshi, et al., in *Light Metals 2020*. (Springer, 2020), pp. 168-173’ and ‘A. Priyadarshi, et al., *Ultrason. Sonochem.* **70**, 105260 (2021)’ – Reproduced after permission.

3.1 Introduction

Aluminium based metal matrix composites (MMCs) have recently emerged as a highly desirable and promising advanced structural material that successfully meets the demands in multitude of industrial applications, but more specifically in automotive, aerospace and construction sectors [6,236,237]. Incorporation of particulate reinforcements into Al matrices in the form of ceramic particles or whiskers of carbides and oxides provide excellent physical and mechanical properties in terms of high specific strength, corrosion resistance and lower thermal expansion coefficient [6,197,238,239]. The strength of these Al MMCs depends on the interfacial bonding (physical and/or chemical) between the matrix and the reinforcing particles. Enhancement in wettability of the reinforcements further facilitates the improvement in the adhesion properties between the different phases in the composite. Since last few decades, the use of transition metals trialuminide (Al_3X) intermetallic compounds (IMCs) such as Al_3Zr and Al_3Ti as reinforcements in Al alloys has attracted a lot of attention in developing high quality MMCs [197,240–243]. These IMCs have densities close to that of ceramics and comparable elastic modulus making them a good candidate for reinforcements in Al alloy matrix. Above all, these trialuminides are also in thermodynamic equilibrium with the Al matrix with strong physico-chemical bonding unlike ceramics with intermediate interfacial zones.

A lot of work have been focussed on developing particle reinforced light MMCs either by the use of casting [141,149,238,239,244,245] or mechanical alloying [199,200,241–243] techniques described in the literature. Processes such as stir casting and liquid metal infiltration involves the incorporation of particulates extrinsically to the molten metal similar to mechanical alloying which involves mixing of solid particles into the solid matrix. It is therefore very important to make sure that a good wettability is achieved between the particulate and the matrix. The formed primary intermetallic crystals tend to have a needle or plate like cross-section with propensity to develop into large shaped particles that can adversely affect the mechanical properties of the alloy. Hence, their fragmentation or changed morphology would be beneficial for the mechanical properties of the as-cast alloy. It has been also observed that the refined primary crystals can nucleate Al grains and therefore refine them [246]. To this end, IMC reinforced MMCs have been produced that promotes wetting and structural refinement (as explained in section 2.3.3 of Chapter 2) through the mechanism of heterogeneous nucleation and/or cavitation-induced fragmentation/de-agglomeration of secondary phases/oxide inclusions within the melt [141,149,238,244,245,247] increases the

nucleation potency of such refined crystals. However, lack of information related to mechanical properties of these IMCs especially at high temperatures, prevents the analysis and modelling of this process.

Work in this Chapter 3 focuses on the determination of mechanical properties of Al_3Zr IMCs at elevated temperatures (from room temperature and up to 700°C). Properties such as hardness (H), elastic modulus (E), and fracture toughness (K_{IC}) can also act as vital inputs for accurate numerical modelling of the intermetallic fragmentation response under range of temperatures in order to realize the optimum ultrasonic treatment conditions. Different experimental (ultrasonic acoustic wave, microhardness indentation) and theoretical (first principle method) approaches have previously been undertaken to evaluate the physical properties of Al_3Zr crystals at room temperature (RT) [178–181,192,195,204,209,211,212]. However, to the best of our knowledge, very limited number of studies have been conducted that discuss the effect of temperature on the mechanical properties of intermetallic phases. High temperature (HT) DSI measurements can help fill this existing gap in literature.

DSI is an established nanoindentation technique that primarily operates at nanometer resolution level with sub-micron depth ranges under nano/mili Newton load conditions [185,248]. It is considered as a very reliable source for probing the physical properties mainly elastic modulus and hardness at finitely small length scales through continuous capturing of indentation force and the resulting indentation depth [217]. As with all metallic materials, mechanical properties such as E and H determined via depth sensing indentation are largely temperature dependent. Thus high temperature indentation becomes highly relevant to engineering applications related to production and processing of materials that requires the fundamental understanding of their in-service behaviour at elevated surrounding temperatures. The involvement of small length scales allows a better control and/or selection of microstructural features of interest used for property examination using this technique. In addition, this method also reveals the changes in the material characteristics from a dynamic temperature loading conditions perspective in a unique manner in cases where the conventional techniques fails. The use of high temperature nanoindentation technique however renders number of technical challenges involving thermal drift, surface oxidation and heat flow regulation due to the evolution of temperature gradient. Thus, high temperature indentation is often carried under high vacuum conditions to prevent the atmospheric oxidation of samples. The advent of state of the art elevated temperature DSI systems and the growing popularity has now enabled the adoption and its implementation as a standard method of probing temperature dependent properties [249,250]. The commercial DSI

systems are capable of performing stable indentation testing at temperature up to 800°C with minimal thermal drifts similar to those observed at RT [251].

3.2 Materials and methods

3.2.1 Al₃Zr crystal extraction and sample preparation

Three kinds of samples were used for the mechanical property measurements i.e., 1) Al₃Zr phase in Al matrix, 2) arc-melted pure Al₃Zr polycrystalline sample for room temperature measurements and 3) embedded Al₃Zr crystals in a cement matrix for high temperature measurements. These different intermetallic specimens were prepared in order to check of any variation in the measurement at RT between the single and polycrystalline and to compare with the cement matrix specimen that alone qualifies for high temperature measurements.

Intermetallic crystal extraction and preparation of polycrystalline specimen was performed in collaboration with BCAST, BRU. The author of this thesis contributed in this section by preparing other two intermetallic specimens from the extracted single crystals and analysing their microstructure. Approximately 350 g of an Al-3wt% Zr alloy were produced by melting pure Al (99.97%) and an Al-5wt% Zr master alloy. The formed alloy was re-melted in an electrical furnace and solidified at a very slow cooling rate in a cylindrical graphite mould ($\varnothing = 50$ mm) with a thermal cycle as shown in Fig. 3.1, with temperature accuracy of up to 3 K. The cooling cycle was kept slow (see the 6-h slope from 1100°C down to 690°C and 2-h slope from 690°C to 660°C) in order for the formed intermetallic crystals to grow to a large size (up to 7 mm). The different cooling rates were decided for different temperature zones based on the nature of formation of Al₃Zr intermetallics. The first temperature zone between 1100-690°C with liquidus close to 1046°C, was the temperature range where the primary crystals were formed. The cooling rate was further decreased between 690-660°C where the formed crystals grew. Finally, the last temperature zone between 660 and RT corresponded to natural cooling of the alloy ingot to room temperature. During this slow cooling, formed primary crystals grew and sedimented to the bottom of the crucible.

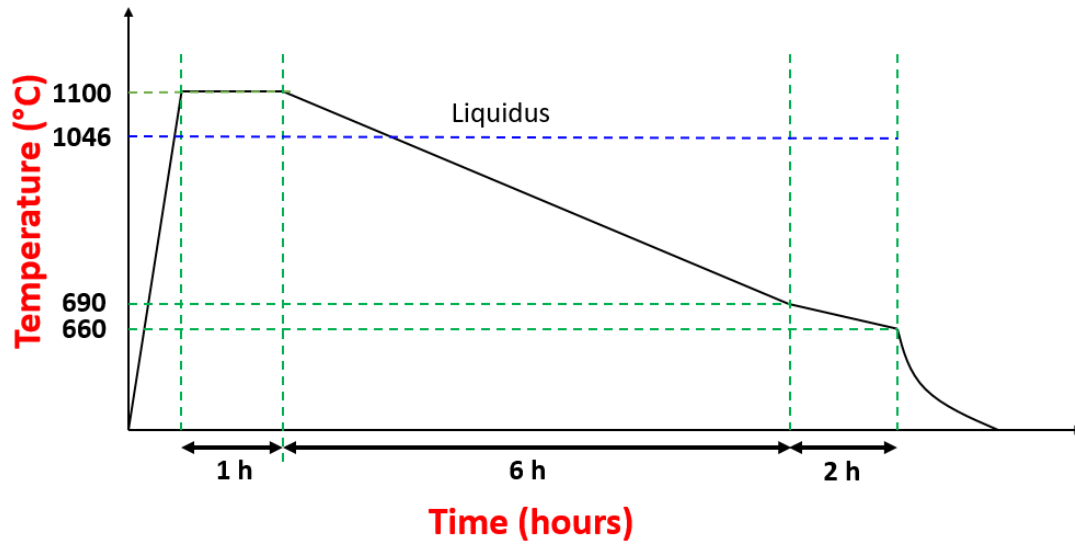
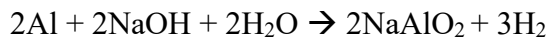


Fig. 3.1 Thermal cycle to produce Al_3Zr intermetallic crystals.

$5 \times 5 \times 5$ mm cubes were cut using a SiC rotating blade from the bottom part of the ingot. To extract Al_3Zr intermetallics, a cube sample was immersed in a 15% NaOH water solution for 24 hrs (or until the Al-matrix was completely dissolved, leaving the Al_3Zr intermetallic crystals). The dissolution of Al matrix to extract the intermetallic crystals from the alloy followed the chemical reaction below:



The resulting solution was filtered out and the extracted intermetallics were then collected and thoroughly rinsed using ethanol and left to dry out. These extracted primary intermetallics exhibited a well-faceted and thin tabular morphology as also observed by Zhen and Davies [252]. Figure 3.2 shows the optical images of typical extracted crystals. The dimensions of these crystals were approximately L_c : 3 ± 1 mm $\times$ W_c : 5 ± 1 mm $\times$ T_c : 0.06 ± 0.01 mm. Numerous similar crystals were collected and used for the experimental investigations described later in Chapters 4 and 6.

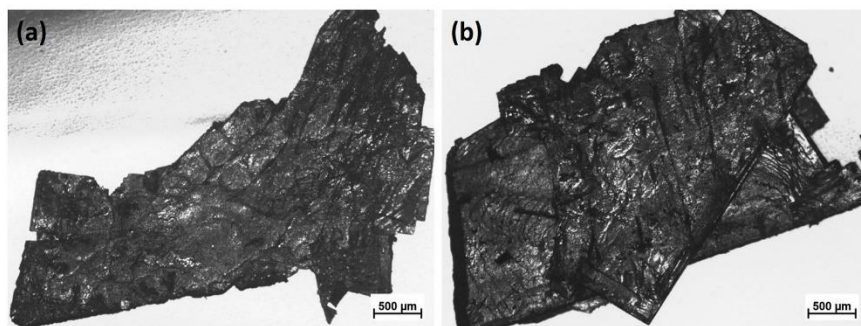


Fig. 3.2 Optical micrographs of typical extracted primary Al_3Zr crystals.

3.2.1.1 Arc-melted pure Al_3Zr polycrystalline sample

3-4 grams of extracted Al_3Zr flakes were arc melted using a non-consumable electrode arc-melting device to produce a 'T' shaped rod of length 10-12 mm and approximately 1.5 mm thick (Fig. 3.3a) in order to comply with the testing requirements (see section 3.2.2). Due to extreme brittleness of the intermetallics, the sample was then embedded and moulded using a low melting Sn-Bi alloy for easy grinding and polishing. After polishing, the Sn-Bi alloy was melted at 150°C and the extracted polycrystalline sample was used for nanoindentation experiments. In Fig. 3.3b, a microstructure of polycrystalline intermetallic specimen is shown. The presence of grains can be clearly seen indicative of a polycrystalline dendritic morphology upon intermetallic solidification. Note that Fig. 3.3b represents the microstructure of Al_3Zr formed upon melting of multiple single crystal flakes and is not the micrograph of a single crystal.

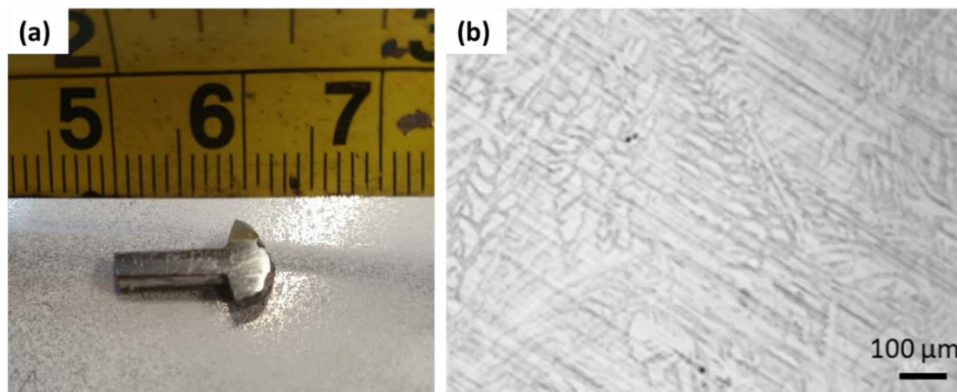


Fig. 3.3 Image showing (a) arc-melted polycrystalline pure Al_3Zr bulk specimen and (b) its microstructure in an optical microscope showing polycrystalline Al_3Zr solidified as dendritic grains.

3.2.1.2 Embedded crystals in cement matrix

For preparing the sample with intermetallics embedded in the cement matrix, the extracted primary Al_3Zr crystals of dimension approximately $2 \pm 1 (L_c) \times 3 \pm 2 (W_c)$ mm and thickness of 60-70 μm were distributed uniformly on the surface of a glass slide (coated with thin layer of oil/grease). The high temperature cement/ceramic adhesive paste (Pelco High Performance Ceramic Adhesive, Ted Pella, Inc, USA) was then poured onto the glass slide and was confined within the circular ring of diameter 25 mm. The adhesive paste was then carefully covered by another glass slide from the top to make the surfaces flat from both ends. The thickness of the sample was kept close to 5 mm to limit the potential thermal shock and the flatness between the two faces was adjusted to be within 20 μm . The adhesive was subsequently air dried and

solidified at room temperature. The dried cement adhesive embedded with intermetallic crystals was then removed from the slides and cured at 93°C for approximately 2 hrs (following the manufacturer instructions for this particular paste). This was deliberately done to achieve good mechanical properties of the solidified matrix at elevated temperatures. The samples were then mechanically polished to a mirror finish with average roughness (S_a) maintained around 0.4 μm for the both sample faces before using for the nanoindentation experiments. Fig. 3.4 shows the intermetallics embedded in the ceramic matrix (encircled in red in Fig. 3.4a) and optical image of the polished crystals (Fig. 3.4(b-c)).

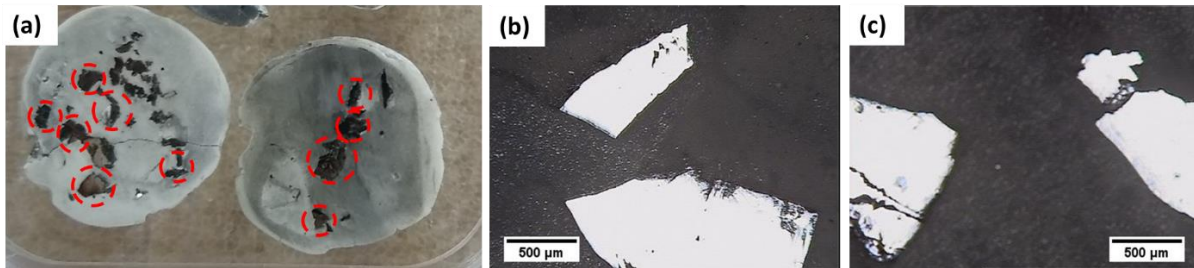


Fig. 3.4 Image showing (a) Al_3Zr crystals embedded in ceramic matrix and (b, c) optical micrographs of the polished specimens.

3.2.1.3 Al_3Zr phase in Al matrix

For the preparation of Al_3Zr phase in Al matrix, a part of the cast ingot was cut longitudinally and sectioned along the central axis from the bottom where the primary intermetallics tend to settle during solidification because of the high density of Al_3Zr . These sectioned samples were then cold mounted on a polymer resin, ground and polished up to a mirror surface finish with S_a of the order of 0.2 μm for optical microscopy examination and nano-indentation studies. Figure 3.5 shows typical micrographs of Al_3Zr phase (indicated by the red dashed lines) in the Al alloy matrix.

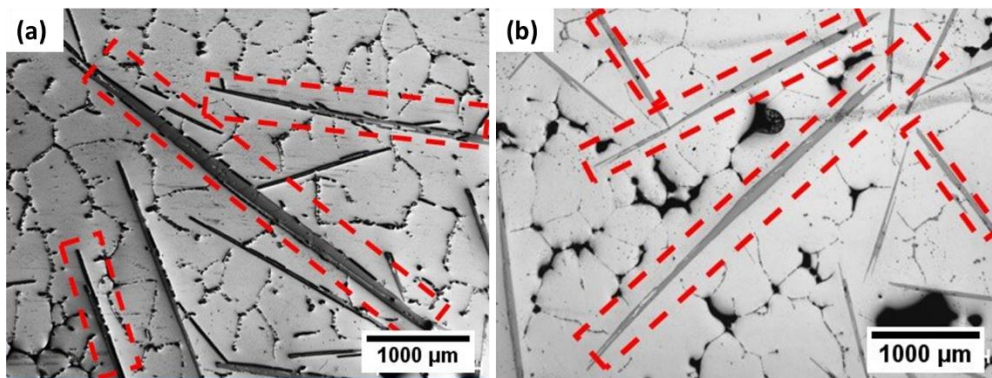


Fig. 3.5 Optical micrographs of Al_3Zr intermetallics phase in Al matrix.

3.2.2 Nanoindentation experimental setup

An ultra-high temperature nano-indentation setup (UNHT HTV, Anton Paar, Switzerland) working on a principle of active surface referencing and infrared heating of the sample and the indenter was used to measure the mechanical properties of Al_3Zr intermetallic specimens at both room and elevated temperatures. This principle employs measuring and referencing axes, each with their own means of computing the applied load and the corresponding displacement. The active reference principle ensures high thermal stability of the instrument even at temperatures up to 800°C and eliminates to a great extent the need to correct the frame compliance. This could be attributed to the excellent thermal stability of the instrument, which does not have to be corrected.

This novel indentation tester can perform measurements up to 800°C under vacuum conditions necessary to avoid surface oxidation of sample and indenters under consideration. The operating load and the corresponding displacement of the indenter can range up to 100 mN and 100 μm respectively having load and displacement resolution of 6 nN and 0.006 nm. The indentation system comprises a diamond or tungsten carbide (WC) indenter tip and utilises infrared heating for high temperature measurements. Application of load on individual axis is constituted by means of piezoelectric actuators connected with springs-based force sensor. The applied force is controlled via a separate feedback loop. The displacement (indentation depth) is measured by a capacitive sensor. The gap between the indenter and the reference axis is ~ 9.25 mm, which dictates the minimum dimension of the sample. Figure 3.6 shows the schematic of the indentation system used in the present study. The additional details regarding the instrumentation setup and configuration are provided elsewhere [251].

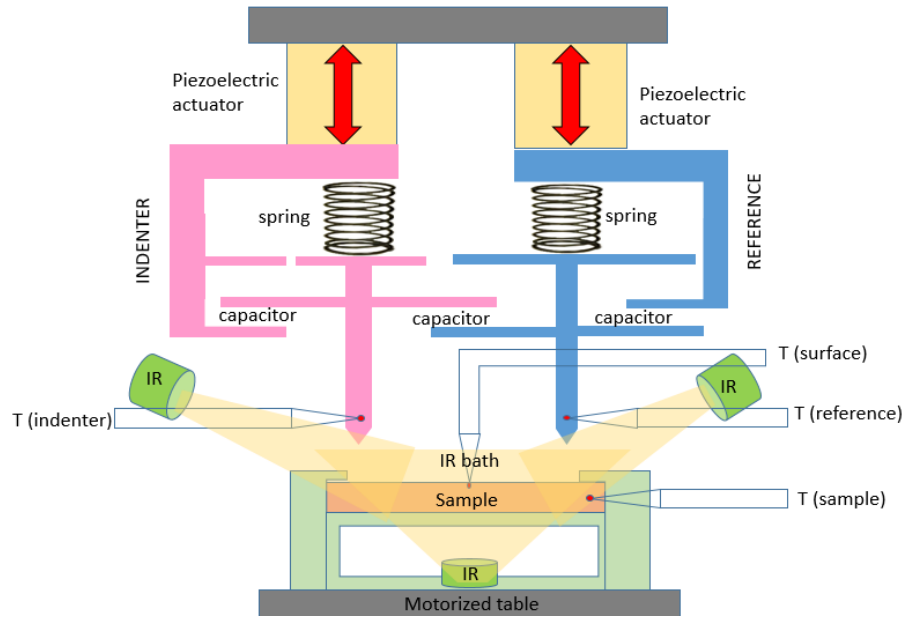


Fig. 3.6 Schematic diagram of the ultra-high temperature nano-indentation state-of-the art system used for the indentation experiments. Adapted from [251].

3.2.2.1 Room temperature measurements

For RT measurements, successive indentations were performed on intermetallic specimens with a continuous loading and unloading speeds of 20 mN/min and a dwell time of 5 sec using a geometrically well-defined Berkovich diamond nano-indenter. The load–displacement characteristics were acquired with a linear quasistatic loading of 10 mN and an acquisition frequency of 10 Hz. Intermetallic phases in the Al matrix sample were further subjected to fracture indentation mode using a diamond cube corner indenter with a maximum load of 100 mN. Other indentations such as continuous stiffness sinus measurement (CSM) and constant multicycle testing (MCT) were also performed over the specimen to measure the depth dependent property variation and fatigue strength of the specimen, respectively. Cyclic (sinus) measurements were carried out using a Berkovich indenter at 100 mN load with employed frequency and amplitude of 40 Hz and 10 mN, respectively, for 5 minutes (12000 cycles). 100 cyclic indentations were performed using a 4 sided pyramidal shape Vickers indenter with maximum and minimum loads of 1 and 0.5 N, 2 and 1 N, and 5 and 3 N, respectively at loading and unloading durations of 10 s, dwell time of 2 sec and acquisition rate of 50 Hz. A minimum of 5 indents were performed for each of the measurement modes and loading conditions to avoid any inconsistencies in the results.

3.2.2.2 Elevated temperature measurements

High temperature nanoindentation measurements were carried out to specifically determine the hardness and elastic modulus of primary intermetallics from RT up to 700°C at intervals of 50°C. The intermetallic crystals embedded in the high temperature cement matrix (section 3.2.1.2) were used for these measurements. To avoid surface oxidation of the specimen, the indentations were performed in vacuum (10^{-6} mbar) with loading and unloading speeds of 120 mN/min and dwell period of 2 sec under high vacuum conditions to avoid oxidation of sample at high temperatures. The waiting time for the vacuum chamber to be buffered was almost 30 h. The load-displacement profiles were obtained with a maximum load of 10 mN with an acquisition rate of 400 Hz. At least 5 indents were done for each measurement conditions to achieve statistically reliable data.

3.3 Results and discussion

Formation and growth of primary intermetallic phases to sizes over 50 μm in the solidifying melt significantly affects the material integrity and mechanical properties of the as-cast alloy. The ultrasound-induced fragmentation potential and refinement of these primary crystals depends, on one hand, on the operating conditions of UST, and, on the other hand, on the fracture strength of the crystal. Knowledge of the latter is a vital input in deciding the acoustic power requirements for efficient and controllable ultrasonic fragmentation. Yet these properties are largely unknown. To fill this gap, we performed this study to evaluate the mechanical properties at room and elevated temperature conditions.

3.3.1 Room temperature measurements

Mechanical properties such as elastic modulus, hardness and fracture toughness of the primary Al_3Zr intermetallics phase in Al matrix have been evaluated here experimentally and compared with the values in literature obtained from first principle calculations [179] and experimental measurements [178]. Figure 3.7 shows the load-displacement profiles (Fig. 3.7a) of an Al_3Zr intermetallic and their corresponding indentation marks (Fig. 3.7b) obtained for a maximum load of 10 mN at room temperature using the nano-indentation setup as described in Section 3.2.2. The mechanical properties have been evaluated from the P_d - h curve using the method introduced by Oliver and Pharr (O&P) [185,217]. To obtain accurate values of the elastic

modulus and hardness from this curve, it is important to measure experimentally certain parameters such as the maximum displacement (h_m), permanent final depth of penetration (h_f) and the contact stiffness of the unloading curve ($S = dP/dh$). The indentation depth in Fig. 3.7a shows substantial elastic recovery ($\sim 24\%$) equivalent to that of quartz [253] with a residual penetration depth of almost 183 nm, which strongly points towards the elastic/plastic behaviour of the crystal being indicative of a typical hard and brittle material.

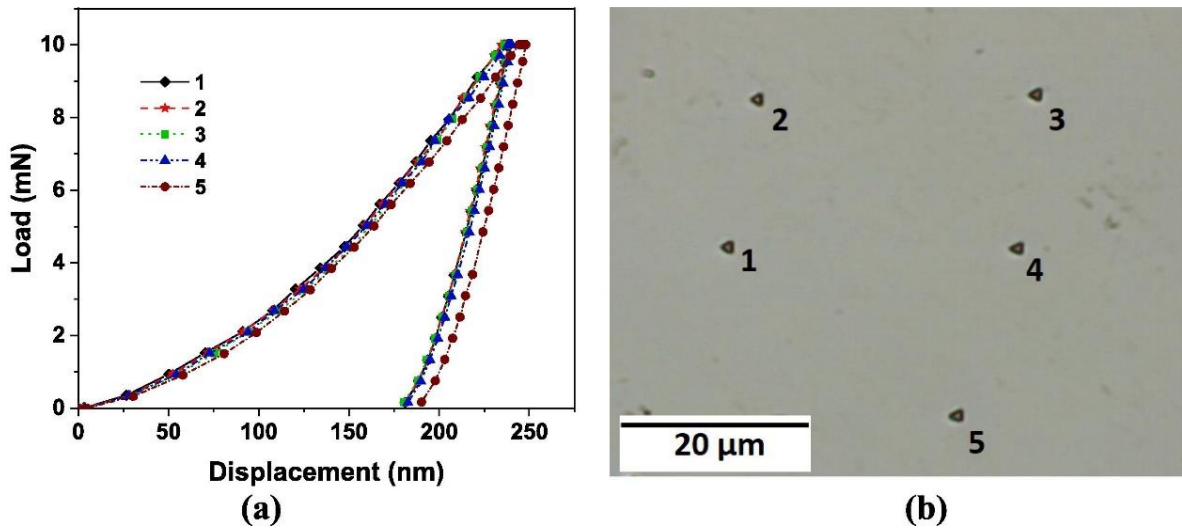


Fig. 3.7 (a) P_h - h curve with maximum and final penetration depth of 240.8 ± 4.14 and 183.1 ± 4.06 nm respectively, and (b) corresponding indentation marks on Al_3Zr crystal with load of 10 mN.

Using the model suggested by O&P, the hardness (H) and the elastic modulus (E) were calculated and found to be in the range of 7.2-7.6 GPa and 194-206 GPa, respectively. The results on the material properties of Al_3Zr based on our experimental measurements are given in Table 3.1 along with some reference data. The values are in good agreement with the current literature data estimated from the first-principle method [178,179,181,209,254,255]. Fracture toughness (K_c) of the intermetallic was also determined from Equation 2.16 (Chapter 2) given by the Lawn Evans Marshall (LEM) model [229,230]. K_c of the Al_3Zr intermetallic was experimentally estimated to be nearly $1 \text{ MPa}\sqrt{\text{m}}$ agreeing well with the value found in literature [180], see Table 3.1. These values have been utilised later in Chapter 4 for accurate determination of fracture mechanics of primary crystals under the influence of ultrasonic cavitation.

Al_3Zr particles in the Al matrix were also subjected to sinus (CSM) mode to account for the variation of properties over penetration depth. Figure 3.8 shows the elastic modulus and

hardness variation with depth of penetration. From the figure, it can be seen that Al_3Zr shows depth dependent properties indicating the indentation size effect (ISE) in accordance with the Nix-Gao model of indentation for crystalline materials [256]. It is important to note that the values of E and H initially increase with the increase in the loading depth, reach the maximum value and then decrease with further penetration. Researchers have reported this ‘initial increase’ in hardness and modulus values as ‘woodpecker effect’ (also coined as ‘nano-jackhammer effect’) observed during dynamic indentation loading, which is mostly pronounced within 200 nm of penetration depth [257,258]. Other possible reasons for this effect could be attributed to the tip imperfections or surface roughness that affect measurements at low depths or instrumental and measurement errors [259]. The maximum values of E and H correspond to the penetration depth close to 160 nm and 66 nm, respectively. Approximately 20% decrease in the values of E and H from the maximum was observed with an applied load of 100 mN.

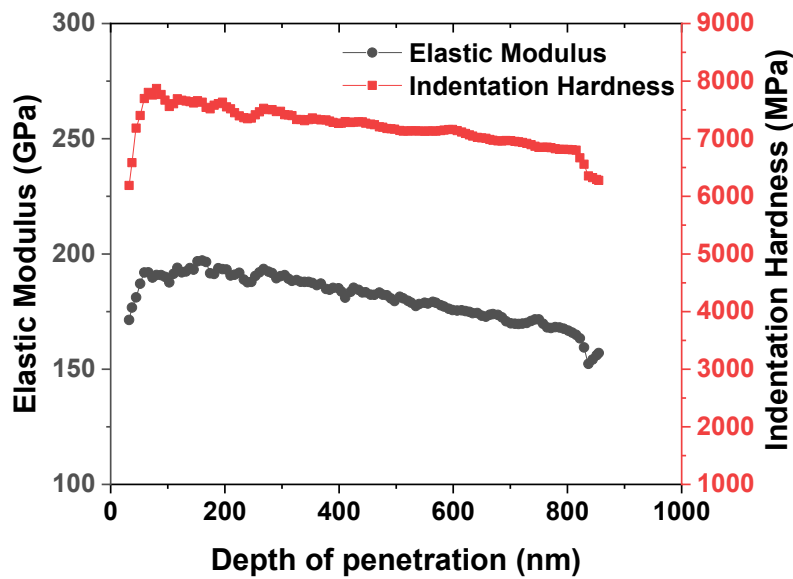


Fig. 3.8 Variation of E & H with the indentation depth measured using dynamic loading of the Al_3Zr phase in the Al matrix.

The indentation curves and the corresponding hardness and elastic modulus values obtained at RT for different intermetallic specimens (as discussed in section 3.2.1) were compared and analysed. Fig. 3.9a shows the typical load-displacement curves and Fig. 3.9 (b and c) shows the bar chart that represents the H and E values of the examined samples, respectively. All the indentations were performed on an unetched samples (the Al_3Zr phase in the Al matrix and

embedded intermetallics in cement matrix) to avoid any plastic response behaviour the surrounding matrix upon application of the indentation force.

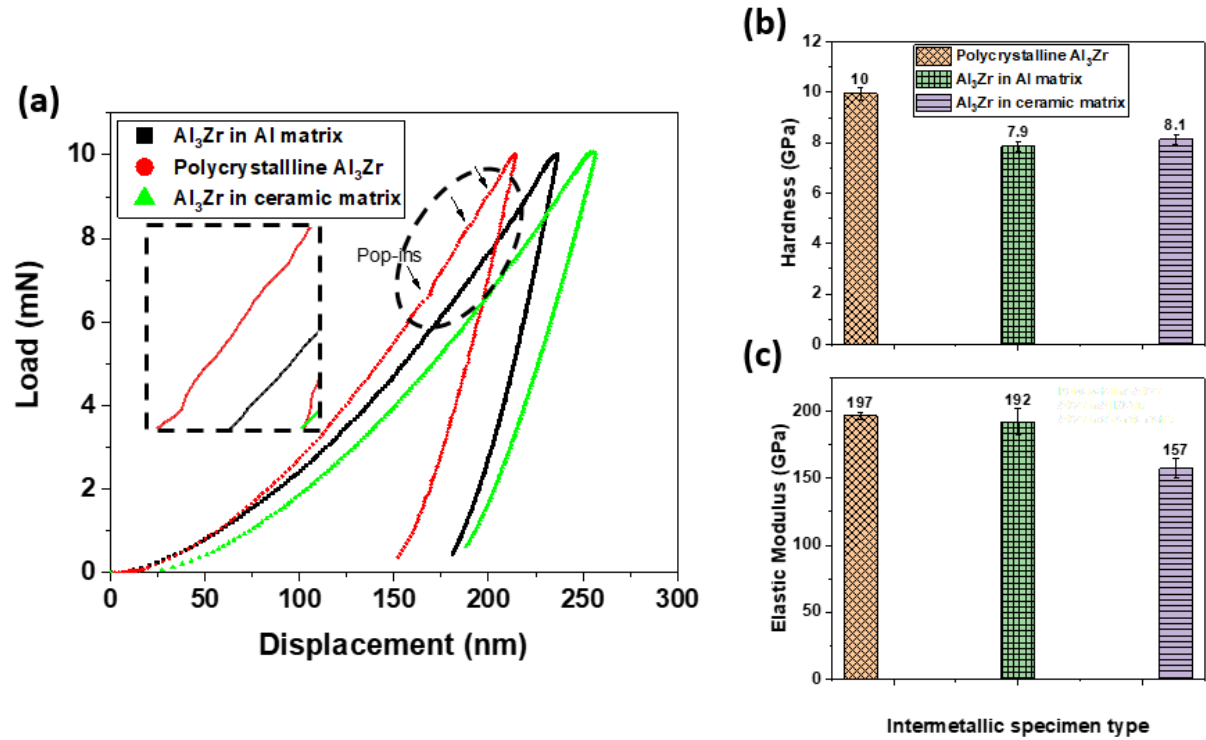


Fig. 3.9 Comparison of nanoindentation response of different intermetallic specimens in terms of (a) Load-displacement curve, (b) indentation hardness, and (c) indentation modulus.

It is apparent from Fig. 3.9a that both single (Al₃Zr in Al phase and those embedded in cement matrix) and polycrystalline Al₃Zr specimens show elastic-plastic response. The load-displacement curves for all the specimens displayed almost similar shape differing only in h_m and h_f , highlighting the resistance of the indenter penetration into the bulk specimens. For a fixed P_m , the intermetallic types can be classified based on h_m . Under maximum indentation load of 10 mN load, h_m was found to be different for all the samples and varied between 214 nm and 252 nm. After the elastic recovery during unloading, variation in h_f was between 152 nm and 188 nm. The indentation curves exhibited approximately similar amount of elastic recovery during unloading, i.e. ~23% for Al₃Zr phase in Al matrix, ~26% for Al₃Zr in cement matrix and about 29% for polycrystalline Al₃Zr. It is interesting to note that the nanoindentation curves for polycrystalline Al₃Zr show some arbitrary discontinuities specifically on the loading curve in contrast to both Al₃Zr in Al and cement matrix. The discontinuities (displacement burst) present in the form of ‘pop-ins’ (see arrows on Fig. 3.9a) can be attributed to the nucleation of dislocations during loading of the indenter [248]. The pop-ins (see Fig. 3.9a inset)

feature are almost negligible for the other two intermetallic specimens and any minor discontinuities may be a result of vibrations present in the measuring device or the feedback cycle occurring during indentation testing.

For the evaluation of E and H from P_d - h curves, another important parameter of measurement is h_c that can be roughly estimated by taking the average of h_m and h_f . From Fig. 3.9b, it can be seen that the polycrystalline intermetallic offers the largest resistance to the localised elasto-plastic deformation (hardness), followed by Al_3Zr crystals embedded in the cement and the Al matrix, which have almost similar values. The P_d - h curve for embedded intermetallics in cement matrix is also a good analogue to Al_3Zr in Al matrix specimens and thus suitable for the high-temperature measurements. However, it should be noted that orientation may play a role as it can be seen that in the case of intermetallics in Al matrix, the crystal is penetrated facing its edges (see Fig. 3.3) whereas in case of intermetallics embedded in cement matrix, the crystals were placed facing its flat (wider) plane (see Fig. 3.5). Therefore, some discrepancy in the measuring values may be expected especially with the flat plane orientation, where chances for underneath/substrate defects are more likely. The differences in the measured hardness values of the intermetallic specimens are also obvious from the variation of h_m as observed in Fig. 3.9a. Fig. 3.9c shows the measured elastic modulus values of different intermetallic specimens. Polycrystalline Al_3Zr and Al_3Zr in the Al matrix showed similar E values in contrast to Al_3Zr crystals in the cement matrix that exhibited the lowest modulus. This difference can be explained by the fact that the indentation modulus is derived from the observed contact area and the stiffness (slope of unloading curve) that is critical in its calculation (see Eq. 2.13 and 2.14 in Chapter 2). It should be noted that the hardness is gauged from the indenter displacement, giving rise to plastic deformation, whereas the modulus is dependent mainly on the elastic stress fields. In addition, the large drop in the modulus value of Al_3Zr in the cement matrix might also be explained in terms of crystal orientation (edge and plane) used for indentation and the effect of the extended plastic zone into the surrounding matrix. This elastic anisotropy is believed to be strongly related with the crystallographic orientation of the material being tested, which has not been examined in the current work. Zhen and Davies [252] observed the growth habit of Al_3Zr crystals and identified the basal (i.e. flat) plane as (0 0 1) while the side orientation with facets (i.e. edge) were identified as {1 0 1} planes of the tetragonal structure. Huang et al. [213] further reported that Al_3Zr with $D0_{23}$ structure exhibits large degree of elastic anisotropy than the one with $L1_2$ type structure with modulus of $D0_{23}$ being higher as seen in Table 2.2. Nakamura and Kimura [178] stated that the

Young's modulus can vary with both the interatomic distance and the atomic distribution along the direction of applied force. The modulus was found to be maximum in $\langle 1\ 1\ 0 \rangle$ direction in which the Al_3Zr atoms are close packed in comparison to $\langle 1\ 0\ 0 \rangle$ or $\langle 0\ 0\ 1 \rangle$ [178]. This is in very good agreement with the current investigation where it can be seen that the room temperature elastic modulus for Al_3Zr in Al matrix is almost 22% higher than the modulus obtained in case of crystals embedded in the cement matrix. Based on these observations, we can say that single (cement matrix specimen) and polycrystalline (arc-melted specimen) intermetallics show similar material behaviour without large differences in the mechanical properties, which means that indentations are localised in tiny areas unaffected by grain boundaries or other defects that do not alter the nano-measurements (as expected). However, the variation in elastic modulus for the cement mono crystal owing high surface to defect ratio. Moreover, the smaller thickness of the specimen with formed crack networks make the indentation measurement prone to interact with a defect present underneath the surface.

Chen et al. [260] pointed out another interesting feature that could be correlated with the elastic modulus, which is the temperature of formation of these intermetallic phases. Based on the thermodynamic modelling, it is predicted that the intermetallic phases which show a higher modulus are actually formed at a higher temperature and vice versa. The higher the formation temperature, the larger the required enthalpy is. The reason of this correlation lies in the notion that a higher formation heat accounts for a tighter and stronger atomic bonding thus resulting in a higher modulus [261]. Such analysis is, however, beyond the scope of this work and is only presented as an overview of nanoindentation measurements.

In order to characterise the fatigue behaviour of the intermetallic phase, Al_3Zr particles in the Al matrix specimens were further subjected to MCT experiments at the maximum and minimum loads of 1, 2, 5 N and 0.5, 1, 3 N, respectively, for 100 cycles simulating the conditions of very low-cycle fatigue. Figure 3.10 (a-d) shows the load-displacement curves and the corresponding indentation marks formed within the intermetallic phase. It can be seen that the indentation performed at 1 N load does not produce any cracks (Fig. 3.10b) within 100 cycles and only undergoes elasto-plastic deformation. Whereas the indentations performed at 2 and 5 N loads show the presence of multiple pop-in and cracking events (see Fig. 3.10a) during initial loading itself. The appearance of pop-ins in the P_d - h curve maybe attributed to either nucleation/slipping of dislocations beneath the indenter tip or instantaneous fracturing of intermetallics (indicated by sudden increase in the penetration depth) as seen in Fig. 3.10 (c and d), which shows the formation of cracks originating at the sides and corners of the indent.

Moreover, the presence of pop-ins could also indicate shifting of intermetallic behaviour from elasto-plastic to plastic deformation. Interestingly, the Al_3Zr intermetallic exhibited first instance of cracking just at 300 mN during loading up to 2 N (see Fig. 3.10a) while there was no sign of any fracture at the same loading point when indented with 1 N load. This strange behaviour can mainly be attributed to the presence of pre-existing cracks within the intermetallic plate used for indentation (see Fig. 3.10d) that may have formed during solidification of an Al-3%Zr alloy due to thermal contraction stresses.

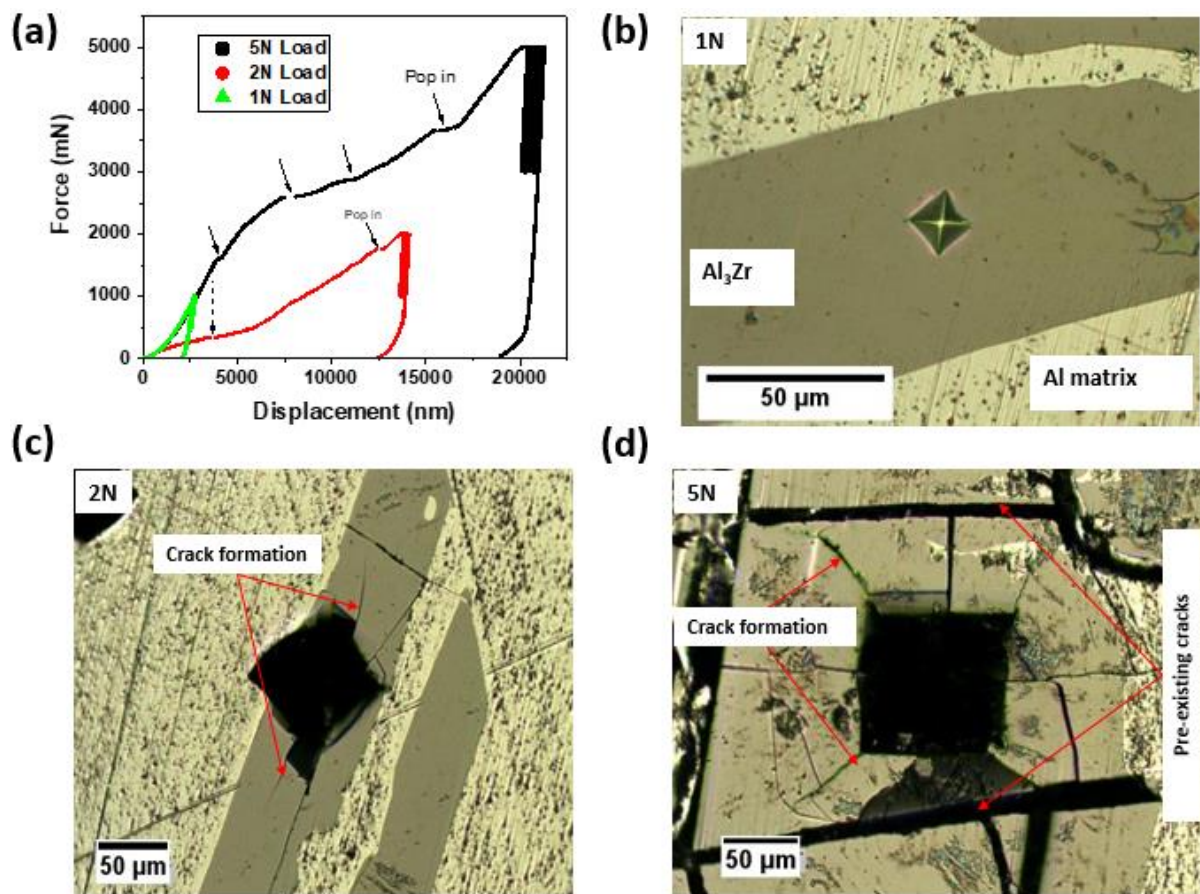


Fig. 3.10 Constant multicycle indentation testing showing (a) P_d - h curves and corresponding indentation marks formed at maximum applied load of (b) 1 N, (c) 2 N, and (d) 5 N after 100 cycles.

In this study, it was not possible to detect the crack propagation in the Al_3Zr phase at the maximum loads of 2 and 5 N as the intermetallic fractured much before the initiation of cyclic loading. Therefore, to understand the fatigue response, we plotted the contact depth of the indenter displacement as a function of indentation cycles. Figure 3.11 shows the same for all three load cases. For the 1 N load, the indentation depth decreased by almost 60 nm during 100 cycles. While in case of the 2 N and 5 N loads, the indentation depth increased by about 300

and 900 nm, respectively. The decrease in indentation depth at the 1 N load could likely be due to stiffening of material during cycles of loading and partial unloading. However, these MCT measurements did not show any evidence of the development of fatigue induced cracks. Instead, the increase in contact depth as observed for the 2 and 5 N loading could just be the propagation of cracks that formed during the initial loading period as discussed above. Based on the MCT measurements, it can be deduced that these brittle intermetallics can only be fractured if the applied contact pressure goes beyond 7 GPa (1 N load) under cyclic loading conditions. However, in reality this is not the case as the fracture toughness is small (see Table 3.1) and cavitation-induced fragmentation of intermetallics occurs via bubbles and emitted shock waves interacting with multiple defects, cracks and discontinuities etc. (as will be discussed in detail in next Chapter 4) resulting in breakage at lower impact pressures.

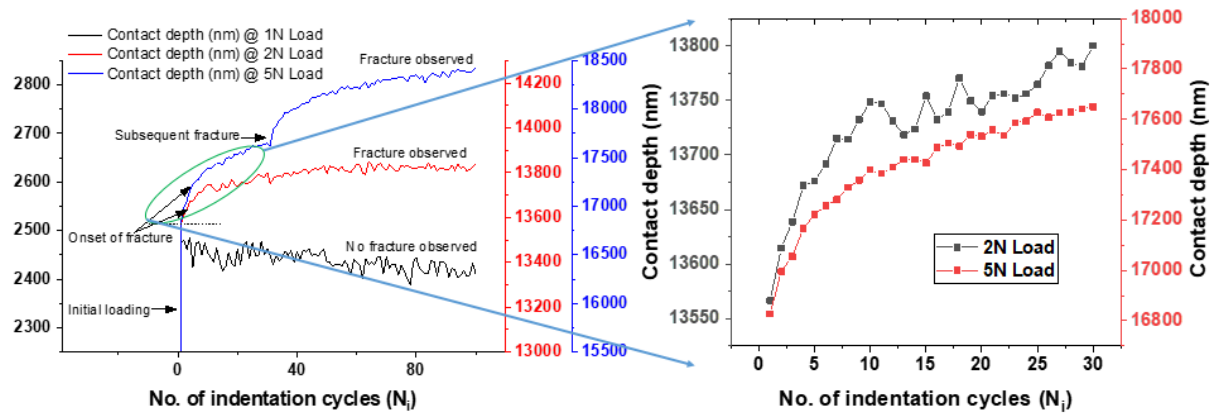


Fig. 3.11 Variation of contact depth of the indenter as a function of indentation cycles (N_i) for maximum load of 1, 2, and 5 N, showing the onset and subsequent fracture observed during loading.

Table 3.1 Measured mechanical properties of Al_3Zr crystal using DSI technique.

Mechanical Properties	This work	Std. dev.	Other work
Hardness (GPa)	7.4	0.2	6 [209]
Elastic Modulus (GPa)	200	5.8	197.6 [179] 201.8 [178] 193.0 [255]
Fracture Toughness ($\text{MPa}\sqrt{\text{m}}$)	1.1	0.1	0.85 [180]

3.3.2 High-temperature measurements

After the evaluation of mechanical properties, i.e., E , H and K_c using quasistatic DSI experiments at ambient conditions in the previous section, Al_3Zr crystals embedded in cement matrix specimens were further subjected to elevated temperature measurements for determining the effect of temperature on the mechanical properties evaluated up to 700°C at 50°C intervals.

Figure 3.12 shows the comparison of typical P_d - h curves for the specimens measured from RT to 700°C . The dwell period of 2 s was kept constant for all the indentation experiments performed at elevated temperatures. As expected, the maximum indentation depth was almost doubled, with the increase in operating temperature from RT to 700°C and measured to be 248 nm and 462 nm, respectively. Between two consecutive indentation temperatures, the increase in the indenter depth was less than 10% except at 650°C and 700°C where this increased up to 22% indicating that the material became softer at such high temperatures. As the temperature was increased, the load displacement curves started to exhibit a steady plateau region during the dwell interval with maximum indentation load (indicated by blue arrow in Fig. 3.12). This can be possibly ascribed to the plastic deformation and development of creep, indicating that Al_3Zr crystals undergo creep at relatively high temperatures (~ 600 - 700°C). However, with a limited dwell period for indentations performed at such temperatures, an intermetallic fails to undergo full plastic relaxation in the creep regime in comparison to low (25 - 200°C) and intermediate temperature (200 - 550°C) ranges, which is noticeable in the form of convex bending (indicated with red arrows in Fig. 3.12) during unloading of the indenter similar to observations made for intermetallic phases such as $\text{Al}_7\text{Cu}_4\text{Ni}$ and Al_2Cu at 350°C [262]. Thus, the determination of elastic modulus values at such a high temperature should be handled with extreme care. Moreover, at this temperature, contribution from the elastic energy to the material deformation is also very small. With the increasing temperature especially in the intermediate and high range, the amount of elastic recovery during indentation unloading also decreases, which indicates larger portion of plastic deformation.

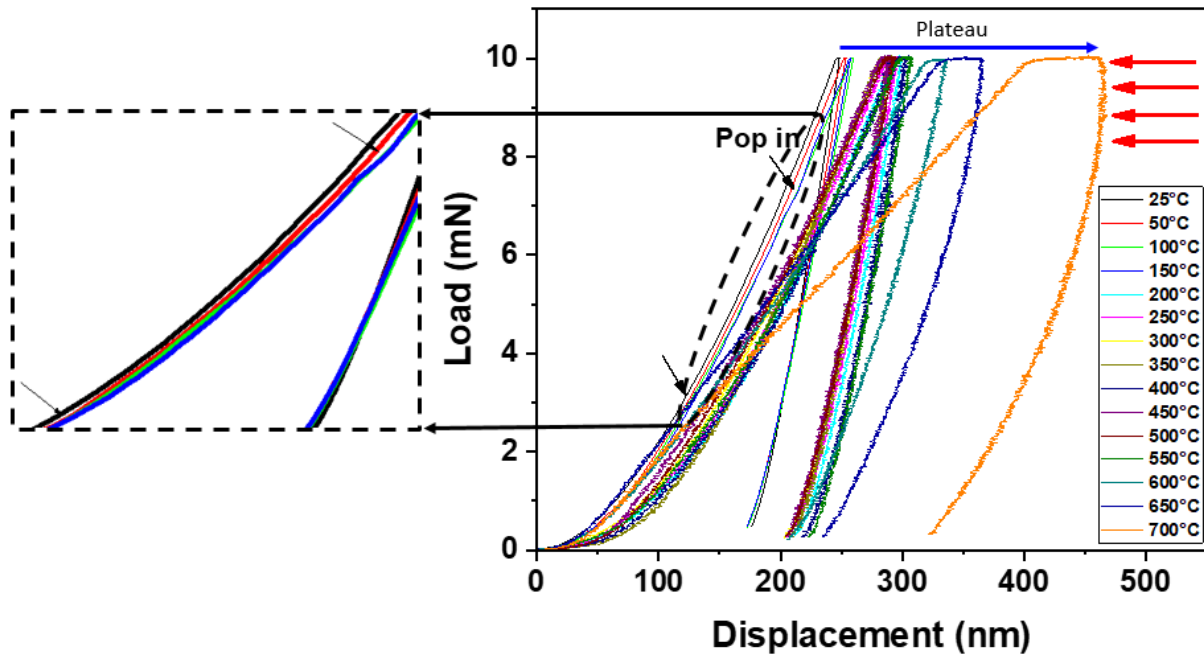


Fig. 3.12 Typical load-displacement curves for Al_3Zr crystals embedded in ceramic matrix measured from RT up to 700°C.

Additionally, a few indentation curves also showed the presence of small pop-ins (see black arrows) during loading of the indenter indicating plastic yield of the material at nanoscale that could be related to dislocation events emerging underneath the indenter tip. The sudden displacement of indenter (pop-ins) typically occur at a penetration load, which is equivalent to the material maximum shear strength that predicates the nucleation of dislocations followed by its propagation. At relatively low temperatures, the movement and interaction of the formed dislocations lead to strain hardening in crystalline materials [263]. Increasing temperature can further shift the plastic yield indentation loads, which is primarily driven by the nucleation kinetics at homologous temperature. There is also severe reduction in the dislocation density and their movement in crystalline materials during annealing at elevated temperatures [262]. This inherent stability of plastic deformation characterises the creep behaviour of crystalline materials at higher operating temperatures ($\sim 0.4\text{--}0.5 T_m$, where T_m is the melting temperature in K). Gupta et al. [264] reported that Al_3Zr crystals are highly stable at creep test temperature of 330°C (about $0.38 T_m$) because of their high melting point, i.e. approximately 1580°C. Moreover, a homogeneous creep deformation in materials is usually observed at temperatures above that of half of the melting point, which is around 654°C (927 K) for these crystals. Therefore, the dislocations events are mainly associated with the discontinuities during indentation loading, which is observed as serrations in the form of pop-ins, whereas the

homogeneous plastic deformation tends to appear in the form of continuous shift, which is affected by the free volume redistribution during indenter penetration [262].

Figure 3.13 shows the variation of mechanical properties i.e. E and H with temperature up to 700°C. As expected, elastic modulus and hardness decreases with increasing temperature. With slight increase in temperature i.e. 25°C from RT, the modulus decreased by almost 12% whereas hardness decreased by approximately 10%. The biggest drop in hardness of about 46% was observed at 700°C from 650°C whereas elastic modulus dropped only by 20% indicating high creep resistance of the intermetallic. Overall, both the hardness and elastic modulus decreased by almost 78% and 55%, respectively from RT to 700°C. At RT, hardness is governed by the evolution of dislocation network, while at HT the change in the indentation hardness has been correlated to creep and plastic flow behaviour [263]. As seen from Fig. 3.12, the higher the temperature, the lesser the elastic recovery during the unloading of the indenter as seen from h_f . For example, the elastic recovery decreased by approximately 29% at RT to 25% at 700°C as seen from the percentage change in h_m and h_f . This partial elastic recovery can greatly influence not only the maximum displacement of the indenter but also slope of the curve during initial unloading that is utilised for evaluating parameters such as E and S . This is not the case for hardness as it is evaluated using the contact depth rather than stiffness. The modulus can also be affected by the surface roughness of the specimen if the indentation is produced at a relatively rough region, which can be very sensitive at HT [265]. In addition, the loading frame compliance can significantly increase during elevated temperature conditions that can lead to an increase in modulus value.

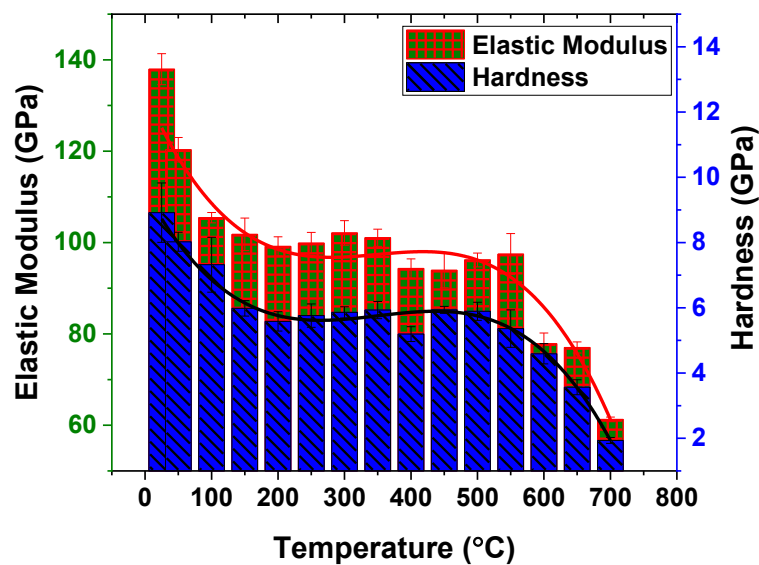


Fig. 3.13 Variation of elastic modulus and hardness as a function of indentation temperature for Al_3Zr intermetallics.

Both hardness and elastic modulus exhibited two regions of large drop in the values with increasing temperature, one at low temperature (50-200°C) and then at relatively high temperature (500-700°C) as shown in Fig. 3.13. Similar behaviour of this intermetallic in terms of microhardness variation with temperature has been previously reported [209]. Fleischer et al. [209] observed that Al_3Zr compound is still susceptible to crack until $\sim 750^\circ\text{C}$. George et al. [266] found that the flow stress and the critical resolved shear stress of the meta-stable titanium tri-aluminide, i.e. $\text{Al}_3\text{Ti}+\text{Fe}$ (having closest crystal structure to D_{023} zirconium tri-aluminide) was very similar to flow stress behaviour realised in the case of ternary polycrystals. A sharp decrease in the flow stress was observed at low temperatures (up to 150-200°C) followed by an atypical plateau region at transitional temperatures and then further steep drop at high temperatures (up to 650-700°C) with very little orientation dependence.

The temperature dependent properties of intermetallics can also be understood in terms of the deformation energy produced during indentation. Since the hardness of the material is related to a combination of various factors such as yield strength, strain hardening coefficient and resulting plastic strain of the material, the most efficient way of evaluating the deformation energy is by using the ratios, H/E and H^3/E^2 , that take into account the creep effects. H/E points towards the cracking resistance to elastic failure indicative of the toughness characteristics and H^3/E^2 defines the plastic deformation resistance during a plane contact [267]. Figure 3.14 displays the variation of H/E and H^3/E^2 with an increasing operating temperature. It is clear from the figure that both ratios decrease non monotonically with temperature. At the same time, the ratio of plastic work (W_p) to total indentation work (W_t) increases non monotonically with temperature. Cheng et al. [268] have previously confirmed that H/E is inversely related to W_p/W_t (plasticity index based on energy approach). For Al_3Zr intermetallics, it can be seen that the H/E is around 0.06 at RT, which means that the material has high propensity to cracking within the elastic limit, which agree well with the low fracture toughness value at RT (Table 3.1). On the other hand, H^3/E^2 is almost zero at an elevated temperature (close to 700°C) with plasticity index of almost 80% indicative of low creep strength of the intermetallic.

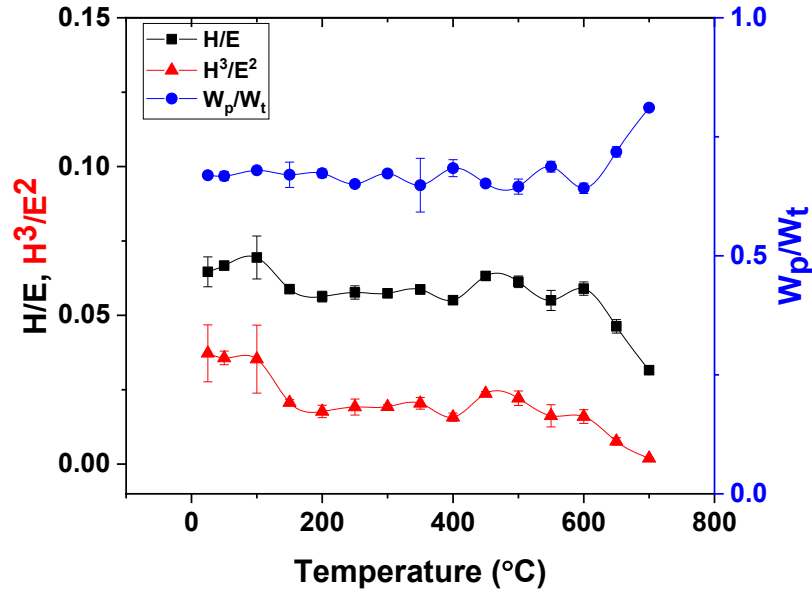


Fig. 3.14 Variation of elastic strain to failure, plastic deformation resistance and plasticity index with indentation temperature of primary Al_3Zr intermetallic.

3.4 Conclusions

In this study, DSI experiments were performed using quasistatic and multicycle indentation loading to evaluate the mechanical properties of three differently produced Al_3Zr intermetallic specimens. High temperature nanoindentation was also performed to determine the variation of hardness and elastic modulus with temperature. The results show that:

1. Room temperature measurement of the elastic modulus and hardness of the primary Al_3Zr phase in the Al matrix demonstrate very close resemblance to values determined using first principle models. CSM measurements on the sample indicate the depth dependent hardness behaviour as per the Nix-Gao indentation model.
2. Polycrystalline Al_3Zr sample exhibits about 24% and 22% higher hardness than the Al_3Zr phase in the Al matrix and the crystals imbedded in the cement matrix, respectively, possibly due to the nucleation of dislocations indicated by the so-called ‘pop-in’ events observed during indenter loading.
3. MCT experiments show that the Al_3Zr intermetallic can sustain contact pressure of almost 7 GPa before failing under low external loading (1 N) with low-cycle fatigue conditions similar to environments encountered during cavitation-induced fragmentation of these intermetallics (as will be discussed in next Chapter 4).
4. High temperature nanoindentation of Al_3Zr crystals show that both hardness and elastic modulus decrease with temperature by 78% and 55% respectively. These intermetallics

offer strong creep resistance at low (RT to 200 °C) and intermediate (200 °C to 500 °C) temperatures.

5. At temperatures close to the melting point of pure Al, intermetallics undergo large plastic deformation indicative of high atomic disorder making the plastic flow inherently unstable.

Chapter 4

Fragmentation mechanism of intermetallic crystals subjected to cavitation[§]

Following the measurement of mechanical properties of Al₃Zr at room and elevated temperature conditions, we now use the extracted intermetallic crystals to study their fragmentation response under the action of controlled cavitation at ambient conditions.

*This chapter describes the cavitation-induced fragmentation behaviour of fixed Al₃Zr crystals. Grain refinement in alloys is a well-known effect of ultrasonic melt processing. However, in-situ observations of the fragmentation process are generally complex and difficult to follow in opaque liquid metals. Among several suggested mechanisms, the fragmentation of primary intermetallics by acoustic cavitation is regarded as very efficient for producing finer and equiaxed grain structures. However, the physical process causing this fragmentation has received little attention and is not well understood. This study correlate the mechanical properties of studied intermetallics obtained in Chapter 3 to those with the in-operando monitoring of the fragmentation process by laser-induced cavitation (single bubble) and by acoustic cavitation (cloud of bubbles) in water. The observed fragmentation mechanism was supported by fracture mechanics and pressure measurements using a calibrated fibre optic hydrophone. **Results demonstrated for the first time that the governing fragmentation mechanism of the studied intermetallics was due to the emitted shock waves from the collapsing bubbles.** The fragmentation caused by a single bubble collapse was found to be almost instantaneous. Results showed that the acoustic pressures produced from shock wave emissions in the case of a single bubble collapse, and responsible for instantaneous fragmentation of the intermetallics, were in the range of 20-40 MPa. On the other hand, sono-fragmentation studies revealed that the intermetallic crystal initially underwent low cycle fatigue loading, followed by catastrophic brittle failure due to propagating shock waves. The shock pressure generated from the acoustic cavitation cloud collapses surged up to 1.5 MPa inducing fatigue stresses within the crystal leading to eventual fragmentation.*

[§] Published as A. Priyadarshi, et al., Ultrason. Sonochem. **70**, 105260 (2021) – Reproduced after permission.

4.1 Introduction

Despite the fact that the benefits of UST on various cast alloy systems is well recognised and reproducible [1,269,270], basic understanding of in-situ ultrasound fragmentation behaviour of the primary solid phases in the melt is very limited while the governing mechanism of sono-fragmentation is not well understood. Recently, synchrotron X-ray imaging of solidification in real metallic melts under the presence of external fields has attracted attention of researchers and is being widely applied in-situ [137,271–273]. Fragmentation of Al_2Cu intermetallic dendrites in an ultrasonically treated Al-35% Cu alloy was observed by Wang et al. using the in-situ X-ray radiography [137]. Other investigations include the dynamic performance of cavitation bubble in relation to bubble growth mechanism [272]. Interaction of phases formed in Bi-8% Zn alloy with the acoustic cavitation bubbles/flow has also been studied by Wang et al. [271]. However, working with real melts is plagued by difficulties, including the handling of liquid metal melts, recording of multi-phase interactions while restricted by the narrow field of view and a continuously growing solid phase during imaging studies. To overcome these limitations, in-situ observations of organic transparent alloys is the proposed alternative [152,153,274].

In-situ grain refinement of organic transparent alloys has been studied using both optical and X-ray imaging techniques [152,153,274]. Chow et al. [153] observed that grain nucleation was accelerated under the influence of ultrasonic vibration causing fragmentation of a dendrite by the pulsating and imploding cavitation bubble. In-situ imaging studies on cavitation-induced fragmentation of calcite crystals present in a CaCO_3 solution revealed that fracture occurred due to the perpetual collapse of the developed bubble cluster [275]. Digital photographic observations of the effect of ultrasonic cavitation on the dendrites formed in a SCN-1-wt.% camphor alloy also revealed that the shock waves emitted from imploding bubbles were mainly responsible for the dendritic fragmentation [274]. However, the behaviour of the growing dendrites offers a very limited fragmentation standpoint as their mechanical properties differ significantly from those of solidifying dendrites or intermetallic crystals in real metallic alloys. Moreover, the physical properties of organic transparent alloys are also very different from the liquid metal alloys to a large extent making this analogy inappropriate [271].

Finding a suitable transparent analogue to liquid metals and conducting in-situ imaging experiments at ambient conditions can be very revealing and worthwhile in terms of profound clarity of the interactions. Water, with similar kinematic viscosity and Newtonian behaviour to

liquid Al, has been found to have a very similar nature in terms of acoustic cavitation development and bubble dynamics behaviour and is frequently a choice as a transparent analogue while conducting UST studies [18,88,276]. Wang et al. [103] recently investigated the cavitation-induced fragmentation and associated fracture mechanism of primary crystals (Si, Al₃Ti and Al₃V) formed in Al alloys. This seems to be the most relevant piece of work on the interaction of cavitation bubbles with primary intermetallic crystals to date. The study confirmed that the fracture of the crystals was caused primarily via the fatigue mechanism initiated by the cyclic pressure exerted by pulsating bubbles, possibly triggering a pre-existing crack to grow to a critical size followed by brittle fracture. Yet, this study was performed at moderate frames-per-second levels, and was not supported by measurements of acoustic parameters or mechanical properties. From other studies, it is also anticipated that fragmentation of dendrites in real melts happens by the combined effect of acoustic streaming jet impact [137] and shock waves propagation [277] from imploding bubbles. On the other hand, a recent similar study on the fragmentation of kidney stones suggested that the potential mechanism of stones' fragmentation is primarily associated with impingement of liquid jet followed by powerful shock wave emissions [278].

Implosion of cavitation bubbles and the resulting shock pressure field has been widely studied in water [279–285]. Cavitation bubbles are generated during the rarefaction phase of the incident ultrasonic wave, grow in size and rapidly collapse when they reach a critical resonance size during the compression cycle producing high-speed jets and local hydrodynamic impact pressures in the range of GPa [69]. However, the exact mechanism leading to the fragmentation of solid phases is still under scrutiny. Understanding the underlying mechanisms of cavitation-induced fragmentation of solid phases will allow us to accurately develop numerical models and advance UST into industrial scale applications [286,287]. To this end, it is of interest to further investigate the fragmentation behaviour of the intermetallic crystals under controlled cavitation using a single laser-induced bubble event, to study the details of cavitation interaction with the intermetallics and then expand the experiment to continuous ultrasonic processing in order to understand the dynamics of this phenomenon in its full complexity. The acoustic parameters and in-situ observations need to be related to the mechanical properties of the fragmented phases.

In this study, the fragmentation of primary Al₃Zr intermetallic under the influence of a single and multiple bubble cavitation has been investigated in deionized water, complemented with in-situ high-speed imaging studies. The fracture mechanism of the intermetallic crystals has

been elucidated using the recorded images and validated using critical stress-fracture mechanics. The results reveal for the first time that the fragmentation of intermetallic crystals was essentially prompted by the interaction with shock waves released from imploding bubbles. The fragmentation criterion has also been supported by the pressure field measured by a high-frequency calibrated hydrophone to account for the shock wave-intermetallic interaction.

4.2. Experimental methodology

4.2.1 Single laser-induced bubble (LIB)

A Nd:YAG laser system (Nano S 130-10, Litron Lasers, UK) was deployed to generate laser-induced cavitation bubbles by focusing a single high-energy laser pulse of 10.5 ± 1 mJ, with a wavelength of 532 nm (Green beam) and duration of 6-8 ns into distilled water. A transparent custom-built chamber of dimensions 420 mm $\times$ 438 mm $\times$ 220 mm equipped with a curved mirror to focus the laser beam was used (Fig. 4.1). The detailed information about the experimental arrangement can be found elsewhere [280]. An extracted intermetallic crystal (as discussed in section 3.2 in Chapter 3) was then fixed on a steel substrate using a cyanoacrylate adhesive. The attached crystal was placed on a bespoke xyz translational stage and judiciously positioned in such a way that laser breakdown occurs in close proximity to the fixed crystal at a radial distance of 3-4 mm. The standoff parameter γ (ratio of the distance of breakdown point from the crystal's surface and the maximum bubble radius) was deliberately kept in the range of 1-1.5 to ensure that the bubble does not touch the crystal upon expanding. In-situ recordings of the interaction of the single laser bubble with the intermetallic crystal were captured using high-speed shadow-graphic imaging performed at 200,000 frames per second with resolution of 400×250 pixels by employing a Hyper vision HPV X2 (Shimadzu, Japan) high-speed camera producing 256 frames for every recorded sequence with shutter time of 200 ns. The illumination and high temporal resolution were provided by synchronous (to frame capture) 10 ns laser pulses of 640 nm (Red beam) via CAVILUX Smart UHS system (Cavitar Ltd., Tampere, Finland). The images (and video in supplementary material) given in this article have been confirmed after 5 similar observations and are found to be repeatable and descriptive. This particular experiment was performed in collaboration at CavLab, GLA. The author of this thesis contributed by identifying and adjusting the camera settings for high-speed filming, preparing and mounting of the crystal within the experimental setup, and capturing the measurements.

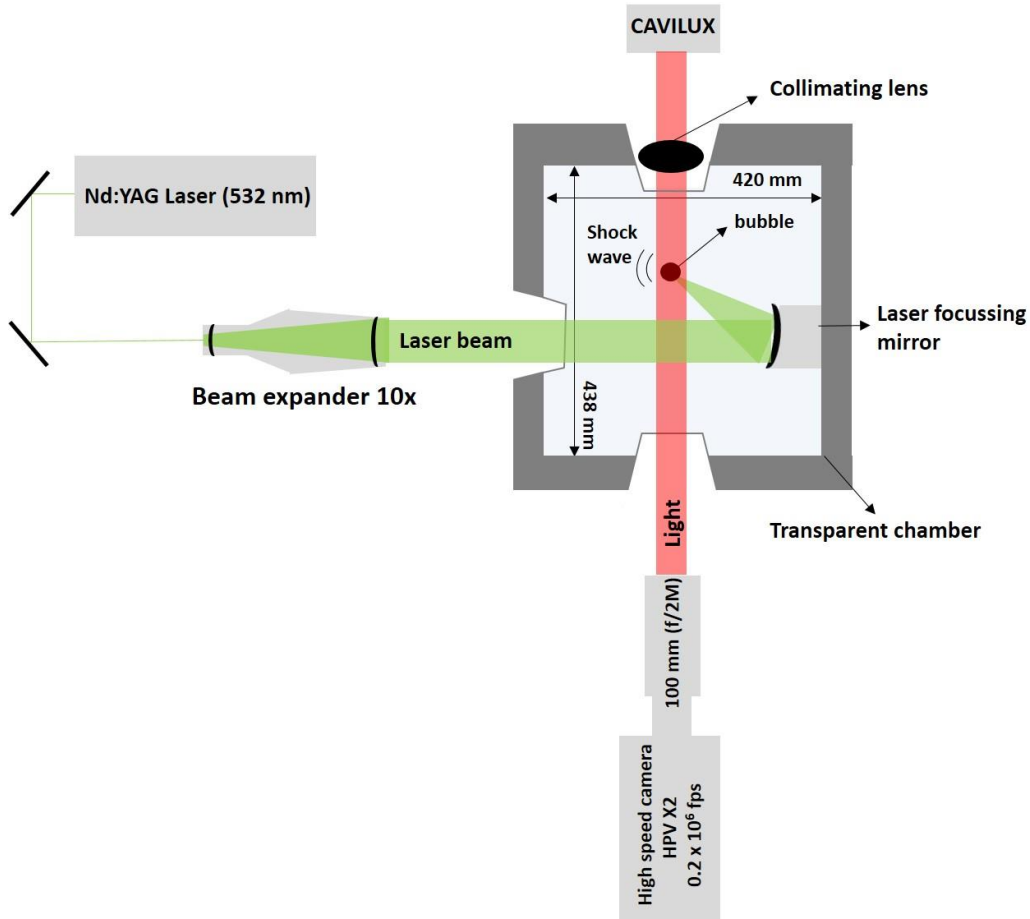


Fig. 4.1 Schematic representation of the experimental setup used for generating laser-induced bubble (LIB).

4.2.2 Ultrasonic processing

The extracted Al_3Zr crystals were fixed onto a steel plate by a cyanoacrylate adhesive and that was deliberately placed on the bottom of the glass vessel of dimensions ($W_v \times L \times H_v$) 75 mm $\times$ 75 mm $\times$ 100 mm (Fig. 4.2a). The tank was then filled with de-ionized water up to a height of 75 mm from the base and placed below the 24 kHz ultrasonic horn (Hielscher UP200S Ultrasonic processor) made of titanium with a tip diameter of 3 mm and an adjustable acoustic oscillating amplitude from 42 to 210 μm peak-to-peak at full power (100%). The detailed technical specification of the ultrasonic processor is listed in the manual [288]. The intermetallic crystals were placed precisely 3-4 mm below and at crosswise direction of the sonotrode tip. The sonotrode was immersed approximately 10 mm below the surface of water. The experiments were performed at a chosen peak-to-peak amplitude of 42 μm (corresponding to 20% input power) and conducted under room temperature conditions.

In-situ imaging of interaction between cavitating liquid and primary intermetallic crystals were captured and recorded using high-speed camera (Photron SA-Z). A frame rate of 100,000 fps

was chosen for imaging the sono-fragmentation behaviour at a resolution of 640×280 pixels with a shutter speed of $8.39 \mu\text{s}$. In this case, front light photography was used in contrast to shadow photography in LIB experiments. A combination of a multi LED flash lamp (GS Vitec) and a high-power light source (Karl Storz Power LED 175) from the front and back of the glass tank respectively was utilised in order to achieve maximum illumination in the direction for filming. Figure 4.2a shows the schematic of the experimental setup made for sono-fragmentation imaging studies. Minimum of 10 consistent and repeatable observations of the fragmented crystals and their interaction with the cavitating field were recorded in real time.

Figure 4.2b exhibits a separate setup that was explicitly used for capturing the propagation of shock waves from the collapsing bubbly clouds using shadow-graphic imaging. The developed cavitation zone nearby the sonotrode surface was recorded at 1 million frames per second in contrast to the crystal fracture observation performed at 100 kfps (due to different time scale of the events) using Hyper Vision HPV X2 (Shimadzu, Japan) ultra-high-speed camera under synchronous 10 ns laser pulses (CAVILUX) illumination in order to capture and quantify the highly dynamic behaviour and propagation of shock waves. Multiple sets of shock wave fronts for a period of 0.25 ms were captured, analysed and related to the fragmentation mechanism (typically occurs after 8-10 ms).

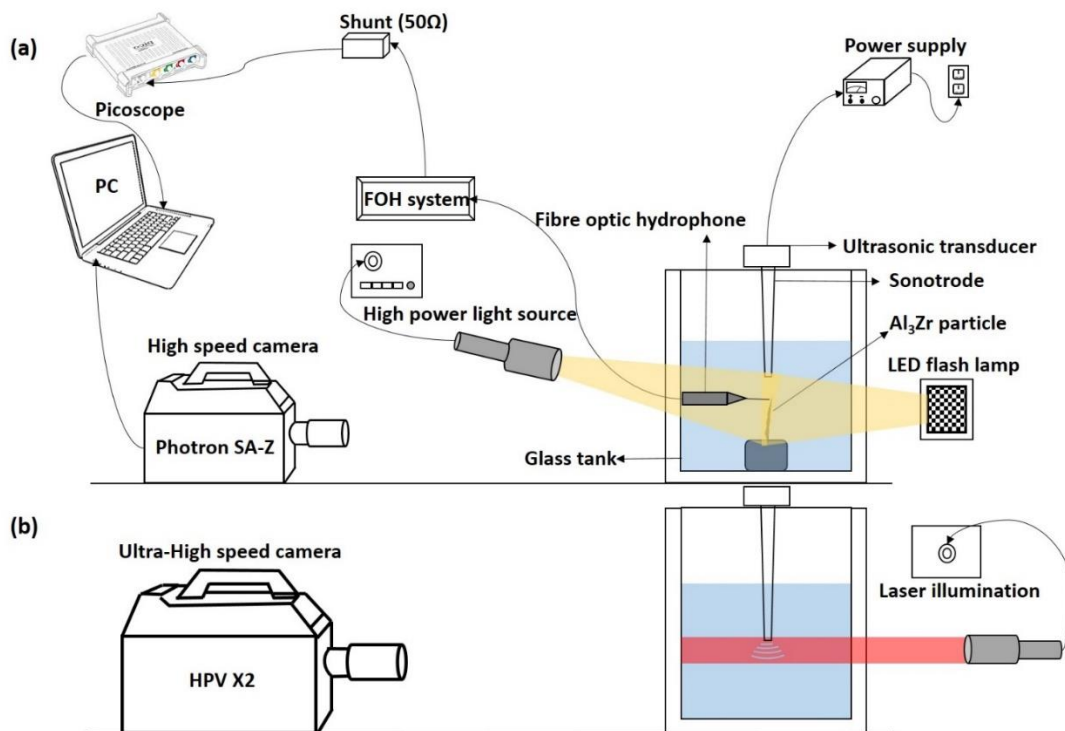


Fig. 4.2 Schematic of the experimental setup involved for (a) sono-fragmentation, and (b) shock wave imaging study.

4.2.3 Acoustic pressure measurements

A fibre optic calibrated hydrophone (FOH) device, with a 125 μm probe sensor (Precision Acoustics Ltd., Dorchester, UK) was integrated to the experimental setup as shown in Fig. 4.2a to monitor the pressures at MHz frequencies associated with transient cavitation and shock wave emissions. The sensor was connected to the digital oscilloscope-3204D (Pico Technology) through the 50 Ω output of FOH system to capture the acoustic signal generated from the ultrasound device. The electronic connection of the sensor is schematically represented in Fig. 4.2a. The hydrophone was calibrated between 1 to 30 MHz at increment of 1 MHz using a PVDF (Polyvinylidene fluoride) membrane hydrophone (0.4 mm diameter) with a sensitivity and its associated uncertainties (grey region) varying as shown in Fig. 4.3. The shock wave pressure was recorded at locations close to the tip (± 0.2 mm) of Al_3Zr crystal placed at 3 mm vertically below the sonotrode (under) along the symmetry axis and 4 mm in the transverse axis (side).

The real time acoustic signal monitoring was captured using the Picoscope data acquisition software. The raw hydrophone voltage signal was obtained over the period of 2 ms (~ 48 acoustic cycles) with a sampling rate of 500 MS/s (Mega samples per second). The raw data was acquired after the steady state condition had been attained. The Fast Fourier Transform (FFT) of the voltage-time signal that was applied to obtain the pressure signal followed the deconvolution process as described in Appendix and previously discussed in our work [289] and in [62]. The pressure values were averaged over 60 waveform signals of 2 ms each to ensure repeatability of the results while noise was subtracted from the raw signal.

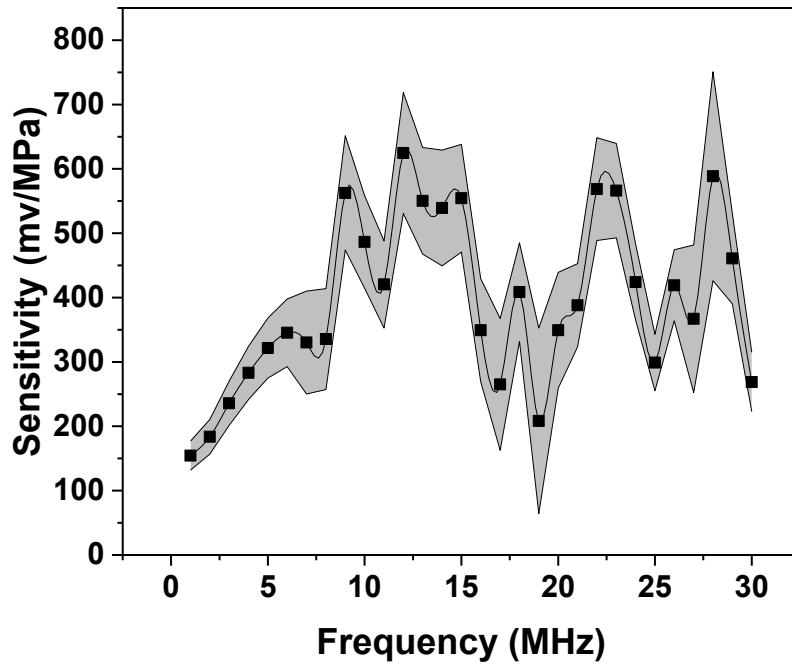


Fig. 4.3 Sensitivity of FOH calibrated in discrete steps of 1 MHz between 1-30 MHz bandwidth frequencies, with calibration uncertainty represented as grey shading.

4.3 Results and discussion

4.3.1 In-situ observations and analysis of fragmentation

4.3.1.1 Single Laser-induced bubble interaction

A sequence of images captured using high-speed filming of primary Al_3Zr intermetallic fragmentation is shown in Fig. 4.4(a-l). An associated video corresponding to this sequence of images (supplementary Video 1) is accessible with the published version of this work (<https://doi.org/10.1016/j.ultsonch.2020.105260>). These real time images demonstrate the interaction of a single laser-induced cavitation bubble with an Al_3Zr intermetallic crystal leading to its fracture. Figure 4.4a shows the studied intermetallic crystal of approximate dimension $3.1 \text{ mm} \times 3.5 \text{ mm} \times 0.06 \text{ mm}$ ($L_c \times W_c \times T_c$) with a pre-existing crack length of 0.5 mm (indicated with a white arrow) at time $t = 0 \text{ } \mu\text{s}$. After about $5 \text{ } \mu\text{s}$, an optical breakdown is triggered using the laser energy source causing bubble nucleation (marked with blue arrow) and release of continuous fronts of shock waves propagating with both compressional and rarefaction phases (indicated with red arrow) within the liquid as shown in Fig. 4.4b. The laser-induced bubble then undergoes the growth phase from $t = 5 \text{ } \mu\text{s}$ to $t = 150 \text{ } \mu\text{s}$, expanding up to a radius of 1.5 mm as illustrated in Fig. 4.4 (b to c) in response to the energy disposition of the liquid medium. The crystal interaction with the first set of generated shock wave fronts

causes the pre-existing crack (at a distance of approximately 3.3 mm from the bubble centre) to propagate through the intermetallic thereby increasing its length (indicated with white double arrow). Thereafter, the inertia of the host medium causes the bubble to shrink and collapse asymmetrically at $t = 325 \mu\text{s}$ (Fig. 4.4d), following the release of next set of shock wave fronts scattering within the liquid.

Following the first collapse, a smaller (secondary) bubble is generated by partially splitting from the main (mother) bubble (encircled in green) with sufficient energy to follow its growth and collapse cycle till a complete separation occurs. The secondary bubble then expands to its maximum size until $t = 405 \mu\text{s}$ causing the crack to further propagate and a secondary crack to develop (indicated with a white arrow) at the bottom of the intermetallic crystal as shown in Fig 4.4e. The smaller bubble then completely splits up from the primary bubble followed by a rebound growth and shrinkage phase and subsequent release of shock waves (indicated with red arrow) upon its final collapse as shown in Fig. 4.4f. To this effect, the crack rapidly propagates to the other end causing complete fracture of the crystal from the bottom left side (indicated with a yellow boundary). Just after next $5 \mu\text{s}$, the primary bubble collapses to generate another set of shock wave fronts (indicated with a red arrow) propagating through the liquid as shown in Fig. 4.4g. Consequently, the secondary crack can be seen spreading from the bottom part to merge with the primary one (marked with red curved arrow) as shown in Fig. 4.4(h-l). Multiple rebounds and collapses of the primary cavitation bubble happen until the bubble's energy is entirely dissipated in the medium and it finally disintegrates into tiny clusters of bubbles as shown in Fig. 4.4l. Even though it seems from the sequence of images in Fig. 4.4 that crack propagation in the crystal results from an immediate bubble collapse event, this may not be entirely true owing to a hysteresis induced from the signal delay after the laser is essentially triggered. Therefore, what may appear as the consequence of crystal-shock wave interaction from a rebound collapse process, could actually be a result of preceding shock waves generated through previous cavity collapses i.e. the damaging effect of the propagating shock fronts on the intermetallic produced after the 2nd and 3rd rebound collapses at $t = 485 \mu\text{s}$ and $t = 565 \mu\text{s}$, respectively, in reality might have induced either from the prior released shock waves $t = 5 \mu\text{s}$ and $t = 325 \mu\text{s}$ or through their synergistic response. It is also likely that the shock fronts generated from the rebound collapses are too weak to cause any severe damage to the crystal compared to the initial high energy disseminated shocks. It has been observed that a split cavitation bubble (as in the present case) produces multiple shock waves with separate centres in the subsequent breakdowns [290]. So, it is fair to say that the whole

crystal fragmentation is essentially a reaction to cumulative shock waves (~ 5 shock fronts typically monitored after the final collapse) impact from a single laser bubble. Similar response was observed in all other cases of single laser bubble experiments where fragmentation essentially occurred from the split cavitation and asymmetric rebound producing multiple shock waves caused by the residual asymmetry during implosion as achieving a perfect spherical shape of the bubble is barely possible [291]. It is also evident from Fig. 4.4 that since there was no direct physical interaction of the laser-induced bubble with the intermetallic crystal with standoff parameter γ being equal or greater than 1 (see supplementary Video 1 for better clarity), the intermetallic fragmentation was solely a result of repeated shock wave cyclic fronts emitted from the breakdown (nucleation) and successive collapse phases of the laser-induced bubble. Also, it is evident from the high-speed images that the crystal underwent almost instantaneous fragmentation befalling in less than a millisecond time. It is worth mentioning here that the asymmetrical collapse of the bubble generated multiple shocks that interacted with the fixed sample leading to almost instantaneous brittle fracture. This type of collapse replicates the real shock pressure conditions occurring in continuous sonicated environments as shown later in section 4.3.1.2.

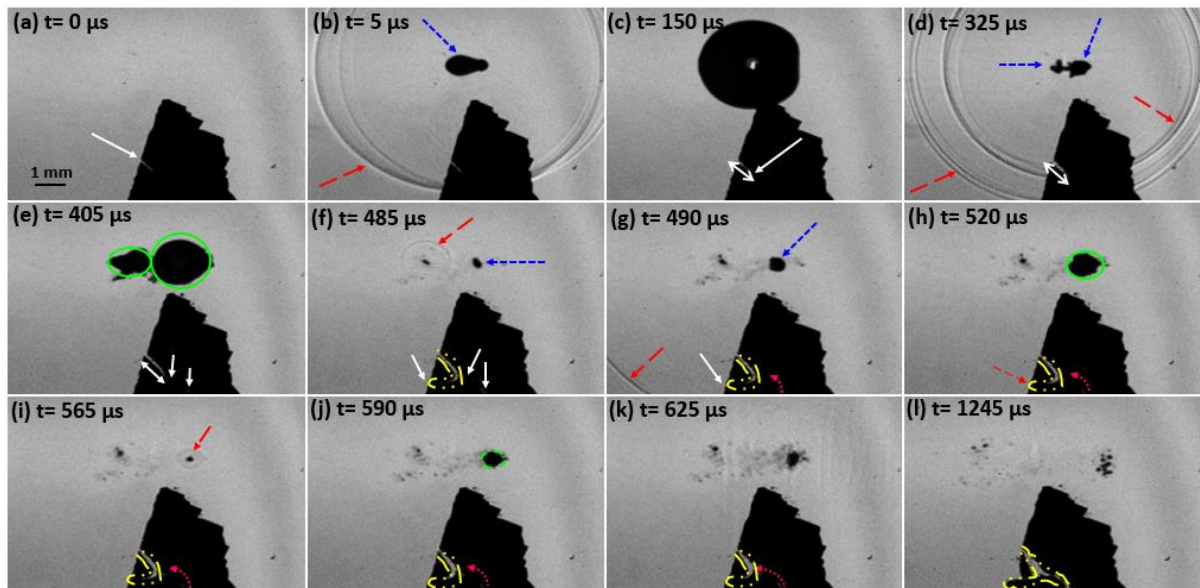


Fig. 4.4 High-speed imaging sequence showing complete fragmentation of primary Al_3Zr intermetallic particle (pre-existing crack) upon interaction with a shock wave from a laser nucleated single bubble recorded at 200 kfps. The supplementary video can be accessed with the published version of this chapter as Video 1.

An attempt to quantify the observed fragmentation mechanism by means of basic fracture mechanics was made. The fragmentation mechanics has been applied in terms of critical stress required to initiate pre-existing crack propagation that completely fractures the intermetallic crystal upon interaction with the laser-induced bubble.

As previously mentioned in this section, the predominant fragmentation mechanism is the surge of shock wave pressures upon bubble collapse. Therefore, it is essential to estimate the strength of shock waves in relation to their pressure amplitude. The following equation suggested by Vogel et al. [279] provides the variation of the pressure amplitude (P_{sw}) of the emitted shock wave from a spherical bubble collapse against the propagating distance, r .

$$P_{sw} = c_1 \rho u_{sw} (10^{(u_{sw}-c_s)/c_2} - 1) + P_h \quad (4.1)$$

where ρ represents the density of the surrounding medium (water) before the emission, u_{sw} denotes the shock wave velocity measured from the $r(t)$ curve, c_s corresponds to the speed of sound in water, c_1 and c_2 are empirical constants equal to 5190 m/s and 25306 m/s respectively as defined in [292], and P_h indicates the hydrostatic pressure.

The maximum shock wave velocity (u_{sw}) for the optical breakdown through laser energy of 10 mJ and 6 ns pulse was reported to be almost 3 times the speed of sound in water [279]. Considering the velocity to be approximately 4500 m/s, the shock pressure amplitude was determined using Eq. 4.1 to be around 7000 MPa. Additionally, using a far-field hydrophone, the shock pressure amplitude, by a similar in nature and energy capacity bubble (10 mJ), was measured in the range of 2.5-10 MPa at a radial distance of 4-4.5 mm from the bubble centre [279,281]. It has been previously reported that the pressure amplitude close to 100 MPa decays approximately as r^{-1} nearby the shock front [279,293]. On a logarithmic scale, the pressure amplitude initially attenuates in an inverse parabolic fashion (r^{-2}) up to a distance of 300 μ m with a value close to 150 MPa and then reduces linearly with the propagating distance until the shock front completely dissipates in the medium [279]. Using these empirical relationships, the shock pressure at a distance of 300 μ m from the laser bubble centre was linearly interpolated to a radial distance of 3.3 mm (the distance of the pre-existing crack from the emission centre) and was estimated to be about 31 MPa. The shock pressure amplitude was estimated to vary between 20-40 MPa for other specific positions of the crystal placed away from the bubble centre (Fig. 4.5a) through careful interpolation, keeping in mind the linear trend of the pressure attenuation.

It is to be noted that these predicted pressure values are for an ideal case of a symmetric bubble collapse that produces a single shock wave. It has been reported that the pressure amplitude of the propagating shock waves emitted from an asymmetric bubble collapse at a distance of 3 mm from the plasma centre is in the range of 4-11 MPa depending upon the focussing angle of the laser beam [291]. This variation is also indicative of the fact that the emitted shock wave is formed through superimposition of signals originating from diverse locations across the elongated plasma region. Therefore, the shock pressure obtained for a spherical bubble collapse clearly exceeds the pressure signal generated from an asymmetric collapse.

To relate the induced shock pressures to those required for the complete fracture of the crystal, the critical fracture stress was determined based on the typical Griffith criterion for a single edge notched Al_3Zr intermetallic (Fig. 4.5b) assuming that Mode I fracture (Fig. 4.5c) is applicable [294]:

$$K_{Ic} = C\sigma\sqrt{\pi a_c} \quad (4.2)$$

Here, K_{Ic} represents the critical stress intensity factor (also called fracture toughness) of the intermetallic crystal, a_c corresponds to the crack length of the pre-existing notch, C is a constant parameter depending on the crack length, and σ denotes the stress needed for complete fracture of the intermetallic. For the present case, the value of K_{Ic} was considered to be 1.1 as obtained from Table 3.1, the crack length, a_c is taken to be 0.5 mm based on the direct observation, and the constant C is taken as 1.12 [295]. Using Eq. 4.2, the critical stress that would result in the brittle fracture of Al_3Zr crystal with a known crack length was estimated to be around 25 MPa. The required fracture stress for crystals having crack length between 0.2 mm to 0.6 mm was in the range of 22-40 MPa (Fig. 4.4d). Therefore, in the ideal case of a spherical collapse, the generated shock pressure is sufficient to break the crystal; however, in our case where multiple collapses are observed due to collapsing asymmetry (elongated plasma breakdown) [292,296], the distributed shock pressure is expected to be comparatively less. Moreover, this exaggeration of the maximum pressure generated from a single shock wave compared to multiple pressure shocks is also in good agreement with experimental measurements as discussed elsewhere [281,291].

Nonetheless, due to the observed almost instantaneous breakage it seems that the pressures generated by shock waves are sufficient to overcome the critical fracture stress of up to 40 MPa as estimated by Griffith's criterion. Also, it is possible that the required stress for fragmentation could be even less than estimated, as the pre-existing crack (as shown in Fig. 4.4a) branches

into two new cracks (Fig. 4.4I) thereby failing not just as per Mode I but by a combination of other fracture modes that the crystal experiences. This implies the presence of other pre-existing flaws facilitating the crack propagation with a multi-directional tendency. Therefore, the resulting multiple shock wave fronts emitted from the collapse of a laser-induced bubble are sufficient to produce brittle failure of an Al_3Zr crystal on the spot.

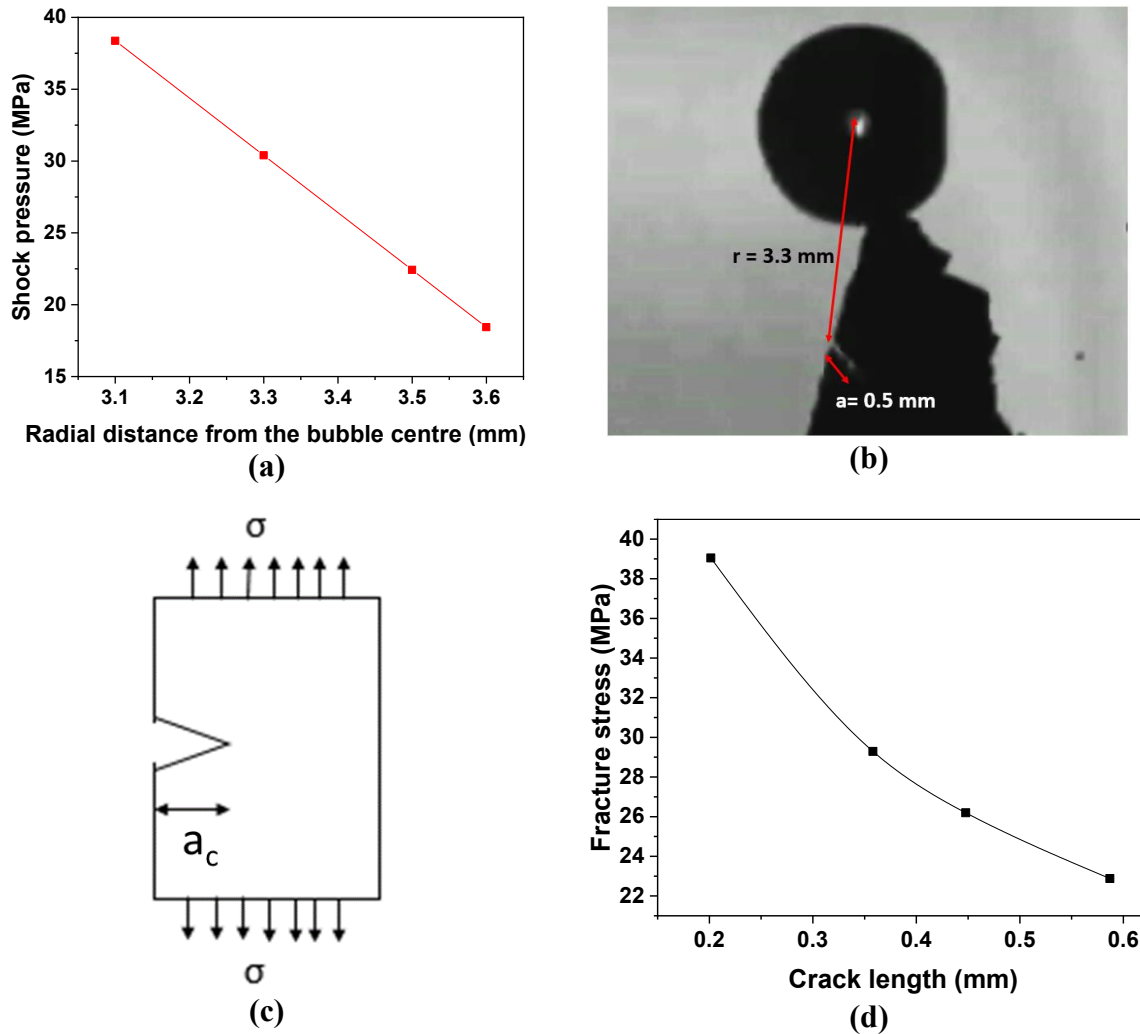


Fig. 4.5 (a) Calculated shock pressure magnitude, (b) image of Al_3Zr crystal showing crack length and its distance from the bubble centre, (c) schematic representation of stresses acting on single edge notched plate, and (d) theoretical fracture stress required for its fragmentation.

4.3.1.2 Ultrasound-induced cloud interaction

Having identified the governing fragmentation mechanism of intermetallics exposed to cavitation impacts, next step is to investigate the fracture of primary Al_3Zr crystals (with and without a noticeable pre-existing crack) when subjected to ultrasonic cavitation induced by a sonotrode.

To start with, the sources of shock waves emissions in this dynamic and highly transient sonicated environment were monitored. Fig. 4.6 shows typical series of images of an already developed cavitation zone at the tip of the sonotrode captured at 1 Mfps using the integrated laser illumination. It is clear that the cavitation phenomena occurring below the sonotrode emit shock waves in a consistent pattern. The red arrows show the emitted shock wave propagating through the liquid at definite time intervals. An associated video corresponding to this sequence of images (supplementary Video 2) is accessible with the published version of this work (<https://doi.org/10.1016/j.ultsonch.2020.105260>). We observe that the tip of the sonotrode is covered by a cavitation cloud which undergoes repetitive expansion and collapse oscillations thus emitting shock waves. The majority of these shocks are generated from the edges: at most locations of the sonotrode surface there is interference of the acoustic waves from adjacent point sources and, therefore, it is only at the edges where there are uncanceled horizontal components and no shielding from the sonotrode [297], resulting in diffractive field effects and spherical spreading of the shock waves. It has been noticed that the collapse of inertial cavitation cloud against the sonotrode face and interaction of the pressure fields within this cloud will also generate complex pressure waves propagating outwards from the perimeter of the sonotrode tip [298]. Video 2 footage shows that around 4 shots of multiple shock wave fronts are released on average in every 0.25 ms from different locations in the vicinity of the ultrasonic source upon collapse of bubbly clouds. It has been argued that these released shock waves have the potential to damage/break the solid crystals in the surrounding area [299–301]. However, the lack of solid evidence in literature have imposed restrictions for the establishment of such a hypothesis.

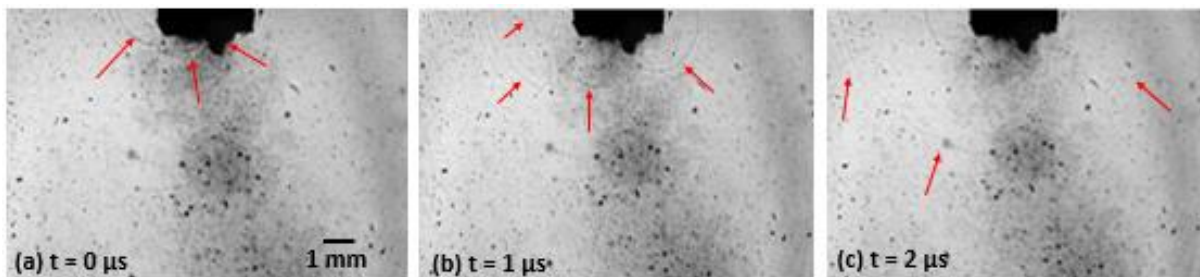


Fig. 4.6 Images of ultrasonic cavitation and shock wave propagation generated from a 3 mm sonotrode recorded at 1Mfps. The supplementary video can be accessed with the published version of this chapter as Video 2.

Fig. 4.7 shows the frame by frame fragmentation process of a single edge notched Al_3Zr crystal by means of acoustic cavitation. An associated video corresponding to this sequence of images (supplementary Video 3) is accessible with the published version of this work (<https://doi.org/10.1016/j.ultsonch.2020.105260>). In this case a lower frame rate speed was deployed using light illumination as explained in section 4.2.2. The first frame ($t = 0$ ms) exhibits a well-illuminated typical Al_3Zr crystal of dimension approximately $2.6 \text{ mm} \times 2.8 \text{ mm} \times 0.06 \text{ mm}$ ($L_c \times W_c \times T_c$) having a crack/notch length of about 1.8 mm (encircled in yellow). Note for imaging experiments, the crystal mounting was done manually on a steel substrate and fixed using a cyanoacrylate adhesive as explained earlier in Section 4.2. The measurement of initial crack length within the crystal was done using high-speed photography and further confirmed via optical microscopy. Based on the image resolution and pixel size, the estimated crack length was found to vary with standard deviation of 0.1 mm from the mean measured value of 5 similar size crystals with noticeable pre-existing cracks used for fragmentation experiments. Prior to switching on the ultrasound (Fig. 4.7a), it has been made sure that there is no presence of microbubbles ($> 10 \text{ }\mu\text{m}$, camera lens cannot resolve smaller size bubbles) in the vicinity of the crystal. Fig. 4.7b shows the formation of small cloud mist near the ultrasonic horn (indicated with red arrow) after the transducer was turned on, which later on forms into a large cavitation cloud covering the whole of the sonotrode surface (Fig. 4.7c). As this cloud collapses in the next frame ($t = 4.34$ ms), a small notch starts to appear at the bottom of the crystal (encircled in blue). Note that since these primary crystals are highly brittle, a crack in any location of the crystal will form depending on the amount of internal flaws that generally act as stress raisers and crack initiation sites. As the cycle of cloud formation and collapse repeats from $t = 4.40$ ms to $t = 4.68$ ms, the crack grows and propagates until it reaches the edge of the crystal (shown in blue rectangular border). Subsequently the crystal fails as the new crack connects to the existing crack (enclosed in a green boundary). From the images, it is apparent that there has been no direct interaction of the cavitation cloud with the studied crystal till $t = 5.02$ ms while the fracture being already initiated. It should be noted that the crystal fragmentation in this case occurs in a very similar fashion as was observed in the case of single bubble interaction. The existing crack propagates and then splits into two secondary crack branches, indicating that the failure occurs through combined (opening and tearing) fracture modes. Unlike the laser-induced bubble, however, the fragmentation here is not instantaneous and occurs in about 7 ms (168 acoustic cycles). It was previously shown that interaction of individual bubbles with intermetallics can be the driving mechanism of

fragmentation [103]. It is unlikely that microbubbles of size in the range of few microns (which cannot be resolved by the camera lens) oscillating far away from source, are capable of damaging the crystal and causing catastrophic fracture in such a short span of time. Indeed, microbubbles with radii in the range of 10-15 μm produces pressure pulses close to 0.1 MPa upon transient collapse that is insufficient to induce fast fracture of the crystal [284,302]. Wang et al. [103] previously reported that large pulsating cavitation bubbles with radii in the range of 50-80 μm that undergo vigorous periodic collapses, damages the nearby crystal after a significant period of 1680 acoustic cycles. So, even if there are non-linearly oscillating bubbles with radii in the range of 10 μm or less attached to the crystal for longer duration, it is unlikely that they would induce severe damage in such a short period of time as they are not likely to collapse [302,303]. Based on the number of acoustic cycles, it is conceivable that the crystal must have survived almost 100 shock waves (based on the shock front approximation as per Fig. 4.6) prior to fracture. It appears that, even though the fragmentation of crystal as observed in the section 4.2.1 is almost instantaneous, the Al_3Zr intermetallic fracture can also be affiliated with fatigue type failure in view of the fact that the crystal survived multiple cavitation cloud collapses before its complete rupture. It is suggested that emitted shock waves from cavitation cloud collapses initially caused the formation of a sub-critical crack that later developed into a critical size crack as observed by Wang et al. [103]. Results show, for the first time, that the governing mechanism is due to the shock waves generated from clouds of bubbles near the sonotrode tip, which may also be complemented by the vigorous oscillation of individual pulsating cavitation bubbles in the vicinity of the crystal.

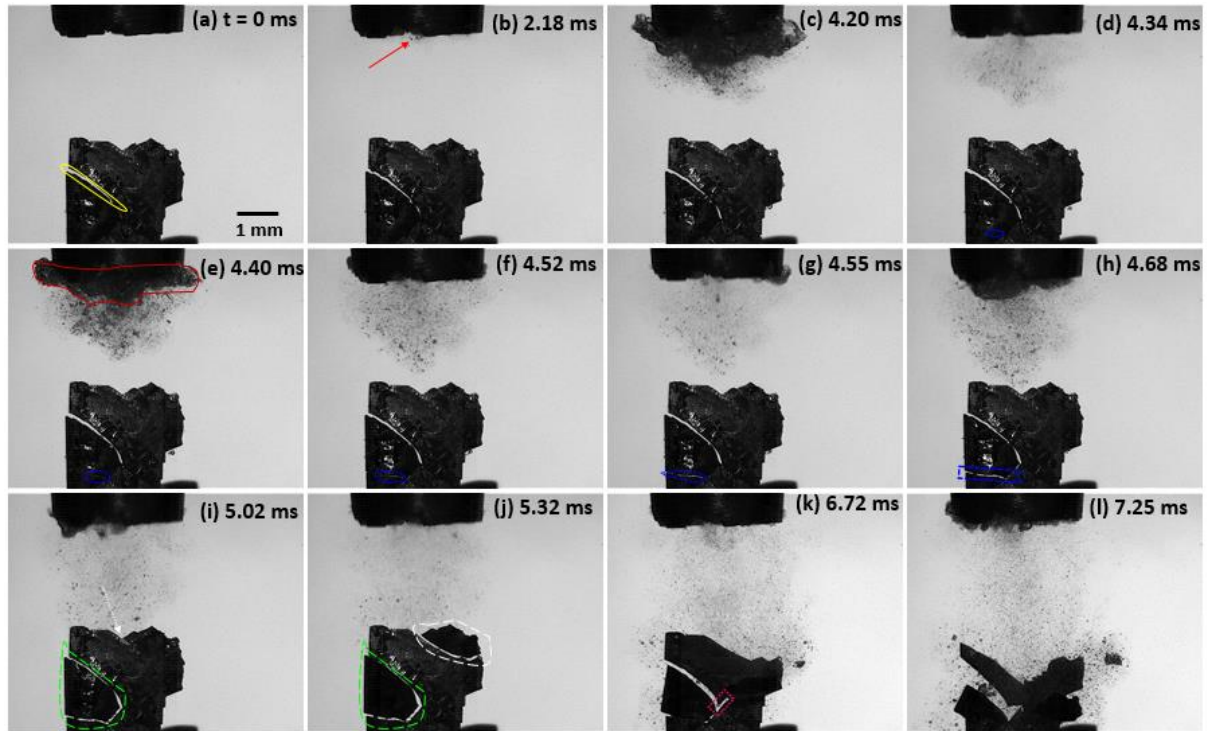


Fig. 4.7 High-speed images of fragmentation of primary Al_3Zr (single edged notch) crystals captured at 100 kfps when subjected to ultrasonic cavitation. The supplementary video can be accessed with the published version of this chapter as Video 3.

In addition to the evaluation of the fracture mechanism of an intermetallic crystal having a pre-existing notch, the fragmentation sequence has also been observed for a perpendicularly oriented crystal placed at roughly 3 mm vertically below and around off-axis 4 mm in the crosswise direction, to account for any bending effects of the fixed crystal from the ultrasound-induced acoustic cavitation pressure field. Again, to avoid any uncertainty caused by microbubbles attached to the crystal's surface as in the case of a crystal in Fig. 4.7, sonication was applied only after making sure that there are no pre-existing bubbles touching the intermetallic that can be resolved by the camera lens. Fig. 4.8(a-o) shows the sequence of sono-fragmentation images of forward-facing and side-facing primary Al_3Zr crystals. An associated video corresponding to this sequence of images (supplementary Video 4) is accessible with the published version of this work (<https://doi.org/10.1016/j.ultsonch.2020.105260>). Only selected frames have been shown for the best representation of the fracture mechanism and brevity of the manuscript.

The first image at $t = 0$ ms displays the well-illuminated crystals placed in two perpendicular planes below the 3 mm sonotrode tip. For clarity, the crystal on the left will be termed as CL and crystal on the right as CR from here onwards. At $t = 1.65$ ms, a few tiny bubbles started

to appear just beneath the sonotrode and a tiny crack is formed at the top of the CL (indicated by red arrow). After about 3.19 ms, clusters of bubble start to cavitate resulting in the possible release of shock waves causing the crack formed on CL to enlarge and notches on CR to form (Fig. 4.8c). At $t = 5.45$ ms, a notch on CR has developed upon increased exposure time of ultrasound and can be clearly seen. Then at $t = 5.9$ ms (Fig. 4.8h), the top right corner of CL has completely separated off and as the propagating bubble cloud becomes denser, the crack starts to develop on CL and a visible cavity forms at the top of the CR (see supplementary Video 4 for clarity). Note that the position where the crack, notch or cavity develops first in the crystal depends, apparently, on the presence of a pre-existing micro crack and defects at those locations, which cannot be resolved in the images. In Fig. 4.8(h to k), as the cavitation bubble cloud approaches the crystals, the top portion of the CR exhibits severe flapping, followed by the fragmentation and a top left corner of CL is detached (indicated by the arrow). The flapping part of the CR ultimately shears away as shown in Fig. 4.8(o). Also, it can be noticed from the sequence of snapshots that a relatively large cavitating bubble in the centre of the images (and within depth of field of 6 mm) has been captured by a standing wave and trapped at the same location changing its vibration (surface/Faraday waves) modes [304] in a stable non-linear motion throughout the sequence without significant variation in its size, indicating the weak effect of the incident pressure waves at that specific position. This confirms evidence that there is almost negligible effect of incident waves and acoustic streaming on the CR located away from the source. Hence, only the powerful surges from shock waves due to the bubble cloud collapse can be responsible for shattering the CR as in Fig. 4.8o.

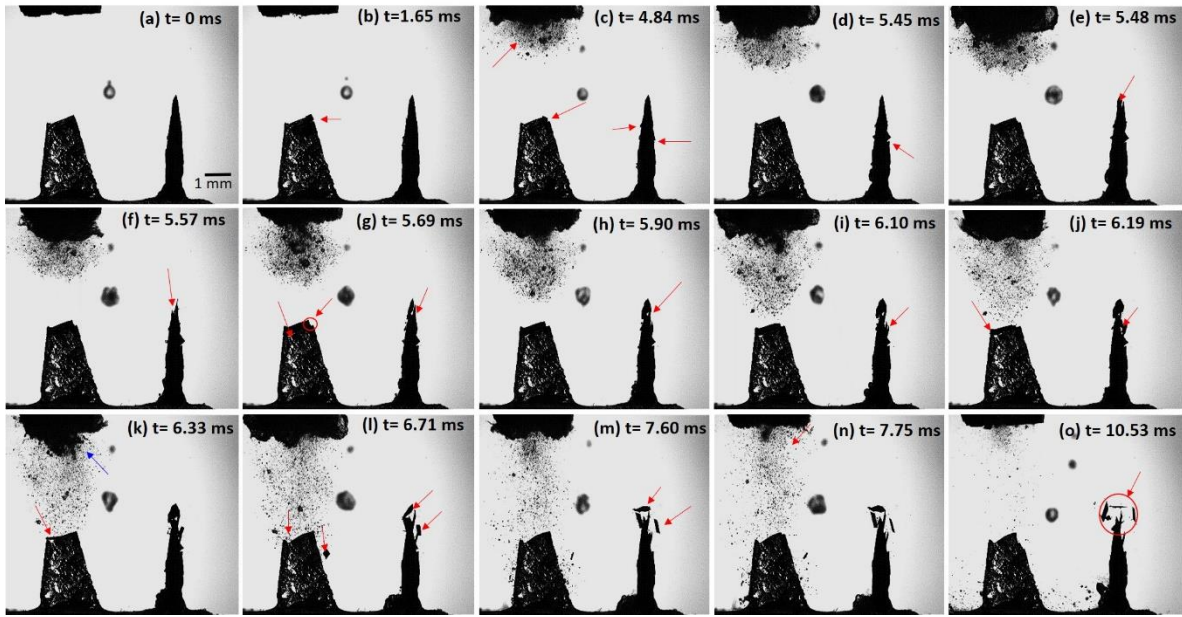


Fig. 4.8 High-speed images of fragmentation of primary Al_3Zr crystals captured at 100 kfps when subjected to ultrasonic cavitation. The supplementary video can be accessed with the online version of the article as Video 4.

The Al_3Zr crystal (CR) underwent just 186 cycles of ultrasonic vibration before its complete fragmentation representing low cycle fatigue type failure. It is worth mentioning that the fracture of crystals at certain locations occurred before the cavitation cloud even approached the intermetallic surface. Also, there is no evidence of a pulsating bubble clusters on the surface of the crystal that can possibly induce damage as a result of liquid jet ejection. So, the only likelihood is that the fragmentation occurs through shock wave interaction causing the crystal to shatter in pieces like that of glass particularly when it is outside the cavitation zone. These observations confirm that the shock waves emitted from the collapse of cavitating bubble cloud act as a crucial agent responsible for the fragmentation of primary crystals, as evaluated in next section. In addition, repeated emission of shock waves impacting the crystal surface intermittently cause low cycle fatigue within the material, eventually fragmenting the crystal thus making the cyclic shock pressure one of the possible fracture mechanism just before brittle failure [103].

As observed from Fig. 4.7 and Fig. 4.8, it is apparent that the acoustically generated large cavitation structure attached to the sonotrode undergoes repetitive dynamic oscillations. It is interesting to note that the oscillating frequency of intermetallic deflection decreases to almost 4.8-5 kHz just before the fragmentation (from $t = 4.81$ ms to $t = 5.62$ ms at steps of 0.2 ms) matching the self-induced subharmonic frequency ($1/5^{\text{th}}$ of the driving frequency) of the large cavitation structure attached to the sonotrode tip as shown in Fig. 4.8k. This sub-harmonic

oscillation of the crystal is indirectly related with the emission of shock waves every time the attached cavitation cloud collapses [305]. The strange behaviour of this large formed cavitation structure has previously been observed by Znidarcic et al. [306]. It was reported that this developed cavitation structure generates its own oscillating frequency that falls in the subharmonic range of the ultrasonic driving frequency. The strength of this subharmonic signal induced from this large cloud can actually be very high and its acoustic intensity in the power spectrum can even come close to the fundamental pressure wave [307]. Johnston et al. [118] found that these strong subharmonic signals are related to the emissions of periodic shock waves from acoustically driven cavitation cloud collapses.

The impact of released shock waves on the CR intermetallic crystal has been explained at different time progressions (see supplementary Video 4 for better clarity). As soon as the ultrasound is switched on, the CR undergoes continuous deflection of about $24.3\text{ }\mu\text{m}$ at $t = 1.05\text{ ms}$ oscillating close to the driving frequency (24 kHz) with simultaneous build-up of cavitation structure near the sonotrode. It was observed that at specific time steps where the bubble cloud collectively collapses, the pressure impulse from the generated shock wave causes the maximum deflection of the crystal viz. $t = 3.62\text{ ms}$, $t = 5.07\text{ ms}$, $t = 5.28\text{ ms}$ and $t = 5.62\text{ ms}$. This peculiar behaviour has been schematically exemplified in Fig. 4.9 for clarity. The cavitation cloud reaches its maximum size at $t = 5.48\text{ ms}$ and with subsequent collapses the CR intermetallic shatter into pieces at $t = 6.71\text{ ms}$ with fragments as small as $50\text{ }\mu\text{m}$. This phenomenon of potential refinement of the primary intermetallic crystals in ultrasonically treated real melt systems is very important in grain refinement with these fragments acting as grain nucleation points without need of any separate inoculation [174].

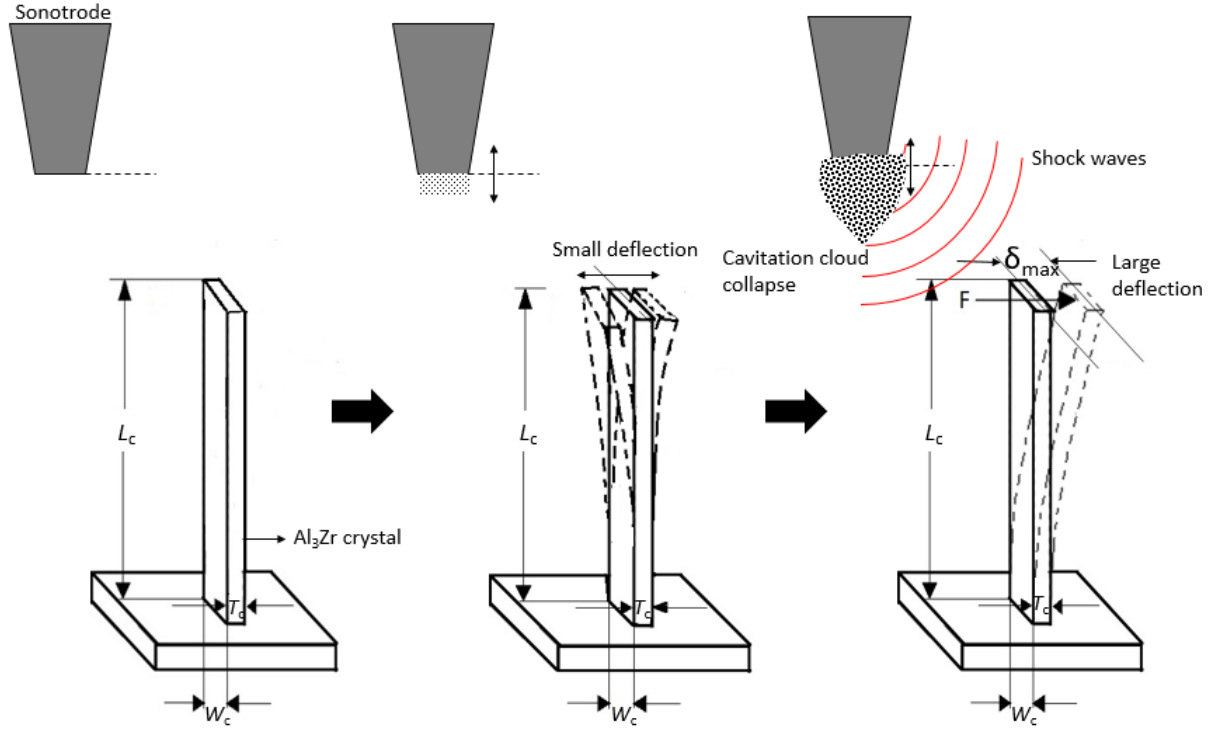


Fig. 4.9 Schematic representation of intermetallic crystal deflecting upon interaction with the incoming shock waves.

This shock wave-induced maximum deflection of CR can be utilised to mathematically estimate the shear stress acting at the tip of the crystal. For calculation, the length (L_c), width (W_c) and thickness (T_c) of CR shown in Fig. 4.9 are taken as 3.6 mm, 2.5 mm and 0.06 mm, respectively. The maximum shear stress (τ_{max}) acting on the crystal was evaluated by adopting a simple cantilever beam model using the following equations as described in [308]:

$$\tau_{max} = \frac{FQ}{IW_c} \quad (4.3)$$

$$F = \frac{3\delta_{max}EI}{L_c^3} \quad (4.4)$$

$$Q = \frac{W_c T_c^2}{8} \quad (4.5)$$

$$I = \frac{W_c T_c^3}{12} \quad (4.6)$$

Here F is the transverse shear force estimated from the maximum deflection of the crystal (δ_{max}), Q is the first moment of area at the neutral axis, I denotes the moment of inertia of the crystal's cross-section and E is elastic modulus of the Al_3Zr crystal taken from Table 3.1. Based on the above equations, τ_{max} was calculated for deflection values (measured using high-speed camera) with accuracies up to 2 μm obtained from at least 3 similar crystals with L_c and W_c in the range

of 3-4 mm and 2-3 mm, respectively, at different time intervals and is presented in Table 4.1. As we can see, the induced shear stress ramps up with the crystal's deflection reaching up to 0.5 MPa at the point of maximum bending of the tip. This gradual increase in the crystal deflection and the associated stress develops from the simultaneously generated acoustic pressure field and agrees well with the findings of Morton et al. [309], where it was shown that the shock pressure increases initially, reaches a maximum value upon the collapse of a fully developed cavitation cloud at $t \approx 6$ ms before becoming steady. A similar approach was also undertaken by Kim et al. [303] where a silicon microcantilever was subjected to oscillating bubbles in a continuous ultrasonic field and its damage potential was assessed through deflection-induced stresses. Their study confirms that deflection of the crystal is not due to acoustic streaming or the developed pressure field, but rather it is driven by the dynamic pressure effects from chaotically oscillating bubble collapses. Interestingly, the deflection produced by the chaotic oscillating bubbles with the pressure in the range of 0.1-0.5 MPa is sufficient to break the Si cantilever, matching very well our findings. Zeng et al. [310] also reported that the cavitation bubble collapse near a rigid solid boundary induces shear stresses in the range of 100 kPa upon liquid jet impact. Even if there is a stable pulsating microbubble attached to the crystal's surface as observed by Kim et al. [303], based on the observed free end deflection (δ), the induced bubble pressure ($P_b = W/W_c$) exerted over the cantilever beam length (L_c) given by $P_b = 2\delta E T_c^3 / 3L_c^4$, is about 0.4 kPa, where W is distributed load. Thus, the imparted pressure by the attached microbubble is almost three orders of magnitude lower than the induced shear stress by the shock waves and liquid jet emitted from the chaotically oscillating bubble cloud just beneath the sonotrode surface. This estimate clearly indicates that the pressure fluctuation due to microbubble undergoing oscillations at the crystal surface is unlikely to induce any rapid damage.

This experiment can also be related to the observations of fragmentation of elongated dendrites in real Al-Cu melts observed in [137]. However, in contrast to study [137] where acoustic flow were suggested to be responsible for the fragmentation of fine and micro-size (5-60 μm) dendrites, we suggest that the stress induced by the acoustic streaming is not sufficient to break-up the crystal via deflection. We have recently showed that acoustic streaming velocities in the range of 0.1-0.3 m/s (typical range from a sonotrode-induced flow in water and in liquid aluminium) generate very small flow pressure fields certainly not adequate to deflect and break the crystal [70]. It is worth noting that there are two factors that differ our study with that of Wang et al. [137], i.e. in their study the crystals were long and thin (different length/thickness

ratio from ours) and the fragmentation in the melt could be assisted by local remelting (which does not take place in our study).

Table 4.1 Calculated maximum shear stress based on the crystal's free end deflection measured at different time intervals.

t (ms)	$\delta_{\max}$ (μm)	$\tau_{\max}$ (kPa)
1.05 ± 0.05	24.3 ± 1.6	141 ± 15.5
3.62 ± 0.05	48.7 ± 1.4	280 ± 58.3
5.07 ± 0.05	73.1 ± 1.2	423 ± 87
5.28 ± 0.05	97.5 ± 1.5	565 ± 114.5

4.3.2 Shock pressure measurements and application to fragmentation

The intermetallic fragmentation has also been complemented by measuring the pressure magnitude of the travelling shock waves in the vicinity of the crystals. Figure 4.10 shows the temporal and peak pressure distribution of the propagating shock fronts, captured using a highly sensitive and calibrated fibre optic hydrophone (section 4.2.3). Quantitative analysis of the pressure distribution in the time domain (Fig. 4.10a & 4.10b) indicates the peak-positive pressure amplitude from the corresponding shock waves. Note, however, that the negative phase has been preserved. The apparent negative phases are most likely associated with the lack of phase calibration (experimental bubble collapse shock wave profiles are magnitude-only deconvoluted) of the fibre optic hydrophone. Although, phase changes may result in alterations of the shape of time domain pressure signal (Fig. 4.10a & 4.10b), they do not affect the integrated energy contained within it and consequently the pressure magnitude (Fig. 4.10c & 4.10d) [62]. This is evident by the work of Johansen et al. [280] where it was experimentally shown that in a cavitating environment, the pressure magnitude is only 3% higher in a deconvoluted phase and magnitude profile than those of magnitude-only deconvoluted profiles. So, for this study, where we are interested on the actual peak pressure values in relation to the fragmentation mechanism of intermetallics, the phase calibration of hydrophone is not essential and is out of scope. Additionally, negative peaks may also be related to the reflection of shock fronts with the bubbly clouds and the myriad of various size bubbles in the bulk liquid as suggested by [311]. The peak pressure averaged across 60 generated waveforms of 2 ms period each for crystals CL (under) and CR (side) in Fig. 4.10c and Fig. 4.10d was measured to be 445 kPa and 357 kPa respectively. However, pressure surges of up to 1.5 MPa were also

observed and these are in a very good agreement with the calculated shear stresses induced by the deflection of the fixed crystal (Table 4.1). Therefore, it can be inferred that the pressure exerted by the repetitive shock waves emitted from the sub-harmonic frequency pulsation of the large cavitation cloud generating impulsive loads with peak pressures in the range of 0.4-0.5 MPa can induce sufficient shear stress to break the studied crystals. It should be noted that shock wave propagation remains virtually undisturbed in the liquid medium at the sides of the ultrasonic horn (Fig. 4.6/Video 2). Whereas, under the sonotrode, the cavitation zone is exceedingly populated with numerous bubbles collapsing and self-interacting with each other. So even if some of the propagating shock fronts get absorbed or lose their energy, on a cumulative basis they are still sufficient in numbers to fragment the weak regions within the crystal present underneath. The pressure of the shock front in the ultrasonic environment is likely to be affected due to the development of cavitation shielding [289], the decrease in the speed of sound and the density of the surrounding medium owing to the presence of a large bubble cloud (half sphere) attached to the ultrasonic horn and other individual cluster or bubbles in the bulk liquid [61]. The observation of this acoustically induced large cavitation structure as it undergoes violent collapses, has been referred to as the phenomenon of acoustic supercavitation elsewhere [306]. It has also been found that the shock pressure induced from the large bubble cloud of radius ~ 1.3 mm is similar to our observation (Fig. 4.7c and Fig. 4.8k) and is three times higher than the pressure measured in the case of single bubble collapse measured at a distance of 10 mm from the ultrasound focus [293]. This clearly indicates that the location of crystals also plays a significant role in producing effective and instantaneous fragmentation. However, since the crystal is placed further away from the acoustic horn, the registered pressure is much lower. Pressure generated from the large cavitation structure attached to a 20 kHz horn tip ($\emptyset = 3$ mm) was found to reach up to 250 kPa during its collapse [306] at a distance of 7 mm, which seems to agree reasonably well with our acoustic pressure measurements.

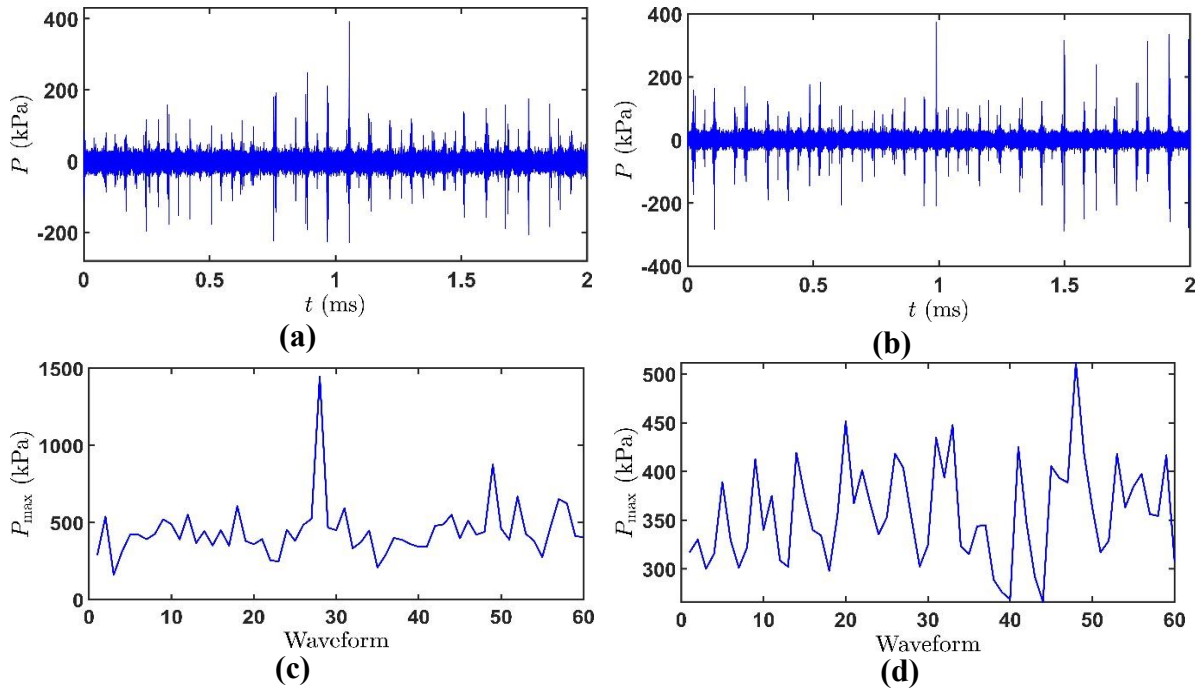


Fig. 4.10 Time evolution of pressure at locations (a) under and (b) at the side of sonotrode, maximum pressure (c) and (d) recorded for 60 acoustic waveform points corresponding to (a) and (b) respectively, measured using fibre optic hydrophone.

As discussed in section 4.3.1.1, the stress required for intermetallic fracture lies in the range of 20-40 MPa depending upon the existing crack length and associated defects. The shock wave emission from a single bubble collapse of ~ 1.5 mm radius also produces pressure of a similar order, causing instantaneous fragmentation. However, the fragmentation of the crystal with (Fig. 4.7) and without (Fig. 4.8) a pre-existing crack under the presence of ultrasound is not instantaneous and occurs between 150-200 acoustic cycles representing fatigue type failure. Results are in very good agreement with the work of Wang et al. [103] where, even if fragmentation occurred in an order of time higher (1680 cycles) as the location of intermetallic crystal was further away (~ 4 mm) from 1 mm sonotrode tip (thus less input energy and shock wave emission), the fatigue mechanism due to the cyclic acoustic pressure was also suggested. According to Wang et al. [103], the probable reason for this prolonged breaking time of crystal corresponds to the emitted pressure waves from the individual pulsating bubbles with radii in the range of 50-80 μm , which decay significantly with increasing distance. Specifically, a recent study by Pishchalnikov et al. [278] reported that a bubble of a similar size as observed in [103] generates pressure as high as 50 MPa at a distance of about 30 μm from the collapsing spot. This essentially indicates that for instantaneous breakage to happen (as in the case of the laser-induced bubble experiments), the bubble collapse should occur immediately next to the crystal. Moreover and according to Ref. [278], pressure surges in the range of 1.5 MPa as

measured with the fibre-optic hydrophone in our study can be achieved at a distance of 100-150 μm from the point of the bubble collapse. So, if an individual bubble of a few tens of microns size collapses beyond this distance, the crystal is not likely to be damaged in a short period of time. However, in the case of a sonotrode where a large cloud of bubbles instantly collapses (Fig. 4.7c-4.7d), a much stronger pressure wave or an instrumental collection of pressure surges impact the specimen. This action is further intensified by the fast acceleration of the sonotrode's mechanical action [306]. Therefore, the incoming multiple shock wave pressures from large cavity collapses near the sonotrode tip are indeed much stronger and carry substantially more energy than the individual stable or transient pulsation/collapse, causing crystal fragmentation at even large distances in just a few tenths/hundreds of acoustic cycles.

Based on the crack length (Fig. 4.7) of 1.8 mm, the stress required for the complete fracture is estimated to be approximately 13 MPa as per Eq. 4.2 with C value of 1.12. Although the stress needed is much higher than the produced acoustic pressure, the fragmentation still happens due to constant interference with propagating shock waves. In statistical terms, and based on Fig. 4.6 (Video 2) observations, the crystal CL and CR in Fig. 4.8 experiences about 100 repetitive and low amplitude shock wave shots, while still strong pressure surges in the range of 0.1 to 0.4 MPa impact the intermetallic surface causing the crystal to fail within 10 ms. Besides, the sono-fragmentation in all the studied crystals occurred in between 5-10 ms. This period of time relates to a few smaller pressure peaks, about 100-200 (~40 peaks every 2 ms according to Fig. 4.10a & 4.10b) in the range of 50-200 kPa and at least 5 maximum pressure surges from the collapsing bubbles in the range of 0.5 to 1.5 MPa according to Fig. 4.10c & 4.10d. Therefore, it is reasonable to say that stresses pile-up on the intermetallic surface under continuous interaction with the ultrasound-induced low-pressure shock waves, generating fatigue in the material that eventually lead to catastrophic failures.

The fragmentation mechanism in a real melt system also bears similarity to our observations. It was reported in [271] that a single bubble implodes in just one acoustic cycle near the ultrasonic source and the breaking up of the solid phase is accelerated by such collapsing bubbles and the high speed acoustic flows in the range of 1-2 m/s. However, this effect may weaken as one moves further away from the ultrasonic source and the cavitation bubbles may survive tens of thousands of acoustic cycles owing to the exponential decrease in the acoustic cavitation intensity with distance [286] and attenuation and sound absorption in the cavitation region [272]. In regions, away from the sonotrode, the fragmentation mechanism of solidifying phases relates to the cyclic fatigue effect induced by the pulsating bubbles and momentum of

acoustic flow (0.05-0.3 m/s) [70]. Wang et al. [271] predicted that pressure amplitude induced by oscillating bubbles in a Bi-8% Zn alloy melt was mostly between 20-30 MPa that was capable to fragment the free floating primary Zn phase in about 3000-5000 acoustic cycles. It has been found that certain intermetallics tend to show a more plastic behaviour (increased yielding and flow stresses) with increasing temperatures thus creating resistance to breakage [312,313]. However, in our case the pressure and time required for fragmentation seems to be much lower considering that the studied intermetallic was different and sonication was performed in water at room temperature. We also anticipate that fragmentation will be much faster in liquid Al than actually predicted, due to higher and more prominent dynamics of the cavitation bubbles [276,289] as well as the fact that the crystal will interact with the cavitation zone more frequently as it is likely to be freely floating. Local remelting at necking and initial cracks may further assist fragmentation of intermetallics in the melt.

Following the elucidation of the governing fracture mechanism of primary aluminium crystals, it can be confidently inferred that the high-speed in-situ real time sono-fragmentation imaging, detailed in this chapter, provides substantial understanding of the fragmentation induced intermetallic crystal refinement upon UST of real metallic melts. All the experiments discussed in this paper were performed by fixing the extracted primary crystals onto a solid substrate. However, this may not be the case in real Al melts where primary crystals also exist in a free-floating condition. It is believed that the mechanism observed for the fixed primary particles is still valid considering the high frequency repetitions of cyclic pressures and the short impact application duration. The catastrophic fracture occurs in very short period of time and within the very first millisecond depending on the position of the sample (the closer to the sonotrode the faster the rupture should be) as well as the deflection that occurs as intermetallic grows as previously discussed in [271].

This study also highlights that shock waves emitted from the active cavitation zone (just below the sonotrode surface) travel up to considerable distances carrying sufficient potential energy to damage intermetallic crystals upon impact; this is unlike other studies [103,278,284,310] which demonstrate that cavitation bubbles should be in very close proximity to the solid boundaries in order to produce severe damage. Thus, the limits of the active cavitation zone can be potentially quantified and optimised promoting effective cavitation treatment. Apart from metallurgical applications, the results of this study are of significance for applications in relevant scientific fields such as surface cleaning [314], bacterial cleaning and water decontamination [315], exfoliation of 2D nanomaterials [316] as well as tumour treatment

[317] and medical lithotripsy [278] dealing with cavitation bubbles' interaction with solid surfaces.

4.4. Conclusions

In this study, interactions of single and multiple cavitation bubbles against fixed individual intermetallic Al_3Zr crystals with quantifiable mechanical properties were investigated. After analysing the real time recorded high-speed images of cavitation bubbles interaction with the studied samples, the governing mechanism of Al_3Zr fragmentation was elucidated. The following major findings of this research are:

1. Controlled interaction of laser-induced cavitation bubbles with the intermetallic crystals revealed that the governing fragmentation mechanism is the exerted shock wave pressure upon bubble collapse.
2. In a continuous sonicated environment, crystals should not necessarily be in the vicinity of the collapsing bubbles for fragmentation to occur. Fragmentation occurs in a range of distances from the acoustic source and involves two-steps: (i) the propagating shock wave fronts continuously interfere with the nearby intermetallic crystals causing a low cycle fatigue (around 100-200 shocks arriving at the sample surface in less than 10 ms) until the existing crack reaches its critical length; (ii) fragmentation occurs immediately afterwards, via brittle fracture.
3. In the case of a laser-induced cavitation bubble, the pressure amplitude required for the instantaneous fragmentation of the intermetallic samples is in the range of 20-40 MPa based on critical crack length measurements. In contrast, in the case of ultrasonic cavitation, the fragmentation occurs between 150-200 acoustic cycles, indicating a low fatigue cycle mode with surges of acoustic pressures from corresponding shock waves in the range of 0.4-0.5 MPa.
4. For a crystal with an existing crack length, the crack propagation occurs both in and out of the shear plane indicating that the crack separation happens through combined fracture modes.
5. The repetitive sub-harmonic collapse of a large cavitation structure attached to the ultrasonic horn is responsible for repeated bending and brittle fracture of the fixed intermetallic crystals, relevant to that of the growing dendrites in the solidification front in a real melt, with corresponding shear stresses in the range of 0.1-0.5 MPa.

Chapter 5

Characterization of cavitation induced shock waves[§]

After establishing the fact that the intermetallic crystals are primarily fragmented by the propagating shock wave fronts emerging from cavitation bubble collapses, we now focus on understanding the shock wave dynamics under the presence of ultrasound and acoustically characterise their behaviour using sophisticated state-of-the-art measurement devices.

*This chapter discusses about the frequency response and shock pressure field characterisation of propagating shock waves. The application of cavitation-induced shock waves generated at low driving frequencies, known as Power Ultrasound, is essential for a wide range of fields, such as sonochemistry, lithotripsy, nanomaterials, emulsions and casting, to name but a few. In this study, we present measurements of the shock wave pressures emitted by cavitating bubbles in water, under ultrasonic excitation produced by an immersed probe oscillating at 24 kHz. A broad-spectrum fibre-optic hydrophone (FOH) calibrated in the range of 1-30 MHz was used for this purpose. Spectral analysis of the data reveals a consistent resonance peak at a very narrow range of frequencies (3.27-3.43 MHz). **This is the first ever observation reported in relation to shock wave propagation that exhibits a unique acoustic identity that falls within the this narrow frequency range.** Results were confirmed using real time analysis of high-speed recordings. By eliminating other possible sources, we propose that this new peak might be associated with shock wave emissions from collapsing bubbles. Spatial maps obtained by collating individual shock wave pressures, highlight the effect of pressure shielding with increasing input power, attributed to a cloud of bubbles surrounding the probe. This work contributes towards the elucidation of the key properties of cavitation-driven shock waves and the underlying mechanisms, essential in controlling the effectiveness of the external processing conditions on various physical, chemical, and biological systems.*

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*Both authors contributed equally on this publication

5.1 Introduction

Shock waves occurring during cavitating bubble collapse have always fascinated scientists as one of the most destructive forces in nature. Cavitation is the phenomenon where individual bubbles or bubble clouds vigorously oscillate and violently collapse due to instantaneous pressure fluctuations in a liquid. As they implode, cavitation bubbles produce high-speed liquid jets (typically above 100 m/s) [69] and omnidirectional shock waves with local pressure spikes in the range of GPa [278]. Accurate determination of the shock wave characteristics is essential in controlling the effectiveness of the external processing conditions on various physical, chemical, and biological systems. Shock waves are of importance due to their extreme dynamics, and underpin many of the applications that utilize acoustic cavitation, notably melt treatment [1,18,318–320], sonochemistry [321], lithotripsy [278,322–327], ocular surgery [328], food processing [329] and pharmaceuticals [330,331], to name but a few. Furthermore it has recently been discussed as part of the present studies, that shock wave emission is the governing mechanism for intermetallics fragmentation [277,332] as well as for graphite exfoliation [309]. However, the key properties of cavitation-driven shock waves and the underlying shock wave mechanisms are not well understood and therefore remain a topic of great interest.

Acoustic pressure measurements can be essential for quantifying and understanding shock wave propagation. There have been several works dealing with experimental pressure measurements and numerical predictions in the presence of a shock wave [37,38,279,285,293,333–335]. However, to the best of our knowledge, a full spectrum analysis (especially in the MHz range) and pressure mapping of the acoustic cavitation-induced shock waves associated with the high-intensity ultrasonic energy generated at low driving frequencies, i.e. 17-30 kHz (so called Power Ultrasound) have not been performed yet, whereas the application of power ultrasound is widespread and essential for many applications. The majority of reported studies on shock waves have been focused on medical applications and were related to transducers with significantly higher driving frequencies, e.g., 692 kHz [122], 254 kHz [118,336], 1.1 MHz [293], with results showing that shock waves are responsible for the rise of subharmonic peaks and the noise floor. Furthermore, previous studies with low driving frequencies [110,337,338] were carried out for low acoustic power intensities ($0.3\text{--}3\text{ W/cm}^2$) with pressure amplitudes being mostly scrutinized for the harmonics and subharmonics to the driving frequency in the kHz range. In contrast, this work employs a

system combining high power densities ($90\text{--}460\text{ W/cm}^2$) with a low acoustic driving frequency (24 kHz), known to produce a broad spectrum of pressure peaks associated with shock waves arising from inertial cavitation events, resonating nodes due to the container dimensions and harmonics from stably oscillating bubbles.

Highly sensitive fibre-optic hydrophones (FOH) that are calibrated for a broad range of MHz frequencies (associated with shock wave emissions) have been deployed [339], since the strong adhesion between their optical fibre and the liquid enables the sensor to seize the tensile phase of the shock wave, avoiding the possibility of cavitation taking place at the surface of the probe [326,339] to ensure that no additional noises or signals are captured. This allowed the frequency spectrum of shock waves in the range above 1 MHz produced by a low frequency transducer (24 kHz) to be resolved via detailed pressure measurements. We present a comprehensive experimental study to understand in detail the shock wave mechanisms and dynamic features in a sonicated environment with high-precision measurement tools. We intentionally used a broadly calibrated FOH at high frequencies to capture all the detailed spectral features in the MHz range associated with transient cavitation and shock wave emissions (as also described in section 4.2.3 in Chapter 4). Pressure measurements were supplemented with visualization techniques. A spatial pressure map was constructed by collating individual pressure measurements taken in the vicinity of the ultrasonic source (and up to 10 mm distance) to provide a better understanding of the physics of acoustic cavitation and associated emission of shock waves produced by collapsing bubble structures.

5.2 Experimental setup

A schematic of our experimental setup is shown in Fig. 5.1. An FOH (Precision Acoustics (PA), Ltd.), was fixed on a plastic holder and mounted at the bottom of a glass tank with internal dimensions $300 \times 75 \times 100\text{ mm}$. The probe has an outer diameter of $125\text{ }\mu\text{m}$ and the optically illuminated core (which defines the active element) has a diameter of $10\text{ }\mu\text{m}$. The very small active element ensures that the FOH has a very broad directional response below 15 MHz [339]. All probe type hydrophones, including the FOH, have a peak in their directional response when their active element is pointed at the source of ultrasonic signal. For the measurements reported here, it is not possible to know, a priori, the precise location of a bubble that is undergoing cavitation. Therefore, the hydrophone should be, as far as is possible, equally responsive to acoustic signals, regardless of their angle of incidence upon the hydrophone. The FOH was calibrated over the range of 1-30 MHz at 1 MHz increments. Fig. 5.2 shows the sensitivity of

the probe for this range. The red spots are the calibrated data points for each discrete step and the blue line shows the interpolated values used for other frequencies. Sonication was applied by a 24 kHz transducer (UP200S, Hielscher Ultrasonics GmbH) to the deionised water (DIW) inside the tank. The water level was 80 mm and the diameter of the cylindrical Ti sonotrode tip was 3 mm. Across the tank, 136 locations were chosen for the measurement of acoustic pressure emissions. All experiments for each position were performed for three different input transducer powers: 20%, 60% and 100%, corresponding to peak-to-peak displacement amplitudes of 42, 126 and 210 μm and nominal intensities of 92, 276 and 460 W/cm^2 respectively. These power intensities are much larger than similar studies with low driving frequencies (3.2 W/cm^2 in [337], 0.3-0.95 W/cm^2 in [338] and 0.53 W/cm^2 in [110]). The inset plot in Fig. 5.1 shows where the probe was placed: at $-10 \leq x \leq 10$ mm and $1 \leq y \leq 10$ mm, with the centre of the sonotrode tip taken as the origin. This gave us an extensive symmetric map of the pressure distribution around the sonication source.

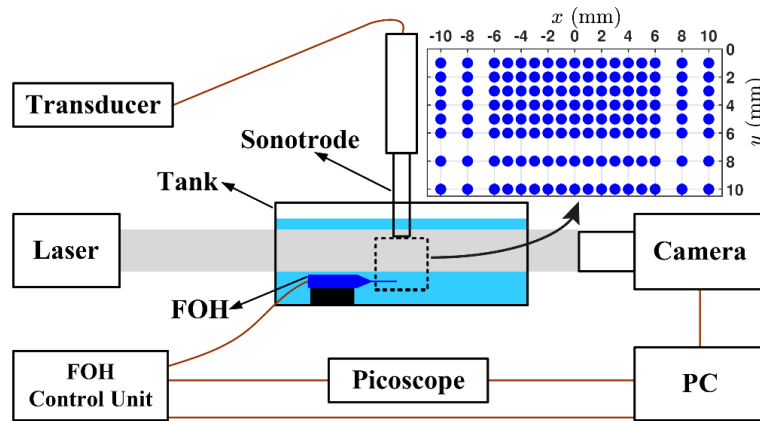


Fig. 5.1 Experimental setup for pressure measurement by FOH. A small sonotrode is immersed in the glass tank filled with DI-water. The signals are captured by a PicoScope, setting the sampling rate (resolution). A high-speed camera (HPV X2, Shimadzu) captures the shock wave propagation. 10 ns laser pulses (640 nm) by CAVILUX Smart UHS provides the required illumination.

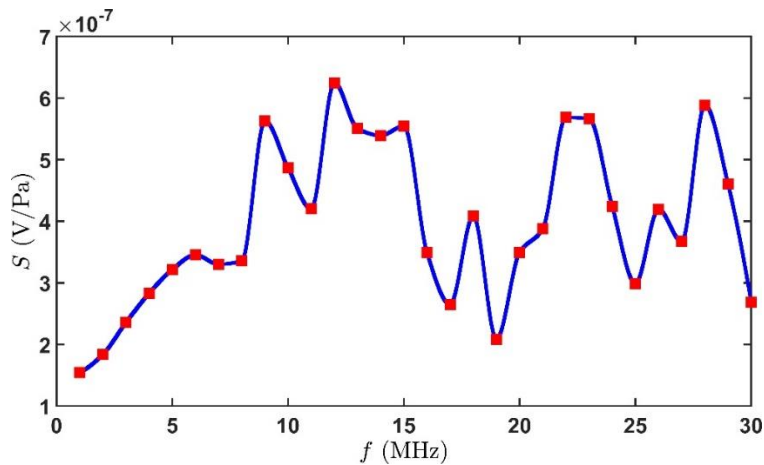


Fig. 5.2 Sensitivity of the FOH vs. frequency (Precision Acoustics, Ltd.).

To ensure the safe functionality of the FOH sensor, each experiment lasted for 5-10 seconds (until steady-state conditions were achieved) and the closest distance of the hydrophone tip from the source was chosen to be 1 mm. The temperature was kept constant at 25°C during the experiments. Furthermore, we used a high-speed camera (HPV X2, Shimadzu, Japan) to capture the shock wave emission. High-speed recordings were carried out at frame rates of up to 1 Mfps, with a resolution of 400×250 pixels and 200 ns exposure time. The illumination was delivered by 10 ns laser pulses (640 nm) from a CAVILUX Smart UHS system (Cavitar Ltd.) to create an effective temporal resolution of emitted shock waves. Shock wave imaging was performed at CavLab, GLA, where the author of this thesis contributed to these experiments by adjusting the camera settings and recording the measurements. The detailed experimental setup for high-speed recordings of shock waves facilitates shadowgraphic imaging such that pressure transients are directly imaged via refractive index variations imposed as the shock wave propagates and is described in [305,336]. The FOH was manually fixed on the tank (as shown in the Fig. 5.1), but for each experiment, the tank was traversed using translational stages to place the FOH at the desired position measured precisely by high-speed camera.

Acoustic pressure emissions were captured using a digital oscilloscope PicoScope-3204D (Pico Technology) through the output of the FOH system. The electronic connection of the sensor is schematically represented in Fig. 5.1. The PicoScope captured and recorded real-time acoustic data for 60 random waveforms (to ensure repeatability and to average out the effect of the random nature of cavitation) under steady-state conditions. The sampling rate was 500×10^6 samples/s. The entire analysis of the experimental data was carried out via an in-house MATLAB code based on the deconvolution process (see Appendix) as described in [62,289,340] and Appendix D in Ref. [63] to correctly apply the sensitivity of the FOH. Our experimental results show that as the input power increases, we observe a smaller number of prominent peaks in the $P - t$ profile though with higher pressure amplitude (Fig. 5.3) and therefore, the time between those peaks increases. This may be attributed to cavitation shielding, extended periods of non-collapsing deflations and distribution of shock energy to other lower band frequencies (see further relevant discussion to Fig. 5.14).

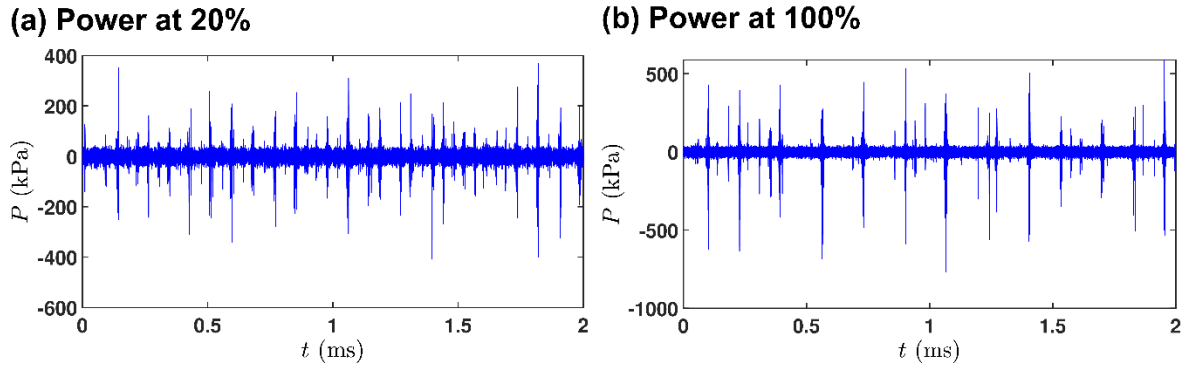


Fig. 5.3 Comparison of pressure distribution in time domain for the same position ($x = 3$ and $y = 2$ mm) and two input powers: a) 20% and b) 100%.

The MATLAB code ultimately calculates the desired pressure magnitudes in the time domain from the original voltage data acquired by the PicoScope. The pressure-time profile allows to evaluate the P_{RMS} and P_{max} by averaging the 60 waveforms of acoustic data (see discussion on P_{RMS} and P_{max} in Appendix). Background noise (~ 10 mV) was recorded and subtracted from the raw signals, and bandpass filters (in the calibration range 1-30 MHz) were applied to avoid the contribution of the non-calibrated range of FOH. Furthermore, from the high-speed recordings, we utilized image-processing techniques to measure the wavelength of the shock wave disturbance and consequently to infer its frequency. The MATLAB code used for FFT of the raw data and image processing algorithm for wavelength estimation was prepared in collaboration with UltraMelt2 group and PA. The author of this thesis contributed to this part of the study by designing the experimental methodology, performing acoustic measurements, analysing and discussing the obtained results.

5.3 Results and discussion

5.3.1 Frequency response of propagating shock wave

Figure 5.5 shows a sample of pressure in the frequency domain clearly demonstrating a distinct peak in a high-frequency range of 3 to 4 MHz. The inset plot in Fig. 5.4 shows the magnified area near the peak frequency, which shows that the peak occurs within a frequency bandwidth of 3.27 to 3.43 MHz. This high-frequency peak was observed for all the experiments irrespective of position or input power. See Supplementary Video SV1 for the entire $P - f$ plots (with their prominent peak) for all 136 positions and input powers of 20%, 60% and 100% along with their corresponding probe position marked around the sonotrode, accessible with the published version of this work (<https://doi.org/10.1017/jfm.2021.186>). Our hypothesis is that this distinct peak in the pressure spectrum is the result of cavitation activity and the shock

wave emissions due to bubble implosions. To investigate whether acoustic cavitation is responsible for this, we performed a number of additional experiments for different conditions to eliminate other possible sources that can potentially contribute to that frequency peak, such as interference from acoustic resonance, effects of transducer, different probe, sonotrode size, presence of glass walls and possible electromagnetic interference.

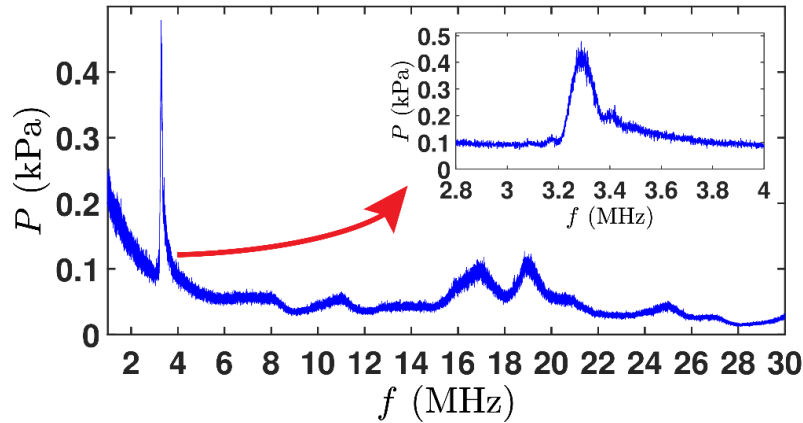


Fig. 5.4 Pressure vs. frequency measured by FOH. The inset magnifies the plot near the distinct peak frequency. For this experiment, the probe was at $x = 0$ and $y = 1 \text{ mm}$ and input power was 60%. The pressure was averaged over 60 waveforms. The pressure at the peak frequency is $0.479 \pm 0.06 \text{ kPa}$.

To confirm the independence of the observed peak of the transducer and the sonotrode diameter, we performed a few experiments with another transducer (Hielscher, UIP500hdT, 20 kHz) with a much bigger sonotrode tip ($d_s = 22 \text{ mm}$). The acoustic cavitation created by the second sonotrode also creates the peak at the same range of frequencies, with a bigger amplitude (compared to our main sonotrode for the same position). Figs. 5.5 and 5.6 show the comparison of the pressure in frequency domain for both sonotrodes for the same position ($x = 0, y = 5 \text{ mm}$) for two input powers (20% and 60%). The inset plots show the proximal region of the peak. Note that we used the same FOH probe for these measurements. Table 5.1 exhibits the maximum and RMS pressure magnitudes for these cases. Therefore, higher transducer power and larger sonotrode diameter will lead to higher peak pressure amplitude.

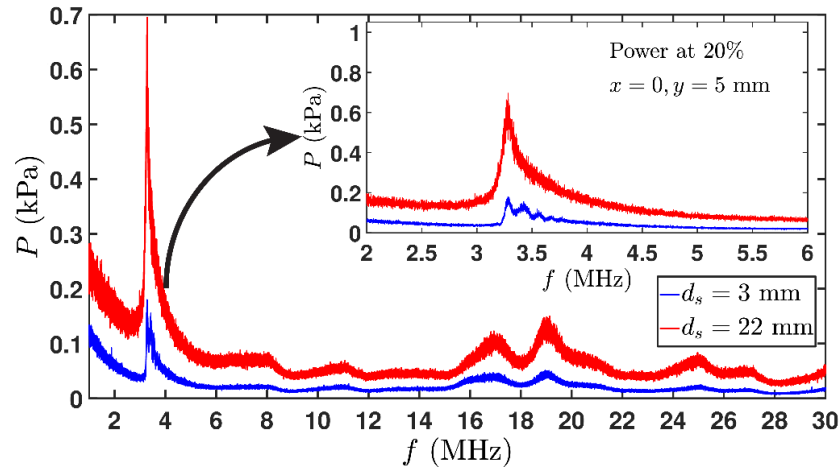


Fig. 5.5 Pressure vs. frequency measured by the same FOH probe for two different transducers (and different sonotrodes) for the same position ($x = 0, y = 5 \text{ mm}$) and input power of 20%. The pressure was averaged over 60 waveforms. The inset plot magnifies the region of the peak in question.

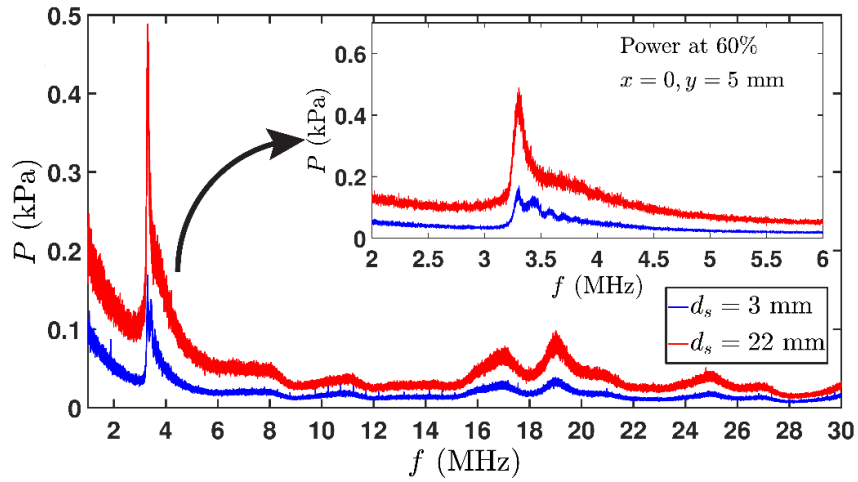


Fig. 5.6 Pressure vs. frequency measured by the same FOH probe for two different transducers (and different sonotrodes) for the same position ($x = 0, y = 5 \text{ mm}$) and input power of 60%. The pressure was averaged over 60 waveforms. The inset plot magnifies the region of the peak in question.

Table 5.1 Comparing the maximum and RMS pressures for two different sonotrodes and two different input powers for the same position ($x = 0, y = 5 \text{ mm}$). The pressure values are averaged over 60 waveforms (of 2 ms each, see Fig. 5.3(d)) for the calibration range (1-30 MHz).

	P_{max} (kPa)		P_{RMS} (kPa)	
	Power at 20%	Power at 60%	Power at 20%	Power at 60%
Sonotrode 1 ($d_s = 3 \text{ mm}$)	222.5	189.1	12.2	10.5
Sonotrode 2 ($d_s = 22 \text{ mm}$)	1213.8	1205.9	36.7	26.2

We performed several experiments with our main transducer (24 kHz, 3 mm sonotrode) and a second FOH sensor (Precision Acoustics Ltd.) having its own calibration over the exact same range (1-30 MHz). The experiments were carried out for several different positions and input powers. The peak at the same frequency range was observed for all cases. Fig. 5.7 shows the pressure profile in frequency domain for the second probe and compares it with the main sensor for the same position ($x = 3 \text{ mm}, y = 3 \text{ mm}$) and input power of 20%. The peak is clearly observed for the second probe as well, occurring at the same range of the first probe.

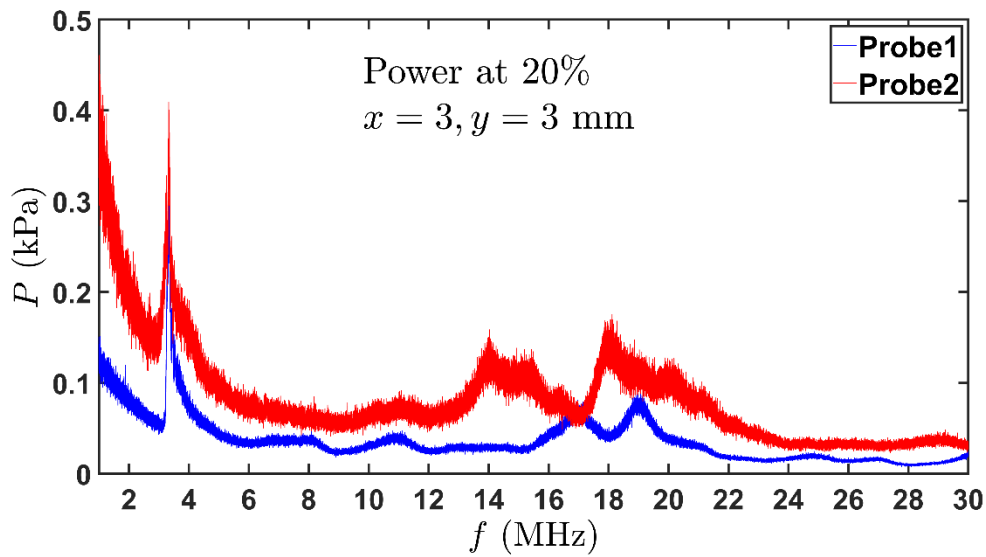


Fig. 5.7 Pressure vs. frequency measured by two different FOH probes for the same position ($x = 3, y = 3 \text{ mm}$) and input power of 20%. The pressure was averaged over 60 waveforms.

To further confirm that the observed peak was due to shock wave propagation, we performed several experiments in different configurations. Fig. 5.8 shows the results for these cases. The inset schematics show the top view of the glass tank and display how the probe and sonotrode are positioned. First, we placed the sonotrode and FOH probe in separate compartments (each filled with water) and different lines at the furthest possible distance (180 mm). Fig. 5.8(a) shows how the insertion loss of these glass walls (separating the probe and sonotrode) leads to the suppression of the peak at $\sim 3.3 \text{ MHz}$. Fig. 5.8(b) shows a similar configuration, except that this time the probe and sonotrode are on the same line, but still in separate compartments. The peak is once again significantly collapsed. For these two cases, we used our main 24 kHz transducer (UP200S with 3 mm tip diameter). We then placed the FOH probe and sonotrode at the two far corners (Fig. 5.8(c)) of the glass tank and used our stronger transducer (Hielscher, UIP500hdT) with bigger sonotrode (22 mm). All other compartments were also filled with water for this case. The input power for all cases was 20%. As seen from the Fig. 5.8(c),

because of the suppression of the ultrasonic cavitation in this long distance and the losses due to the presence of the glass walls, the peak completely disappeared. All these experiments further imply that the observed peak at ~ 3.3 MHz could be related to shock wave emission.

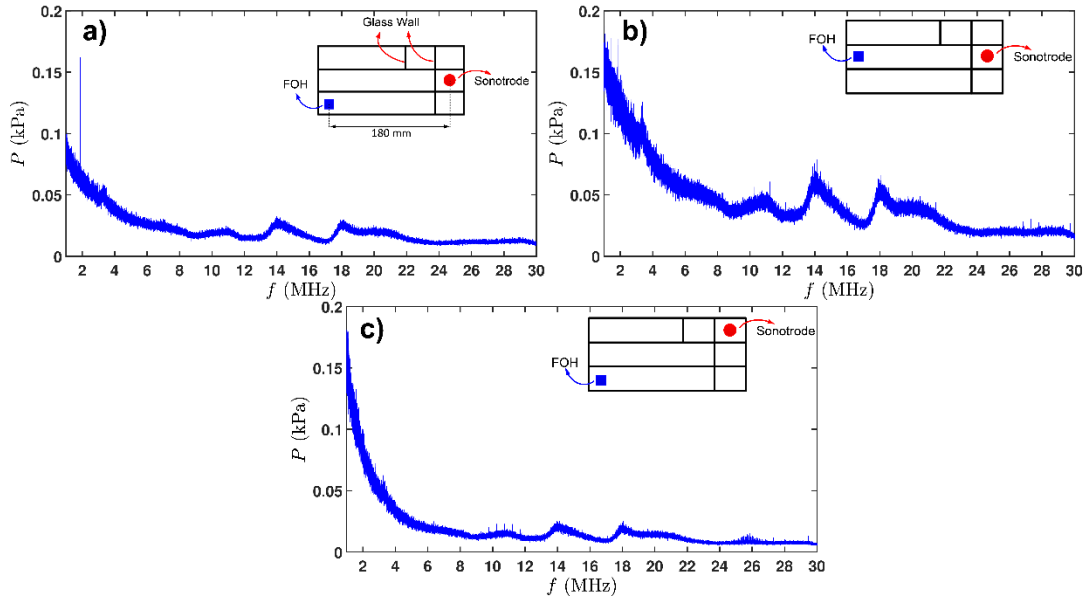


Fig. 5.8 Pressure vs. frequency for different configuration of sonotrode and FOH probe. The inset schematics (the top view of the glass tank) show how they are positioned: a) sonotrode and probes at two separate compartments and different lines; b) sonotrode and probe at two different compartments but on the same line and c) sonotrode and probe at two far corners of the glass tank, with all other compartments filled with water. For all cases, input power was 20%. For (a) and (b), we used our main transducer (24 kHz, 3 mm tip) and for (c), we used the powerful transducer (22 mm tip). The pressure was averaged over 60 waveforms.

Eventually, to eliminate the role of electromagnetic interference, we did a few experiments with the probe tip being covered with an air-filled finger cot (the air/water boundary is acoustically reflective). As seen from the result shown in Fig. 5.9, the peak is no longer present.

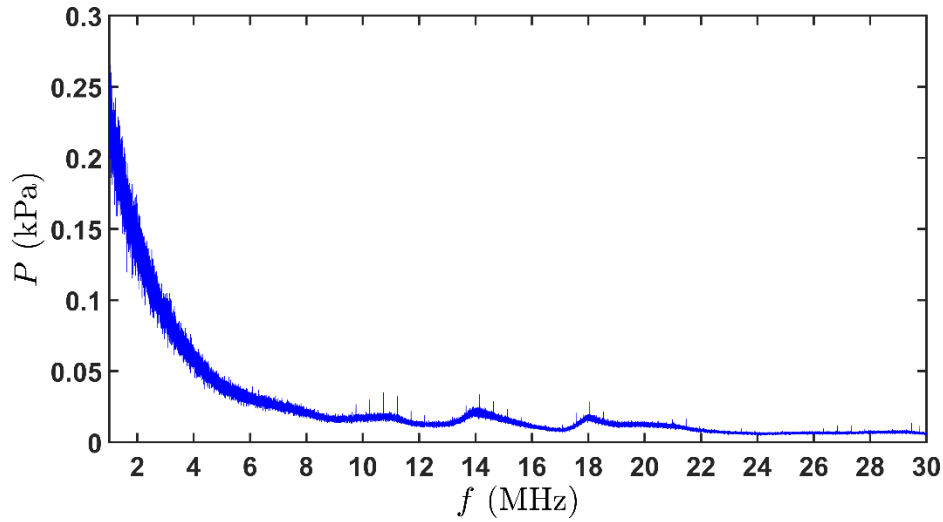


Fig. 5.9 Pressure vs. frequency for a case where the probe tip was covered with an acoustically reflective material. The peak is no longer present. We used our main transducer (24 kHz), main glass tank and second probe for this case. Input power was 100% and the distance between probe and sonotrode was 30 mm.

We propose that the observed peak might be associated with the shock wave. To see the relation between this peak and overall shock-wave energy, we applied an additional bandpass filter within the range containing the peak (3-4 MHz) to remove the contents of these frequencies. Fig. 5.10(a) shows the pressure vs. frequency plot with and without this filter, clearly showing how the filter suppresses the information within this range (see the inset plot for magnified region). Fig. 5.10(b) shows the pressure profile in time domain for both cases (with and without filter) for a single waveform depicting a drop in peak pressure magnitudes. This drop is around $25\% \pm 6\%$. This indicates that the observed peak contains some of the shock wave power, however most of its energy is, as expected, distributed among all other frequencies (broadband noise). These results are obtained for the studied case in Fig. 5.4, i.e., the probe was placed at $x = 0$ and $y = 1$ mm and input power was 60%.

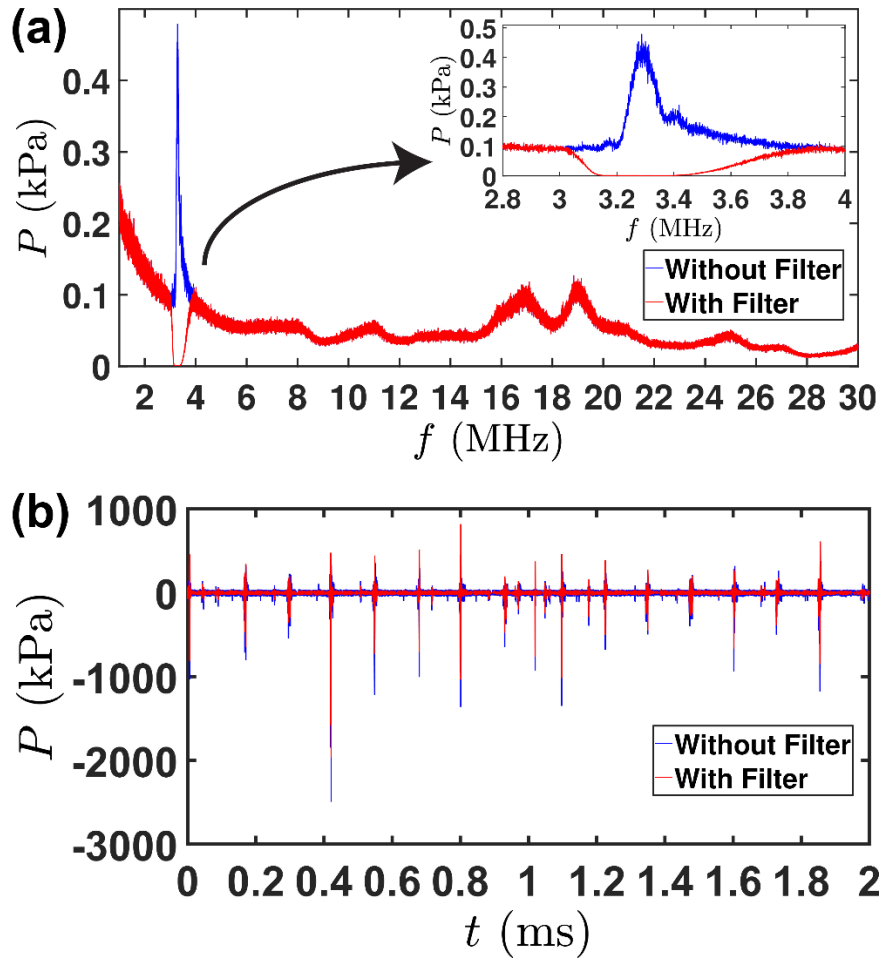


Fig. 5.10 The effect of applying an additional bandpass filter on 3-4 MHz (the frequency range containing the peak). a) Pressure vs. frequency for both with and without this filter for the entire calibrated range. Inset: magnified zone of the filtered range clearly showing how the additional filter suppresses the data within this range. b) The resultant $P - t$ plot for both with and without filter. The peak pressure magnitudes for the filtered data are dropped. The probe was at $x = 0$ and $y = 1 \text{ mm}$ and input power was 60%. The pressure at (a) was averaged over 60 waveforms. The pressure distribution at (b) is for one waveform.

When we used a different transducer and sonotrode (Fig. 5.6 and 5.7) and a different probe (Fig. 5.8), we still observed the peak. Placing the probe and sonotrode far from each other, putting a glass wall between them (Fig. 5.8) and covering the probe with an acoustically reflective material (to see if electromagnetic interference can contribute to the peak, see Fig. 5.9) either weakened or suppressed the peak. Therefore, these additional experiments strengthen our hypothesis that the shock wave propagation due to bubble collapses might be the plausible cause of the observed peak at 3.27-3.43 MHz frequency. It should be noted that the broadband nature of the shock wave distributes its power (not necessarily equally) over almost all frequencies, across a flat-wise spectrum (see Fig. 5.10). Therefore, this peak contains a portion of the power content of the shock wave, while the rest of its power is distributed over all other frequencies.

The majority of the previous studies on shock wave measurements and visualizations were performed for a single bubble collapse and the consequent analysis of a single or a few shock waves showed that apart from the energy that is spread over a very large frequency range, a prominent though obscured peak can be also observed, indicating that even those individual shock waves can still lead to a peak in the frequency domain [280,326]. However, in our case, we are facing multiple shock waves, due to the continuous formation and collapse of cavitation-induced bubbles. Thus, an ensemble of imploding bubbles and the consequent piling up of numerous shock waves may lead to this prominent peak that is sensed by FOH. However, the energy of these bubble collapses is not strong enough for the probe to pick up the subsequent harmonics.

To further examine the measured shock wave frequency, using the Schlieren [341,342] method, we analysed the high-speed images of shock wave emission to extract the wavelength of the disturbance and consequently the frequency. Fig. 5.11 shows a snapshot of a propagation of the shock wave along with the distribution of optical intensity across the shock wave (distance d from point a towards b). The shock wave and the sonication source (sonotrode) are specified in the figure. The intensity profile shows a full cycle of the wave from which the wavelength (λ) and consequently the frequency of the emission can be measured. The optical intensity is proportional to the second derivative of the index of refraction [341,343] as well as that of pressure [344]. Thus, the change in the optical intensity (diffraction of light) is due to the change in acoustic pressure as the pressure waves propagate through the liquid bulk. Therefore, the wave front can be considered as the compression phase, while the tail as the rarefaction phase, typical to a shock wave profile [326]. As a result, measuring the speed of sound and the wavelength from the high-speed recordings can give us the frequency of the wave propagation.

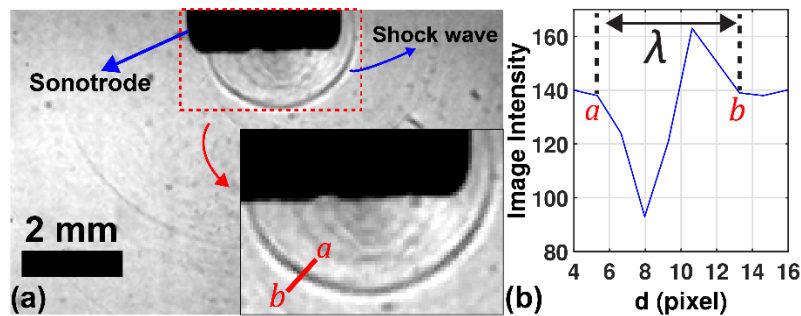


Fig. 5.11 A snapshot of shock wave propagation (a) along with the intensity profile (b) across the shock wave. Intensity profile shows how the wavelength (λ) and consequently the frequency can be calculated. Arrows show the sonotrode and shock wave. The red dashed rectangle (colour online) magnifies the shock wave for better visualization. Scale bar is 2 mm.

Fig. 5.12 shows the measured frequency for numerous shock waves (around 300) for six different experiments with different input powers (20%, 40% and 60%) at different time stamps. For each case, several measurements were performed for the wavelength (and frequency), the average of which is also shown in the legend. The mean frequency of all experiments was 4.78 ± 0.3 MHz (the corresponding average wavelength was 315 ± 20 μm) which is in the same order though $\sim 30\%$ off to the calculated value from the deconvolution process of pressure measurements. The tolerance in the measurements from the high-speed recordings are due to the image resolution (pixel size 39.02 ± 4 μm) and measurement of the speed of emission. A detailed discussion of this discrepancy is further presented below.

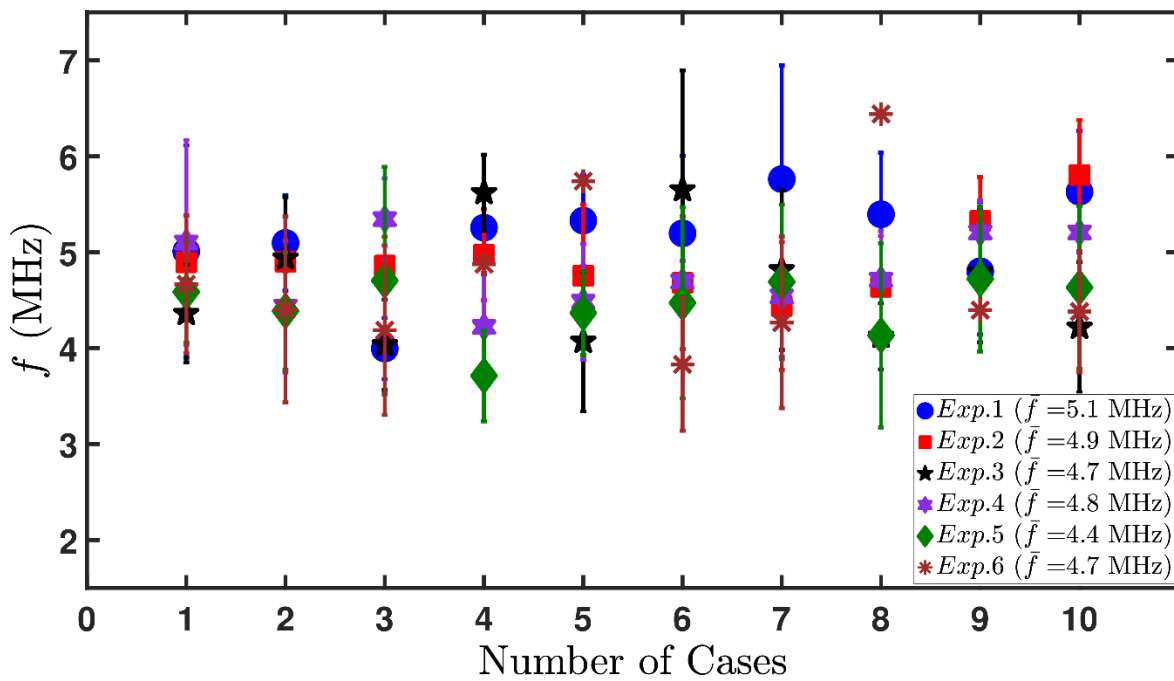


Fig. 5.12 Frequency of the shock wave emission from high-speed recordings for different experiments. The frequencies in the legend are the mean frequency for each experiment.

After monitoring the propagation of multiple shock fronts in our entire experiments, the mean speed of the shock wave emission (speed of sound) was measured to be 1464 ± 5 m/s and pixels size was 39.02 ± 4 μm . For the case in Fig. 5.11, this frequency was found to be 4.2 MHz. This value is reasonably close to the calculated value from the deconvolution process, i.e., 3.27 – 3.43 MHz (see Fig. 5.12 for the measured frequency for different cases of different experiments and their corresponding mean value for each experiment).

We suspect the reason for this discrepancy lies on the selected approach for identifying the borders of the spatially propagating shock waves. For all the shock waves, the frequency was

determined by the analysis of the wave pattern captured by the high-speed recordings and the corresponding measured wavelength (see Fig. 5.13). For the sake of consistency and clarity, for all the 300 cases, we decided to use two distinct points (points a and b in Fig. 5.13) as the absolute borders of the studied shock waves which indicate a well-defined sinusoidal or so-called N-wave (Fig. 5.11(b)), associated with propagation of shock waves. However, as shown in Fig. 5.13, careful visual inspection by scrutinizing the individual pixel intensity revealed that the borders of the shock waves (bow to tail) are not within the designated area defined initially (blue dash arrow and distance s_1 in Fig. 5.13(b1) and (b2)) that corresponds to the waveform of Fig. 5.11(b), but they extend, on average, by 1-2 pixels. For the case of Fig. 5.13, this extension is by 1 pixel in the tail (see Fig. 5.13(c1) where the red solid arrow and distance s_2 indicate the actual borders of the shock wave). This corresponds to a much larger wavelength as indicated by Fig. 5.13(c2) (points a_0 and b). This discrepancy may well occur due to the fluid turbulence that can generate artefacts in bows and tails of the shock wave as shown in [345]. This will affect the diffraction of light and pixel contrast and therefore prevent a perfect distinction of the borders of the shock wave. These larger wavelengths will drop the average values of frequency in Fig. 5.12, bringing them closer to the frequencies measured by the FOH probe (3.27-3.43 MHz).

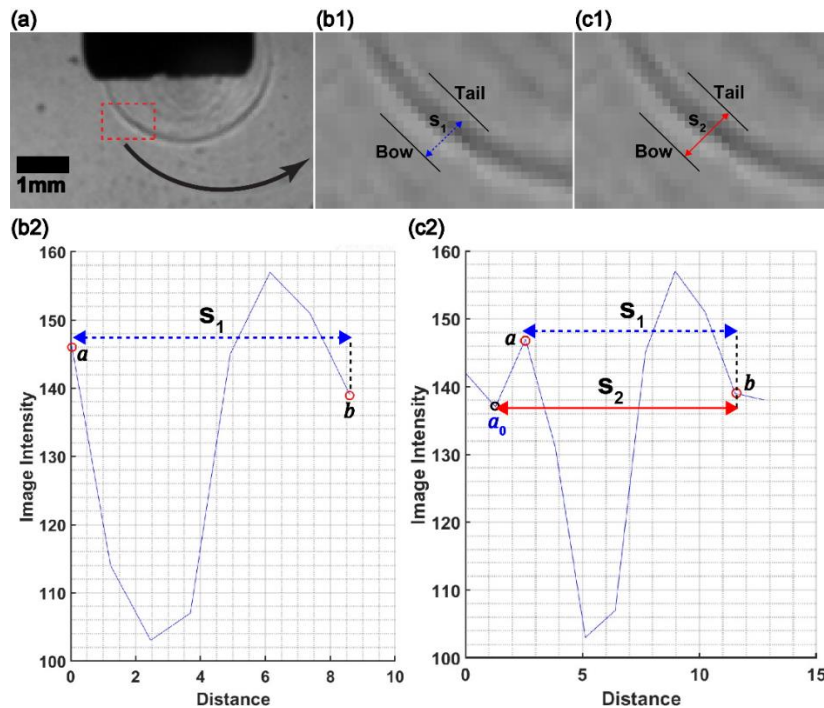


Fig. 5.13 (a) Shock wave around the sonotrode; (b1) Magnified area near the shock wave with its bow and tail, corresponding intensity profile (b2) and the selected distance (s_1) considered for wavelength measurement; (c1) The same case with the actual distance (s_2) and its intensity profile (c2). Blue (color online) dash arrow is the selected distance (s_1) for measuring the wavelength and red solid arrow is the actual distance s_2 being 1-2 pixels larger than s_1 .

5.3.2 Shock pressure field characterization and mapping

The formation of shock waves has a profound effect on overall pressure distribution in the liquid. We are going to demonstrate this by measuring the pressure profiles and then correlating these observations to the shock waves. The final output of the deconvolution process is the desired pressure profile in the time domain used to measure the maximum and RMS pressures ($P_{\max}$ and P_{RMS}), averaged over 60 waveforms for each experiment. Figs. 5.14 and 5.15 show the contour plots of $P_{\max}$ and P_{RMS} distribution vs. horizontal and vertical position surrounding the sonotrode for three different transducer powers: a) 20%, b) 60% and c) 100%.

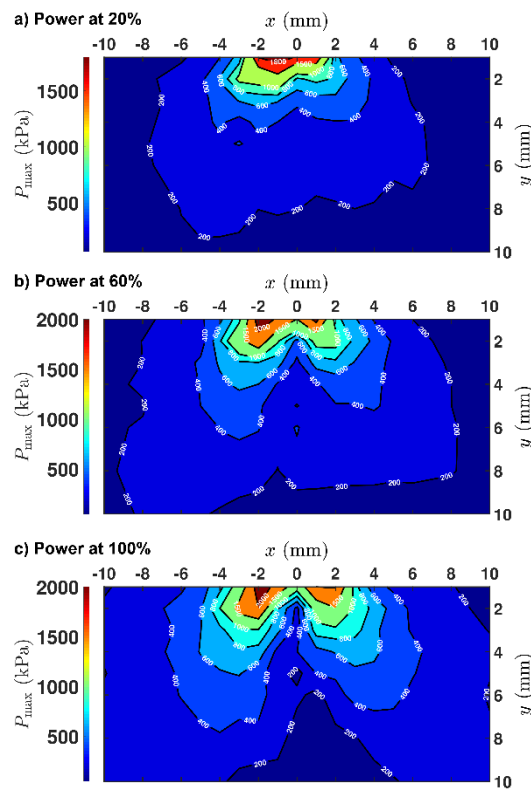


Fig. 5.14 Contour plots of $P_{\max}$ around the sonotrode for three different transducer powers: a) 20%, b) 60% and c) 100%. The sonotrode is at (0,0).

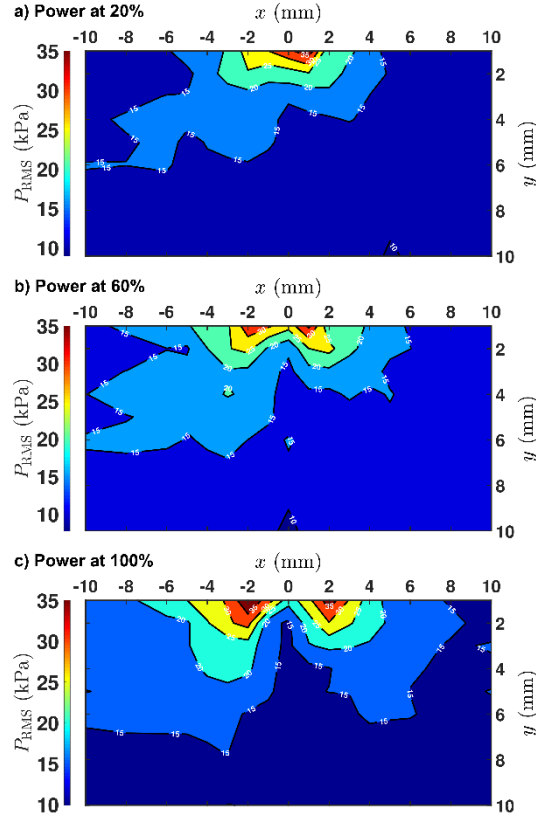


Fig. 5.15 Contour plots of P_{RMS} around the sonotrode for three different transducer powers: a) 20%, b) 60% and c) 100%. The sonotrode is at (0,0).

Figs. 5.16 and 5.17 show the contour plots of P_{max} and P_{RMS} vs. input power and vertical position from the sonotrode for four different horizontal positions. These results belong to the right side of the sonotrode. For small x (< 2 mm), the pressure does not depend much on the input power for $y = 1 - 4$ mm, while far from the sonotrode, the pressure increases as the input power is raised, thus shock wave impact would be more effective in the vicinity of the source.

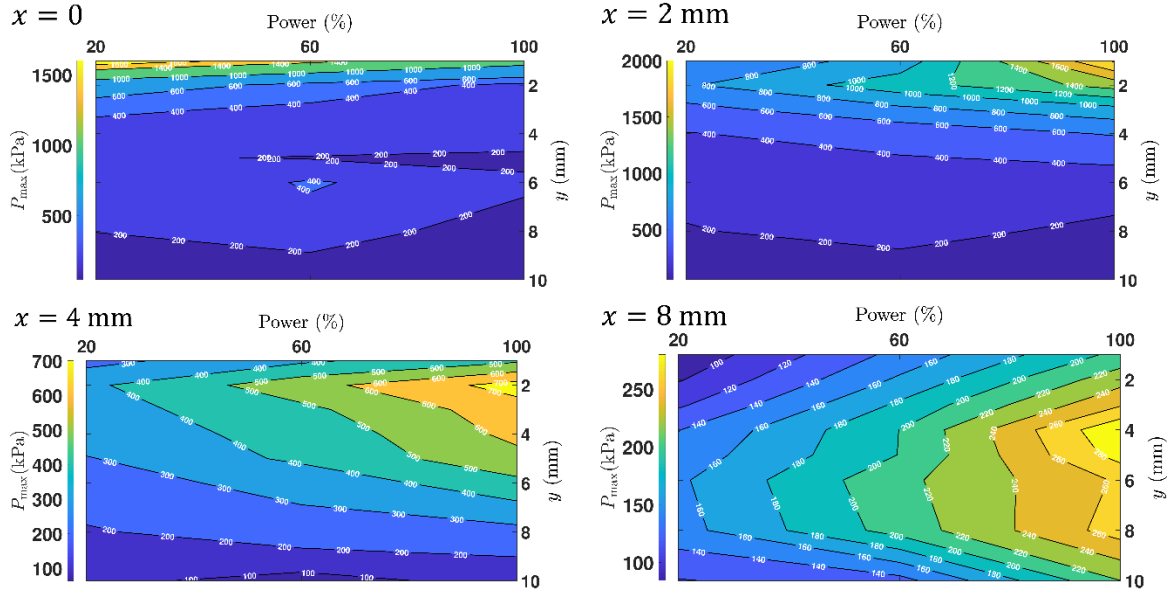


Fig. 5.16 Contour plots of P_{max} vs. input power and vertical position for 4 different horizontal positions on the right side of the sonotrode.

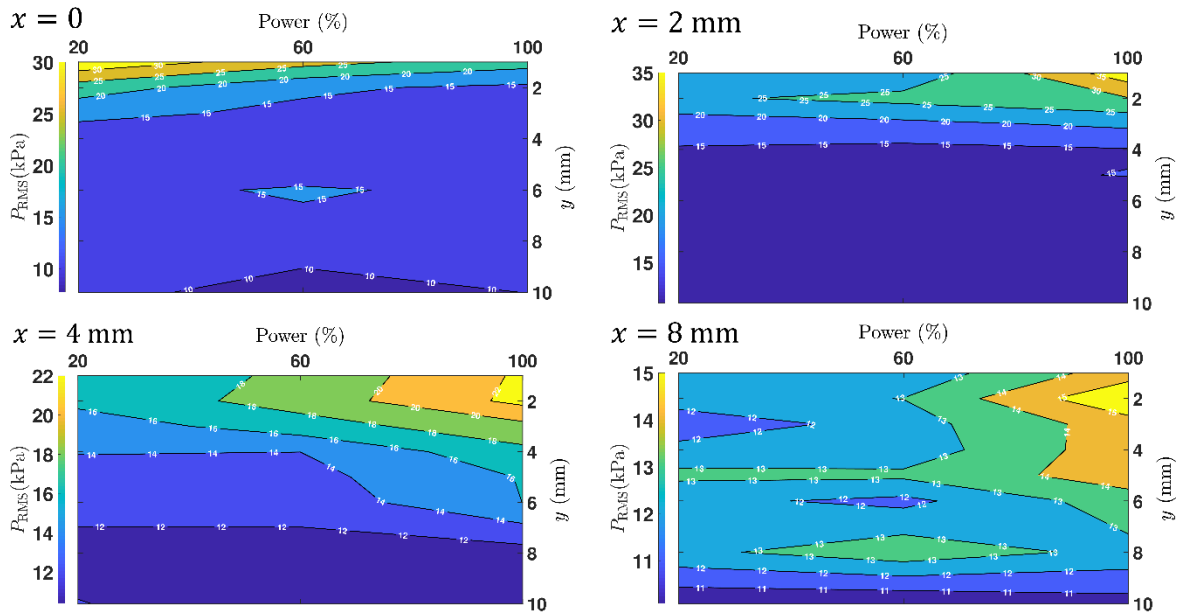


Fig. 5.17 Contour plots of P_{RMS} vs. input power and vertical position for 4 different horizontal positions on the right side of the sonotrode.

It is evident from Fig. 5.14 that P_{max} is largest just under and in the closest proximity to the sonotrode, but as the FOH probe moves away from the source, P_{max} drops significantly. A similar behaviour is observed for RMS pressure near and far from the source (Fig. 5.15). In fact, our measurements show that within the 10 mm distance in the map of observation, P_{max}

drops by 97-98% for all input powers. The corresponding drop for P_{RMS} was 75-78%. Furthermore, it is clear from these plots that considerably larger peak pressure magnitudes are obtained only in the regions very close to the sonotrode, i.e. in areas where bubble concentration is likely to be the highest indicating a strong non-linear vibration mode of bubbles (transient cavitation) [346–348]. Additionally, the contour plots show high pressure regions near the source as well as the non-symmetrical shape of the cavitation zone, the latter becomes less symmetrical with increase in power (the oscillation amplitude of the sonotrode). As the cavitation intensity near the sonotrode increases (increase of input power), a significant drop in the measured acoustic pressure close to the centre of the radiating surface can be observed. Note how the maximum pressure (P_{max}) drops almost one order of magnitude over a distance less than 10 mm away from the source for all input powers.

This decrease in the peak pressure amplitude, especially for the case of 60% and 100% power, can be attributed to the cavitation shielding effect caused by the bubble cloud formation [349] at the horn surface that restricts the propagation of the driving acoustic field and corresponding cavitation emissions into the medium [289]. This is in good agreement with previous observations, where the conical shape structure is believed to absorb the acoustic emissions weakening the cavitation impact [61,88,289,297,349]. As the cavitation cloud intensifies with the input power, the shielding becomes stronger which leads to weakening of the pressure field at some short distance [350]. Another possibility for a weakening pressure field and decreasing cavitation intensity is the absence of periodic bubble collapses as observed in [305]. In this recent work, an erratic behaviour of cavitation intensity for different input powers associated with shock wave emissions was shown. It was attributed to the local minima in the acoustic data observed with increasing sonotrode intensity (increased input power) caused by extended periods of non-collapsing deflations and thus absence of shock waves generation. This is in line with previous observations [88] where a similar behaviour was noticed.

On the other hand, the study by [338] showed that the increase in input power resulted in an increase in the acoustic emissions only at derivative frequencies such as harmonics and subharmonics. However, it should be noted that this might also be related to the shock wave propagation and spatial distribution of the cavitation energy at those frequencies, as it is known that subharmonics arise from transient cavitation events and the associated shock waves, while their interaction with bubbles in their pathway (as bubbles absorb part of shock wave energy) triggers more stable cavitation events that are superimposed to the existing harmonic or superharmonic spectral features [119,351] of the fundamental frequency. Hence, the magnitude

of cavitation intensity is inextricably linked to the shock waves and their propagation towards the bulk liquid.

It is evident that at input power of 20% (Figs. 5.14(a) and 5.15(a)) where bubbly structures are rather weak and disjointed [88], a rather uniform pressure field is formed below the sonotrode with a lower shielding effect as compared to that of 60% (figure 5.14(b) and 5.15(b)) and 100% (Figs. 5.14(c) and 5.15(c)) power regimes. Furthermore, as it can be seen more clearly in Fig. 5.16, P_{RMS} (being statistically more robust than P_{max}) does not exhibit a symmetric pressure distribution (as expected), since the cavitation zone is “dancing” continuously and propagating at various directions. This is a characteristic feature of the stochastic cavitation phenomenon. As seen in Fig. 5.15, in our case the cavitation zone mostly points towards the left ($-x$) regions (possible structural tilt of the sonotrode tip) and consequently gives rise to more bubble collapses there, as the bubbly clouds are thrust to the left; therefore, the pressure is expected to be higher in those regions and this is well captured by the FOH probe.

Furthermore, the presence of bubble clouds indicates the propagation of the shock waves and most importantly where the shock waves are mostly absorbed. At low input power (see Supplementary Video SV2 at power 20%, accessible with the published version of this work (<https://doi.org/10.1017/jfm.2021.186>)), the shock wave, while passing through the right side of the sonotrode, interacts with tiny cavitation nuclei and generates bubbles (i.e., the nuclei grow to form bubbles) which means that the shock wave should be less strong at this side than at the left side where the shock wave propagates undisturbed [351]. This agrees well with the pressure contours in Fig. 5.15. On the other hand, at higher power (see Supplementary Video SV3 at power 60%, accessible with the published version of this work (<https://doi.org/10.1017/jfm.2021.186>)), the majority of the bubbles are observed in the central region just below the source (sonotrode axis) leading to energy absorption in that zone. Therefore, the shock waves are weakened around the axis of symmetry and are stronger at the edges, again in agreement with the pressure contours in Fig. 5.14.

Fig. 5.18 shows the maximum pressure P_{max} of our entire sets of experiments for all horizontal (left and right) and vertical positions for all three transducer powers (20% , 60% and 100%), versus the radial position (r) measured from the source ($r = \sqrt{x^2 + y^2}$). Interestingly, the data fit well with the $1/r$ scale, as was previously suggested based on theoretical grounds [279] or numerical calculations of shock wave velocity [285,352]. We can now verify this scale by direct experimental pressure measurements. According to Fig. 5.18, the pressure drop away

from the sonotrode may be explained from the fact that the shock wave is briefly supersonic upon formation and loses its energy quickly afterwards [279,353]. The individual fitting equations for each input power are $P_{20\%} = 2.29/r^{-1.1}$, $P_{60\%} = 2.31/r^{-0.99}$ and $P_{100\%} = 2.22/r^{-0.85}$. The reason for the multiple pressure magnitudes for the same position in Fig. 5.18 is that several different positions with the same r value have different x and y coordinates.

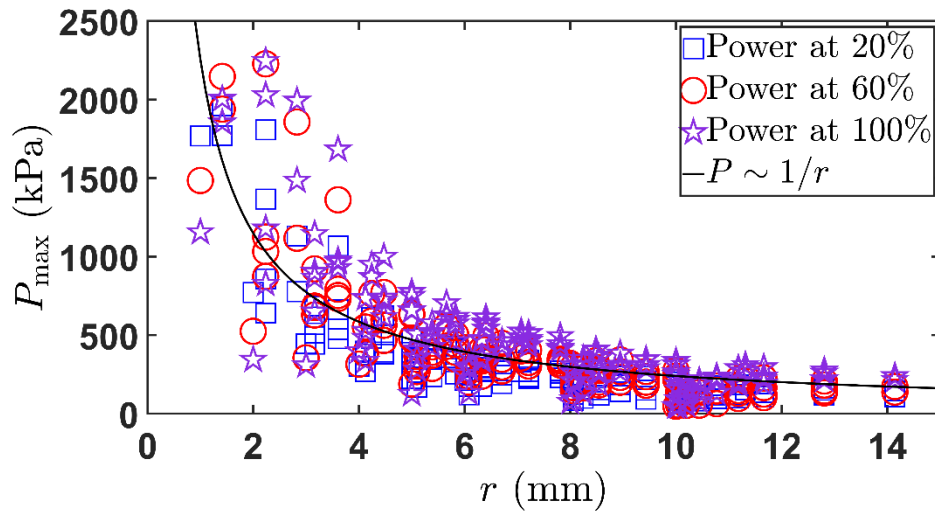


Fig. 5.18 P_{max} vs. r for the entire experimental matrix (all horizontal and vertical positions and input powers).

This is expected as the strength of the shock wave pressure across the spatial positions hugely depends on the speed of the propagating shock fronts. It has been reported that the speed of shock wave within 100 μm from the acoustic source is close to 2500 m/s and becomes equal to the speed of sound beyond the source [38]. Also previous studies confirm the significant dissipation of shock wave mechanical energy within the first 10 mm of its propagation [279]. Note that 10 mm is the outer limit of our experimental map (see Fig. 5.1). The spatial pressure mapping (Fig. 5.15) clearly shows that the pressure in the centre of the sonotrode is considerably reduced with increase in input power, while pressure on the sides is increased (see also Figs. 5.16 and 5.17). The reason for that is that persistent bubble clouds are barely present at the sides of the sonotrode and therefore, the shock waves are emitted to the liquid bulk without being disturbed.

Fig. 5.19 shows a series of snapshots for shock wave emission for different time steps (see Video SV2 accessible with the published version of this work (<https://doi.org/10.1017/jfm.2021.186>) for the full recording) where sonotrode, bubble clouds and shock waves are specified. It is clearly seen in several snapshots (Figs. 5.19 (c-h)) that, in

steady-state conditions, the shock waves emitted near the sides of the sonotrode propagate to the bulk uninterrupted, since the bubbles in those regions collapse in isolation or coincide with the borders of the bubble cloud (Fig. 5.19 (b)). Additionally, the attenuation of shock wave pressure with radial distance from the sonotrode ($P_{\max} \sim r^{-1}$) in Fig. 5.19 can now be explained as the energy dissipation resulting in pressure field modification during shock front propagation in the medium [38].

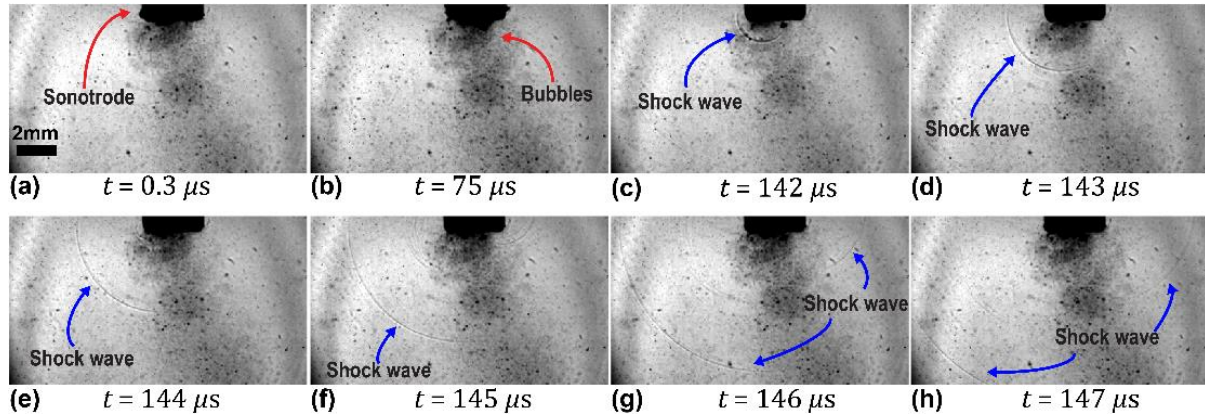


Fig. 5.19 Snapshots of acoustic cavitation and shock wave propagation. The red arrows (color online) mark the sonotrode and bubble clouds surrounding it. The blue arrows indicate the shock wave at different time steps and various positions. The shock waves are emitted to the bulk of the liquid undisturbed. The scale bar is 2 mm.

Finally, to investigate how the frequency (f_{peak}) of this new peak (see Fig. 5.4), caused by shock wave emission, is changing with distance from the source, a 3D bar plot with respect to horizontal and vertical positions for input power of 20% is shown in Fig. 5.20 (the corresponding plots for input powers of 60% and 100% follow the same trend and are shown in Figs. 5.21 and 5.22). The frequency of the peak is highest in the vicinity of the sonotrode and slightly reduces (4%) at farther distances. This tendency indicates the broadband nature of the peak source with significant broadband intensity contribution in the short bandwidth range.

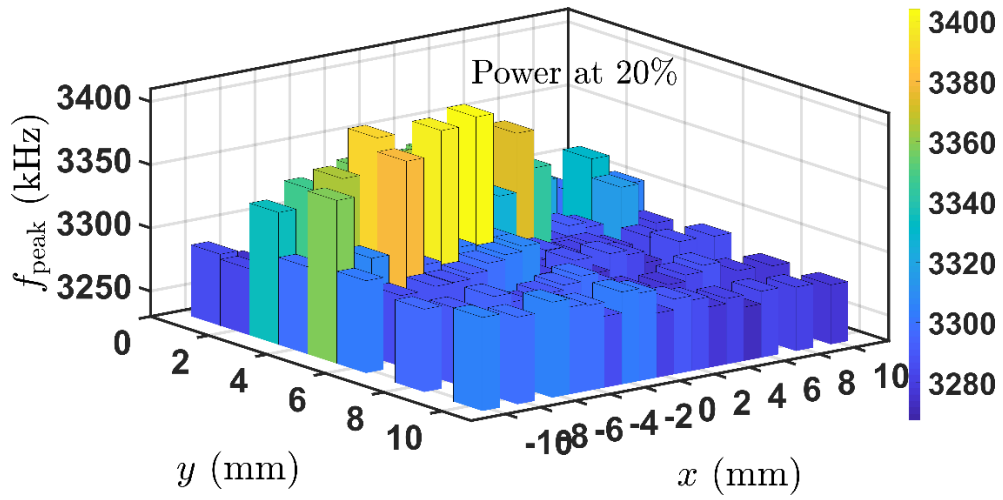


Fig. 5.20 3D distribution of the peak frequency vs. horizontal and vertical position for transducer power of 20%.

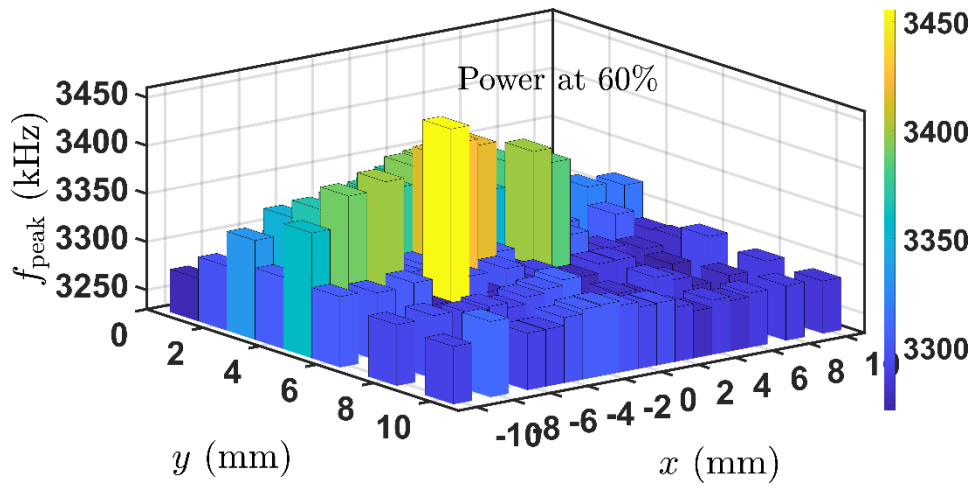


Fig. 5.21 3D distribution of the peak frequency vs. horizontal and vertical positions for transducer power of 60%.

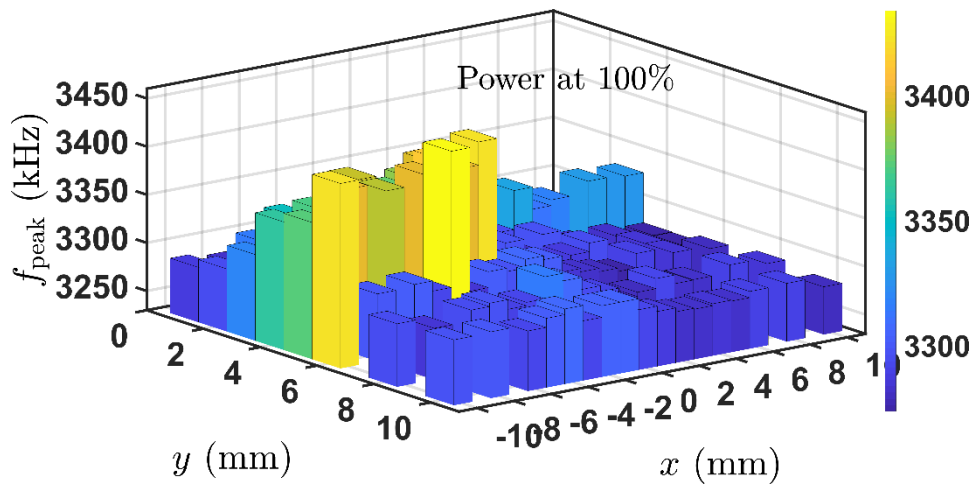


Fig. 5.22 3D distribution of the peak frequency vs. horizontal and vertical positions for transducer power of 100%.

Table 5.2 presents the minimum and maximum magnitudes of the peak frequency and peak pressure for three different input powers. In order to further confirm this tendency, bandpass filters were applied within the range of 3-4 MHz that includes the measured prominent peak. A drop of $25\% \pm 6\%$ in pressure magnitudes was identified showing that the observed peak contains some of the shock wave power, however most of its energy is, as expected, distributed among all other frequencies (see Fig. 5.10). This can be seen in Supplementary Video SV1 accessible with the published version of this work (<https://doi.org/10.1017/jfm.2021.186>), where we also observe some local maxima in $P - f$ profile at higher frequencies, particularly between 15-20 MHz, which become prominent in the vicinity of the sonotrode. This is due to the presence of multiple intensified collapsing spots near the cavitation zone that emit shock waves and raise the cavitation noise floor. The prominence of these humps near the sonotrode shows that most of shock wave energy is, as expected, distributed among all other frequencies including the high frequency values.

Table 5.2 Minimum and maximum magnitudes (of all positions) of the peak frequency and peak pressure for three different input powers. The pressure values are averaged over 60 waveforms.

	f_{peak} (MHz)		P_{peak} (kPa)	
	Min	Max	Min	Max
Power at 20%	3.27	3.40	0.124	0.715
Power at 60%	3.27	3.46	0.125	0.946
Power at 100%	3.27	3.43	0.156	1.16

Fig. 5.23 shows the acoustic level in dB scale vs. frequency (for low frequency range) for the case study presented in the manuscript. The probe was at $x = 0$ and $y = 1$ mm and input power was 60%. Note that for this plot, the bandpass filter is not applied, since this low frequency range is outside the calibrated range of FOH. For this plot, we used a fixed value for sensitivity (sensitivity at 1 MHz). The probe is capable of detecting the driving frequency and its harmonics, ultra- and sub-harmonics as indicated by the arrows in Fig. 5.23.

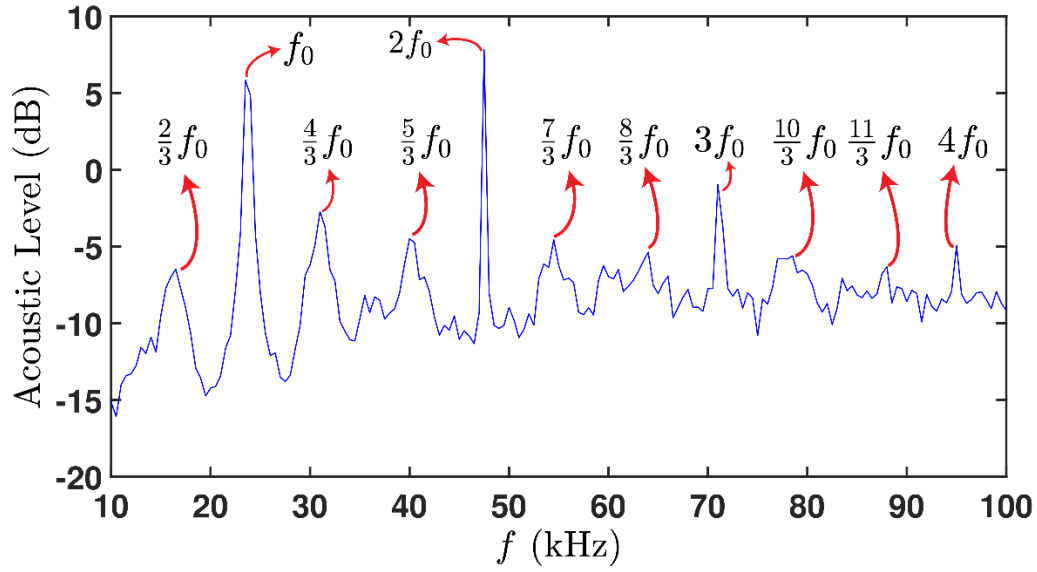


Fig. 5.23 Acoustic spectrum level (dB) vs. frequency (without bandpass filter) for $x = 0$ and $y = 1 \text{ mm}$ and input power of 60%. The pressure was averaged over 60 waveforms. Along with the driving frequency (24 kHz), the probe detects its harmonics, ultra- and sub-harmonics.

It should also be noted that a typical spectrum in the low frequency range including the driving frequency shows the capability of the sensor to resolve the emissions at these frequencies as well. The FOH captures, as expected, the driving frequency along with its harmonics, sub- and ultra-harmonics (see Fig. 5.23 for acoustic level in dB scale for our case study (without the bandpass filter)). For our entire set of experiments, f_{peak} changes between 3.27-3.40, 3.46 and 3.43 MHz for input powers of 20%, 60% and 100% respectively. The corresponding ranges for pressure at this frequency (P_{peak}) was 0.12-0.72 kPa, 0.12-0.95 kPa and 0.16-1.17 kPa.

5.4 Conclusions

In this Chapter, a comprehensive experimental study of accurate pressure measurements for horizontal and vertical distances close to an ultrasonic source (up to 10 mm) was conducted. The characteristics of acoustic cavitation-induced shock waves from a low frequency source (24 kHz) associated with power ultrasound applications were resolved. The main outcomes can be listed as follows:

1. A prominent frequency peak within the range of 3.27-3.43 MHz was detected. A hypothesis was made that this newly observed peak is associated with the accumulative effect of shock wave emissions.

2. A similar value for frequency of the shock wave emission was measured using high-speed photography at 1 million fps.
3. The data for the maximum pressure fits well with $1/r$ scale confirming that this is the reliable scale for the proximal distances (1-10 mm) from the sonotrode.
4. Our contour mappings also showed how the shielding effect can weaken the pressure field right below the sonotrode for high input powers.

This has not been previously reported and is in contrast to the current views where shock waves are in general characterized by a broadband acoustic impulse, described by a short rise of a sharp peak in the time domain and held to be solely responsible for raising the “noise floor” in the frequency domain. It can be observed that whilst the broadband acoustic pulses are undoubtedly present, the experimental configuration used here clearly gives rise to a consistent additional peak in the 3.23-3.47 MHz region. The new observations reported in this study can provide fundamental insights and another stepping-stone into the world of the shock wave emissions induced by acoustic cavitation and can be effectively used for developing and validating the numerical models and optimization of various industrial processes. The hypothesis proposed in this study, i.e. the shock wave emissions being the source of the observed peak, should be studied further and is the subject of our upcoming investigations. Nevertheless, this work could be a starting point for a complete understanding of the nature of shock waves generated by the collapsing bubbles.

Chapter 6

Spatial and temporal mapping of the fragmentation process of primary intermetallics[§]

Subsequent to the disclosure of cavitation-induced shock wave characteristics in a more profound manner (Chapter 5) and their effect on breaking fixed intermetallics (Chapter 4), we advance into a more complex and a real-case UST scenario of understanding the ultrasound-induced fragmentation and erosion mechanism of free-floating crystals.

*This chapter is a continuation of Chapter 4 where we first identify the best possible treatment domain for breaking intermetallics in terms of fragmentation time and then understanding the breakage and erosion process of floating crystals. In the present study, we developed a transparent test rig to observe in real time the fragmentation potential of free-floating primary Al_3Zr particles under ultrasonic excitation in water (an established analogue medium to liquid aluminium for cavitation studies) replicating the real-time casting conditions. An effective treatment domain was identified and fragmentation time determined using acoustic pressure field mapping. **For the first time, real-time high-speed imaging captured the dynamic interaction of shock waves from the collapsing bubbles with floating intermetallic particles that led to their fragmentation confirming the long-standing hypothesis that shock waves are responsible for the dynamic fracture of solid phases in a sonicated environment.** The breakage sequence as well as the cavitation erosion pattern were studied by means of post-treatment microscopic characterisation of the fragments. Fragment size distribution and crack patterns on the fractured surface were then analysed and quantified. Application of ultrasound is shown to rapidly (< 10 s) reduce intermetallic size (from 5 mm down to $10\ \mu m$), thereby increasing the number of potential nucleation sites for the grain refinement of aluminium alloys during melt treatment.*

[§] Published as A. Priyadarshi, et al., Ultrason. Sonochem. **80**, 105820 (2021) – Reproduced after permission.

6.1 Introduction

As discussed earlier in Chapter 2, there are two commonly recognised mechanisms of grain refinement acting upon conventional casting: enhanced heterogeneous nucleation on activated non-metallic inclusions through improved wetting and the sono-capillary effect and, fragmentation of primary intermetallics/dendrites through cavitation-induced shock waves [1,354,355]; with the latter process being very efficient and generally known as sono-fragmentation. Application of ultrasound to achieve particulate refinement has been widely studied in the areas related to sonocrystallisation and precipitation processes [138,356–358]. The phenomena of potential refinement of such particulates have previously been ascribed to stable-inertial bubble implosions, high pressure shock waves (order of GPa), powerful microjets and enhanced mixing of particles [138,300,359]. However, no concrete evidence of the same were provided leaving it as a hypothesis yet to be validated. Recently, a number of studies have been made to discern the ultrasound-induced fragmentation dynamics of various dendrites and crystals by application of in-situ synchrotron X-radiography imaging [137,271,360,361]. All these studies were done on fixed dendrites or intermetallic crystals. Moreover, real-time capturing of cavitation bubble dynamics and their interaction with solid phases in an actual melt system has been constrained due to working temperatures, opacity and temporal and spatial limitations of even the most advanced X-ray imaging [361]. This calls for alternative analysing approaches, whereby detailed cavitation dynamics can be recorded and resolved in-situ. A suitable transparent candidate for such studies is water. Water shares similar cavitation behaviour with liquid aluminium, though the acoustic pressure can be up to 2 times larger in Al melts as reported elsewhere [289]. For this reason it has been systematically used to replicate the conditions of acoustic cavitation in liquid Al during UST [18,88,276].

Additionally, in-situ synchrotron observations revealed that the induced acoustic flow can also play a major role in the redistribution and fragmentation of growing dendrites [361]. Intermetallics play a significant role in the formation of Al alloys structure and properties. Their fineness and uniformity of distribution are of great importance, as large particles are detrimental for mechanical properties acting as stress concentrators. The majority of intermetallic compounds are deemed to be structurally strong at ambient temperatures and maintain their hardness with increasing temperature [362,363] without drastic change up to the melting point (660°C) of aluminium, though the specific properties such as strength and ductility of Al-based intermetallics at high temperatures cannot be found in literature.

Nevertheless, the use of transparent media at ambient temperature seems appropriate for elucidation of the fragmentation mechanisms involved. Very few studies related to fragmentation of primary intermetallics has been reported until now. Wang et al. [103] recently studied in-situ fragmentation of various fixed primary crystals such as Al_3Ti , Si and Al_3V subjected to ultrasound in water. Also the fragmentation of fixed-in-space Al_2Cu primary intermetallics in aluminium melt subjected to UST was observed upon in-situ synchrotron studies [137]. Further works [277,332] have concluded that shock waves generated by cavitation bubble collapses are predominantly responsible for the fragmentation of primary intermetallics. Fragmentation of these crystals to appropriate shape and sizes is also vital for an effective grain refinement [172,174]. However, due to limitations of studying fixed crystals or having a small field of view in X-ray radiography, understanding the combined role of acoustic cavitation and streaming in the overall refinement process remains elusive and, therefore, calls for the need of further research in this regard.

The work presented in this chapter is a continuation of Chapter 4. Here we aim to first characterize the fragmentation process conditions in terms of breakage time and associated pressure field, using fixed intermetallic crystals and then move on to more realistic conditions of intermetallic fragmentation that represent the real case scenario in liquid metal during UST, i.e. identifying the fragmentation mechanism in the case of free-floating crystals within a dynamic cavitating environment. The latter has not been done before, to the best of our knowledge. Quantifying the cavitation-induced fragmentation of floating dendrites and primary intermetallics and finding their temporal and spatial fragmentation patterns are crucial in realising the optimal treatment conditions for effective up-scaling of the UST process. It is known that these crystal fragments act as source of heterogeneous grain nucleation points in real melt system subsequently leading to grain refinement and optimum equiaxed structure [137,147,174,176,364]. The role of Al_3Zr in the grain refinement of aluminium alloys upon UST has been established elsewhere [365]. Wang et al. [176] observed the formation of primary Al_3Zr particles in Al-0.4% Zr alloy after UST was applied at different temperature ranges. Their study mainly focussed on the particle refinement under the influence of UST. It has been reported that grain refinement in ultrasonically treated Al alloys is dependent on the nucleation potential and number density of primary intermetallic particles [163–165]. Another important characteristic of UST-induced grain refinement is that the fragmented dendritic crystals can also significantly improve the microstructure, homogeneity, and quality of the casting, without the need of substantial amount of grain refining particles or addition of AlTiB

master alloys [366]. Jung et al. [367] reported that primary phase particles of the order of 10 μm or less was sufficient for $\alpha\text{-Al}$ nucleation. The final microstructure observed after solidification of treated melts is therefore systematically connected with the refinement capability of the formed primary phases. Although, these investigations provided a general overview of the microstructural refinement obtained after the UST process, there is no evidence yet available in the literature that quantifies the time-based size-reduction potential of the intermetallic crystals. These studies also seldom provided the statistical data that would eventually lead to a clear criterion of fragmentation and did not report the extent of effective treatment domain that is essential for the fragmentation response to UST. Understanding of the primary crystal fragmentation potential under the influence of ultrasound by outlining the temporal and spatial behaviour of these fragments thus becomes vital in predicting actual grain refinement in Al based alloys.

The present work, therefore, focuses on firstly determining the extent of the treatment domain in terms of fragmentation time for a fixed crystal subjected to acoustic pressures measured across the treated liquid volume. Subsequently, the effect of ultrasonic treatment on the mechanism of floating-crystal fragmentation under various sonication periods in de-ionised water (DIW) is investigated using in-situ real-time high-speed imaging and post-mortem characterisation.

6.2 Experimental setup

The following experiments were strategically designed to quantify the fragmentation behaviour for fixed and a free-floating primary intermetallics. Firstly, the treatment domain defined as the region where fragmentation occurs within a very short period of time (less than 100 ms) was outlined for a fixed intermetallic at different input powers of ultrasound. The treatment domain was also effectively characterised through maximum acoustic pressure mapping across the cavitation field by using a calibrated needle hydrophone system. Thus by observing the fragmentation process while monitoring the acoustic pressure field, we could resolve the effective range of pressure amplitudes where fragmentation occurred. Secondly, the crystal break-up and the flow pattern resolved by the floating fragments were captured in-situ by high-speed imaging. The cavitation erosion pattern of free-floating primary crystals was characterised with respect to the sonication period using scanning electron microscopy (SEM). Finally, the number and size distribution of fragments were subsequently evaluated at different sonication time intervals.

6.2.1 Fixed intermetallic

An extracted primary crystal was first fixed on top of a steel substrate as described in Chapter 4 and positioned at the base of a glass container with dimensions $W_v: 75 \text{ mm} \times L: 75 \text{ mm} \times H_v: 100 \text{ mm}$. The container was filled with DIW to a height of 75-80 mm and was then placed below a 500 W piezoelectric horn transducer (Hielscher UIP500hdT) operating at 20 kHz. The ultrasonic waves were introduced into the water-filled container through a cylindrical titanium sonotrode ($\varnothing = 22 \text{ mm}$) immersed approximately 10 mm below the water surface. The driving amplitude of the vibrating sonotrode was chosen to run at 3 different power levels: 11.4 μm peak to peak (p-p) corresponding to 24 W (20%), 34.2 μm p-p to 65 W (60%) and 57 μm p-p to 108 W (100%). The experiments were conducted in ambient ($\sim 25^\circ\text{C}$) conditions. After each experimental run, a fresh crystal was placed across varying locations in transverse (X-axis) and longitudinal (Y-axis) directions with co-ordinates, $0 \leq x \leq 30 \text{ mm}$ and $5 \leq y \leq 30 \text{ mm}$, respectively at a gap of 5 mm between two consecutive positions. A schematic of the experimental setup is shown in Fig. 6.1. The fragmentation time of the crystal leading to first breakage from the onset of cavitation was obtained. At least 2-3 readings were taken for each position of the crystal for reproducibility of the results. The actual fragmentation time and boundaries of the effective treatment domain where crystals seemed to be prone to breakage by the action of ultrasound were defined.

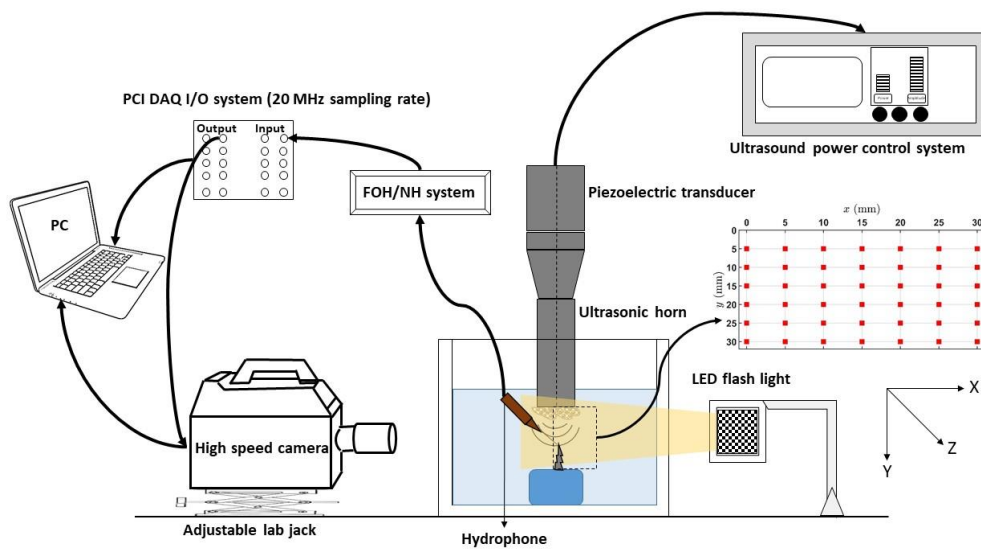


Fig. 6.1 Experimental setup to identify the effective treatment zone via crystal fragmentation time and acoustic pressure mapping in transverse (X-axis) and longitudinal (Y-axis) direction.

Acoustic emissions were recorded with a 4-mm PVdF Needle Hydrophone (NH) and a 125- μm Fibre Optic Hydrophone (FOH) sensor (Precision Acoustics Ltd.) calibrated in the range of low (8-400 kHz) and high (1-30 MHz) frequencies, respectively, with the sensitivity function shown in Fig. 6.2 (a, b). The acoustic measurements were captured across the treatment domain by using NH at each of the defined co-ordinates ($5 \leq x \leq 30$ mm, $5 \leq y \leq 30$ mm) as previously described for the fixed position (Fig. 6.1). In addition, synchronised acoustic emissions and in-situ fragmentation imaging measurements were recorded by placing the FOH sensor in the vicinity of a fixed crystal to monitor as accurately as possible the shock wave pressure amplitude required for fragmentation. The raw voltage data were acquired with a Peripheral Component Interconnect (PCI) data acquisition device with sampling rate of 20×10^6 samples/s which allowed real-time signal tracking and recording of high-speed images and the FOH data. Fast Fourier transformation was applied to the voltage-time data to obtain the pressure values following the deconvolution process defined in Appendix and earlier works [62,289]. For repeatability of the results, the experiments were conducted at least 4-5 times for each position and input power, including 3 extra runs without the presence of intermetallics.

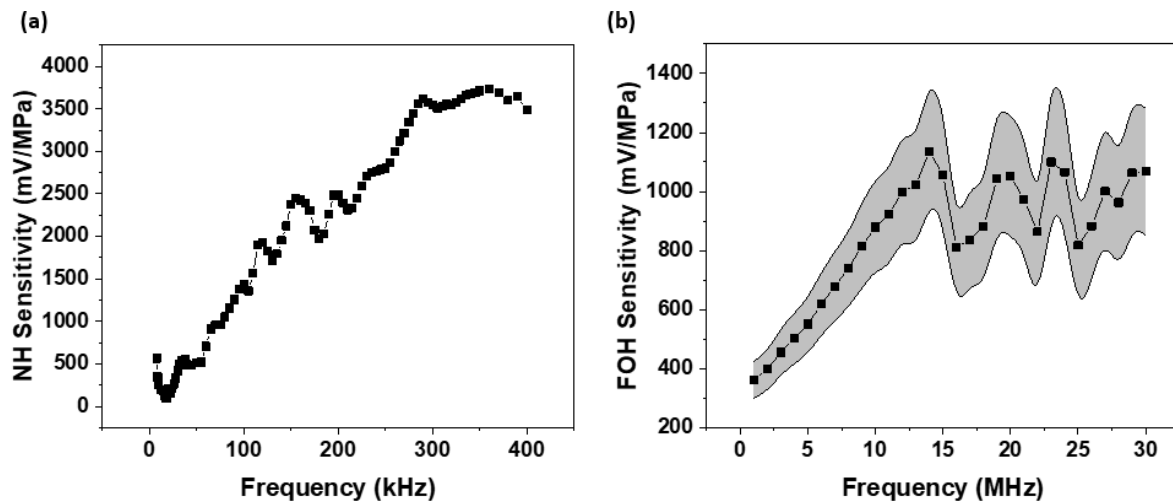


Fig. 6.2 Sensitivity of (a) NH calibrated between 8-400 kHz, (b) FOH calibrated between 1-30 MHz bandwidth frequencies.

6.2.2 Free-floating intermetallic

An extracted primary Al_3Zr crystal was placed in a transparent cuvette of dimension L : 25 mm $\times$ W_v : 10 mm $\times$ H_v : 45 mm containing 4 ml of DIW and allowed to settle at the bottom. The container was then placed below a 200-W piezoelectric ultrasonic transducer (Hielscher UP200S) operating at a frequency of 24 kHz. Detailed specification of this ultrasound device can be found elsewhere [288]. In this case, a titanium tapered sonotrode with a tip 3 mm in

diameter was used that allowed for detailed observations of the highly dynamic bubble/fragment interactions. The sonotrode-tip was vertically submerged into the liquid up to a depth of 5 mm to sonicate the medium at room temperature conditions (25°C). The liquid was sonicated for different time intervals: 3, 6 and 9 seconds from the onset of cavitation with a sonotrode-tip vibration amplitude (A_s) fixed at 210 μm peak to peak.

The in-situ fragmentation of the free-floating intermetallic crystals upon ultrasonication was captured using Photron SA-Z Fastcam high-speed camera (Photron Inc.). The camera was combined with Navitar 12 $\times$ adapter lens and nominal frame rates of 3,000 and 100,000 frames per second (fps) were chosen to capture the whole fragmentation sequence with imaging resolution of 640×512 pixels and 384×256 pixels, respectively. The background illumination was supplied by a multi LED flash lamp (GS Vitec) arranged from the rear of the container. A schematic illustration of the in-situ high-speed imaging setup is shown in Fig. 6.3 (a). The crystal fragmentation was repeated 5 times, with a new extracted crystal used each time. In this chapter, we only show the most illustrative sequence of images. After sonication, the liquid was filtered over a 2.5- μm pore-sized filter paper to separate the fragmented crystals. The particles were then air dried and preserved for SEM examination. The crystal velocity and size distribution during and after sonication, respectively was measured using image tracking processing techniques by ImageJ 1.8.0.

To capture the sono-fragmentation of a crystal by the propagating shock waves emanating from cavitation cloud collapses beneath the horn-tip, shadowgraphic imaging (Fig. 6.3 (b)) was performed using an ultra-high-speed camera (HyperVision Shimadzu, Japan) with a resolution of 450×200 pixels. In order to resolve the emitted shock waves, a similar Schlieren imaging setup was used as discussed elsewhere [305]. The fragmentation sequence was captured with high temporal resolution of 500 kfps over a short period of 512 μs . The spatial resolution of 17 $\mu\text{m}/\text{pixel}$ was obtained using a Milvus 100-mm macro lens (Zeiss, Oberkochen, Germany) with 10 ns synchronous laser pulse illumination (CAVILUX Smart, Cavitar, Finland) coupled to a collimating lens.

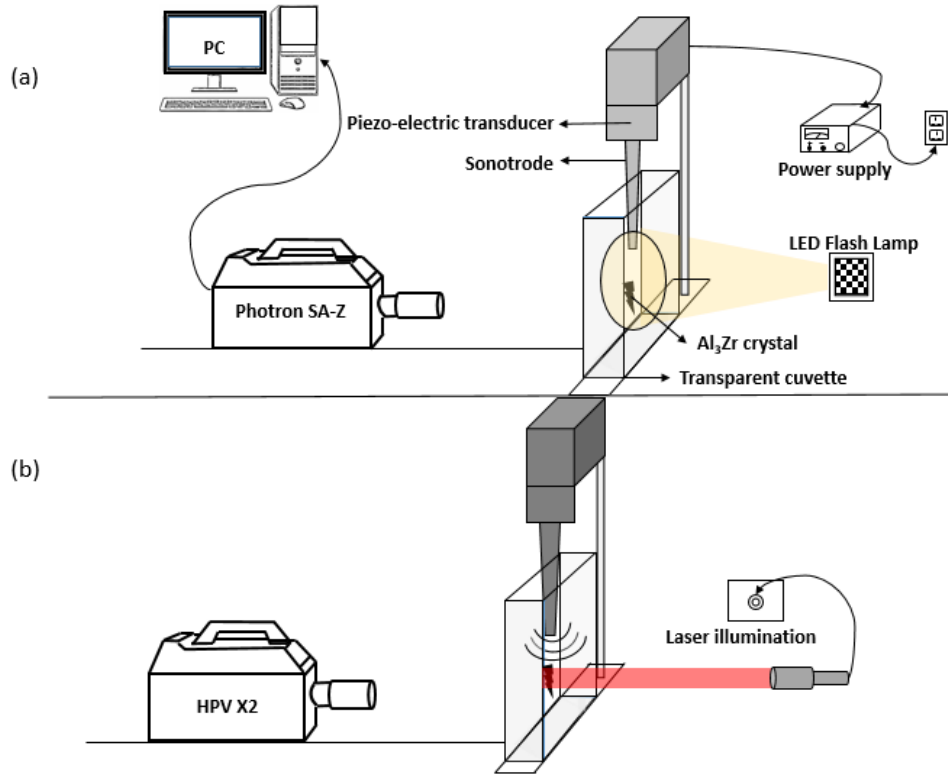


Fig. 6.3 Schematic of a high-speed imaging experimental setup to (a) capture the sequence of fragmentation process, spatial and temporal distribution as well as the dynamic size reduction of the fragments under light illumination; (b) capture sequence of crystal fragmentation by shock waves under laser illumination.

6.3 Results and Discussion

6.3.1 Fragmentation zone mapping of the treatment domain

In a real liquid metal system subjected to UST, it is essential that the entire melt volume undergoes treatment. Therefore, identifying the borders of the effective treatment domain becomes very important to ensure the effectiveness of ultrasonic treatment on crystal fragmentation, in order to optimise the processing of large melt volumes by using a single energy source (single sonotrode) [366,368]. In this section, we outline the spatial treatment domain in terms of the time required to fracture a single fixed crystal and relating it to the acoustic pressure field generated by the ultrasound.

Figs. 6.4a and 6.4b show respectively the 2D mapping of the measured maximum acoustic pressure ($P_{\max}$) obtained using a NH at specific positions as described in section 6.2.1 and the associated crystal fragmentation time (t_{frag}) distribution for different sonotrode amplitudes as mentioned in section 6.2.1. The sizes of all the crystals that were subjected to cavitation action from ultrasound were in the range of 3-5 mm. For clarity, we define the cavitation zone as the

area within the limits of the tip of the sonotrode (marked as the rectangular region below the horn-tip in Fig. 6.4(a, b)) where the cavitation cloud is formed i.e., up to a distance of 11 mm away from the centre of sonotrode with pressure amplitude fluctuating between 600 to 1300 kPa along its borders. The region beyond that is referred as outside the cavitation zone. The fragmentation time of the crystal was measured by placing the intermetallics within and outside the defined cavitation zone in order to check the effective treatment volume depending on the position and operating transducer power. As it can be seen in Fig. 6.4b, the fragmentation time of a crystal remains largely unaffected throughout the treatment domain measured within the cavitation zone ($x < 11$; $5 \leq y \leq 30$ mm) irrespective of transducer powers of 20% and 60% and varies in the range of 20-100 ms from the cavitation inception. However, for 100% power, the fragmentation time dramatically rises from 80 ± 10 ms at 20% up to 240 ± 30 ms in the location $x = 0$ mm and $y = 30$ mm below the sonotrode surface. The reason for this discrepancy could be the developed acoustic shielding effect [109,297,349] caused by the dense bubble cloud formation near the sonotrode or due to the extended periods of non-collapsing bubble deflations [305]. For crystals positioned immediately outside the cavitation zone ($11 \leq x \leq 30$; $5 \leq y \leq 30$ mm), there is only about 5-10% increase in the fragmentation time of the intermetallic crystals. The measured acoustic pressure (Fig. 6.4a) on the other hand is highest in close proximity to the sonotrode surface and attenuates with increasing distance away from the source as expected. The maximum pressure outside the cavitation zone varies between 180 and 1000 kPa for transducer powers operating at 20%, 60% and 100%. Even with the attenuation of the acoustic pressure, the fragmentation time remains mostly unaffected immediately outside the cavitation zone. For regions farther from the active treatment domain ($x > 30$; $y > 30$ mm), no fragmentation was observed, possibly owing to reduced acoustic pressures. It is interesting to note here that the fragmentation of these crystals is effectively occurring both inside and outside the cavitation zone which means that the breakage response is also somewhat dependent on the physical condition of the material as explained below.

It is usually expected that fragmentation will occur faster at higher pressure amplitudes and closer to the ultrasonic source. However, this was not the case in our experiments. Almost all intermetallic crystals broke within 100 ms of cavitation onset and the fragmentation time did not vary much with the position of a crystal for the 20% and 60% transducer power. This interesting behaviour may be attributed to the morphology of intermetallic crystals. Al_3Zr intermetallics are highly brittle in nature with the fracture toughness close to $1.1 \text{ MPa}\sqrt{\text{m}}$ [277] and usually contain many micro-cracks/defects formed during solidification that act as stress

concentration points resulting in failure of the material upon continuous interaction with shock waves emitted from the cavitation bubble collapses. It has been previously reported that crystal failure under the presence of acoustic cavitation occurred through a fatigue mechanism. During certain number of acoustic pressure cycles, the micro-cracks present within the crystal propagate until the critical crack size is reached leading to its brittle fracture [103]. In the case of 100% power, however, the fragmentation time increased by a factor of 2-3 compared to 20% and 60% input power, with the breakage time being about 250 ms farthest below the horn ($y = 30$ mm). This is better depicted in Fig. 6.4c where the plot of pressure amplitude versus the number of acoustic cycles obtained for the 100% input power indicates that the number of acoustic cycles to failure inside the cavitation zone is almost 2 times higher than outside the cavitation zone for each depicted position (x, y). This can then be attributed to strong shielding (due to formation of a larger cavitation cloud beneath the sonotrode) or extended non-collapsing periods of the numerous bubbly structures as previously discussed that obstruct and cushion the propagation of shock wave emissions, which are known to be the driving force for fragmentation of intermetallic crystals [277], within the cavitation zone. This also causes the suppression of the pressure field within the cavitation zone at 100% compared to 20% as seen Fig. 6.4a. Thus, even though the pressure amplitude (predominantly associated with the fundamental/driving (f_0), subharmonics, harmonics, and ultra-harmonics arising from the cavitation activity) is of the same order as in case of 20% and 60% input power, the fragmentation time is actually larger. This is however not the case outside the cavitation zone, where there are always some prevailing horizontal components of the propagating shock waves generated from the edges of the sonotrode that remains unaltered as previously observed in Chapter 5. Therefore, based on the fragmentation time and acoustic pressure measurements obtained from NH (Fig. 6.4 (a, b)), and since the measured pressure field, in the range of up to 400 kHz, spans within the same order of pressure amplitude for all input powers, it can be hypothesised that shielding of shock waves at the higher input power (100%) may be the reason for increase in the critical fragmentation time within the cavitation zone.

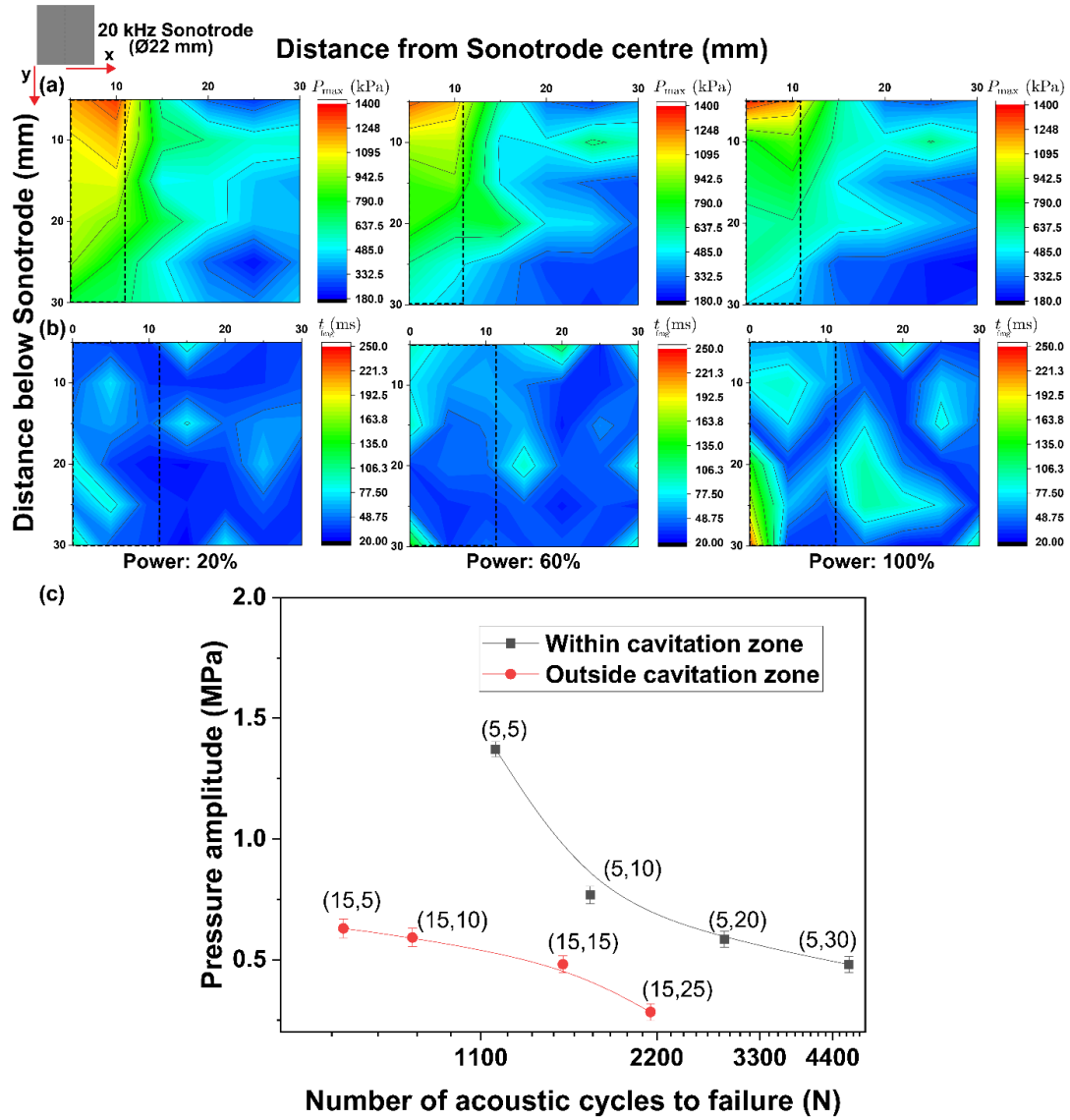


Fig. 6.4 Contour plots of (a) effective treatment domain with maximum pressure (P_{max}) distribution obtained from NH, (b) fragmentation time (t_{frag}) of fixed intermetallic crystals, obtained at 20%, 60% and 100% input power. (c) Variation of cyclic pressure amplitude with respect to the acoustic (sonotrode motion) cycles to failure of the crystal measured from the onset of cavitation activity at 100% input power at (x, y) position in mm away from the horn.

For that reason, the pressure field generated from the shock wave emissions was further studied using the FOH probe calibrated in the MHz range (see section 6.2.1) through synchronised high-speed imaging of crystal fragmentation and shock pressure measurement setup as described in section 6.2.1. This allowed us to test this hypothesis and verify if the cloud formation with the parallel suppression of shock waves is the main reason for the delay of the fragmentation.

Fig. 6.5 (Supplementary Video 1 accessible with published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105820>)) shows the fragmentation process of a fixed crystal with the dimensions L_c : 4.2 mm $\times$ W_c : 2.4 mm $\times$ T_c : 0.06 mm positioned 10 mm below and 15 mm in the transverse direction from the centre of the sonotrode operating at 11.4 μ m p-p tip amplitude. Fig. 6.5a shows the pressure–time profile captured from the onset of cavitation ($t = 0$ ms) up to maximum bubble cloud formation ($t = 283.64$ ms) obtained from the FOH sensor tip placed near the crystal. Once the cavitation initiates, the shock pressure peaks started to appear with gradual increase in the pressure amplitude. This continuous exposure to shock waves, indicated by the sharp pressure peaks from the periodic implosions of cavitation cluster below the horn-tip arguably generated low-cycle fatigue within the material, leading to crystal fragmentation. Fig. 6.5b shows the shock pressure peak and the corresponding fragmentation snapshot of crystal at $t = 20$ ms and $t = 43.3$ ms when a bundle of high intensity shock waves is emitted. The major fragmentation occurs at $t = 43.3$ ms when the shock wave intensity was the strongest with the peak positive pressure amplitude about 300 kPa. Along with this major breaking event, various smaller fragments were also formed simultaneously from the fractured region indicative of the typical brittle material failure (see Supplementary Video 1 accessible with published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105820>)). Interestingly, just before the 2nd breakage occurred, a small bubble was seen to grow and oscillate close to the crystal fracture location and the FOH tip. However, in our opinion the collapsing bubble had no role to play in the fragmentation of the crystal in this case, as these tiny cavitation bubbles cannot produce pressure surges of the magnitude that is responsible for the breakage of an Al₃Zr intermetallic. Even if it did, the acoustic cycles required to break the crystal should be significantly higher as previously discussed in [103]. Also, the rise of shock pressure at the same instant as the bubble collapses and the fragmentation occurs can be purely coincidental. Supplementary Video 2, accessible with published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105820>) shows a high-speed video recording demonstrating the fragmentation response of a primary crystal captured under same experimental conditions as done for Supplementary Video 1 (accessible with published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105820>)). From Video 2, it can be clearly seen that the 1st fragmentation event occurred just after the inception of cavitation at the horn tip followed by the 2nd breakage and also there was no bubble oscillating close to the crystal or the FOH tip this time. This further shows that the shock waves are the primary reason for the intermetallic fragmentation as also reported earlier [277,332]. Moreover, as observed from Fig. 6.5 (Supplementary Video 1), the crystal breakage happened within 100 ms of the onset of

cavitation and much before the fully developed cavitation regime was reached. It should be noted that after the 2nd breaking event, no further fragmentation was observed until much later, i.e. ~284 ms following the onset of cavitation. It is apparent that the developed cavitation cloud beneath the sonotrode-tip shields the propagation of shock waves causing the pressure amplitude to suppress as seen in Fig. 6.4a (100%) and previously observed in Chapter 5 and in [309]. Thus, the subsequent fragmentation takes much more time to occur until the existing crack/ flaw size reaches its critical length.

As shown in Fig. 6.4b, the treatment domain that was responsible for crystal fragmentation extended up to 30 mm from the sonotrode axis in both the vertical and horizontal plane. With taking into account the 22 mm diameter of the sonotrode, this falls within the well-known 1.5D rule of thumb for the cavitation zone [369]. It should also be noted that the fragmentation occurred well before the cavitation cloud under the sonotrode ever reached its maximum size (Fig. 6.5, Video 1). Therefore, the crystal breakage occurring between 20 and 100 ms after cavitation inception can be regarded as the effective treatment period caused by high intensity shock waves emissions, as long as the crystals were within the fragmentation domain ($x < 30$; $y < 30$ mm) at low input powers, where shock waves obstruction is suppressed. Upon real cavitation in liquid metals, there should be a trade-off between the input power and bubbles formation (cavitation activity) that define the effective treatment domain as has been previously highlighted in [370].

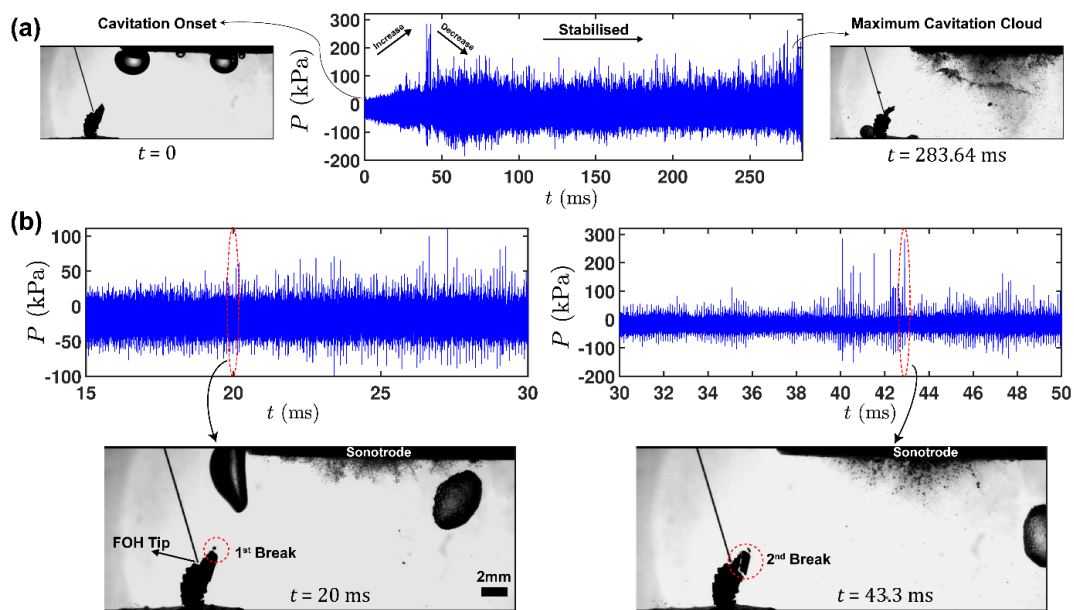


Fig. 6.5 Synchronised capture of in-situ high-speed imaging and acoustic pressure obtained by the high frequency calibrated FOH sensor; (a) pressure–time profile indicating the onset of cavitation and maximum bubble cloud, (b) the crystal breakage snapshot with the corresponding pressure peak. Supplementary Video 1 can be accessed with the published version of this work.

6.3.2 Fragmentation characteristics of free-floating intermetallics

After identifying the actual fragmentation zone and relating it to the corresponding acoustic pressure field and dynamics of shock waves, the next step is to monitor and reveal the fragmentation process of free-floating intermetallics. These primary intermetallic crystals that are formed in real metallic melts are typically free-floating under conventional UST. Thus, the fragmentation dynamics of these primary crystals is governed not only via the ultrasonic cavitation regime but also through the developed acoustic flow streaming within the liquid medium. The following section discusses the breakage mechanism of a free-floating intermetallic particle in the liquid irradiated with power ultrasound.

Fig. 6.6a (i) shows a faceted crystal (marked with an arrow) with approximate dimensions of L_c : 5.2 mm $\times$ W_c : 4.1 mm $\times$ T_c : 0.06 mm freely floating in water at time, $t = 0$ ms. Forced convection induced by acoustic flows prevented settling of this particle. After about 34 ms, the crystal driven by the streaming forces reached near the horn-tip as shown in Fig. 6.6a (ii). As soon as the crystal approaches the cavitation cluster formed beneath the vibrating horn, catastrophic fracture “instantly” occurred with it disintegrating into small fragments as shown in Fig. 6.6a (iii). Subsequently, the fragmented crystals were seen to follow a recirculating streaming path, for example the encircled crystal in Fig. 6.6a (iv) flowed back towards the cavitation zone (Fig. 6.6a (v)) thereby coming into contact with the bubble cloud again causing the crystal to further break down into smaller fragments, as shown in Fig. 6.6a (vi) (marked with an arrow). Some of the fragments tended to accelerate after interacting with the strong cavitation cloud formed beneath the sonotrode (see Supplementary Video 3, accessible with the published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105820>) for clarity). The velocity of fragments after passing through the cavitation zone varied in the range 1-2 m/s (see more on that below). Note, the recirculation flow pattern may be different for each fragment depending on its size and initial momentum, and may also change course to follow different paths as shown in Fig. 6.6a (vii). Nevertheless, it is certain that each and every fragment will follow some acoustic flow pattern and will pass through the strong cavitation region multiple times during its motion. It is also evident from Video 3 (accessible with the published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105820>)) that some of the fragments did not come in contact with the cloud and remained unaffected. In addition, multiple small and large cavitation bubbles were also observed vigorously coalescing, splitting and changing their oscillating pattern surface (Faraday waves) continuously as shown in Fig. 6.6a (viii-ix) (see Supplementary Video 4, accessible with the published version of this work

(<https://doi.org/10.1016/j.ultsonch.2021.105820>)). These bubbles were also seen moving against the streaming motion, attaching themselves to the fragmented particles (Fig. 6.6a (x-xi)) and transporting them back to the cavitation zone (see Supplementary Video 5, accessible with the published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105820>)). Further breakage of crystal fragments that recirculate back to the cavitation zone was almost instantaneous and occurred within 2 ms (Fig. 6.6a (xii-xv)). It is evident from Supplementary Videos 3-5 (accessible with the published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105820>))) that only some of the crystal fragments undergo further breakage after recirculating back towards the vibrating source. We also did not observe any fragmentation of smaller-sized crystals as capturing such fine details could be constrained by the optical resolution and depth of field limitation of the high-speed camera. The role of acoustic streaming as seen here was mostly to promote the recirculation of crystals back to the cavitation zone (vicinity of the cavitation cloud beneath the horn tip) for further treatment where the acoustic pressure intensity is highest. It should be however noted that the floating fragments when entering the cavitation zone did not break by coming into direct contact with the vibrating horn as the tip was covered by the cavitation bubble clouds for almost all the sonication period, even during the compression cycle of the vibrating source. Other possibilities of the fragments breaking through crystal – crystal, crystal – horn and crystal – wall interaction were also ruled out elsewhere [300,301]. It can be seen in Supplementary Video 6 (accessible with the published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105820>))) recorded at 5 kfps that a large crystal approaching the ultrasonic source rebounded and did not break even after colliding with the horn surface, validating the observation made by Zeiger et al. [300]. It has been found that the fragmentation response of materials during ultrasonic treatment of different solid-liquid phase systems essentially depends on the type of material being sonicated. In the case of softer metals, the particle – particle collision leads to surface deformation and interparticle melting [371–373]. Whereas, in the case of hard brittle materials like in our study, the fragmentation of materials is primarily through direct particle – shock wave interaction [300]. However, to be able to attribute such mechanism to the case of sono-fragmentation of primary intermetallics, we have performed high-speed imaging at high frame rates further below in this section in order to validate this hypothesis.

Fig. 6.6b shows the velocity-time profile obtained after real-time tracking of three free-floating fragments (see Supplementary Video 7, accessible with the published version of this work

(<https://doi.org/10.1016/j.ultsonch.2021.105820>) with sizes of the order of 1.48 ± 0.8 mm with Fragment 1 being the largest and 3 being the smallest; as they come into the vicinity of the cloud beneath the oscillating horn and pass through the cavitation zone. It can be seen from Fig. 6.6b that the average instantaneous velocity of the fragments before interacting with the cavitation zone was approximately 0.34 ± 0.1 m/s, consistent with acoustic flows based on previous Particle Image Velocimetry (PIV) measurements [70]. As soon as the fragments entered the cavitation zone, their velocity rapidly increased to 1.6 ± 0.5 m/s due to the instant push from violent cloud collapses. This change of the velocity reflected the collapse of large cavitating cloud that imparted a strong shock impulse (rate of change in momentum) to the nearby fragment inducing sufficient stress to cause particle breakage.

As observed in Fig. 6.6a (vii), vortices formed on the sides of the main cavitation flow stream brought the fragments back towards the sonotrode as demonstrated by their motion monitored up to 15 mm below the tip of the sonotrode. Acoustic streaming in liquid metals exhibits a typical acoustic flow pattern with a strong downstream jet motion along with a toroidal vortex surrounding the jet. According to [18] and [374], for sonotrode operating at 20 kHz in transparent liquids such as water with p-p amplitude of 51 μm , the average acoustic streaming velocity near the tip can reach up to 0.5 m/s. The presence of dominant vortices developed near the cavitation zone was shown to maximise the entrainment and enhanced treatment of floating phases [18]. A similar pattern in the acoustic streaming profiles was also observed in other transparent liquids with such different physical parameters as water and glycerine [88]. UST of an Sn-30wt% Cu alloy performed during the solidification revealed that the generated acoustic streaming helps to draw the fragmented dendrites back into the melt bulk, thus confirming that disintegration and distribution of solid phases by acoustic cavitation and streaming led to grain refinement in metallic alloy melts [18]. Wang et al. [137] also confirmed that acoustic streaming played a significant role in the fragmentation of a primary solid phase. It was found that the dendritic crystals tended to vibrate upon ultrasonic irradiation and were subsequently detached by the acoustic flow. These crystals were then propelled back into the cavitation zone following the upward path of the recirculating loop where they underwent further breakdown caused by violently imploding bubbles thereby, producing smaller fragments that would act as nucleation sites for secondary phase solidification leading to microstructural refinement. Lebon et al. [70] earlier reported that the acoustic streaming response in water and liquid aluminium is very similar. Although the specific flow and acoustic patterns in the setup used and in metal casting moulds are different, we do not expect large

differences in the underlying mechanisms that happen on microscopic rather than macroscopic scale. Note that depending on the acoustic streaming path (as shown in Fig. 6.6a (vii)) followed by the crystal, the time taken by each fragment to re-enter the cavitation zone can vary from 17 – 120 ms (Fig. 6.6b). However, the majority of the fragments took close to 100 ms to recirculate back to the cavitation zone following their respective trajectories as shown in Fig. 6.6a (vii). This is in very good agreement with recent investigation by Beckwith et al. [3], where it was shown that the effective residence time in a real case scenario of UST performed in direct-chill casting launder was close to 100 ms meaning that every fragment should essentially recirculate almost 50 times before moving downstream towards a hot top mould. Therefore, the synergy of strong collapses inside the cavitation zone and adjacent to the sonotrode-tip, in conjunction with the rapid collision of fragments with the bubble cloud may lead to crystal breakage after few acoustic cycles.

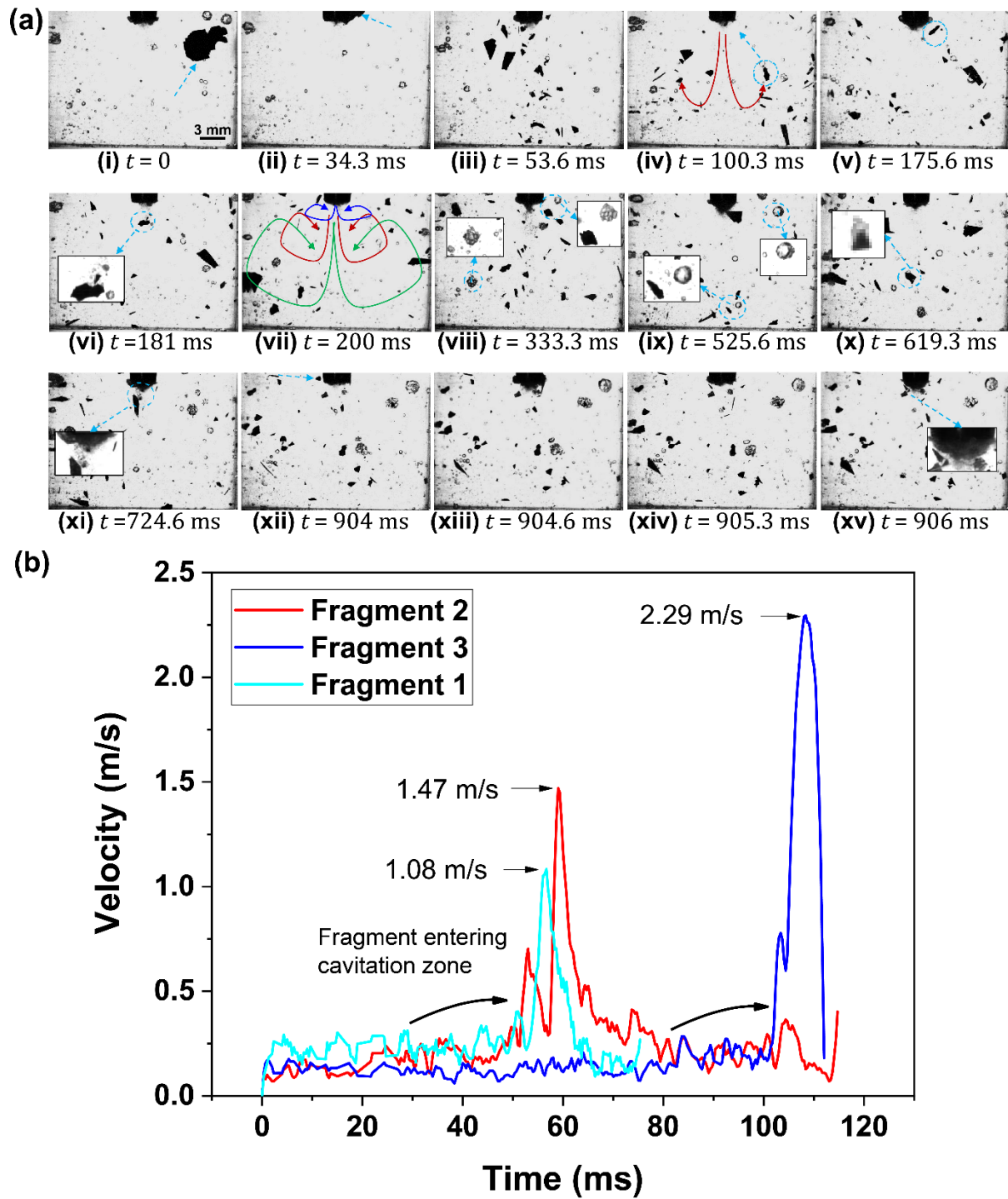


Fig. 6.6 (a) High-speed image sequence showing the break-up mechanism of free-floating primary crystal recorded at 3000 fps. The corresponding videos 3, 4 and 5 can be accessed with the online version of the article. (b) Measured instantaneous velocity–time profile of recirculating intermetallic fragments flowing towards and through the cavitation zone. Supplementary Video 7 can be accessed with the published version of this work.

In order to clarify the exact fragmentation mechanism of free-floating crystals recirculating and re-entering the cavitation zone, high-speed imaging at higher frame rates, under visible light and laser illumination was carried out. Fig. 6.7a (i-viii) shows a sequence of images captured at 100 kfps with a zoomed view on the fragmentation of a floating crystal as it approaches the sonotrode. At $t = 0$ ms, the crystal was seen to flow towards the vibrating sonotrode as shown in Fig. 6.7a (i). The crystal then started to vibrate with its frequency matching the oscillating frequency (24 kHz) of the cavitation cloud collapse at $t = 0.37$ ms (Fig. 6.7a (ii)). As the crystal approached the tip of the sonotrode, the amplitude of crystal vibration increased with its oscillating frequency reducing to 5 kHz equivalent to the $f_0/4$ subharmonic collapse of primary bubble clusters [305]. At $t = 2.36$ ms, the crystal experienced the maximum deflection and almost came in contact with the cavitation cloud when it was at its maximum size (Fig. 6.7a (iii)). With the bubble cluster collapsing at $t = 2.51$ ms, the crack initiated in the crystal and propagated until a section broke off at $t = 2.77$ ms as shown in Fig. 6.7a (iv-vi). The remaining parent crystal however continued to flow towards the ultrasonic source and again almost touched the cloud at $t = 3.99$ ms (Fig. 6.7a (vii)). Soon after, the crystal was deflected away as the cloud started to grow and another small breakage occurred at $t = 4.03$ ms (Fig. 6.7a (viii)). This whole sequence of images can be clearly seen in Supplementary Video 8 (accessible with the published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105820>)). It was suggested that the shock waves emitted from these subharmonic cluster collapses are responsible for the fragmentation. To verify this, another set of high-speed imaging experiments (at a higher rate of 500 kfps), represented schematically in Fig. 6.3 (b), was performed to confirm that crystal breakage is caused by the shock waves close to the ultrasonic source.

Fig. 6.7b (i-vi) outlines the series of images showing the crystal breakup occurring near the horn-tip caused by the propagating shock waves (see Supplementary Video 9, accessible with the published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105820>)). Initially ($t = 0$ μ s), a crystal (circled in red) was seen floating near the source (Fig. 6.7b (i)). As the primary bubble cluster beneath the sonotrode started to collapse, multiple fronted shock waves were released (marked by blue arrows) and incident to the fragmented crystal (Fig. 6.7b (ii)). Upon complete collapse of the bubble cluster as shown with a red arrow in Fig. 6.7b (iii), another set of shock waves was released (blue arrows). Frame-by-frame analysis indicates that around 10 shock waves were emitted for every 50 μ s (~ 1 acoustic cycle). After exposure to around 20 shock waves, delamination seems to occur followed by crack inception on the side

of the floating crystal (marked with an arrow in Fig. 6.7b (iv)). The crystal then eventually broke as the crack propagated further ultimately causing its complete fragmentation at $t = 232 \mu\text{s}$ (Fig. 6.7b (v-vi)). It should be noted that the direction of the shock wave propagation with respect to the crystal position or point of defect (pre-existing micro-crack) may contribute to the fragmentation process.

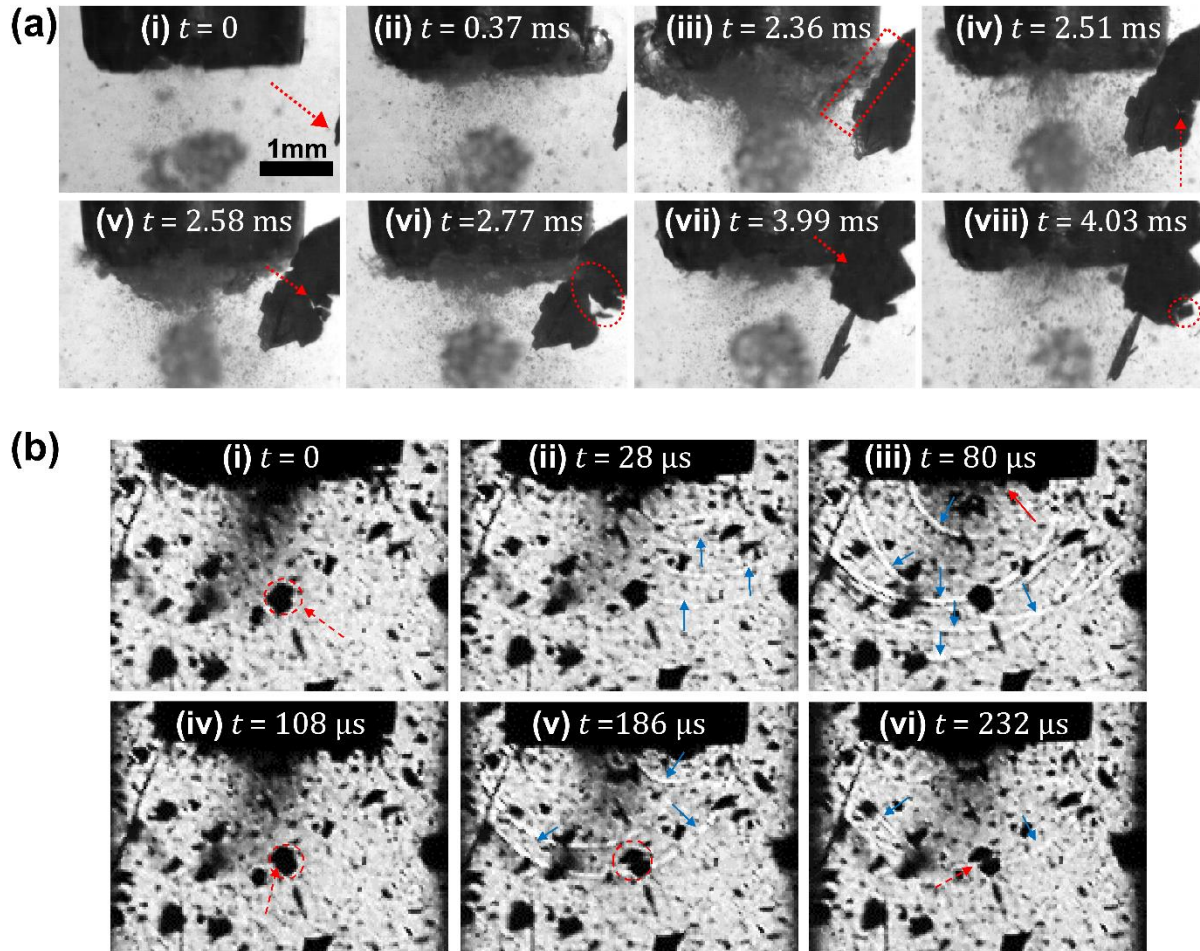


Fig. 6.7 (a) High-speed image sequence showing the crystal break-up mechanism near the cavitation cloud recorded at 100 kfps. Supplementary Video 8 can be accessed with the online version of the article. (b) Series of in-situ high-speed shadowgraphic imaging showing the crystal fragmentation caused by multiple shock wave impacts in the vicinity of cavitation cloud recorded at 500 kfps. Supplementary Video 9 can be accessed with the published version of this work.

The observations of Figs. 6.6a, 6.7a and 6.7b reveal that sono-fragmentation of intermetallic crystals is a result of both acoustic streaming and acoustic cavitation-induced shock waves. The fragmentation is primarily governed by the impact of propagating shock waves produced from subharmonic cloud collapses, while the acoustic streaming is responsible for bringing the crystals into the effective cavitation region. Crystal fragmentation mostly occurs near the source as a result of shock-induced bending/torsion, where the majority of high amplitude

shock waves are generated. Interestingly, the eventual breakage of floating crystals occurs by the same fatigue failure from repetitive shock wave impacts as in the case of fixed crystals [103]. However, the fragmentation, refinement and dispersion of such particulates can also be realised through the mechanism of cavitation induced micro jetting and de-agglomeration and remains a subject for further research. The high-speed images (Fig. 6.6a, 6.7a and 6.7b) and the corresponding Supplementary Videos (accessible with the published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105820>)) that show the fragmentation of intermetallics in real-time did not indicate any crystal breakage occurring within the cavitation zone that transpires through the mechanism other than propagating shock waves. Any such fragmentation events realised away from the horn tip maybe further related to mechanical and hydrodynamical effects induced by the cavitation bubbles, but were not observed in our study.

6.3.3 Ultrasonic cavitation erosion of floating intermetallics

Having revealed the main fragmentation mechanism that leads to fragmentation for free-floating crystals, we now turn our attention the micro-fragmentation response of free-floating crystals from the microstructural perspective.

Fig. 6.8(a-c) displays the morphology of an extracted Al_3Zr intermetallic crystal prior to ultrasound exposure. The untreated intermetallic exhibited a layered and faceted structure as shown in Fig. 6.8a (i) and 6.8a (ii) reflecting its growth morphology as discussed elsewhere [252]. In addition, these crystals with thicknesses in the range of 60-70 μm contained pre-existing macro- (Fig. 6.8b (i)) and micro-cracks (Fig. 6.8b (ii)) due to released residual stresses during solidification and extraction process as described in section 3.2.1 of Chapter 3. A considerable number of foreign particles were also found in various locations on the surface layer of the crystals, as shown in Fig. 6.8c (i). Energy-dispersive X-ray spectroscopy (EDS) examination of these particles indicated the presence of various oxides with sizes of 5-10 μm such as Al_2O_3 , ZrO_2 , Na_2O , TiO_2 , FeO (Fig. 6.8c (ii)) some of which might have formed during storage and material preparation while other represent indigenous oxide particles that can potentially act as an additional source of nucleation sites for the growth of Al grains [375] and primary intermetallics [376]. The surface morphology and internal defects of these crystals can have a substantial impact on their fragmentation response characteristics as previously discussed in Section 6.3.1. Campbell [377] has shown that primary intermetallics that form during solidification of Al melts may (actually he claims – always) nucleate onto oxide bi-films

that act as internal cracks within the intermetallic particles. Therefore, the fragmentation dynamics of these extracted crystals can provide new insights into their refinement mechanism in a real melt processing environment.

A detailed post-exposure SEM examination of the single crystal after ultrasonic treatment was performed to analyse the morphology of cavitation-induced damage as shown in Fig. 6.8(d-f). Fig. 6.8d shows the morphology of intermetallic fragments after 3 sec of ultrasonic treatment. As it can be seen from Fig. 6.8d (i), the crystal broke into several small fragments with sizes as small as 50 μm . In addition, zooming onto the bigger fragments showed a well-defined fracture network developed along the existing micro-cracks as shown in Fig. 6.8d (ii) and 6.8d (iii). It is interesting to note that the surface of the fragment showed round protrusions 5-20 μm in size with well-defined edges, bulging out from the cracked upper layer matching their peripheral boundaries (Fig. 6.8d (iv)). Fig. 6.8e displays the morphological images of fragmented crystals after 6 sec of exposure to ultrasound. Increased ultrasound exposure led to delamination of the top layer (indicated with red arrow) as shown in Fig. 6.8e (i). Also, the formation of a micron-sized hierarchical crack pattern, in the range of 20-100 μm , can be observed on the upper layer of the fragmented crystal (arrowed red, Figs. 6.8e (ii) and 6.8e (iii)). The presence of plastic pits (round punch marks) of size $6 \pm 2 \mu\text{m}$ can also be seen on the fractured surface as shown in Fig. 6.8e (ii). In addition, peeling of the cracked upper layer (as indicated with red contour) can also be seen at certain regions of the fragmented crystal as observed in Fig. 6.8e (iv). Fig. 6.8f exhibits the microstructural images of cavitation-induced damage of the primary crystal after UST for 9 sec. Further increase in the treatment duration generated more fragments of smaller size (Fig. 6.8f (i)) and also resulted in the formation of a finer hierarchical crack network in the range of 1-5 μm (Fig. 6.8f (ii)). Extensive erosion and ‘chipping off’ of the upper crystal layer can also be seen for the fragmented intermetallics as shown in Fig. 6.8f (iii). Individual fragments with sizes in the range of 10-50 μm , broken from the fractured surface can be seen in Fig. 6.8f (iv).

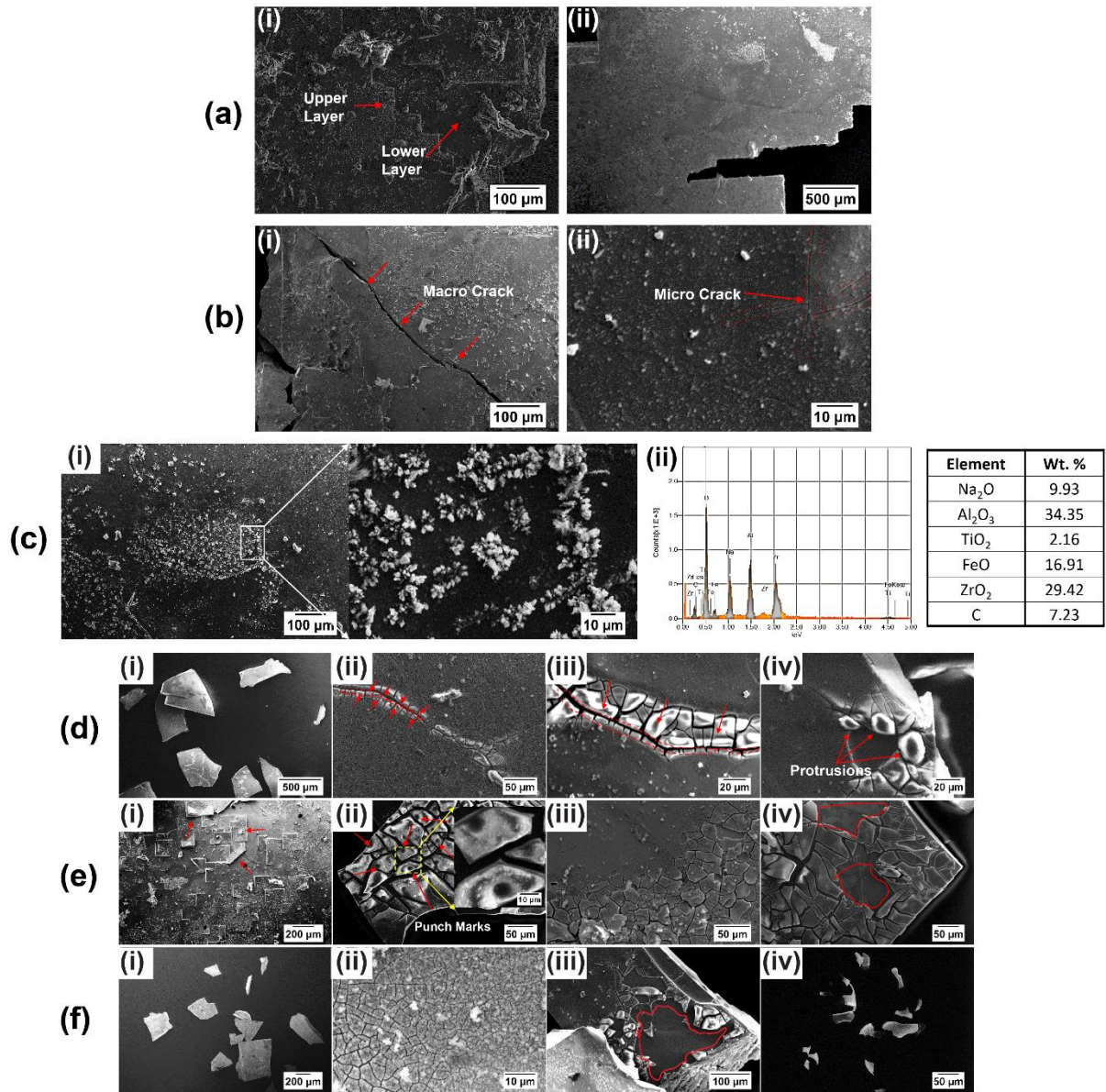


Fig. 6.8 (a) SEM images of an extracted Al_3Zr crystal showing layered and faceted morphology, (b) presence of pre-existing micro-cracks, and (c) oxides and the EDS spectrum with elemental composition. (d) SEM morphological images of cavitation damage induced after 3 sec, (e) 6 sec, and (f) 9 sec sonication, obtained at ultrasonic amplitude of 210 μm peak-to-peak.

Strong impact pressures from collapsing bubbles generating powerful shock waves and high-speed liquid-microjets are deemed likely to be responsible for the induced fracture, surface delamination and erosion as discussed in section 6.3.2 and elsewhere [69,378,379]. In addition to emitted shock waves, these collapses also generate liquid jets with velocities in the order of 100 m/s near the crystal surface, producing water-hammer pressures P_w on impact, given by, $P_w = \rho_c v_i$ [102], where ρ_c is the density times the speed of sound in water and v_i is the liquid

jet velocity, of up to 0.1 GPa sufficient to generate plastic pits (Fig. 6.8e (ii)) arising from multiple micro-jet impacts as previously shown in [69,379]. Outside the cavitation zone, the crystals are less likely to be damaged by liquid jets and are mostly accompanied by stably pulsating ultrasonic bubbles that undergo distortion of interface resulting in splitting, shape and chaotic oscillations as shown in Fig. 6.6a (viii-ix). It has been reported that these chaotically oscillating bubbles also emit liquid jets upon splitting, but the values are substantially lower, i.e. about 1 m/s and a corresponding dynamic pressure of only 10 kPa, which is unlikely to induce any significant damage of the solid surface nearby [303]. Kim et al. [303] were first to observe the damage of a silicon wafer caused by the ultrasonically splitting bubbles. It was found that the damage was possible only if the bubble split occurred directly over the surface. Ishida et al. [380] reported that the impulsive pressure due to the emitted shock wave generated by a splitting of a spark-induced bubble when confined within the narrow surface is enough to induce microstructural damage/erosion patterns on the solid structures. Therefore, it is possible that the microstructural damage in the form of hierarchical crack patterns on the surface of fragments as shown in Fig. 6.8(d-f) was predominantly generated by shock waves and complemented by high-speed liquid jets produced from the periodic collapses of the cavitating cloud near the sonotrode-tip [69,379,381]. Whereas, chaotically oscillating ultrasonic bubbles present outside the cavitation zone may only scrub the surface of attached fragments, facilitating the removal of some exogenous non-metallic inclusions, as observed in Fig. 6.8c rather than damaging the surface [303,380].

As the Al_3Zr primary crystals in Al melt grew in steps, it is likely that repetitive exposure to cavitation bubbles induce delamination of several atomic layers, prior to cracking. The exposed layer thus became loose and then cracked owing to the stress generated by bubbles and potential discontinuities with the properties of the bulk material underneath and partially delaminated top layer. Subsequently, the loosely bonded sections of the outer layers of the crystal began to peel off, and the large cracks grew and opened up causing further breakage as it recirculated back into the cavitation zone, by induced acoustic streaming. Safonov et al. [382] previously observed that the material degradation of a multilayer brittle material by cavitation occurs in stages. It was reported that in the regions of low cavitation load, the outer layer degradation occurred through multiple impacts of cavitation bubbles inducing brittle fracture. Therefore, delamination followed by further crack formation and growth (as seen in Fig. 6.7b) explains the observed ‘peeling off’ of layers governing the micro-fragmentation behaviour of Al_3Zr

primary crystals, similar to the mechanism discussed elsewhere for thermal-sprayed coatings [383].

6.3.4 Fragment size distribution

The final step in this study was to identify the statistical distribution of the fragments based on the sonication time, which is important to control the treatment duration within the cavitation zone and optimise flow management techniques for continuous casting as recently discussed in [366,384].

Fig. 6.9a shows the size distribution of fragmented particles after sonicating for 3, 6 and 9 seconds based on the results of SEM imaging. As expected, the average size decreased with treatment time. With just 3 sec of treatment, almost all fragments had a size smaller than 1000 μm down from the initial size of 5 mm. The smallest crystal size from the analysis of at least 3 sets of collected fragment batches was $12 \pm 1 \mu\text{m}$ with approximately 20% of fragments having sizes below 100 μm . The fragmentation potential of UST increased by almost 150% after 6 sec of sonication, however, the total number density of all the produced fragments remains approximately the same after 6 sec. With a further increase in the sonication time to 9 sec, the fragment number density increases by almost 200% with more than 50% of the fragments being smaller than 100 μm .

Fig. 6.9b shows the fragmentation potential of UST for intermetallic crystals represented in terms of average fragment size with respect to ultrasonic treatment durations up to 120 sec. A significant decrease in the fragment size was visible after 3 sec of treatment, indicating the severity of particle breakage. The mean size reduced by more than 10 times from the initial crystal dimension showing high propensity of intermetallics to fragment under the combined action of acoustic cavitation and acoustic streaming. The average size dropped to almost 500 μm within the first 6 sec of treatment. The slope of the fragment size with respect to sonication time, however, only slightly decreased thereafter reaching a plateau after 9 sec indicating a stabilised fragmentation process. This was possibly because the fragments were not sufficiently large to achieve the required flexing/bending upon shock wave incidence, as described previously. The average size of fragments decreased to 100 μm and remained constant until 120 sec of sonication duration. The majority of the fragments of sizes less than 100 μm produced after 9 sec of treatment, were more likely to be the result of delamination and breakage of the fractured crystal surface, as observed in Fig. 6.8f. The results indicate that the

effective treatment time of intermetallics within the active fragmentation zone (defined in section 6.3.1) in water medium should be in the range of 10-15 sec which coincides well with the time required for efficient intermetallic fragmentation upon casting of Al alloys [174,384]. It is important to note here that in a real casting processes, the choice of effective treatment time will also depend on the process scale dimensions and various other important factors such as casting speed, horn dimension etc.

As identified in Fig. 6.8(d-f), many of the large broken fragments also showed the presence of micron-size crack patterns in the form of grains/platelets and, with the increase in sonication time, a much finer crack network was generated on the exposed surface of the fragments with the individual sections measuring 100 μm or less. It is expected that these tiny sections will eventually break off from the surface and play the role of effective nuclei within the Al melt, further promoting heterogeneous nucleation of new Al grains. With this in mind, we also analysed these crack patterns generated after 3, 6 and 9 sec of treatment.

Fig. 6.9c shows the section size and its number distribution obtained from micron-size hierarchical crack network pattern for different sonication periods as discussed in relation to Fig. 6.8(d-f). It can be seen that overall section count increased with the treatment time from 3 sec to 6 sec by a factor of 7 and then subsequently decreased for the 9 sec sonication for sections with sizes between 10-100 μm . The number of the individual sections with the size below 10 μm however, increased by a factor of almost 8, from 3 sec to 9 sec. The average size of the grains formed after 3 sec decreases from approximately 50 μm to 38 μm after 6 sec and then remains almost unchanged even with 9 sec with fewer number of grains ranging from 10-100 μm . It might be that with a further increase of treatment time beyond 6 sec, the resulting cracked sections broke out from the damaged layer of the intermetallic crystal, thereby increasing the number of smaller size fragments as shown in Fig. 6.9a.

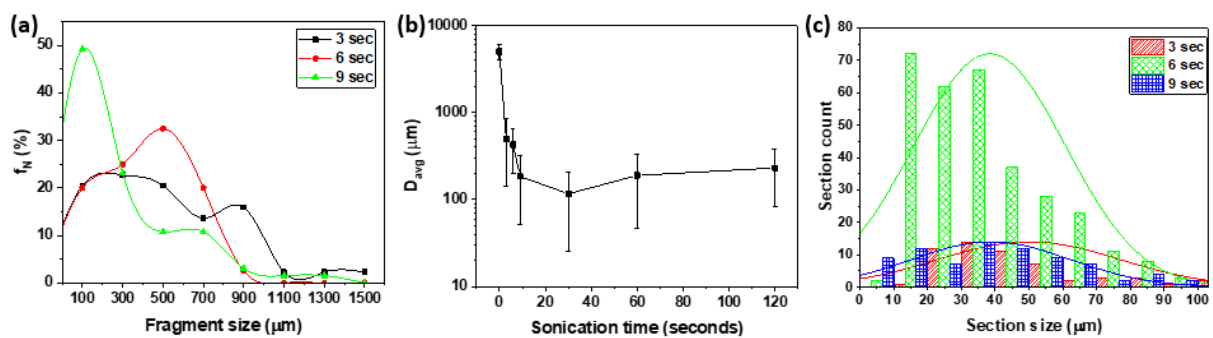


Fig. 6.9 (a) Relative fragment number density vs. size distribution measured after 3, 6 and 9 sec of sonication, (b) Average crystal diameter as a function of sonication duration up to 120 sec. (c) Section size distribution and number measured after 3, 6 and 9 sec of sonication, obtained from micron-size hierarchical crack pattern images.

A similar qualitative trend in particle size reduction and number distribution as a result of sono-fragmentation has been reported in a number of studies [138,299–301,385]. Although the effect of sono-fragmentation on the particle size reduction was observed at different operating frequencies, most of the papers reported a significant size reduction for low sonication frequencies (circa 20 kHz), where the effect of shock wave was more pronounced, making it ideal for treating liquid metals as compared to higher frequencies [356,385–387]. In the case of UST of real Al alloys, however, such big crystals 5-7 mm in dimensions would be not formed under normal casting conditions. Therefore, although fragmentation of intermetallics in Al melts under cavitation does happen and has been observed experimentally (ex-situ) before, the specific results obtained from the fragment size distribution are confined to the experimental conditions used, i.e. crystal/particulate breakage in water.

Fig. 6.10 shows a schematic of the free-floating intermetallic fragmentation mechanism summarizing the fragmentation observations made in our study. The continuous interaction of the floating intermetallics with the periodic shock wave emissions from high-energy collapses of the cavitation cloud with the pressure field in the range of 0.2–1 MPa facilitated by the recirculating acoustic flow results in the formation of numerous small fragments (10–100 μm) within just a few seconds of treatment (10-15 sec). The effective fragmentation zone can extend up to 1.5 times the diameter of the ultrasonic source in longitudinal (Y-axis) and up to 3 times in transverse (X-axis) direction, as observed in Fig. 6.4b. The rapid reduction in fragment size can be due to the brittle nature of the intermetallics and the presence of various micro-cracks and defects making them more susceptible to fragmentation. With the progression in fragmentation, the possibility of fragments to further break up is expected to reduce, making the subsequent rate of fragmentation slower as is demonstrated upon UST longer than 9 sec. This may be a result of the smaller aspect ratio of remaining fragments increasing their inherent strength.

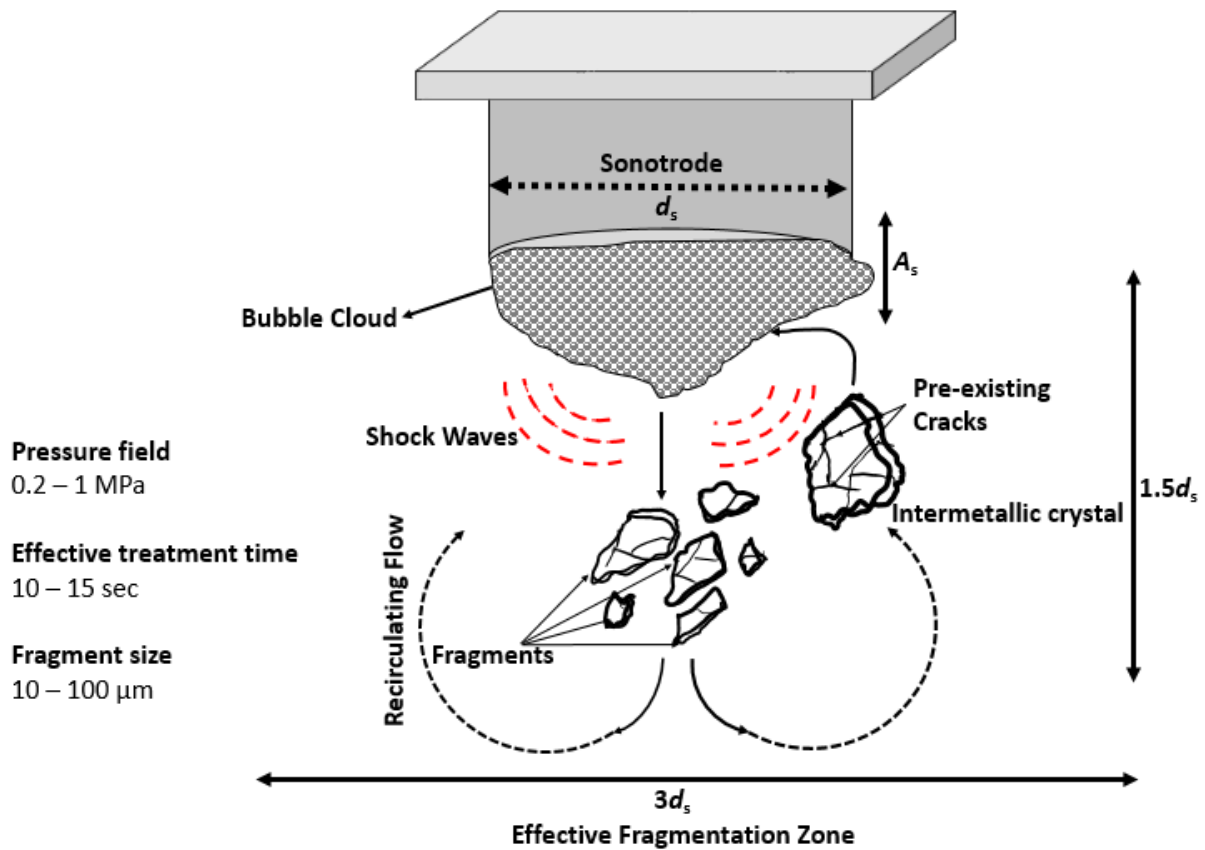


Fig. 6.10 Schematic representation of free-floating crystal fragmentation mechanism showing the extent of effective treatment domain.

In this work, temporal and spatial statistics for crystal fragmentation were generated in water for fixed and free-floating conditions important for identifying the optimum treatment duration and domain for a larger scale real melt processing units. It is likely that the crystal fragmentation will be even more pronounced in liquid aluminium leading to increased particle number and even smaller particles compared to observations made here, in water. Tzanakis et al. [276,388] observed that the cavitation dynamic response in liquid Al is almost twice as intense in terms of acoustic pressure field generated. Moreover, the higher density of liquid Al will prevent fast sedimentation of the primary crystals increasing their exposure to further fragmentation. In real ultrasonic melt processing, the estimation of treatment time or residence time becomes very important in order to ensure that the whole liquid volume passing through the cavitation zone is uniformly treated [389]. Therefore, based on the temporal and spatial characteristics of the crystal fragmentation as described in this chapter, the optimum size of the treatment vessel, size of sonotrode and sonication time can be estimated and used for numerical modelling of ultrasonic processing.

6.4. Conclusions

In this study, the fragmentation potential of fixed and free-floating primary intermetallics was examined based on the effective spatial and temporal domain treatment characteristics that maximize the extent of crystal refinement when subjected to ultrasonic treatment. Following investigations of fragmentation of fixed and free-floating intermetallics through in-situ high-speed imaging, acoustic measurements, and post-exposure SEM study of the crystal fragments, the following conclusions can be drawn:

1. Effective cavitation zone mapping experiments for fixed intermetallics reveal that time required for first breakage of a crystal mostly lies in the range of 20-100 ms irrespective of its position as long as crystal lies within the actual treatment zone ($5 \leq |x| \leq 30$; $5 \leq |y| \leq 30$ mm) and the developed pressure field that spans from 200-1300 kPa for all the input powers (20%, 60%, and 100%). However, what regulates the breakage of the studied crystals is the bubble volume fraction that surpasses the developed pressure field and cushions the propagating shock waves (predominantly responsible for the fragmentation). Therefore, the crystal fragmentation time may be delayed even by 2-3 times, as seen in the case of 100% power.
2. For the first time high-speed filming captured the dynamic interaction of shock waves with floating intermetallic particles that led to their fragmentation. Repeated fragmentations are induced as the crystals recirculate with the acoustic streaming generated from the vibrating sonotrode.
3. Microscopic observations of fragmented free-floating crystals show the formation of protrusions, plastic pits and micron-sized hierarchical crack network on the surface of the fragments. The size of crack network decreases with the increasing treatment time, beyond 6 sec and are in the range of 5 to 50 μm . SEM imaging of the fragmented crystals suggests that the intermetallic fracture occurs through delamination/fracture of the exposed top layer. The fragmentation is likely to occur within the cavitation zone (close to bubble cloud) upon repetitive shock wave impacts. The smaller fragments, with sizes below 100 μm , are most likely produced through the breakage of the delaminated surface layer.
4. The size reduction potential of intermetallics assessed by the post-treatment fragment analysis (using SEM) indicates that the average fragment size and relative density decreases and increases, respectively, with the extended sonication period. The crystal

fragmentation initially occurs rapidly, and subsequently slows down, generating crystals smaller than 100 μm in just 9 sec of treatment.

Chapter 7

Ultrasonic de-agglomeration of metal oxides[§]

Having understood the fragmentation response of intermetallics under the influence of power ultrasound, we now turn our attention to the ultrasound-induced de-agglomeration process of oxides which also plays a crucial role in grain refinement of Al alloys and production of Al metal matrix composites.

*This chapter addresses the de-agglomeration and dispersion mechanism of different metal oxides that are commonly found within the melt as inclusions. Ultrasonic de-agglomeration and dispersion of oxides is important for a range of applications. In particular, in liquid metal, this is one of the ways to produce metal-matrix composites reinforced with micron and nano sized particles. The associated mechanism through which the de-agglomeration occurs has, however, only been conceptualized theoretically and not yet been validated with experimental observations. Owing to the opacity of liquid metals, a de-agglomeration imaging experiment was carried out in de-ionised water with sequences captured at frame rates up to 50 kfps. In-situ observations were further accompanied by synchronised acoustic measurements using an advanced calibrated cavitometer, to reveal the effect of pressure amplitude arising from oscillating microbubbles on oxide de-agglomeration. In this study, the influence of ultrasonic cavitation on SiO₂ and MgO agglomerates (commonly found in lightweight alloys as reinforcements) with individual particle sizes ranging between 0.5 and 10 µm was monitored **For the first time in-situ using high-speed imaging revealed that the complex nature of de-agglomeration is dictated by a combination of processes described as the “sandwich mechanism”**. In specific, results showed that ultrasound-induced microbubble clusters pulsating chaotically, were predominantly responsible for the breakage and dispersion of oxide agglomerates. Such oscillating cavitation clusters were seen to capture the floating agglomerates resulting in their immediate disintegration. De-agglomeration of oxides occurred from both the surface and within the bulk of the aggregate. Microbubble clusters oscillating with associated emission frequencies at the subharmonic, 1st harmonic and low order ultra-harmonics of the driving frequency were deemed responsible for the breakage of the agglomerates.*

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7.1. Introduction

UST of metallic melts favourably impacts material quality through grain refinement, particle mixing and, dispersion, cluster fragmentation, and degassing [1,390]. This equally applies to liquid metal processing with added nanoparticles/powders or grain refining agents used to produce metal matrix composite materials [149,391]. Incorporation of oxides such as alumina, silica and magnesia as reinforcements offers superior strength to the majority of aluminium alloy composites [392–394]. The use of such ceramic materials in Al matrix composites is considered suitable as it acts as particulate reinforcement that offers high hardness, wear resistance, compressive strength, and thermal stability [239]. Other than in composite materials, the use of oxides like MgO have been found to be useful in other applications such as waste water treatment [395], antacid for heartburn and dyspepsia [396] and also as an anticaking agent in food additives [397]. In all these applications, there is a challenge of agglomeration that needs to be addressed. Nevertheless, there are issues with the introduction of such particles in melts and more specifically to liquid aluminium [244]. Owing to large surface tension, poor wettability, oxidation and hydrogen adsorption, particles added externally, or indigenous oxides, often form agglomerates with absorbed hydrogen on their surface [1]. Thus, these agglomerated particles cannot be wetted by the surrounding melt and are particularly difficult to disperse and distribute uniformly within the liquid metal matrix. UST has been found to assist in both distribution and dispersion of particles added or formed within the melt through the process known as ultrasonic de-agglomeration [398,399]. The ultrasound-induced acoustic cavitation and related streaming effects, both play an important role in de-agglomeration and subsequent dispersion of particles in the liquid. Note that this is important not only for the metal-matrix composites but also for “conventional” grain refinement that is based on the distribution of secondary phases or activated substrates, which is facilitated by de-agglomeration/dispersion. Beyond liquid metal processing, de-agglomeration using ultrasonic effects can be important in other applications ranging from pharmaceuticals to food industry [400].

It is hypothesized that the increased wettability of the particles under cavitation conditions allows the molten metal to reach their surface and subsequently penetrate the agglomerate through capillaries [401]. This has been resolved experimentally using synchrotron studies where the sono-capillary mechanism in molten aluminium was captured, showing that the high-speed liquid jets from the collapsing bubbles lead to the de-agglomeration of oxide particles

trapped within a groove during the solidification process [104]. However, the role of ultrasonic cavitation on the particle de-agglomeration and the underlying mechanisms have not yet been clearly understood and have only been qualitatively described. For example, Kudryashova and Vorozhtsov [398] demonstrated analytically that the cavitation-induced microscopic bubbles pulsate and collapse near the agglomerate, developing overpressure that pushes the melt into the narrow pores of an agglomerate by overcoming the capillary pressure threshold. The liquid thus enters the capillary channels and pores of the agglomerates. The infusion of liquid metal into the agglomerated particles considerably alters the properties of the agglomerates and expedites the breakup of the particle cluster (de-agglomeration) through viscous and shear forces caused by the cavitating bubbles and propagating ultrasonic waves. The high intensity ultrasonic waves produce numerous microscopic cavitating bubbles that are distributed within the liquid volume by the generated acoustic and secondary flows. Moreover, as the bubbles favourably nucleate at gas pockets and interfaces, pores within the aggregate and individual particles act as ideal sites for cavitation nucleation. Eskin and Eskin [1] postulated the de-agglomeration mechanism in a slightly more comprehensive manner. The mechanism was described as follows: The formation of microbubbles initially occurs at the particle/liquid interfaces (gas pockets). As the bubbles tend to pulsate vigorously under the influence of ultrasound, this causes the loosening of agglomerates from within. The resulting pressure and momentum impulses as bubbles collapse break the agglomerates apart. The generated localised pressure, which reaches up to 500 MPa [69,278] is sufficient to overcome the capillary and adhesive bonds between the particles (~ 1 MPa) within the agglomerate [402]. The acoustically induced flows further distribute the particles within the treated volume. Up to now, most experiments on ultrasonic de-agglomeration in metallic melts have been performed in ex-situ and post-mortem conditions and the associated effects were interpreted based on microscopic examination of the formed particle clusters in the solidified product. For example, Eskin et al. [403] experimentally observed the partial de-agglomeration of TiB_2 clusters by remelting a commercial Al-3%Ti-1%B master alloy and by ultrasonically treating the alloy melt using a 5-kW transducer operating at a frequency of 18 kHz. It was found that the cavitation treatment of an AlTiB master alloy resulted in the release of individual TiB_2 particles of sizes between 1-3 μm from the agglomerates and they further became available as active substrates to promote heterogeneous nucleation of new aluminium grains. However, in-situ studies to understand the de-agglomeration mechanism are scarce, owing to the liquid metal opacity that makes real-time observations difficult. Water has long been recognised as a suitable liquid analogue system for studying the effects of intermetallic fragmentation and de-agglomeration

[1,18,103,277,332,388,404]. Eskin et al. [18] recently showed through in-situ high-speed observations that cavitation assisted de-agglomeration of MgO aggregates in water was initiated from their outer surface and not from within. The de-agglomeration process was thought to resemble the ‘chipping-off’ of individual constituent particles from the surface rather than occurring within the bulk. Nevertheless, there is still a deficit in the literature on studying the process of de-agglomeration of particles within ultrasonically treated liquid and analysing the effect of cavitation bubbles and streaming on particle dispersion and distribution.

The present work focuses on understanding through real-time high-speed imaging, of the overall de-agglomeration process of silica (SiO_2) and magnesia (MgO) agglomerates with individual particle sizes up to $10\text{ }\mu\text{m}$ exposed to cavitation action in water, under the influence of ultrasound. In addition to being model oxide agglomerates, silica and magnesia are widely used in cosmetics, food, and nutritional supplements; hence, their de-agglomeration behaviour has broader practical significance. The underlying mechanism of group and individual agglomerates has been explained in terms of ultrasonic cavitation and induced acoustic streaming effects. The de-agglomeration process has also been further characterised in terms of the frequency components observed within the cavitation emission signals.

7.2 Materials and methods

7.2.1 In-situ high-speed imaging

High purity SiO_2 (99.999%) and MgO (99.998%) were obtained from Fisher Scientific, UK having particle density of 2.65 and 3.58 g/cm^3 , respectively. Agglomerates of these oxides with particle sizes in the range of $0.5\text{--}10\text{ }\mu\text{m}$ were used for ultrasonic de-agglomeration experiments in deionised water. Fig. 7.1 shows the microstructural images of silica and magnesia aggregates and individual oxides particles (as inset) obtained using scanning electron microscopy (SEM) prior to exposure to ultrasound. The in-situ high-speed observations were performed in a transparent cuvette of dimensions, L : 12 mm ; W_v : 12 mm ; H_v : 44 mm , using a 200 W piezoelectric transducer (UP200S, Hielscher Ultrasonics GmbH, Germany) operating at 24 kHz with a coupled titanium sonotrode (tip diameter $\varnothing = 3\text{ mm}$). Detailed specification of this ultrasonic device can be found elsewhere [288]. The liquid height in the cuvette was maintained at $20 \pm 2\text{ mm}$ and the sonotrode was submerged $15 \pm 1\text{ mm}$ below the liquid surface. The tip-vibration amplitude of the sonotrode was chosen to be $210\text{ }\mu\text{m}$ peak to peak (for developed cavitation). The experimental test rig designed for the experiments is depicted schematically in Fig. 7.2. The high-speed imaging of the de-agglomeration effect was undertaken using Fastcam

SA-Z 2100K (Photron, UK) and the cavitation activity was recorded at 20,000-50,000 frames per second (fps), with a shutter speed of 18.39 μ s through a Navitar 12 $\times$ zoom lens (0.5 $\times$ 0.009-0.051 NA 1-50012). At 50 kfps, imaging was obtained over 896 $\times$ 448 pixels with a resolution of 11.2 μ m/pixel. High intensity light illumination was provided by a GS VITEC Multi LED flash lamp and a Fibre Optic Haloid lamp from front and rear end of the focussing plane, respectively. This illumination allowed for observing bubbles in both the transient and stable oscillation modes. The main purpose of this imaging was to capture the de-agglomeration sequence of the oxide agglomerates under the influence of ultrasonic cavitation and acoustic streaming effects.

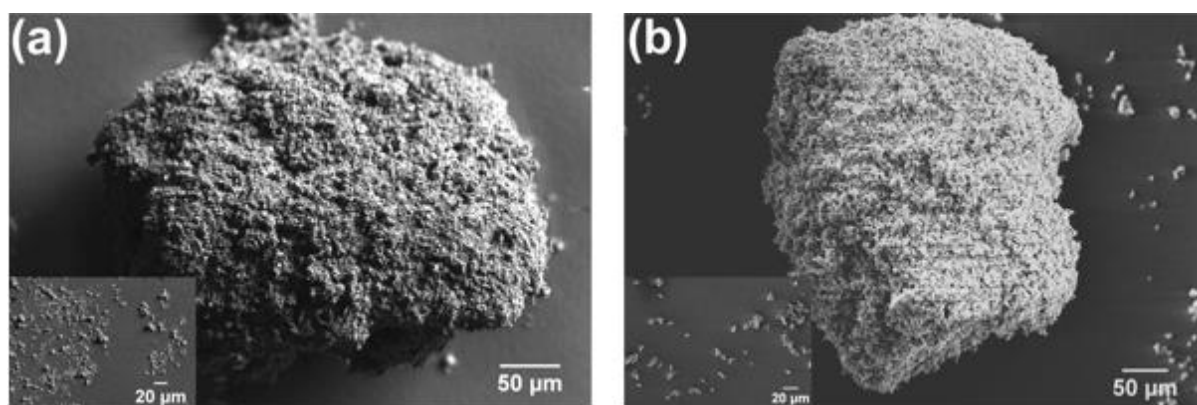


Fig. 7.1 Microstructural images showing the typical surface morphology of (a) SiO₂, and (b) MgO agglomerate with individual particle size up to 10 μ m depicted as an inset.

7.2.2 Acoustic detection

The acoustic emissions were detected using a bespoke low-frequency (in the range of kHz) calibrated cavitometer mounted 3 ± 0.2 and 0.8 ± 0.1 mm away from the centre of the horn tip in transverse and longitudinal direction, respectively (Fig. 7.2). This bespoke cavitometer comprised of an in-built tungsten waveguide ($\varnothing = 4$ mm) connected to a piezoelectric sensor that converted the acquired mechanical vibrations into a voltage signal. The cavitometer had a spatial resolution of 40 mm and was calibrated in the National Physical Laboratory (NPL, UK) over a frequency range of 8-400 kHz with a sensitivity function (shown later in Chapter 8). Spatial resolution of any sensor defines its ability to resolve the cavitation activity occurring within the ultrasonically treated volume. The significance of spatial resolution is that it allows for the characterisation of the whole cavitating environment with greater understanding of the treatment volumes, which can help in scaling up the sonication systems. The treatment volumes used for de-agglomeration studies in this study were very small with a cuvette length of 12 mm,

therefore the spatial resolution of 40 mm was adequate to acoustically characterise the overall treatment volume. Detailed information regarding the performance, design and specification of this cavitometer can be found elsewhere [297]. The bandwidth of the cavitometer extended up to 10 MHz [88], which was sufficient to enable monitoring of the broadband acoustic emissions resulting from the cavitation activity. The calibration sensitivity of the cavitometer at the driving frequency of the ultrasound was around -279 dB re 1V/ μ Pa. For the experiments described below, the cavitometer was strategically synchronised with the camera and the ultrasonic device using a data acquisition (DAQ) system, at a sampling rate of 20×10^6 samples per second. The acoustic measurements were acquired from the onset of cavitation activity extending for up to tens of milliseconds to account for the de-agglomeration of particles confined within the imaging field of view. The analysis of the raw data (voltage-time) obtained from the cavitometer was performed using an in-house developed MATLAB code (see Appendix) by applying a Fast Fourier Transformation to the captured signal as described in Appendix and elsewhere [289], to appropriately apply the sensitivity values of the sensor. The output of the acoustic emissions was displayed in the pressure-time domain after subtracting the background noise. The obtained spectrum was averaged over 60 measurements, each corresponding to the FFT of ~ 50 ms signal with a resolution of 0.02 kHz (or 20 Hz). The acoustic measurements were then related to the observed de-agglomeration sequence obtained using high-speed imaging.

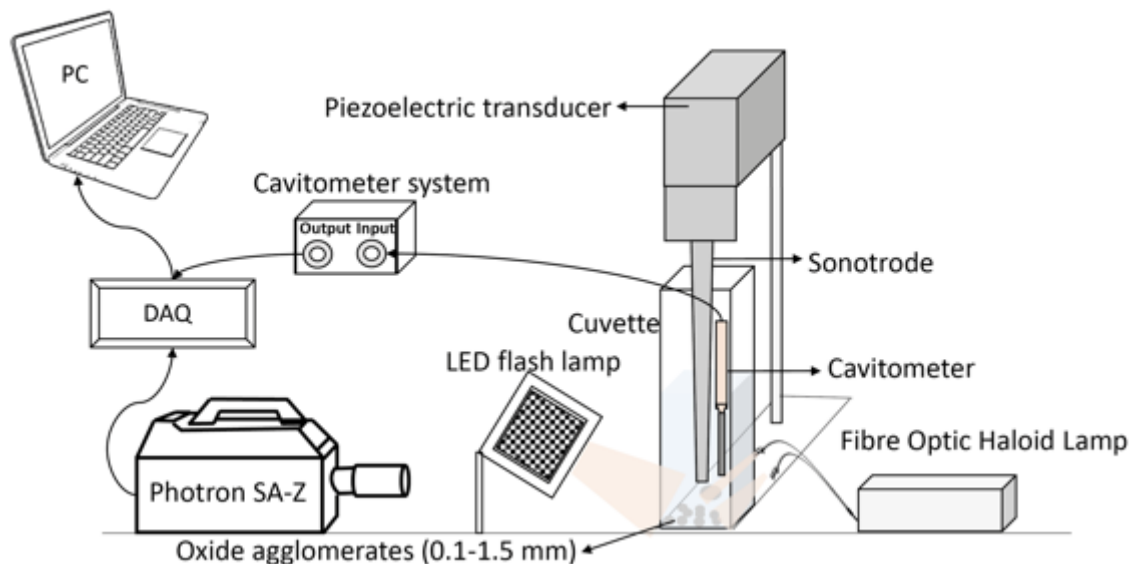


Fig. 7.2 Schematic representation of the experimental setup used for obtaining synchronised acoustic pressure measurements and in-situ imaging of ultrasonic de-agglomeration.

7.3. Results and Discussion

7.3.1 High-speed observations of ultrasonic de-agglomeration

7.3.1.1 Silica (SiO_2) aggregates

Fig. 7.3 (see Supplementary Video 1, accessible with the published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105792>)) represents a high-speed image sequence of SiO_2 aggregates subjected to de-agglomeration captured from the onset of cavitation. Time, $t = 0$ ms shows the number of agglomerates of varying sizes positioned ~ 3.5 mm below the sonotrode tip (Fig. 7.3a). Once the ultrasound was turned on, numerous microbubbles were formed and propagated from the horn tip, forming a cavitation stream extending down to the agglomerate bed as shown in Fig. 7.3b. As the cavitation stream interacted with the agglomerates, those that were in the path of the bubble flow were set in motion to form recirculation vortices apparent on either side of the jet, as shown in Fig. 7.3(c-d). As the agglomerates were uplifted from the base, some of them moved towards the ultrasonic source and de-agglomerated instantly upon interacting with the strong cavitation cloud formed below the tip, generating a fine suspension in this region (Fig. 7.3e). In addition to the formation of primary cavitation bubbles, there were also some small microbubble (μB) clusters generated from the collapse of bubbles in the large cavitation cloud. These clusters underwent continuous splitting and coalescence as shown in Fig. 7.3f (marked with yellow contours). We shall call these bubble clusters, arising due to the Bjerknes forces created by the acoustic waves, ‘ultrasonic splitting microbubbles’. They pulsate chaotically undergoing continuous shape oscillations and move around in the cavitation field as previously reported by Kim et al. [303]. A surprising feature that has not, to the best of our knowledge, been previously reported was that these μB clusters attached themselves to the flowing agglomerates, triggering their immediate breakup. Two agglomerates in Fig. 7.3f (encircled in blue) flowed towards the bubble cluster (encircled in yellow). As the agglomerates reached the vicinity of the cluster, they were caught up in a pulsating μB cluster, causing them to de-agglomerate completely at $t = 44.94$ ms. Also, the aggregates (encircled in pink) de-agglomerated while in motion leaving a trail of very fine particle, like a comet, as shown in Fig. 7.3g (arrowed pink). Similarly, another moving agglomerate as seen in Fig. 7.3h (encircled in red) got captured by the μB cluster (marked with red arrow) and de-agglomerated almost instantly as shown in Fig. 7.3i. It is also interesting to note that in most of the cases the visual impression of de-agglomeration is the increase in size of the aggregates as seen in Fig. 7.3 (h-i). Eventually, owing to the large

number of agglomerates present within the liquid volume, the visibility was impeded following their de-agglomeration, making the field of view too obscured for further meaningful observations. In the next experimental run, fewer agglomerated particles were deployed to overcome this visual constraint.

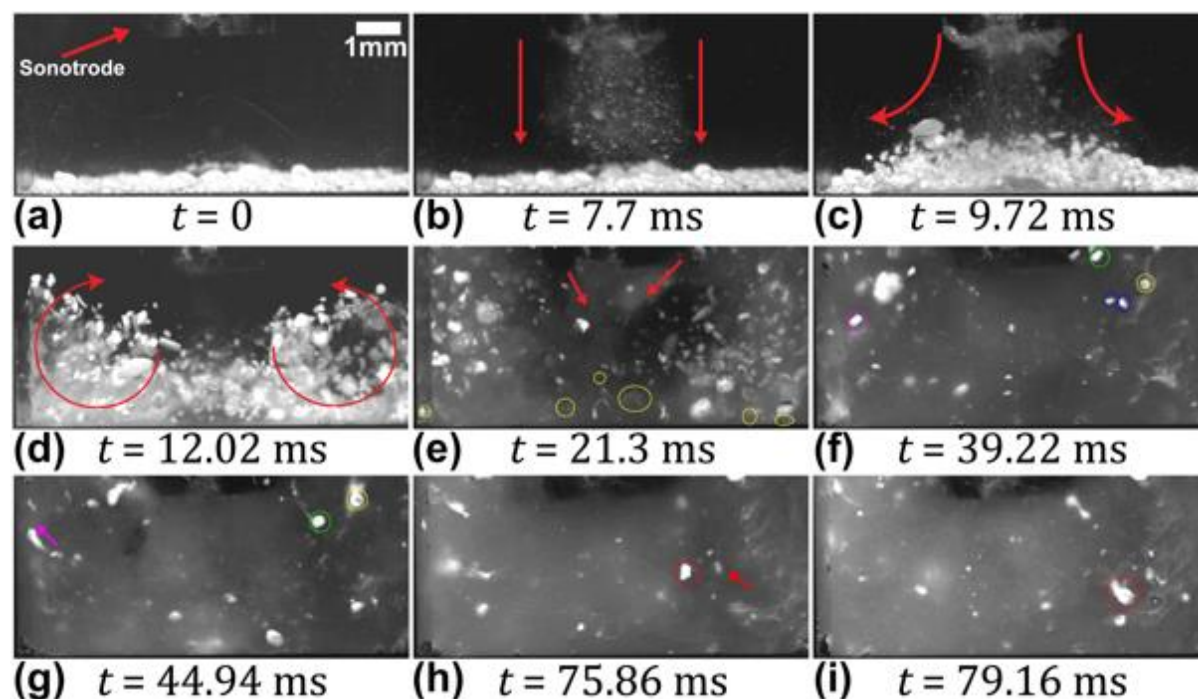


Fig. 7.3 Images of SiO₂ de-agglomeration caused by the cavitation bubble clusters and induced acoustic streaming flow recorded at 50 kfps with sonotrode-tip operating at 210 μ m peak-to-peak amplitude. Note that the resolution is not high enough to resolve individual particles that are seen as “mist” in (e). Supplementary Video 1 can be accessed with the published version of this work.

Fig. 7.4 (see Supplementary Video 2, accessible with published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105792>)) depicts representative frames from a high-speed sequence of SiO₂ de-agglomeration under the same ultrasonic processing conditions as above, but with fewer aggregates this time. Fig. 7.4a shows the snapshot of agglomerates at the bottom of a water-filled cuvette, just before the onset of cavitation. At $t = 0$ ms, a number of gas bubbles (marked with red arrow) were present at the bottom, sidewalls and the corners of the cuvette. As the oxide agglomerates are highly porous in nature, numerous gas bubbles are expected to be present on their surface and the pores then act as preferred nucleation sites. After the transducer was switched on, the sonotrode started to vibrate causing the cavitation to initiate, thereby releasing numerous μ B and μ B clusters generated from strong bubble cloud collapses (Fig. 7.4b). With the onset of cavitation, the gas bubbles also started to undergo vigorous volumetric oscillations and moved towards some of the nearby agglomerates (encircled in blue).

These bubbles then tended to oscillate on the surface of the aggregates shaking them loose from the outside, initiating the de-agglomeration process. This activity occurred even before the cavitation bubble stream reached the base of the cuvette. As soon as the microbubble stream reached the base, the agglomerates were pushed aside and the loosely bonded particles of the agglomerates were dispersed into the bulk liquid (Fig. 7.4c). Subsequently, the recirculation vortices formed on either side of main cavitation stream caused the agglomerates to lift-off from the base and drove them towards the ultrasonic horn-tip, thus producing further de-agglomeration of aggregates from the surface through induced acoustic streaming (Fig. 7.4d). Fig. 7.4e shows the instant when one of the floating agglomerates (encircled in red) with size approximately 576 μm was captured by a μB cluster (encircled in yellow) around 186 μm in size. The pulsating μB attached to and quickly eroded the agglomerate, and dispersed the individual particles into the bulk liquid volume while in motion as indicated with an arrow (Fig. 7.4f). Interestingly, even though these vigorously μB clusters are almost 3 times smaller in size than the oxide agglomerates, they can effectively disintegrate the aggregates into fine powders in just a few milliseconds. The actual mechanism through which the attached pulsating μB clusters caused de-agglomeration of the oxide aggregates could not be resolved in this experiment. Therefore, we deliberately captured the de-agglomeration process of a single SiO_2 agglomerate.

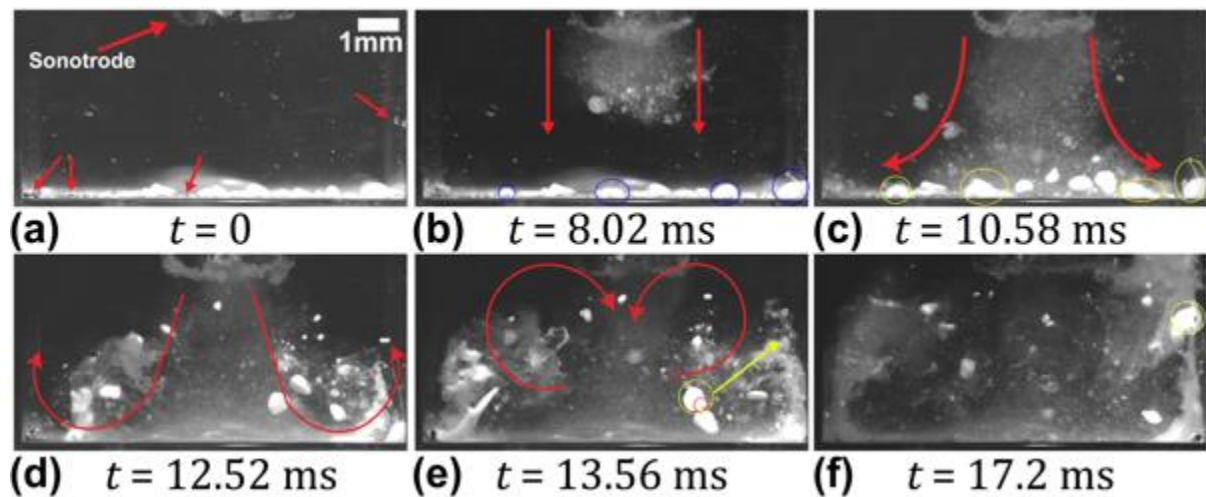


Fig. 7.4 Sequence of images showing de-agglomeration and dispersion of fewer oxide aggregates under the influence of ultrasound captured at 50 kfps with a sonotrode amplitude of 210 μm peak-to-peak amplitude. Supplementary Video 2 can be accessed with the published version of this work.

Fig. 7.5 (see Supplementary Video 3, accessible with published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105792>)) shows the zoomed view of the de-agglomeration sequence of a single SiO₂ agglomerate when exposed to ultrasonic waves. Fig. 7.5a, at $t = 0$ ms, shows a non-spherical agglomerate of 1 mm approximate size positioned at the corner of the cuvette and about ~10 mm away for the horn tip in the longitudinal direction, with some gas bubbles attached to its surface (marked with red arrows). The position of the SiO₂ aggregate for this particular observation was judiciously chosen to allow for capturing the de-agglomeration sequence in more detail, overcoming the visual constraints arising from the obscured field of view. When the ultrasound was switched on, the propagating acoustic waves (AW) in the liquid triggered these gas bubbles to volumetrically oscillate causing them to split and coalesce continuously as shown by blue arrows, Fig. 7.5b. As these chaotically oscillating μ B clusters constantly imploded and rebounded on the surface, they produced erosion from the surface of the agglomerate possibly through the chipping mechanism most likely caused by the emitted micro-jets discussed elsewhere [18,405]. Subsequently, the pulsating μ B cluster tended to coalesce with nearby clusters causing them to collapse and rebound even more violently close to the agglomerate surface (marked in yellow contour) as shown in Fig. 7.5c. Stepišnik et al. [406] also reported that the dissolution of a surfactant could be caused primarily by the by cavitation bubbles imploding in its vicinity releasing multiple microjets leading to material erosion from the surface. These chaotically oscillating but stable μ B clusters triggered, what resembles a landslide, where loose particles started to detach from the agglomerate and slide from the surface to create a suspension cloud (indicated with green arrow) as shown in Fig. 7.5d. Simultaneously, the agglomerate also became slightly distended from the front as the cluster oscillation continued and the bubbles seemed to penetrate inside it as shown by the green encirclement in Fig. 7.5(e-f). With increase in the number of acoustic cycles, the size of the μ B cluster increased gradually causing the agglomerate to inflate even further (Fig. 7.5e). The induced acoustic flow from the ultrasonic source (indicated with red arrow) then pushed the agglomerate in the flow direction and dispersed the de-agglomerated particles into the liquid (Fig. 7.5f).

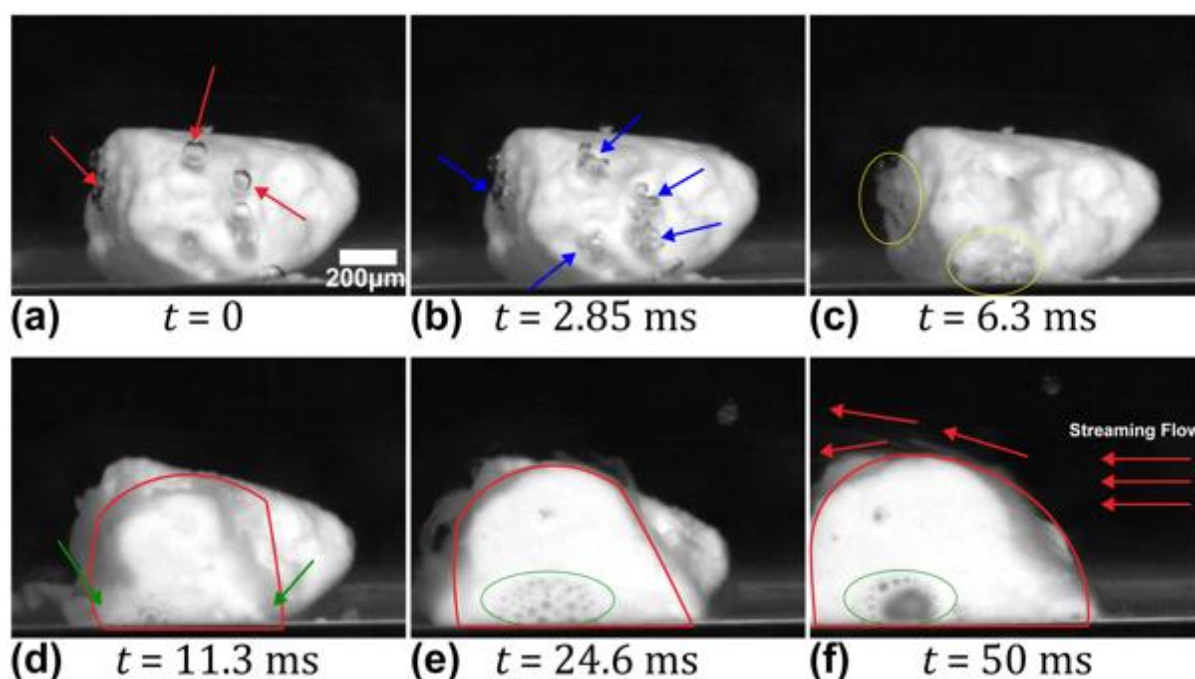


Fig. 7.5 Sequence of zoomed view of de-agglomeration of a single SiO_2 agglomerate under cavitation action captured at 20 kfps with sonotrode operating at 210 μm peak-to-peak amplitude. Supplementary Video 3 can be accessed with the published version of this work.

7.3.1.2 *Magnesia (MgO) aggregates*

Fig. 7.6 (see Supplementary Video 4, accessible with published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105792>)) shows the frame-by-frame capture sequence of cavitation-induced de-agglomeration for MgO agglomerates. The first frame, $t = 0$ ms, shows the agglomerates located almost 3.5 mm below the horn tip, Fig. 7.6a. The frame also shows the presence of gas bubbles located on the bottom, sidewalls and on the surface of the agglomerate (indicated with red arrow). With the onset of cavitation, the gas bubbles began to pulsate, coalesced with other oscillating bubbles (encircled in red), and moved towards the nearby agglomerate (Fig. 7.6b) as was also observed in case of SiO_2 agglomerates. Continued pulsation of these bubbles loosened the surface of the aggregate and initiated de-agglomeration through chipping-off of individual particles from the outer surface as indicated by blue arrows (Fig. 7.6c). The oscillation of the bubble clusters became even more vigorous as they coalesced with other such clusters surrounding the agglomerate surface and subsequently intensified the de-agglomeration rate, well before the cavitation bubble stream reached the agglomerate (Fig. 7.6d). Upon interaction with the cavitation cloud stream, the loosely bonded particles dispersed, moving into the bulk liquid (indicated with yellow arrows) as shown in Fig. 7.6e. The

recirculation vortices formed on either side of the central cavitation stream further caused the broken-off agglomerates to flow into the cavitation zone (beneath the horn tip) for further de-agglomeration as previously seen in the case of SiO₂ (Fig. 7.6f). To understand the role of these bubble cluster oscillations on de-agglomeration, a zoomed imaging of a single agglomerate was performed.

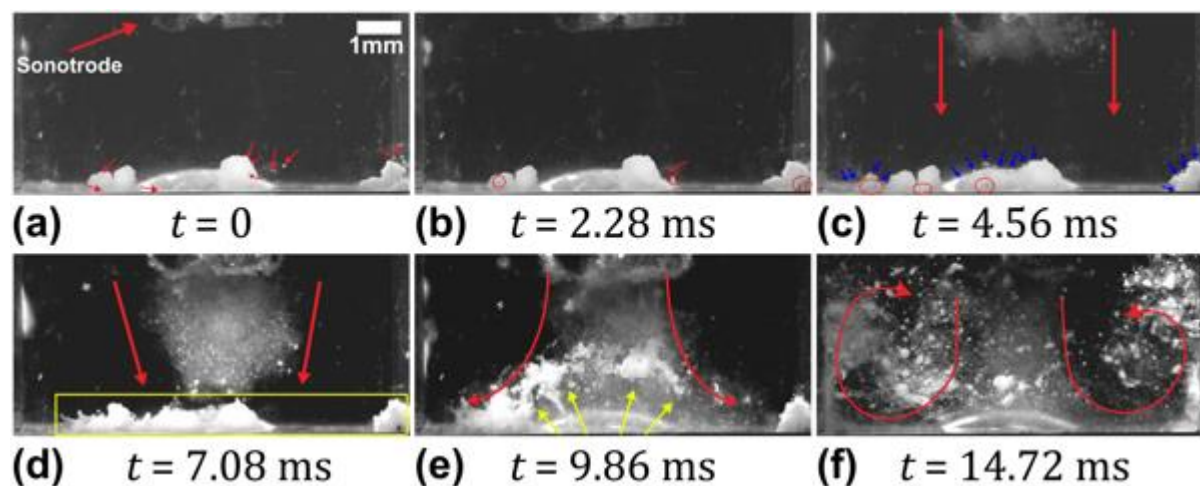


Fig. 7.6 Sequence of images showing de-agglomeration and dispersion of MgO aggregates under the influence of ultrasound captured at 50 kfps with sonotrode amplitude of 210 μm peak-to-peak amplitude. Supplementary Video 4 can be accessed with the published version of this work.

Fig. 7.7 (see Supplementary Video 5, accessible with published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105792>)) displays the sequences of images showing the de-agglomeration process of a single MgO agglomerate caused by the oscillating bubble cluster under the influence of ultrasound. The agglomerate was positioned ~ 3.5 mm away from the sonotrode tip and closer to the centre of the cuvette. Fig. 7.7a shows the agglomerate with visible gas bubbles approximately 20 μm in size on its surface (indicated with arrow). These bubbles started to pulsate stably as soon as the ultrasound was turned on (Fig. 7.7b). As seen in Fig. 7.7b, the tiny gas bubbles coalesced together to form a bubble cluster. A cluster of oscillating bubbles was also seen to move towards the agglomerate (Fig. 7.7c). These oscillating bubbles caused the agglomerate to become loosened from both inside and outside and further initiated surface rupture at the periphery (encircled in red) as shown in Fig. 7.7d. It is possible that the bubble clusters oscillating close to the agglomerate excited the tiny bubbles present within the pores and pushed the particles apart resulting in agglomerate breakage. Another possibility is that the AW generated sufficient pressure that pushed the surrounding liquid inside the pores of the agglomerate inducing breakup through sono-capillary effect

[104,398,399,401]. Once the cluster contacted the agglomerate, its oscillation amplitude further increased, accompanied with the appearance of subharmonics in the frequency spectrum (as seen later in section 7.3.2 and Fig. 7.9(a2)). The subharmonic emissions predominantly occurred as the large bubble clouds formed beneath the horn tip imploded after one or more cycles, emitting high energy shock waves and liquid jets [305], a phenomenon sometimes termed as acoustic supercavitation [38]. In addition to the strong cloud collapses, as microbubble clusters approached the MgO aggregate, the amplitude of its oscillation increased and the cluster underwent repetitive violent collapses from time $t = 9.40$ ms to $t = 10.98$ ms. The frequency of collapse was as low as 1/8th of the fundamental between time $t = 9.70$ ms to $t = 9.98$ ms (see Supplementary Video 5, accessible with the published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105792>)), expediting the de-agglomeration through rupturing the agglomerate as shown in Fig. 7.7(g-h). The de-agglomerated particles were then dispersed in the bulk liquid by the incoming acoustic streaming (Fig. 7.7i).

As observed in Figs. 7.3 through 7.7, it is evident that the de-agglomeration of oxides primarily occurs through cavitation bubbles that are formed within the ultrasonically treated liquid. The stable bubbles (splitting and shape oscillating microbubble clusters) initiate the de-agglomeration of aggregates through the chipping mechanism as described in Fig. 7.5b and Fig. 7.6c and earlier reported by Eskin et al. [18]. These stably oscillating bubbles then lose their shape and their oscillations become extremely violent with chaotic pulsations and continuous splitting thereby releasing multiple daughter bubbles, with the resulting liquid microjets with velocities of the order of 1 m/s [303] making the surface of the agglomerate inflated by the penetration of microbubbles and the induced sono-capillary effect as discussed later in Section 7.3.3. The oxide particles thus become loose from both the surface and the bulk of the aggregate increasing the rate of de-agglomeration. However, the de-agglomeration caused by the transiently cavitating bubbles is more aggressive with powerful emitted shock waves generated from the subharmonic cloud collapses occurring at the tip of the horn. In this case, the de-agglomeration occurs instantly through rupture of the aggregate forming a ‘mist’ like region as seen in Fig. 7.3e when the agglomerates recirculate back towards the ultrasonic source due to the secondary vortex flow. Therefore, the de-agglomeration process is enhanced owing to the contribution from both the cavitation bubbles and the induced acoustic streaming. In the next section, the effect of pressure amplitude and cavitation emissions arising from oscillating microbubbles on oxide de-agglomeration will be presented and linked to the high-speed camera observations.

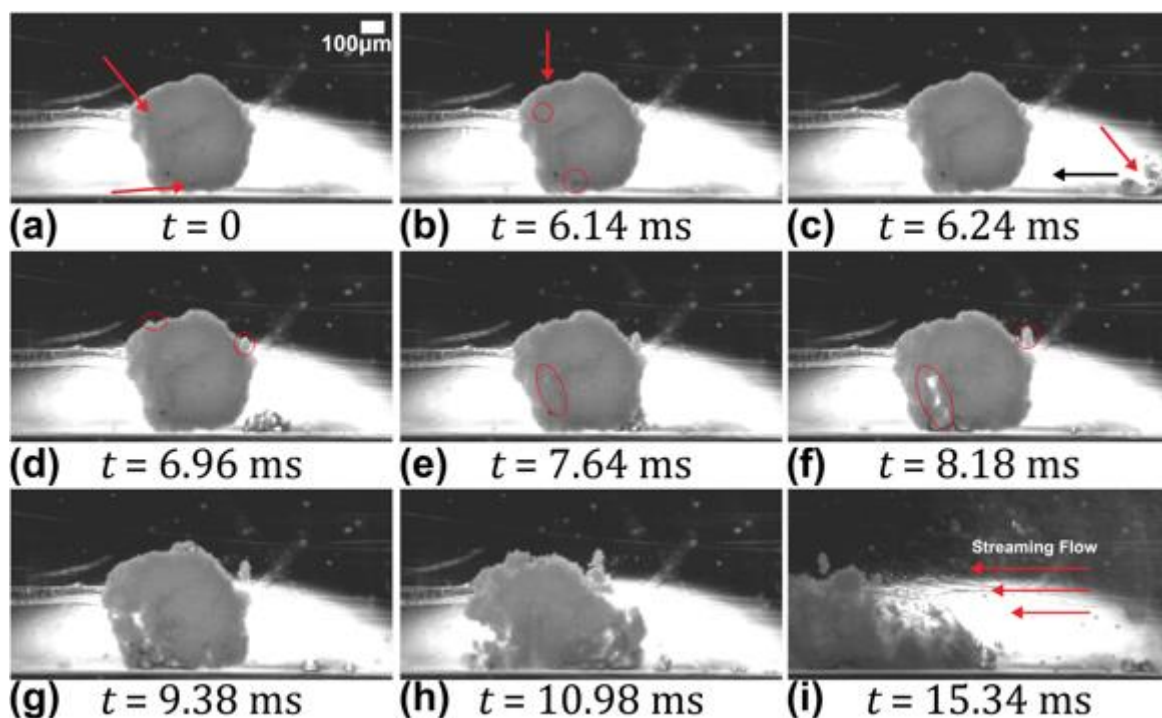


Fig. 7.7 Sequence of zoomed view of de-agglomeration of a single MgO agglomerate under cavitation action captured at 20 kfps with sonotrode operating at 210 μm peak-to-peak amplitude. Supplementary Video 5 can be accessed with the published version of this work.

7.3.2 Acoustic pressure measurement

After detailed observations demonstrating some aspects of the mechanisms of de-agglomeration, we now delve deeper into the acoustic characterisation of the ultrasonic cavitating field that promotes de-agglomeration. Synchronised pressure measurement coupled with in-situ imaging of ultrasonic de-agglomeration were performed using a cavitometer sensor positioned close to the tip of the sonotrode as mentioned in Section 7.2.2. It should be noted that the acoustic pressure values reported here were measured with reference to barometric pressure since the cavitometer was calibrated in water at ambient pressure conditions. Fig. 7.8a (see Supplementary Video 6, accessible with the published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105792>)) displays the synchronised high-speed images (Fig. 7.8(a1)) and acoustic pressure-time profile (Fig. 7.8(a2)) for the de-agglomeration sequence of SiO_2 agglomerates. The root mean square (RMS) and maximum pressures recorded were found to be approximately 32 kPa and 150 kPa, respectively. The de-agglomeration of SiO_2 aggregates started before the bubble cloud stream interacted with them ($t = 11.34$ ms). With the increase in acoustic pressure i.e. after 5 ms, a large agglomerate (marked with double sided red arrow) was seen to break apart at $t = 13.62$ ms. As the pressure stabilised within the cavitating field, the oscillating μB cluster attached itself to one of the

flowing agglomerates (indicated with red arrow) at $t = 19.08$ ms, triggered its breakup ($t = 20.78$ ms). Fig. 7.8b (see Supplementary Video 7, accessible with the published version of this work (<https://doi.org/10.1016/j.ultsonch.2021.105792>)) shows the de-agglomeration imaging (Fig. 7.8(b1)) and acoustic pressure variation (Fig. 7.8(b2)) across the cavitation field for MgO oxides. The RMS and maximum pressures generated within the cavitation field were found to be close to 46 kPa and 300 kPa, respectively. The slight increase in acoustic pressure values can be attributed to a smaller bubble concentration resulting in lower shielding [289], owing to the presence of fewer agglomerates compared to SiO₂. With the introduction of ultrasonic waves to the liquid, gas bubbles with diameters in the range of 50-60 μm in diameter located near the agglomerates started to pulsate and moved closer to the oxides ($t = 2.16$ ms). As the cavitation activity intensified, the bubbles expanded and underwent vigorous pulsations close to the agglomerate ($t = 4.92$ ms) leading to its partial erosion from the surface even before the cavitation stream reached the agglomerate surface ($t = 6.60$ ms) as indicated with a blue arrow similar to observations made in case of SiO₂. The pressure gradually escalated with increased cavitation activity up to 8.28 ms, reaching almost 300 kPa. The increased acoustic pressure thus expedited the de-agglomeration of loosened agglomerates and dispersed the oxide particles in the bulk liquid with the help of induced streaming flow ($t = 11.48$ ms). It is interesting to note from the pressure-time profile in Fig. 7.8 (a and b) that the cavitation output signal first increased after the onset of cavitation, reached a maximum value and then decreased and stabilized with the sonication time. This trend shows that the acoustic pressure generated by ultrasound increased until the cavitation cloud attached to the horn tip attained the maximum size and collapsed, thereby releasing high-energy shock waves and high-speed liquid jets as the cavitation activity increased [309]. The further decrease and stabilisation of the pressure was a result of non-collapsing bubble deflations [305] and collapses occurring after one or more acoustic pressure cycles.

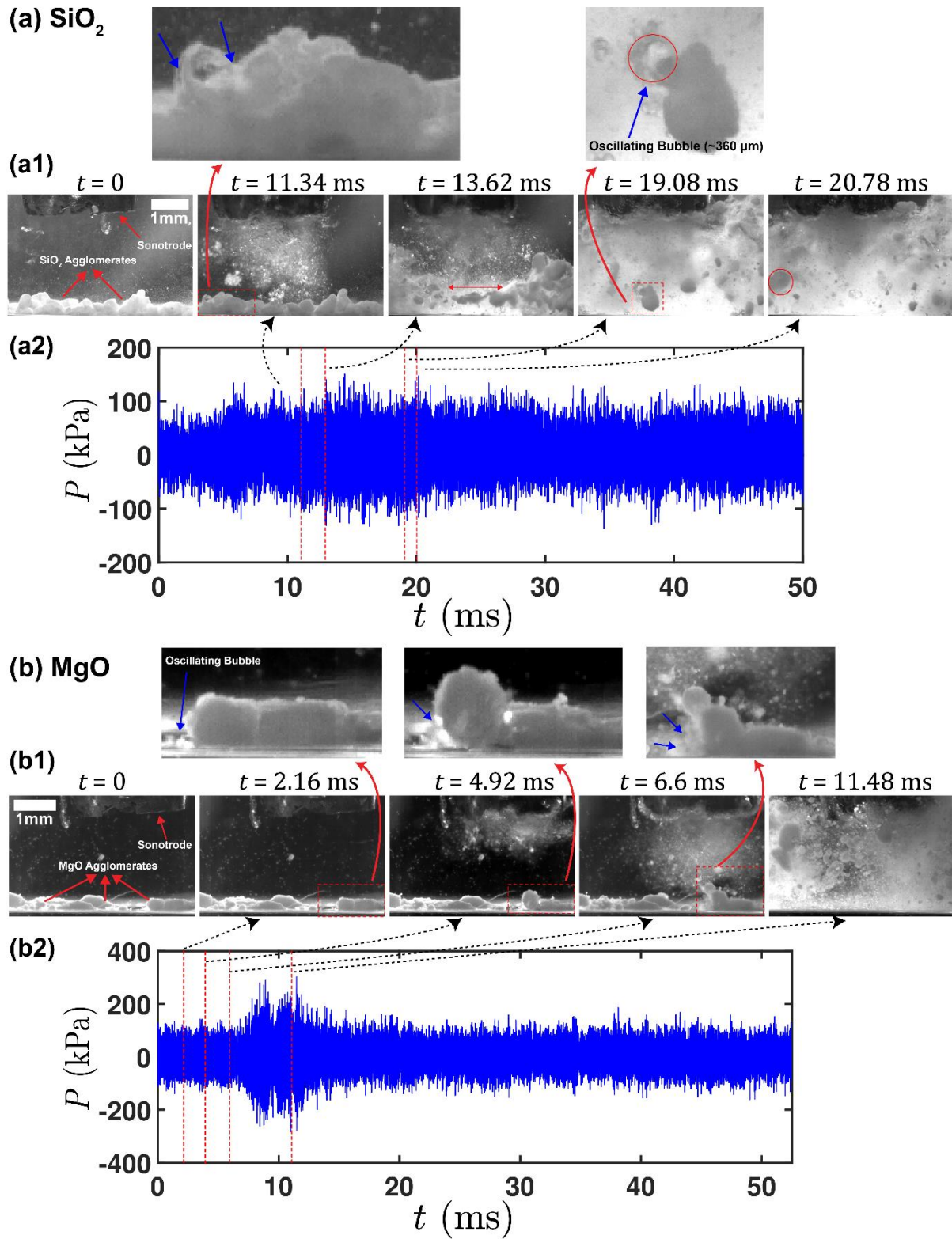


Fig. 7.8 Synchronised high-speed image snapshot and in-situ acoustic pressure emission recorded using the advanced calibrated cavitometer showing de-agglomeration of (a) SiO_2 , and (b) MgO aggregates.

To further understand the frequency content of the acoustic emissions from these μB clusters and its relationship to the de-agglomeration of SiO_2 and MgO aggregates as observed in Fig. 7.8a ($t = 19.08$ to 20.78 ms) and Fig. 7.8b ($t = 4.90$ to 6.60 ms), respectively, the pressure–time profiles for both sequences were isolated and a fast Fourier transform (FFT) was applied to obtain the pressure–frequency spectrum.

Fig. 7.9 shows the acoustic pressure emissions in both time (see a1 and b1) and frequency (see a2 and b2) domains emitted from majority of the oscillating μB clusters responsible for inducing de-agglomeration. To obtain the acoustic spectrum, pressures profiles were carefully selected and isolated for FFT analysis based on the most prominent de-agglomeration events captured by the synchronised camera observations in Figs. 7.8a and 7.8b. Specifically, the time band selected for the analysis in the case of SiO_2 i.e. from $t = 19.08$ ms to $t = 20.78$ ms and MgO , i.e. from $t = 4.90$ ms to $t = 6.60$ ms, was the period when the oscillating microbubble attached to the nearby aggregate and initiated the de-agglomeration process. The time span (acoustic cycles) was kept the same for comparison purposes. As can be seen, the pressure–frequency spectrum obtained from SiO_2 de-agglomeration (Fig. 7.9 (a2)) shows multiple high frequency peaks extending up to 400 kHz, accounting for the non-linear and complex dynamics of microbubbles with prominent peaks at the low frequency region as also seen from camera observations between $t = 19.08$ to 20.78 ms. Zooming on the low frequency spectrum up to 60 kHz showed the fundamental (f_0), 1st harmonic ($2f_0$) and ultra-harmonics with $7f_0/4$, $25f_0/12$ as prominent higher order peaks with pressure magnitude of approximately 8 kPa in addition to lower order ultraharmonic ($4f_0/3$) and subharmonic peaks of $5f_0/8$, $3f_0/4$ with magnitudes in the range of 3–4 kPa. This is in good agreement with the observations made in [303]. It is postulated that these subharmonics emissions arise from stable chaotically oscillating bubbles, and they are much weaker in magnitude in comparison to transiently collapsing bubble structures attached to the horn tip [108]. The spectrum in the case of MgO de-agglomeration (Fig. 7.9(b2)) exhibited similar low frequency pressure spectrum with peaks appearing at the fundamental (f_0), 1st harmonic ($2f_0$), ultra-harmonics ($5f_0/4$, $4f_0/3$, $7f_0/4$, $25f_0/12$) and subharmonic ($2f_0/3$) range. The observed pressure magnitude was found to be highest for $25f_0/12$ with peak amplitude close to 12 kPa followed by $7f_0/4$ with pressure approaching 11 kPa and $2f_0$ with peak pressure of almost 8 kPa. The other low-pressure peaks in the range of 2–7 kPa included $2f_0/3$, f_0 , $4f_0/3$, and $5f_0/4$. These weak subharmonic peaks observed for both silica and magnesia most likely corresponded to large μB clusters that oscillated violently near the agglomerate surface producing de-agglomeration as observed in Fig. 7.8 (a, b). This is evident in Fig. 7.8

(a1) at $t = 19.08$ ms, where a bubbly cluster attached to the silica agglomerate vigorously pulsed with growth and collapse cycle of 0.06 ms reaching maximum size of about 360 μm . This corresponds to a bubble resonance at an oscillating frequency close to 24 kHz, thereby raising a prominent subharmonic peak at $3f_0/4$. Ideally, it is expected that the fundamental peak at 24 kHz would be prominent unlike Fig. 7.9. This incongruity could be due to the small size of the sonotrode and the diminishing of irradiated ultrasonic waves by the formation of numerous bubble clusters within the cavitation zone. Therefore, the bubble cluster dynamics and the overall acoustic emissions can be best described by the range of subharmonic acoustic pressure peaks as previously observed by Tan et al. [407]. The dynamic pressure as a result of shock waves (SWs) and microjets arising from these attached bubbles as they undergo splitting and chaotic shape oscillations can reach up to 100 kPa [303]. Unlike intermetallics [277,332], where the breakage mechanism occurred through the development and propagation of cracks resulting from the SW emissions, the breakage/de-agglomeration of agglomerates was primarily caused by either the gas bubbles present at the surface and within pores of the agglomerate (as also seen with the exfoliation of graphite in [309]) or due to the pressure spikes in the vicinity of the bubble clusters released from the cavitation cloud formed below the vibrating horn producing the pulsations in subharmonics and ultra-harmonics observed in the frequency regime, which are related to the chaotic oscillations and collapse of the bubbly cloud as reported elsewhere [118,305,408–412].

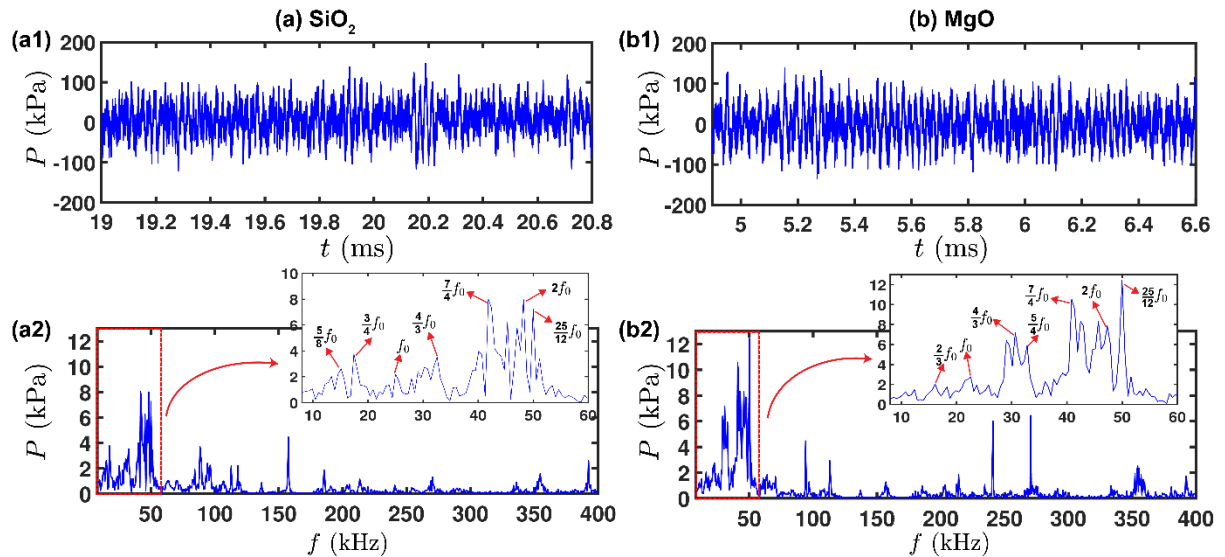


Fig. 7.9 Acoustic pressure spectrum obtained after FFT of isolated pressure-time profiles for de-agglomeration of (a) SiO_2 , and (b) MgO .

7.3.3 De-agglomeration and dispersion mechanism

The mechanism of ultrasonic de-agglomeration of oxide agglomerates as observed in Figs. 7.3 to 7.7 is depicted in Fig. 7.10 (a-c). Fig. 7.10 (a i) shows an oxide agglomerate present at the bottom of a container filled with liquid. There are also gas/vapour bubbles within the pores of the agglomerate and at the surfaces including the container walls. With the inception of cavitation beneath the sonotrode tip, the incoming AW trigger oscillation of these gas bubbles that split and coalesce together to develop μ B clusters pulsating near the agglomerate (Fig. 7.10 (a ii)). As the cavitation cloud becomes bigger and stronger, the μ B clusters undergo violent and repetitive rebound and collapse close to the agglomerate, which induces intense shear forces through combined effect of emitted primary SWs and powerful liquid jets [69,309]. These SWs can further trigger more cavitation cloud collapses generating secondary SWs [351]. It has been previously observed that the overall shock pressure amplitude can range from 1 – 5 MPa at distances up to 3 mm from the horn tip of the same ultrasonic device [309] and is, therefore, sufficient to initiate de-agglomeration by overcoming the interparticle bond strength. This induced pressure can further trigger the gas bubbles present inside and at the surface of the agglomerate to pulsate violently (undergoing splitting and chaotic shape oscillations) promoting de-agglomeration (Fig. 7.10 (a iii)). De-agglomeration thus also happens from the bulk of agglomerate where the oscillating microbubbles push the oxide particles from within. After the cavitation cloud reaches the agglomerate, the induced acoustic streaming and the developed recirculation vortex disperse the de-agglomerated oxide particles into the bulk liquid and push some of the remaining agglomerates towards the cavitation zone for further disintegration by high intensity bubble cloud collapses occurring below the sonotrode tip as observed in case of intermetallics in Chapter 6. The oscillating μ B clusters (acting like drones) also tend to track down the tiny floating agglomerates with size in the range of 300-600 μ m by attaching to their surface, promoting their further breakup and subsequent dispersion into fine particles (Fig. 7.10 (a iv)). The overall rate of de-agglomeration depends on the acoustic pressure generated within the liquid and the amount of stably oscillating and transient μ B's that produce intense stresses upon collapse, sufficient to break the agglomerates to smaller aggregates [413,414]. Sumitomo et al. [415] reported that the rate of dispersion of the agglomerates was enhanced with low-frequency irradiation. The physical effects of de-agglomeration and dispersion arises from the enhanced mass transport caused by high-energy pressure pulses as a result of μ B cluster collapses close to the agglomerate [416]. Therefore, the breakage of agglomerates is not solely induced by SWs as previously reported [415] but also by pulsating and imploding μ B clusters through the phenomenon of sono-capillary effect

[104,398,399]. Fig. 7.10b shows the representative schematic simplified for better understanding of this phenomenon occurring for a single agglomerate within the liquid. Before sonication, the agglomerate contain many voids or air pockets between the oxide particles, in the form of micro pores and cavities. In reality, however, these individual oxide particles are not regular spheroids but contain grooves on their surface as shown in Fig. 7.10c. The only realistic mechanism that can regularly excite bubbles in these tiny grooves is the travelling shock waves (with corresponding wavelength in the range of 0.4 - 0.5 mm) rather than driving ultrasonic/incident wave that is diminished by the formation and collapse of bubbly clouds. As the cavitation kicks in, splitting bubble clusters undergoing chaotic shape oscillations close to the aggregate, plus the induced acoustic microstreaming [70,303,417,418] force push the surrounding liquid to penetrate inside the agglomerate reaching air pockets and grooves or capillaries. The oscillation of μB clusters as well as the incoming AW/SW near the agglomerate then excites the liquid inside, creating overpressure to nucleate more tiny vigorously oscillating microbubbles that generate large shear forces [419,420] leading to de-agglomeration and fragmentation of the oxide particles within the bulk liquid. These sequence of events as demonstrated in Fig. 7.10b is clearly evident with experimental observations made in Fig. 7.5 (a-f), which highlight the sono-capillary effect occurring on the surface of the aggregate. It can be seen that the oscillating bubble clusters undergoing shape, splitting and chaotic oscillations with pressures ranging from 26 to 575 kPa [303] pushes the surrounding liquid into pores of the agglomerate leading to formation of bubbles within the air/gas pockets thereby inflating agglomerate and pushing the oxide particles from inside as observed in Fig. 7.5 (e-f) with shear stresses reaching up to 100 kPa following liquid jet impact [310]. Thus, the de-agglomeration of oxides essentially occurs from both direction i.e., ‘chipping--off’ the oxide particles from outer surface of the aggregate [18] and dynamic pressure produced from the chaotically oscillating bubble [303] that pushes the oxide particles from within, like a “*sandwich mechanism*”. The majority of agglomerate disintegration is done within few milliseconds of the cavitation inception and the agglomerates that remain unaffected are then tracked down by the floating ‘bubble drones’ making the overall de-agglomeration process very effective.

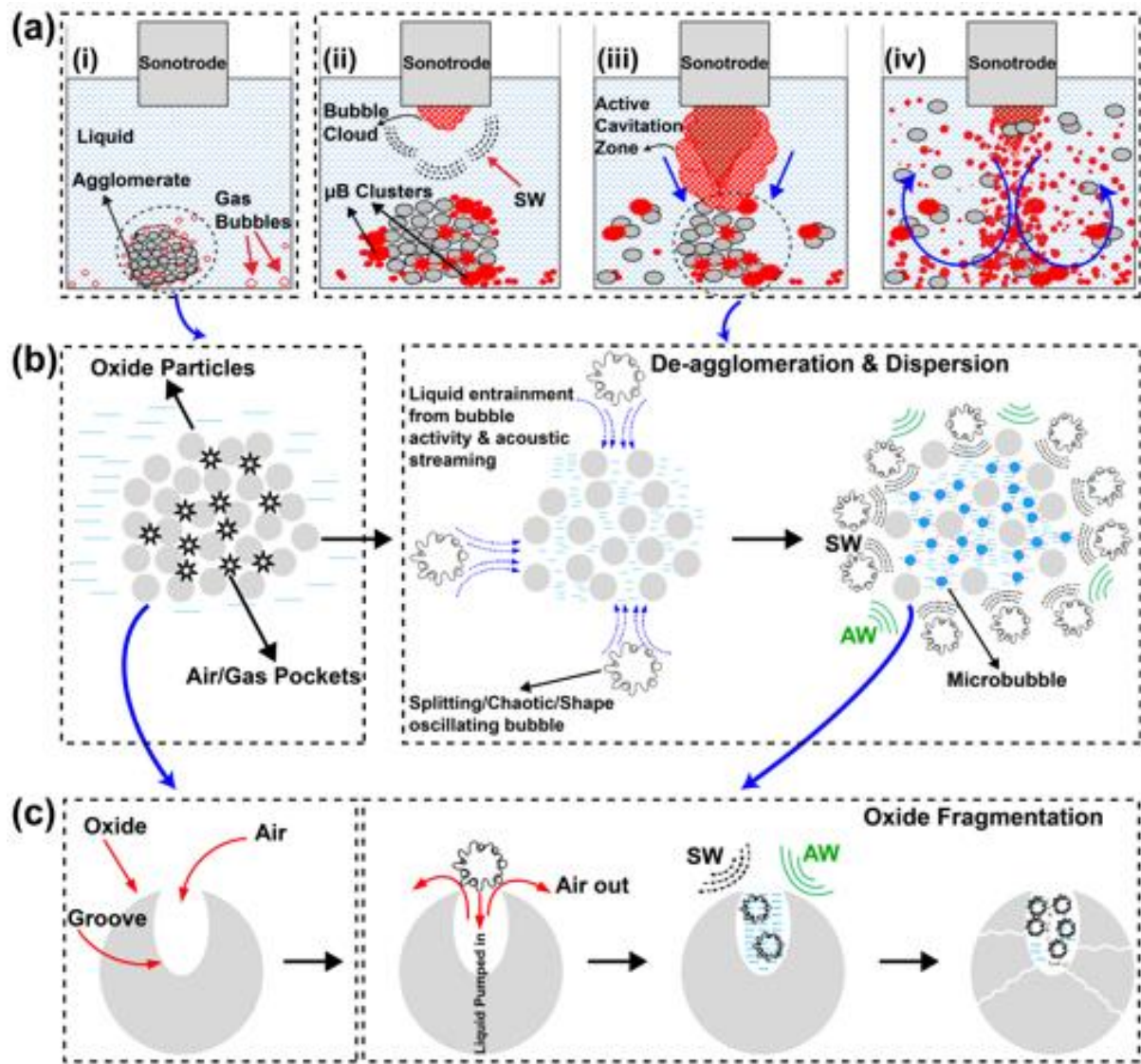


Fig. 7.10 Schematic diagram showing de-agglomeration and fragmentation mechanism of (a, b) an oxide aggregate and (c) single oxide particle, respectively caused by the dynamic pressure effect from oscillating bubbles recognised from the onset of cavitation.

7.4. Conclusions

In-situ high-speed imaging of cavitation-induced de-agglomeration was performed using high-intensity, low-frequency power ultrasound to fundamentally understand the process mechanism using micron-sized particles of MgO and SiO₂ agglomerates. Synchronised acoustic pressure measurements were also carried out to characterise the cavitation field in both the time and frequency domain. The following conclusions were drawn from the aforementioned studies:

1. De-agglomeration processes of both oxide aggregates are mechanistically similar and initially occurred through nonlinear acoustic cavitation generated due to ultrasonic excitation of pre-existing gas bubbles upon the introduction of ultrasonic waves within the liquid. The splitting and chaotic shape oscillating bubble clusters induce intense high-energy pressure pulses and the resulting shear stresses eventually chip-off individual oxide particles from the surface of an agglomerate.
2. The ultrasonic/incident wave has a rather limited contribution to the formation of cavitation bubbles within the oxides and SWs are the dominant source of excitation and cavitation development in tiny grooves/spots. The increased collapse and rebound of the oscillating gas bubble clusters and the ultrasonic microbubble (μB) clusters near an agglomerate create large overpressure facilitated by the ultrasonic-capillary effect thus promoting their de-agglomeration also from within like a *sandwich mechanism*. The acoustic streaming then promotes further surface de-agglomeration and dispersion of the loose aggregates. Smaller agglomerates are subsequently captured and separated into individual particles by the floating ‘bubble drones’ within the cavitating medium.
3. The introduction of ultrasonic waves and cavitation-induced shock waves triggers a strong nonlinear response of the oscillating μB clusters attached to oxide agglomerates raising prominent acoustic subharmonic and ultra-harmonic pressure peaks with multiple high frequency peaks extending up to 400 kHz in the frequency spectrum, which appear to be associated with the cavitation activity that promotes initial de-agglomeration.
4. Synchronised acoustic pressure measurements reveal that maximum de-agglomeration and dispersion of the oxide clusters occur when the maximum pressure has been reached within the cavitating medium. The generated RMS pressure in the range of 30-50 kPa with maximum pressure surges in the range of 300 kPa was found to be sufficient to induce de-agglomeration.

Chapter 8

Acoustic characterisation of water and liquid aluminium under ultrasonic treatment[§]

Having identified the governing mechanism of ultrasound-induced fragmentation of intermetallics and de-agglomeration of oxides, we now move from these fundamental studies to more of applied research by ultrasonic treatment of actual liquid metals. We now try to assess the effectiveness of UST and routes for scaling up by studying the influence of resonance length of the treatment vessel on the developed acoustic pressure field and grain refinement in Al alloys. Parts of the liquid Al experiment reported in this chapter were conducted in collaboration with BCAST at BRU.

This chapter focuses on determining the efficiency of UST of liquid Al and water in terms of the size of the treatment vessel that generates resonance conditions within the container and can play a crucial role in amplifying pressure amplitude for cavitation. To quantify the importance of resonance length during the treatment of liquid aluminium, we used calibrated high-temperature cavitometers (in the range of 8-400 kHz), to measure and record the acoustic pressure profiles inside the cavitation-induced environment of liquid Al and deionized water (used as an analogue to Al) excited at 19.5 kHz. To achieve a comprehensive map of the acoustic pressure field, measurements were conducted at three different cavitometer positions relative to the vibrating sonotrode probe and for a number of resonant and non-resonant container lengths based on the speed of sound in the treated medium. The results showed that the resonance length affected the pressure magnitude in liquid Al in all cavitometer positions, while water showed no sensitivity to resonance length. An important practical application of UST in aluminium processing concerns grain refinement. For this reason, grain size analysis of UST-treated Al-Cu-Zr-Ti alloy was used as an indicator of the melt treatment efficiency. The result showed that the treatment in a resonance tank of $L = \lambda_{Al}$ (the wavelength of sound in Al) with the largest recorded cavitation activity gave the best structure refinement as compared to other tested lengths. The data given here contribute to the optimisation of the ultrasonic process in continuous casting, by providing an optimum value for the critical compartment (e.g. in a launder of direct-chill casting) dimension.

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*Both authors contributed equally on this publication

8.1 Introduction

The acoustic pressure amplitude and distribution generated by the immersed sonotrode and the resultant extent of cavitation region are the main process parameters that need to be controlled and optimised. Optimisation requires deep understanding of the parameters affecting the process. However, inherent difficulties such as the opacity of the liquid metals and (until recently) lack of high temperature experimental tools that enable direct measurement of cavitation activity, limited the understanding of acoustic bubble dynamics and associated flow field effects. This imposes difficulties in process optimisation and control and eventually scaling up for adoption by industry. Typically, the effectiveness of UST is assessed through indirect post-process observations, such as microstructure analysis (e.g. grain size analysis [1], size and distribution of primary particles [175,176]) and degassing efficiency [421].

So far, controlling UST in industrial processes is rather qualitative and intuitive; current efforts are concentrated on 1) characterizing the cavitation regime and the acoustic pressure spectrum in a range of frequencies and 2) achieving high efficiency in processing large melt volumes by using a single ultrasonic source coupled with a cleverly designed flow arrangement. The latter is a challenging task that requires, for example, strategically fitted partitions to exploit resonance leading to higher pressures, excite a larger liquid volume and increase the melt treatment residence time within the cavitation zone [422–424]. This approach showed promising results in direct-chill casting experiments [287,366]. Nevertheless, for a technological step up, we feel a more systematic study of the salient physical phenomena is required. There have been recent studies in optimising an ultrasonic reactor [425,426], albeit these have been mostly done for low-temperature liquids.

A powerful tool in analysing and optimising the cavitation dynamics via synchrotron observation [272,427,428] (where only small-scale experiments are feasible and observations restricted in small volumes) is by measuring acoustic pressure emissions within the sonicated volume. Only handful of studies has been conducted so far on the characterization of cavitation-induced acoustic emissions in molten metals using high-temperature advanced sensors [1,88,276,289,297,370,388,404,424]. The recent advent of direct measurements of the acoustic pressure and cavitation intensity using cavitometers – calibrated for a broad range of frequencies – has opened new avenues for characterizing UST in various metallic melts, enabling insights in the fundamental governing mechanisms and the optimisation of melt processing.

Previous acoustic pressure measurements in liquid Al have mostly been confined to narrow-band frequency domains i.e. 15-50 kHz (with excitation frequency in the range of 17-24 kHz) [289]. These cover the effect of the driving frequency and up to the second harmonic and the corresponding ultra-harmonic emissions, partially neglecting the sub-harmonics and higher order harmonics and prominent peaks plus broadband components (associated with cavitation bubble collapses and non-linear/transient cavitation) that are important for the characterization of different cavitation regimes and precise quantification of generated acoustic pressures.

It has been reported [276] that the cavitation-induced pressure intensity in liquid Al is much more pronounced than that in water (otherwise a reasonable analogue to liquid Al in cavitation behaviour). The effectiveness of UST also relies on the volume of the liquid metal being treated and is governed by the size of the tank utilized for processing. Lebon et al. [289] numerically studied and experimentally validated the effect of the experimental vessel size (around 1λ) on the pressure field in water and showed that the resonance may play role in the magnitude of acoustic pressure. This work was, however, limited to small vessels (with a length at 65 mm ($\sim 0.85\lambda$) and 75 mm (1λ)) with water and narrow-band calibrated cavitometers (neglected the effect from cavitating bubbles). The dependence of the acoustic pressure on the resonance may be particularly important for the ultrasonic processing of flowing liquid aluminium (e.g. in a launder of direct-chill casting) when the processing (residence) time needs to be increased by all means. The acoustic pressure variation and dependence on the dimensions of the experimental tank or partition has, however, not yet been confirmed explicitly for processing of liquid Al.

To this end, the present work aimed at closing the existing knowledge gap, related to acoustic characterization of cavitation activity in liquid Al in vessels with resonant and non-resonant dimensions, using cavitometer pressure sensors calibrated for a wide frequency range of 8-400 kHz as in [297]. Deionized water (having the closest cavitation properties to liquid aluminium) was used for comparison. In order to map the full pressure domain, cavitometer measurements were taken at different positions in the process tank. The measured cavitation activity was delineated with respect to the observed frequency spectrum and conclusions have been made in relation to the choice of the treatment domain that would result in pressure field amplification, increased cavitation activity and presumed increased UST efficiency. As an additional measure in verifying the treatment efficiency in liquid Al, microstructural observations (i.e. average grain size) were performed for the samples cast after UST of the melt in tanks of different lengths (with fixed width and depth).

8.2 Methods and Materials

8.2.1 Experimental setup

Fig. 8.1 shows a schematic of the experimental setup. Two different working liquids (deionized water (DIW) and liquid Al) and various tanks for each liquid with dimensions $L \times H_V 75 \times W_V 100$ mm (DIW) and $L \times H_V 95 \times W_V 100$ mm (Al, based on industrial laundries [384]) to maintain the same resonance and off-resonance conditions were deployed. Despite the different heights of the tanks, we made sure that liquid height in the vessels remained the same. The resonance length was defined as $L = n\lambda = c_s/f_0$ where f_0 is the driving frequency and c_s is the sound speed in the liquid (see Table 8.1). It is known that cavitation may change the speed of sound in the liquid in the vicinity of the sonotrode [429], though it was neglected in this study as there are currently no means to know what is the extent of this effect.

The following tank lengths were used: for liquid Al – $L = 115, 230, 250, 390$ and 460 mm corresponding to $L = 0.5\lambda, \lambda, 1.1\lambda, 1.7\lambda$ (for microstructure analysis) and 2λ ; for DIW – $L = 50, 75, 98$ and 150 mm corresponding to $L = 0.7\lambda, \lambda, 1.3\lambda$ and 2λ , as $\lambda_{Al} = 230$ mm and $\lambda_{DIW} = 75$ mm. We had, therefore, selected two resonance lengths (λ and 2λ) and a number of off-resonance lengths based on the geometrical features of each container. In water, we could not consider a $L = 0.5\lambda$ measurement as the cavitometer device would not fit. Note that in order to have consistency in the measurements, we decided to use similar sonotrode diameter/resonance length ratio (based on the available commercial sonotrodes) for DIW and liquid Al (0.29 for DIW and 0.21 for Al). Table 8.1 summarises the experimental conditions. Sonication was applied using a 19.5 kHz 1-kW piezoelectric transducer (Hielscher Ultrasonics GmbH). The tank was filled with the working liquid and a ceramic (SiAlON) sonotrode (48 mm in diameter) for liquid Al and a Ti sonotrode (22 mm in diameter) for DIW were submerged in the centre of the tank, 10 mm below the liquid surface. The input power was adjusted to give a peak-to-peak displacement amplitude of 33 μ m for both cases. The liquid level within the tank was maintained at 60 mm. A calibrated cavitometer [297] was immersed at three different positions inside the liquid, i.e., referring to Fig. 8.1, under the sonotrode (P1), at a quarter-length (P2) and at the edge of the tank (P3). Each experiment was repeated at least twice. For liquid Al experiments (except for the microstructure analysis), we used commercially pure 99.7 wt% Al, and a K-type thermocouple to constantly monitor the temperature during the experiments with all measurements recorded in the range of 710 ± 30 °C. The temperature was kept constant at 25°C for DIW experiments.

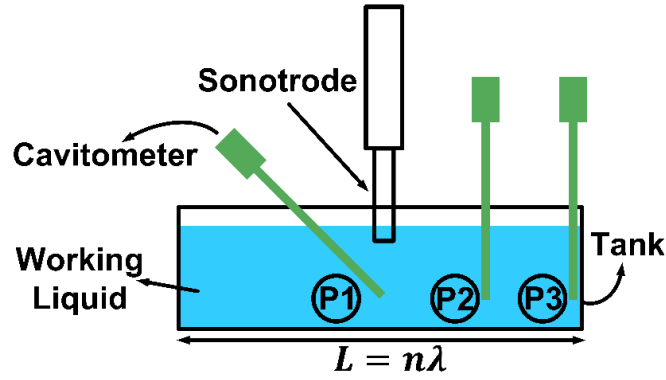


Fig. 8.1 Experimental setup for pressure measurement via cavitometers. The sonotrode is immersed in the tank filled with working liquid (either DIW or liquid Al). The cavitometer is placed at three different positions, under the sonotrode (P1), quarter-length or middle (P2) and edge of the tank (P3).

Table 8.1 Descriptions of experimental conditions.

Working Liquid	Tank Material	Vessel Length L/λ	Cavitometer Calibrated Range (kHz)	Driving Frequency f_0 (kHz)	Sound Velocity c_s (m/s) [289]
DIW	Glass	0.7, 1, 1.3, 2	8-400	19.5	1482
Liquid Al	Refractory Board	0.5, 1, 1.1, 1.7, 2	8-400	19.5	4600

A digital oscilloscope PicoScope-3204D (Pico Technology) monitored and captured in real-time the acoustic pressure emissions as voltage signals that were amplified by a calibrated pre-amplifier. For each experiment, we recorded the acoustic data for 60 random waveforms of 2 ms each (with sampling rate of 500×10^6 samples/s) under steady-state conditions to ensure the repeatability of the experiments and to account for the randomness of the cavitation phenomenon. The high temperature cavitometer with a spatial resolution of 40–50 mm and a bandwidth of up to 10 MHz [297] was calibrated over the range of 8-400 kHz at 0.5 kHz increments at the National Physical Laboratory (NPL), UK. The rationale behind this calibration range was to capture the associated emissions from collapsing bubbles at higher order frequencies as has been previously explained in the Introduction. Figure 8.2 shows the calibration of the cavitometer as function of its sensitivity for the calibrated range (8-400 kHz) for two cases, under the sonotrode and to the side of it. The red markers are the calibrated data points for each discrete step and the blue lines are the interpolated values used for the intermediate frequencies. All pressure measurements were taken with respect to the ambient pressure, since the cavitometer had been calibrated at atmospheric pressure.

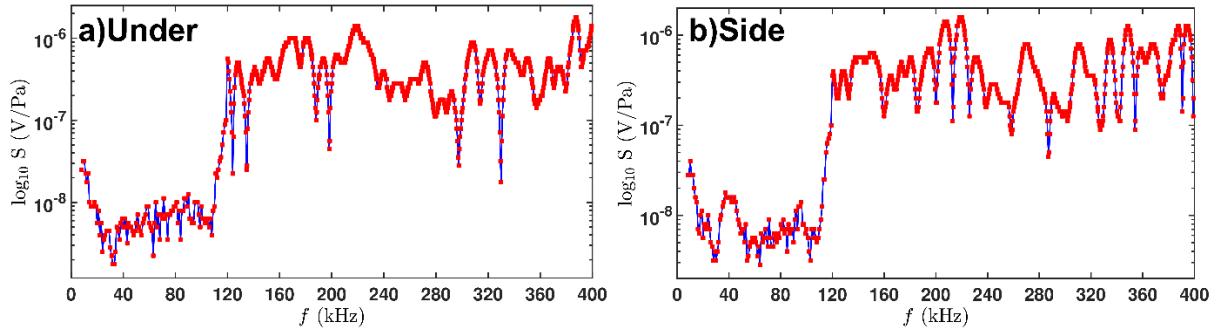


Fig. 8.2 Sensitivity of the cavimeter vs. frequency (NPL) for two probe positions: a) under (position P1 in Fig. 8.1) and b) side (positions P2 and P3 in Fig. 8.1).

8.2.2 Microstructure experiments

As an indicator of ultrasonic melt treatment efficiency, the average grain size was measured from solidified samples cast from the melt subjected to UST. Grain refinement in Zr and Ti-containing aluminium alloys is known to be an indicator of UST efficiency [1,18]. In this work, an Al-Cu-Zr-Ti alloy was prepared using a commercially pure aluminium alloy (99.7 wt% Al) with the addition of the alloying elements (i.e. Cu, Zr and Ti) through master alloys. The chemical composition of the alloy was determined by optical emission spectroscopy shown in Table 8.2. UST was performed using the same parameters and equipment as described above for liquid Al as we do not expect any noticeable variation in acoustic parameters of the alloy versus pure aluminium. Four experiments were carried out in tanks that were used for acoustic pressure measurements (as described in Section 8.2.1). One reference experiment was performed without UST, and three remaining ones were with UST at three different container lengths ($L = \lambda$, 1.7λ (off-resonance condition) and 2λ). For each experiment, the alloy was heated to 750°C and poured into the preheated tank, then UST was performed using the preheated sonotrode immersed approximately 10 mm into the melt. Experiments were repeated three times with consistent results. The treatment was performed for about 1 min, with liquid Al cooling down from $740 \pm 10^\circ\text{C}$ to approximately 700°C , then the melt was scooped using a preheated ladle and poured into a preheated steel mould. Microstructural samples were cut from the solidified cast, then mechanically ground, polished, and subsequently anodized using Barker's solution (5% HBF₄ in water solution) for approximately 60s at 20 VDC. The grain size analysis was performed using the linear intercept method and statistical analysis was carried out afterwards. Liquid Al experiments and microstructure analysis were done in collaboration with BCAST, BRU. The author of this thesis contributed to these experiments by assisting with the identifying resources, designing the experimental methodology for acoustic measurements, analysing and discussing the recorded data.

Table 8.2 Average composition of the alloy obtained through OES.

Composition	Al	Cu	Zr	Ti
Amount (wt %)	Balance	4.1	0.16	0.06

The deconvolution procedure and the MATLAB code used for obtaining acoustic pressures has been described in Appendix. Fig. 8.3 shows the pressure distribution in the time domain (the final output of the deconvolution analysis) for a single random waveform for liquid Al for all cavitometer positions: edge (Fig. 8.3(a)), quarter length (Fig. 8.3(b)) and under the sonotrode (Fig. 8.3(c)) each for three tank lengths $L = 0.5\lambda$, λ and 2λ . The significant drop in the pressure magnitudes for 2λ is observed for all probe positions.

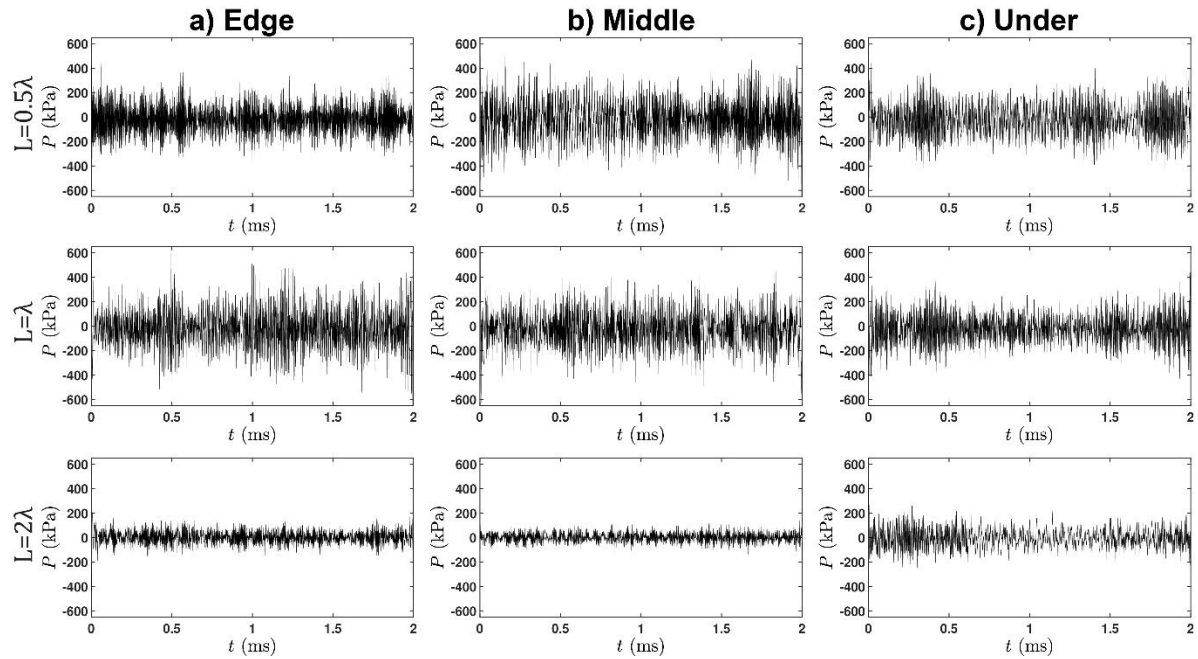


Fig. 8.3 Pressure distribution in the time domain for a single random waveform for liquid Al for different cavitometer positions; edge (a), quarter length (middle) (b) and under (c), each for three tank lengths $L = 0.5\lambda$, λ and 2λ .

8.3 Results and discussion

8.3.1 Acoustic spectrum analysis

Fig. 8.4 shows the pressure in the frequency domain for three different values of $L = 0.5\lambda$, λ and 2λ for liquid Al (a) and for $L = 0.7\lambda$, λ and 2λ for DIW (b), each for three cavitometer positions: under, quarter length (middle) and edge. In retrospect, Fig. 8.5 compares

the frequency response at various cavitometer positions for each L for liquid Al (a, b and c) and the position ‘under’ for DIW (d). Direct comparison of the frequency response of liquid Al and DIW is given in Fig. 8.6. It was decided for the frequency spectrum comparison (Figs. 8.4 and 8.5) to use only one off-resonance length ($L < \lambda$) for each case as it exhibits a higher pressure magnitude for both liquids (and among all the off-resonance lengths) in the majority of the studied cases (see Fig. 8.7).

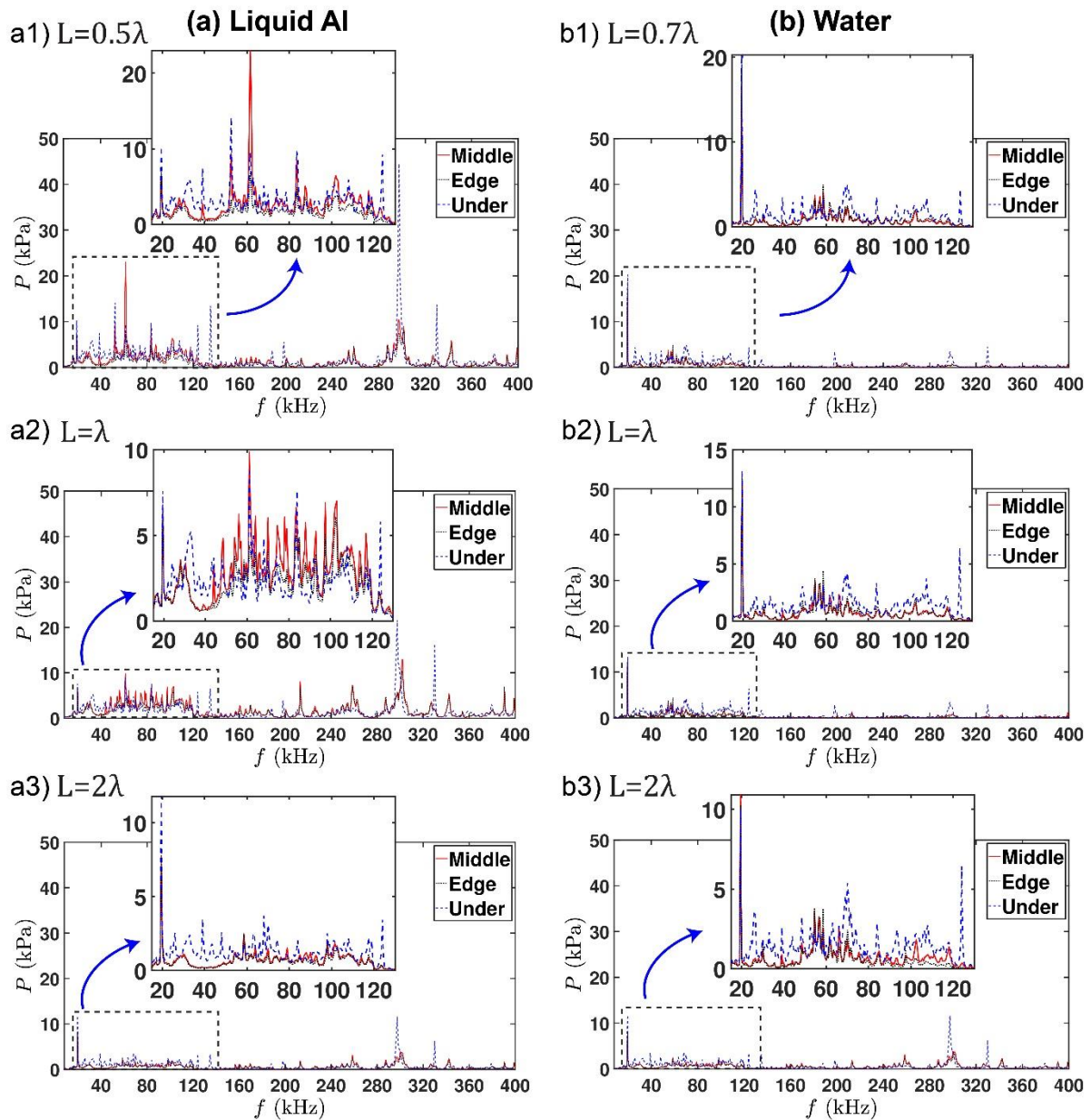


Fig. 8.4 Pressure vs. frequency for three different tank lengths (L) for both liquid Al (a) and DIW (b), each for three different cavitometer positions; under, quarter-length and edge (colour online). Note the driving frequency and ultra-harmonics being captured by the cavitometer. Red solid line is for the pressure at quarter-length, dotted black line is for edge and dashed blue line is for under positions. The pressure for each case was averaged over 60 waveforms. Note different Y-axis scale in the insets.

The analysis of the frequency response for liquid Al in Fig. 8.4 shows that large pressure magnitudes were recorded under the sonotrode for every tank length. Specifically large pressure spikes were observed at high frequencies (~ 300 kHz). For $L = 0.5\lambda$ (Fig. 8.4(a1)), the maximum peak pressure was ~ 45 kPa at 300 kHz under the sonotrode (P1), while the amplitude of the peak at this frequency reduced to 11 kPa for quarter-length (P2) (with the maximum peak pressure for this position calculated to be 23 kPa at 62 kHz), and to 8.5 kPa for edge (P3). At the driving frequency ($f_0 = 19.5$ kHz), the peak pressure for this L slightly dropped as the probe moved away from the sonication source and is 10.3, 6.8 and 7.3 kPa for P1, P2 and P3, respectively. For $L = \lambda$ (Fig. 8.4(a2)), the maximum peak pressure for all three positions was at 300 kHz and was calculated to be ~ 22 , 13 and 10 kPa for P1, P2 and P3 positions, respectively. The pressure at the driving frequency ($f_0 = 19.5$ kHz) for this L varied only slightly with position, being 7.5, 6.8 and 6.8 kPa for P1, P2 and P3, respectively. However, as we show in Fig. 8.4(a3), the peak pressures for $L = 2\lambda$ were significantly smaller than those in the shorter tanks. For $L = 2\lambda$, the largest peak pressure for all probe positions was recorded at the driving frequency ($f_0 = 19.5$ kHz) as 11.7, 7.8 and 7.8 kPa for P1, P2 and P3, respectively. At the high frequency $f = 300$ kHz for which we observed large spikes at smaller vessel lengths, the peak pressures are recorded to be 11.3, 3.9 and 3.3 kPa for P1, P2 and P3, respectively.

Unlike liquid Al, for DIW (Fig. 8.4b), no significant differences were observed for the pressure magnitudes or peaks for quarter-length and edge positions, while under the sonotrode, we observed higher pressure values and larger pressure spikes in the entire spectrum, a similar behaviour to liquid Al. Also, the maximum peak pressures for DIW were typically recorded at the driving frequencies of 19.5 kHz for all positions and lengths.

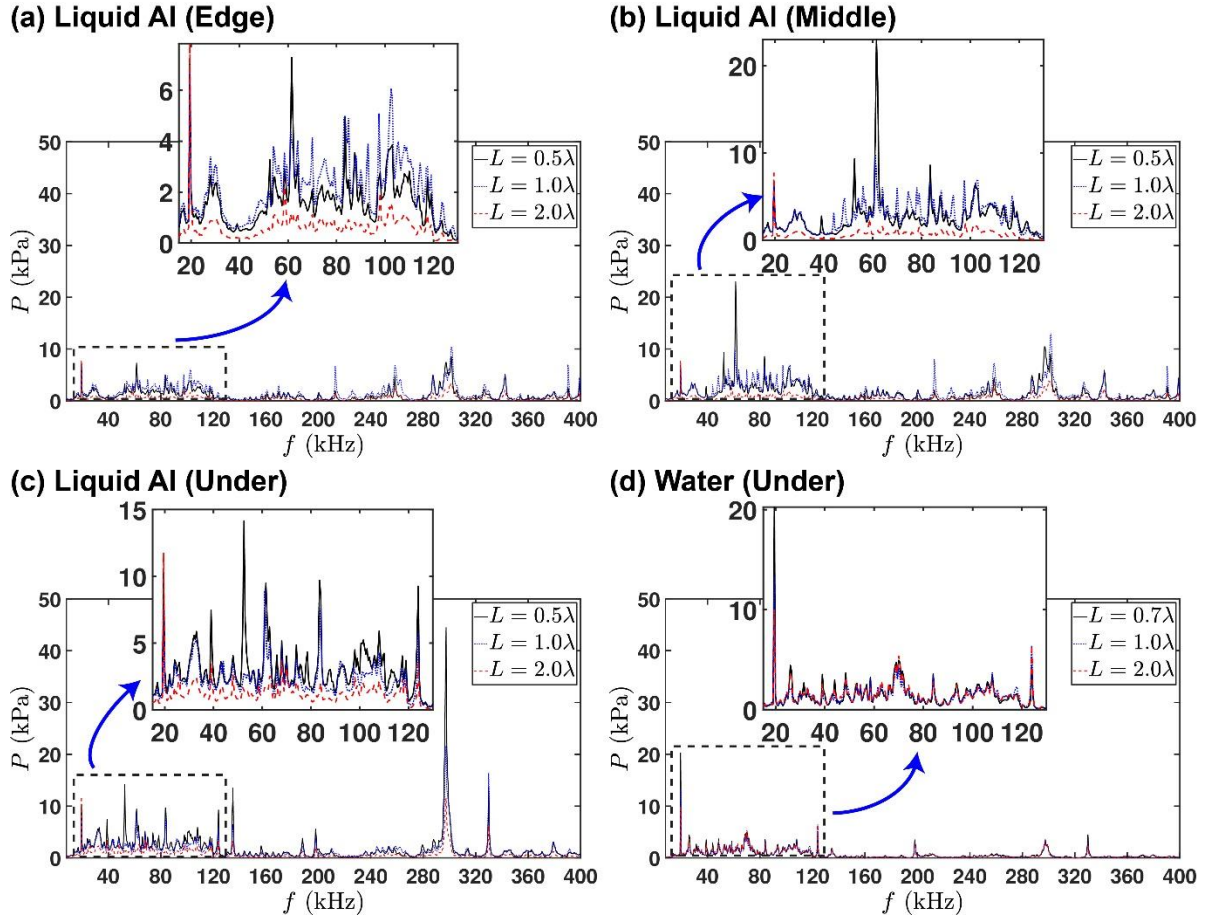


Fig. 8.5 Pressure vs. frequency for three λ for different positions for liquid Al (a, b and c) and for position ‘under’ for DIW (d) (colour online). Dotted blue line is for $L = \lambda$ and dashed red line is for $L = 2\lambda$ for both liquid Al and DIW. Solid black line is for $L = 0.5\lambda$ for liquid Al and $L = 0.7\lambda$ for DIW. The pressure for each case was averaged over 60 waveforms. Note different Y-axis scale in the insets.

For DIW, the pressure magnitudes under the sonotrode seemed to be independent of L (Fig. 8.5(d)) and similarly there was no significant difference for the response for the other two positions (quarter-length and edge). This is in contrast with what was reported before [289]. The reason for this disagreement could be attributed to the narrow frequency range (15-50 kHz) of calibration as well as only short ($L = \lambda$ or less) tanks used in the earlier study with the size of the sonotrode (48 mm) occupy most of the available space promoting strong shielding and attenuation of the acoustic emissions. Because for this range, the shielding and damping of the acoustic field was significant and the bubble emissions were not captured properly, while in the present study, a finer resolution in the spectral calibration range of 8-400 kHz allowed us to capture cavitation phenomena and contributions in more detail. The insensitivity to resonance length (vessel dimensions) in the case of water could be impactful for applications such as in 2D nanomaterials [309], or emulsions [405] where cavitation treatment is carried out

in water. An observation that may potentially simplify the complexity of treatment vessel designs.

For liquid Al, as seen in Fig. 8.5(a)-(c), we observed a distinct drop in the pressure magnitudes for $L = 2\lambda$ in all positions, along with several resonance peaks at high frequencies (200-400 kHz) and a rise of the fundamental frequency component. However, these peaks were not significant for this large tank (2λ), considering that the rate of dissipation of energy is high in liquid Al [286]. Additionally, the fact of lower pressure peaks may indicate a smaller number of cavitating bubbles (bubble volume fraction) in the bulk liquid, allowing the sound wave at the driving frequency to reach farther distances (less shielding). This could be related to the absence of standing waves and corresponding antinodes that could promote bubbles growth/collapse (formation of bubbly clouds), for larger tanks ($L = 2\lambda$) with liquid Al, which led to a pressure drop. It is worth noting that the peaks at higher frequencies for liquid Al have not been reported before, as previous studies did not use probes with this range of calibration.

For DIW, in contrast, the pressure peaks at high frequencies are suppressed due to the smaller lifetime of bubbles (compared to those in liquid Al) and, therefore, the driving frequency gives the most prominent peak (see Fig. 8.4(b) and Fig. 8.5(d)) with contributions from the cavitating bubbles. This could be the determining factor in defining the extent of the cavitation zone for liquid Al and DIW and can be complementary to the previous explanations that the borders of the cavitation zone were typically controlled by the acoustic impedance and the attenuation factor [276,297].

On the other hand, for smaller tanks ($L = 0.5\lambda$ and λ) in liquid Al, the prominent peaks at higher frequencies overwhelmed the fundamental frequency. This is especially pronounced in the very active area of 50-100 kHz, represented by harmonics of the driving frequency and the corresponding ultra-harmonics as well as superimposed cavitation emissions from vigorous bubble oscillations and shock wave emissions from the inertial (transient) cavitation [353]. This observation is interesting as it clearly shows that in liquid aluminium for $L < \lambda$, and in contrast to water, the fundamental frequency does not give the prominent peak, with the rise of the 3rd harmonic (see Fig. 8.5 (a-c)) indicating a resonance mode that may be related to the harmonic cascading as explained in [430] or the non-linearity parameter of the host medium that promotes waveform distortions (similar to harmonic imaging technique where the resonance frequency from the body fluids is typically a multiple of the original frequency). In addition, the bubbles in smaller vessels ($L < 2\lambda$) being confined to a smaller melt volume

(compared to $L = 2\lambda$), were expected to amplify the cavitation activity within this limited zone. This suggests a much higher bubble volume fraction for $L < 2\lambda$ than $L = 2\lambda$. On the other hand, these populated bubbly structures could lead to a stronger shielding effect [88,349] and might as well interfere with the standing waves expected due to the resonance length and may suppress the number of antinodes [431] that would be considered beneficial for formation and collapse of bubbles. So the outcome is a trade-off between the two effects. Additionally, a more compact space of small tanks provided more reflections for the acoustic waves that could not be attenuated (as they could for larger tanks of $L = 2\lambda$).

In Fig. 8.6, we compare the pressure in frequency domain for DIW and liquid Al for three cavitometer positions and different resonance lengths: off resonance ($L = 0.5\lambda$ for liquid Al and $L = 0.7\lambda$ for DIW, first row), $L = \lambda$ (second row) and $L = 2\lambda$ (third row). For the smaller tanks, the pressure magnitudes in liquid Al were higher than those of DIW, as expected, but the difference increased as we moved away from the cavitation zone. However, the pressure magnitudes for DIW for all three positions were comparable with liquid Al for 2λ .

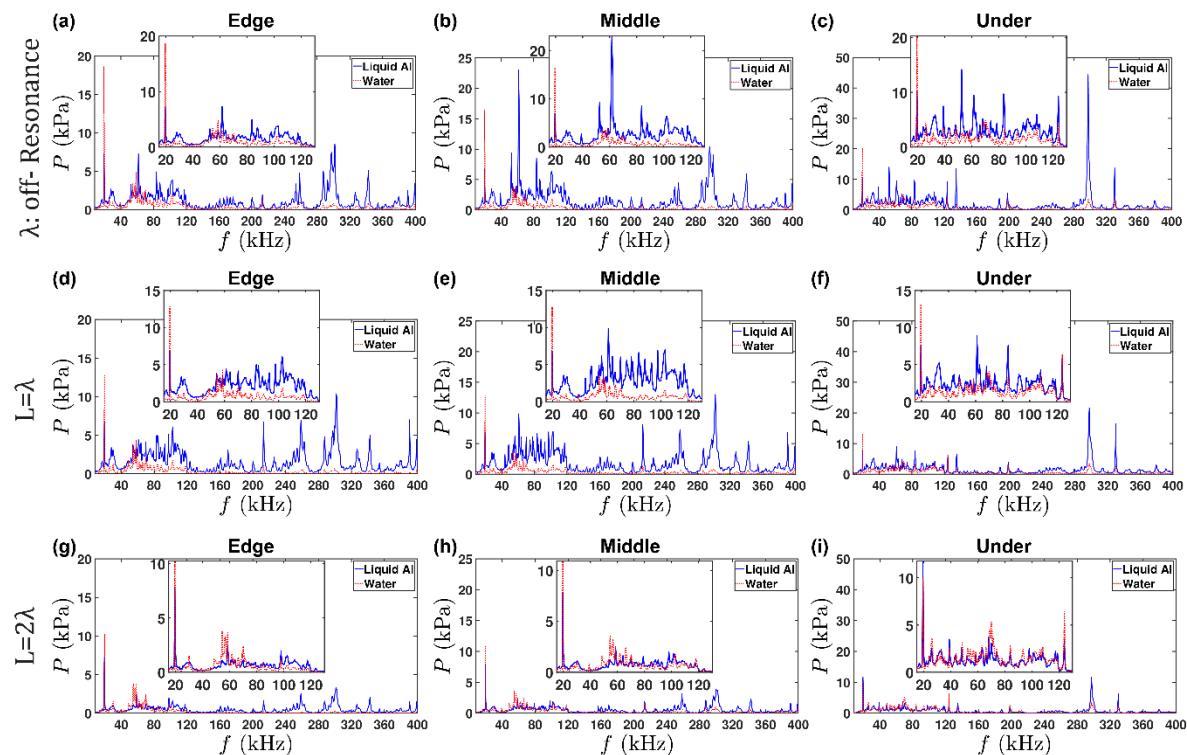


Fig. 8.6 Comparison of pressure in frequency domain for DIW and liquid Al for different cavitometer positions and different tank lengths: off resonance ($L = 0.5\lambda$ for liquid Al and $L = 0.7\lambda$ for DIW, first row), $L = \lambda$ (second row) and $L = 2\lambda$ (third row). The pressure for each case was averaged over 60 waveforms.

Furthermore, previous studies [49,272] have shown that in liquid Al, cavitation bubbles behave in a non-linear stable manner and are capable of surviving in the molten liquid for long periods of time. This will amplify the intensity of the recorded cavitation signals at the bubble resonant frequency and improve the potential of cavitation treatment. This could be a reason for the observation of the prominent peaks in 200-400 kHz range for liquid Al (with 19.5 kHz excitation frequency), as seen in Fig. 8.4(a) and 8.5(a)-(c). The most plausible explanation is the oscillation of cavitation bubbles at their resonance size (with a natural frequency within this range of 200-400 kHz as shown below) or the periodic collapses (bubbles collapse and rebound for a few hundred of milliseconds as seen in [49]). The size of these oscillating cavitation bubbles in liquid Al can be estimated by the Minnaert equation [432,433]: $f_m = 1/2\pi\sqrt{[3\gamma P_{abs} + 2(3\gamma - 1)\sigma_s/R_0]/(\rho R_0^2)}$ where γ is the gas specific heat ratio, ρ and σ_s are the density and surface tension of the liquid, P_{abs} is the absolute pressure and f_m is the natural frequency of the oscillating bubbles. Solving this complete form of the Minnaert equation numerically for R_0 and using $\gamma = 1.33$, $\sigma_s = 0.079$ N/m and $\rho = 1000$ kg/m³ for water [434] and $\gamma = 1.41$, $\sigma_s = 0.86$ N/m and $\rho = 2375$ kg/m³ for liquid Al [286], the resonance radii of oscillating bubbles for all prominent frequencies (Figs. 8.4 and 8.5) and their corresponding absolute pressures ($P_{abs} = P_\infty + P_{RMS}$) from the time domain for the entire set of experimental data were estimated for both water and liquid Al and all three positions of the cavitometer.

The tabulated results are presented in Tables 8.3 (liquid Al) and 8.4 (water). These estimates (excluding the driving frequency) give a range of 10-50 μ m for the bubble radius for liquid Al, which is close to the previously reported theoretical linear resonance size of 20 μ m at similar frequency of 20 kHz [289]. We do not observe any significant effect of cavitometer position on bubble radius. These calculated bubbles radii qualitatively represent the pressure peaks in the frequency domain captured by cavitometer during in-situ monitoring (as it is unlikely that the fundamental frequency in a relatively viscous and controlled by energy diffusion environment contributes to any peaks in the range of the 10th to 20th harmonic, i.e., 200-400 kHz). The bubbles in the cavitation zone are very unstable and multiply continuously, while most of the bubbles that are typically located outside the cavitation zone possess longer lifetimes, and their oscillations contribute to the emissions and rise of spectrum peaks at high frequencies.

Table 8.3 Bubble radius for all peak frequencies in pressure spectrum for liquid Al, all tank lengths and three different probe positions.

$L = 0.5\lambda$						$L = \lambda$					
Edge		Middle		Under		Edge		Middle		Under	
f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)
19.5	161.3	19.5	172.1	19.5	175.3	19.5	170.3	19.5	171.9	19.5	158.7
61.5	53.0	52.5	65.5	39	88.9	61	56.2	28	120.5	33	95.0
83.5	39.7	61.5	56.2	52.5	66.6	102.5	34.4	61	56.6	61	52.7
103	32.7	83.5	42.0	61.5	57.2	170	21.5	103	34.5	84	39.0
258.5	14.3	102	34.8	83.5	42.7	213	17.6	213	17.7	124	27.2
287.5	13.0	258.5	14.9	124	29.5	258.5	14.8	258.5	14.9	135	25.2
301.5	12.5	297	13.2	135	27.2	287.5	13.5	287.5	13.6	198	17.9
342.5	11.2	342.5	11.7	198	19.2	301.5	12.9	302	13.0	297.5	12.5
				297.5	13.3	327	12.1	327	12.1	330	11.5
				330	12.2	342.5	11.6	342.5	11.7		
						390.5	10.4	390.5	10.4		
$L = 1.1\lambda$						$L = 2\lambda$					
Edge		Middle		Under		Edge		Middle		Under	
f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)
19.5	161.4	19.5	164.8	19.5	170.4	19.5	134.9	19.5	135.5	19.5	138.7
65.5	50.0	28	115.6	33	101.8	58.5	47.5	58.5	47.7	39	71.2
88	37.8	39	83.8	39	86.5	98	29.7	98	29.8	68	42.3
103	32.7	48	68.6	63	54.5	213	15.1	169.5	18.4	124	24.6
169.5	20.7	65.5	50.9	84	41.4	258.5	12.9	213	15.2	135	22.8
200.5	17.9	79	42.6	117.5	30.3	287.5	11.8	258.5	12.9	156.5	20.0
213	16.9	93	36.6	124	28.8	301	11.3	287.5	11.8	198	16.4
258.5	14.3	103	33.3	135	26.6	326.5	10.6	300	11.4	297.5	11.6
287.5	13.0	117.5	29.4	156.5	23.2	342.5	10.2	342.5	10.2	330	10.7
301.5	12.5	160.5	22.1	188	19.7	390.5	9.2	390.5	9.2	379	9.5
327	11.7	169.5	21.1	198	18.8						
342	11.2	200.5	18.1	257.5	14.9						
379.5	10.3	213	17.2	297.5	13.1						
390.5	10.0	226	16.3	330	12.0						
		258.5	14.5	345.5	11.5						
		287.5	13.2	379	10.6						
		301	12.7								
		326.5	11.8								
		342.5	11.4								
		379.5	10.4								
		390.5	10.2								

Table 8.4 Bubble radii for all peak frequencies in pressure spectrum for DIW, all tank lengths and three different probe positions.

$L = 0.7\lambda$						$L = \lambda$					
Edge		Middle		Under		Edge		Middle		Under	
f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)
19.5	133.1	19.5	131.0	19.5	138.9	19.5	128.4	19.5	129.2	19.5	135.6
58.5	46.9	58.5	46.3	26	105.1	58.5	45.6	54.5	48.9	48.5	56.8
102.5	28.2	102.5	27.9	39	71.3	102.5	27.5	102.5	27.6	70	40.4
213	15.0	213	14.9	48.5	58.0	118	24.3	118	24.4	84	34.2
259.5	12.7	259.5	12.6	70	41.2	213	14.7	213	14.8	108	27.3
287	11.7	287	11.6	84	34.9	259.5	12.5	259.5	12.5	124	24.2
299.5	11.3	299.5	11.2	108	27.8	287	11.5	287	11.5	135	22.4
328.5	10.5	328.5	10.4	124	24.6	299.5	11.1	299.5	11.2	198	16.1
342.5	10.1	342.5	10.1	135	22.8	342	10.0	342	10.0	210	15.3
				198	16.4					297.5	11.5
				297.5	11.6					330	10.6
				330	10.7						
$L = 1.3\lambda$						$L = 2\lambda$					
Edge		Middle		Under		Edge		Middle		Under	
f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)	f_m (kHz)	R_0 (μm)
19.5	127.0	19.5	128.6	19.5	137.8	19.5	126.5	19.5	128.3	19.5	135.7
30	84.1	30	85.1	26	104.4	30	83.8	30	85.0	26	102.8
48.5	53.6	54.5	48.7	48.5	57.6	54.5	48.0	54.5	48.6	48.5	56.9
58.5	45.1	102	27.7	70	41.0	58.5	45.0	66	40.8	70	40.5
102.5	27.3	118	24.3	84	34.7	70	38.2	102.5	27.5	84	34.3
213	14.6	200	15.5	124	24.5	97.5	28.4	118	24.3	108	27.3
287	11.5	213	14.7	135	22.7	213	14.6	213	14.7	124	24.2
299.5	11.1	259.5	12.5	198	16.3	299.5	11.0	259.5	12.5	135	22.5
342	9.9	287	11.5	297.5	11.6	342.5	9.9	287	11.5	198	16.1
		299.5	11.1	330	10.6			299.5	11.1	211.5	15.3
		342	10.0					342	10.0	297.5	11.5
										330	10.6

8.3.2 Acoustic pressure measurements

Fig. 8.7 presents the $P_{\max}$ (a) and P_{RMS} (b) of liquid Al and DIW for different positions of the probe and all lengths of the vessel. For liquid Al, we observed a dependence of pressure on L , in particular for $L > 1\lambda$, while the pressure was independent of the cavitometer position for $L < 1\lambda$. This is seen for both $P_{\max}$ and P_{RMS} . For DIW, however, we observed an opposite behaviour, as the pressure did not seem to depend on L at all, but indeed decreased as the cavitometer moved away from the cavitation zone, therefore, we observed the largest pressure magnitudes for DIW right under the sonotrode for any L value. This is, apparently, because the speed of sound in water in the cavitating environment changes significantly and makes the resonance conditions (λ) irrelevant (unlike in liquid aluminium as verified by microstructure

analysis, see Section 8.3.3 and Fig. 8.8). Furthermore, the pressure magnitudes for liquid Al were much higher than those of water for any position or resonance length, except for $L = 2\lambda$ for which the pressures in liquid Al and water became comparable.

The magnitude of the acoustic pressures in a sonicated liquid also influences the cavitation activity. As seen in Fig. 8.7, the maximum pressure in liquid Al is more than 400 kPa for all positions and dimensions (except for $L = 2\lambda$) within the vessel. Whereas, in case of DIW, the maximum pressure lies in the range of 100-200 kPa under and side of the ultrasonic source. This further supports the observation of Figs. 8.4 and 8.5, where high frequency peaks close to 300 kHz were readily captured in case of liquid Al indicating the sustained oscillatory motion of cavitation bubbles. However, in the case of DIW, these high frequency peaks were suppressed and only substantial peaks up to 100 kHz were captured, confirming that smaller cavitation bubbles (Table 8.4) undergo inertial oscillation and catastrophically collapse after a few acoustic cycles. Yasui et al. [435] reported that the energy of acoustic waves radiated from oscillating bubbles corresponding to resonance frequency peak at each acoustic cycle increases with the rise in pressure amplitude. The radiated acoustic energy further increases in bubble clouds within the liquid.

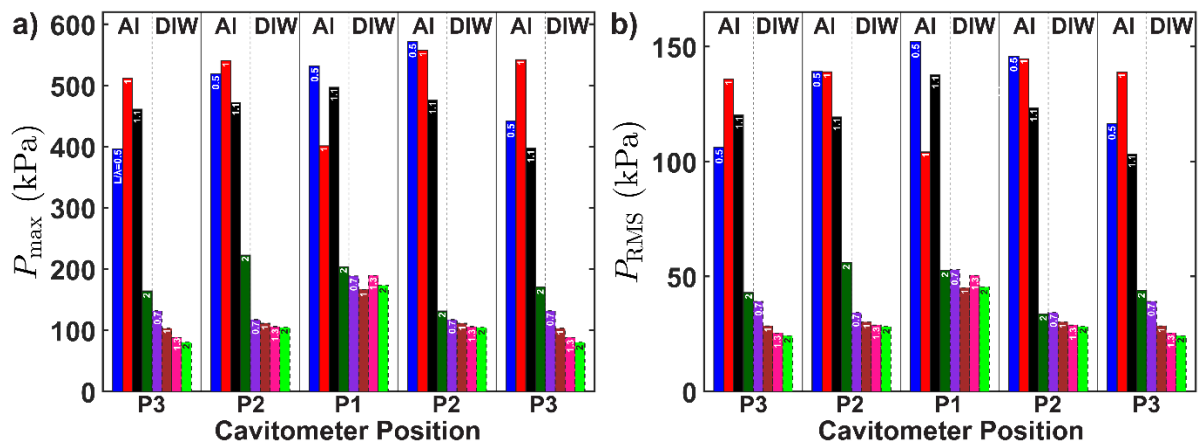


Fig. 8.7 Bar plot of P_{max} (a) and P_{RMS} (b) for both liquid Al and DIW vs. the cavitometer position (see Fig. 8.1) for all resonance lengths for each liquid. Positions are under the sonotrode (P1), quarter-length or middle (P2) and edge of the tank (P3). The tank length for each case is shown as the L/λ ratio inside each bar. The four left bars for each sensor position belong to liquid Al and the four right bars belong to DIW. Note that the relative positions reflect different lengths of the tanks for each case.

8.3.3 Microstructural analysis

Fig. 8.8 shows the microstructures (a–d) and their quantification in terms of average grain size (e), along with their corresponding acoustic pressure measurements under the sonotrode. It should be noted that for this investigation only the resonance lengths of λ and 2λ were

considered (as in section 8.3.1) with the off-resonance length at 1.7λ for comparison. We chose $L = 1.7\lambda$ as an off-resonance comparison based on the previous work which shows a trend that larger partition distances increase the residence time [423]. In this work, we try to find an off-resonance length which still gives reasonable acoustic pressure, while obtaining longer residence time (Fig. 8.8(f)). Furthermore, $L = 1.7\lambda$ provides almost the same resonance ratio (0.85) to 2λ (which gives the maximum volume melt) as the ratio of $L = \lambda$ (typically a desirable vessel length) to the off-resonance 1.1λ used in our acoustic pressure measurements in section 8.3.2.

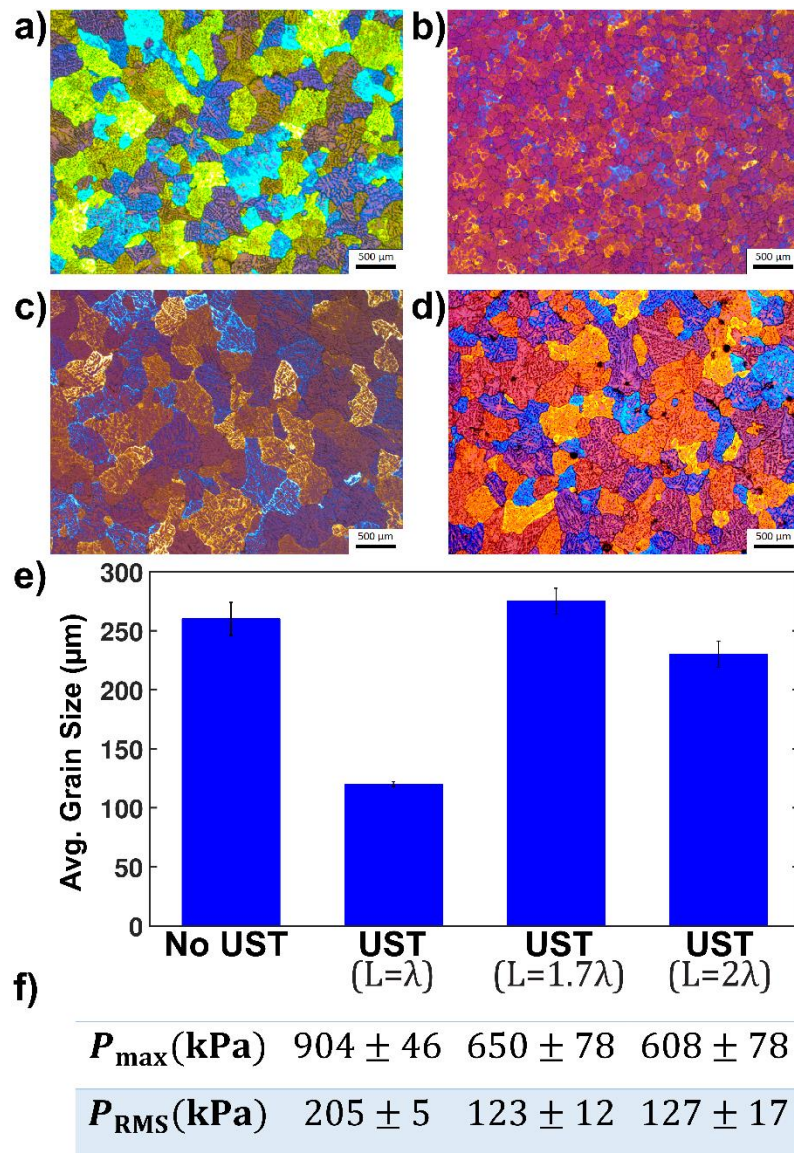


Fig. 8.8 Typical anodized microstructures of samples in different tank lengths: (a) without UST, (b) with UST for $L = \lambda$, (c) with UST for $L = 1.7\lambda$ (off-resonance) and (d) with UST for $L = 2\lambda$. (e) Bar plot of the average grain size for different processing condition. (f) P_{max} and P_{RMS} for microstructure experiments in liquid Al for the three different tank lengths. Note that these experiments were performed under the sonotrode (position P1).

The case of $L < \lambda$ that showed the highest pressure in some locations (and discussed in Section 8.3.1 from a spectral point of view) has less practical meaning in a continuous casting environment as it significantly restricts the treated volume and especially reduces residence time as in [384] and thus it was not considered for microstructural analysis and comparison. The best result in terms of grain refinement (the indicator of UST efficiency) was obtained when UST was performed in the tank with $L = \lambda$ (with grain size of 120 μm vs 260 μm for the untreated melt). This is consistent with the results of acoustic pressure measurements (Figs. 8.5 and 8.7): tank with $L = \lambda$ produced highest acoustic pressure (the maximum pressure for $L = \lambda$ is 39% higher than that of $L = 1.7\lambda$ and 49% higher than $L = 2\lambda$), because the tank length was at the main resonance mode where the cavitation activity was amplified [389] and the reflection from the tank walls was still quite strong (despite a larger bubble volume fraction as previously explained) as compared to when the tank walls were further apart. The important areas to consider for a homogeneous and effective treatment of the melt are the ones farther away from the obvious cavitation zone under the sonotrode, where cavitation treatment occurs anyway, and it seems that for the particular resonance wavelength $L = \lambda$ the middle and edge points maintain the highest pressure magnitude, implying a more intense treatment throughout the melt volume. Furthermore, another advantage of $L = \lambda$, in contrast to the closely followed in pressure magnitudes $L = 0.5\lambda$ (Fig. 8.7), is that this particular configuration can treat 2 times more volume with the same pressure efficiency over the same period of time.

UST for $L = 2\lambda$ gave slight grain refinement (230 μm) reflecting the significant drop in the acoustic pressure (see Figs. 8.5 and 8.7). Most interestingly, the lowest treatment efficiency was obtained when the tank is at off-resonance yet shorter length ($L = 1.7\lambda$) producing average grain size of 275 μm which means no grain refinement at all (the average grain size is even larger than without UST, but can be considered the same within the statistical error). This hints at the presence of higher-order resonance at $L = 2\lambda$ which was observed in our previous work [422] and also here (Fig. 8.5). This also supports our assumption that the resonance conditions in liquid Al are more sustainable than in DIW, being less susceptible to the changes in acoustic properties induced by cavitation.

8.3 Conclusions

In this work, we measured experimentally the acoustic pressure induced by ultrasonic processing in both liquid Al and DI water with a broad frequency-calibrated cavitometer (8-400 kHz) for different tank lengths – in both resonant and non-resonant conditions – keeping all other dimensions constant and for various positions of the sensor. By conducting a comprehensive analysis based on a deconvolution algorithm, we reported detailed observations and comparison of the pressure spectra for various conditions. The effect of the ultrasonic treatment on liquid Al was verified by metallographic examination. The following conclusions can be drawn from this study:

1. For liquid Al, the pressure field is sensitive to the length of the vessel and drops significantly for $L = 2\lambda$ (from 150 kPa to 50 kPa) with a drop of almost 66%. Nevertheless, resonance conditions can be maintained in the liquid Al even in the presence of cavitation.
2. Significant high-frequency peaks (at around 300 kHz) are observed for liquid Al due to intensified pressure fields assumed to be caused by a large number of oscillating bubbles.
3. The acoustic pressure in DIW does not appear to depend on λ (presumably the speed of sound changes significantly upon cavitation and the resonance conditions are not met), but it depends on the position of the cavitometer for every given length, i.e. the pressure decays as the probe moves away from the sonotrode.
4. Microstructure observation through an averaged grain size analysis shows that the main mode of resonance ($L = \lambda$) gives the finest grain with average size of approximately 100 μm which also reflects the highest cavitation activity (with P_{RMS} and P_{max} surging up to 200 kPa and 1 MPa, respectively) and treatment efficiency as compared to other conditions.

Chapter 9

Concluding remarks and future outlook

Based on the research presented in this dissertation titled '**Influence of ultrasonic cavitation treatment on fragmentation and de-agglomeration of primary intermetallics and oxides formed in Al alloys**', there are a few key take away points from the experimental results that recapitulates the overall significance of this work from a fundamental perspective and may further serve as a gateway and open new directions for future research by both experimenters and modellers. Each point includes brief description of the experimental results followed by the brief discussion of potential future work.

1. Measurement of mechanical properties of primary Al_3Zr intermetallics using DSI technique reveal that these intermetallics exhibit hardness, elastic modulus and fracture toughness close to 8 GPa, 200 GPa and $1 \text{ MPa}\sqrt{\text{m}}$, indicative of a typical hard and brittle material at room temperature. With dynamic indentation under high load-low cycle conditions, these intermetallics can sustain the contact pressure of almost 7 GPa without failing at RT. Both hardness and elastic modulus tends to decrease with the increase in operating temperature exhibiting high creep resistance at low and intermediate temperatures, while undergoing large deformation at temperatures close to the melting point of pure Al. However, this study fails to measure some critical factors such as fatigue strength of the material based on crack propagation characteristics and fracture toughness values at elevated temperature conditions, which would have allowed better understanding and interpretation of the deformation and fracture of intermetallics at HT with greater confidence. Measurement of such parameters could be an area of future work.
2. In-situ high-speed imaging unveils that the intermetallic breakage in water at ambient conditions is primarily governed by the cavitation-induced shock waves fronts emitted from the collapsing bubbles. In case of single bubble collapse (LIB), shock pressure in the range of 20-40 MPa is necessary for the instantaneous (fracture occurring in less than a millisecond) fragmentation of crystal depending on the critical crack length, whereas in case cloud of bubbles (ultrasound), fragmentation occurs in stages: the continuously propagating shock wave fronts (with pressure surges in the range of 0.4-0.5 MPa) first induces violent cyclic defection (low cycle fatigue) of crystal until a

critical size crack is formed. This is followed by immediate fracture following a brittle failure happening both in and out of the shear plane which typically transpires after 8-10 ms. The breakage is predicated mainly by the repetitive bubble cloud collapses occurring sub-harmonically at the horn-tip, which could be closely applicable to the fragmentation of a growing dendrite (possibly faster) across the solidification front in actual metallic melts considering the aggressiveness of cavitation activity (higher acoustic pressure). However, using water medium as an analogue does not necessarily replicate the scenario of any real melt environment and further research is needed to confirm such speculations. Therefore, in-situ fragmentation studies pertaining to floating intermetallics in Al melts using advanced X-ray synchrotron methods could be an area of future work.

3. Cavitation-induced shock waves in conjunction give rise to an inherent pressure peak frequency in the range of 3.27-3.43 MHz in addition to well recognized broadband noise floor confirmed by both FOH and shadowgraphic imaging performed at 1Mfps of the shock wave front. The acoustic pressure measured by the highly sensitive hydrophone show that pressure decays logarithmical fashion for proximal distance (1-10 mm) away from the ultrasonic horn. The pressure field can however be very weak just beneath the sonotrode tip at high input powers owing to strong cavitation shielding effect. Although, the evidence of this peak is only valid in case of water medium with certain ultrasonic conditions at room temperature, future research should focus on identifying the frequency peak in case of other organic liquids with different physical properties ranging from low to high surface tension, viscosity and density.
4. Synchronised in-situ high-speed fragmentation imaging and acoustic pressure measurement elucidate that the crystal breakage is subjugated mainly by volume fraction of the cavitation bubbles within the cavitation zone. These can significantly alter the pressure field by cushioning the emanating shock waves, thereby delaying the crystal fragmentation inside the cavitation zone at large input powers. High-speed filming investigation further revealed that the free-floating intermetallics also happen to break predominantly by emitted shock waves as in case of fixed intermetallic. Repetitive fragmentation occurs when the fragment recirculate back towards the cavitation zone (close to bubble cloud) as a result of induced acoustic streaming. Microscopic observations show that these extracted intermetallics are layered materials with pre-existing micro/macro cracks and oxides on the surface before sonication, which could significantly impact their fragmentation potential. After sonication, the

broken fragments show the formation of plastic pits, protrusions and crack network surrounding the pre-existing crack. Fragmented crystals show that the crack network becomes finer with the increase in treatment time with size ranging from 5-50 μm . SEM images of fragmented crystals further reveal that the intermetallic breakage of individual layers occurs via delamination of the exposed surface producing even smaller fragments of size of the order of 100 μm . Fragment size analysis indicates that the mean fragment size and their relative density decrease and increase, respectively with the increase in sonication time. The fragments reach the average size of 100 μm or less in just 9 sec of sonication. What this study fails to answer is the viability of these observations in regards to treatment in actual Al melts where the size of intermetallics present may be much smaller and less ductile than discussed in the present work. Moreover, the crystals used in this study exhibit large surface cracks and defects and therefore the results obtained using such particles cannot be generalized as representative scientific findings for metallic alloy systems at temperature close to melting points and therefore strictly should be applicable to present experimental conditions. One of the important findings missing from this study is the fragmentation of different particle structures at different stages of melt solidification under ultrasonic excitation. So, to address such concerns, more study is needed involving the use of X-ray synchrotron imaging of crystal fragmentation in Al melts during ultrasonication as also mentioned in point 3 above, which can be one of the areas of future work.

5. Ultrasonic de-agglomeration of silica and magnesia aggregates occur in a similar manner with regards to the process mechanism as observed in water medium at ambient temperature. The de-agglomeration process initiates purely through the nonlinear cavitation of pre-existing gas bubbles excited by the acoustic waves causing chaotic splitting and shape oscillation. The large shear stresses and the intense pressure pulses can cause effective chipping-off of oxide particles from the surface of the aggregate. The intensified implosions and rebound of oscillating microbubble clusters close to an aggregate can create a pressure surge as a result of sono-capillary effect promoting the de-agglomeration from inside of the bulk aggregate. The loose agglomerates get dispersed by the acoustic streaming in the bulk liquid volume and are further captured by the floating 'bubble drones' for separation into individual particles. Microbubble cluster oscillations responsible for de-agglomeration raise the prominent pressure peak at subharmonics and low order ultraharmonic frequencies that appears to be related to overall cavitation activity. This study can be further strengthened by some actual de-

agglomeration of oxides observed in the UST treated Al alloy melt either-in-situ or ex-situ measurements as a potential future work.

6. Ultrasonic treatment of liquid Al and water highlights and re-confirm the notion that the generated acoustic pressure field measured by the cavitation sensor in molten Al is almost twice as strong in comparison to the pressures induced in water. In case of liquid Al, the pressure regime is highly sensitive to the size of the treatment domain for maintaining resonance condition during cavitation. The amplified pressure fields emerging from the vessel length equivalent to main resonating mode of λ produces smaller average grain size indicative of the high cavitation activity and treatment efficiency assumed to be produced from large number of sustained oscillatory motion of bubbles at frequencies close to 300 kHz. Water, in contrast show little or no effect of vessel dimension on the acoustically generated pressures presumably due to compressible nature of the medium with significant changes in the sound propagation speed due to presence of cavitation resulting in loss of resonance conditions. Even though this work determines the best possible vessel dimension of treating liquid Al with ultrasound, it only considers the static processing conditions which is far from what is realized during continuous flow in launders of DC casting setup. Therefore, the future work should deal essentially with characterizing these liquids in a flow condition and identifying the best possible treatment conditions that maximizes the melt residence time and UST effect in terms of grain refinement of the ingot/billet.

To address this, Ultramelt 2 (with the author of this thesis being the part of) group conducted a pilot-scale trial testing involving the UST DC casting setup for process optimization assisted by the numerical modelling studies with the aim of scaling up this technology and to be further adopted by the industry as a standard step in the aluminium production and casting. This work is however beyond the scope of this PhD project and therefore has been added as a separate section in the Appendix (see A3).

Appendix

A1. From Voltage to Pressure: The deconvolution Process

The entire analysis of the experimental acoustic data in Chapter 4,5,6,7 and was carried out via an in-house MATLAB code (see below) based on the deconvolution process as described elsewhere [62,289,340] and Appendix D in Ref. [63] taking into account the pressure sensor (FOH/NH/cavitometer) calibration. Fig. A1 shows the steps in the pressure conversion procedure for DIW as the working liquid, glass tank length as λ (~ 75 mm), and sensor position (under the sonotrode). The noise measured before the main experiment was subtracted from the original voltage signals (Fig. A1(a)) in the time domain recorded by PicoScope/data acquisition device (PCI card) and low-pass filters were applied to avoid the contribution of the non-calibrated range of the pressure sensors. We then used the Fast Fourier Transform (FFT) algorithm to compute the discrete Fourier transform of the input signal (Fig. A1(b)). The signal was then converted into a single-sided spectrum [63] to correct for the cavitometer sensitivity. After dividing the resultant signal by its corresponding sensitivity value at each frequency, the signal was converted back to a double-sided spectrum, resulting in the pressure profile within the frequency domain (Fig. A1(c)). For each experiment, 60 random waveforms were recorded. The final frequency response of each experiment was the mean over 60 waveforms of the corresponding values for each waveform of 2 ms. An inverse Fast Fourier Transform would result in the pressure distribution in time domain [62,63,340]. Fig. A1(d) shows the final output of the deconvolution process as pressure-time profile for a single random waveform. The maximum ($P_{\max}$) and root-mean-square (RMS) pressure (P_{RMS}) of each waveform were then calculated from these profiles. Fig. A1(e) and A1(f) shows these values for 60 waveforms for the case study. The final $P_{\max}$ & P_{RMS} for each experiment were averaged over 60 waveforms.

P_{RMS} represents the root mean square pressure averaged across all the 60 waveforms of pressure-time spectrum and is associated with the distribution of the acoustic energy from the source in addition to the emitted cavitation emissions. P_{RMS} is the main parameter that is taken into account for evaluation and validation of numerical models. On the other hand, $P_{\max}$ represents the maximum peak pressure in each waveform which is averaged across 60 waveforms and is associated with the sharp peak of high magnitude mainly recorded from the shock wave emissions. Red and green arrows in Fig. A1(d) shows the $P_{\max}$ and P_{RMS} obtained from a typical pressure-time waveform.

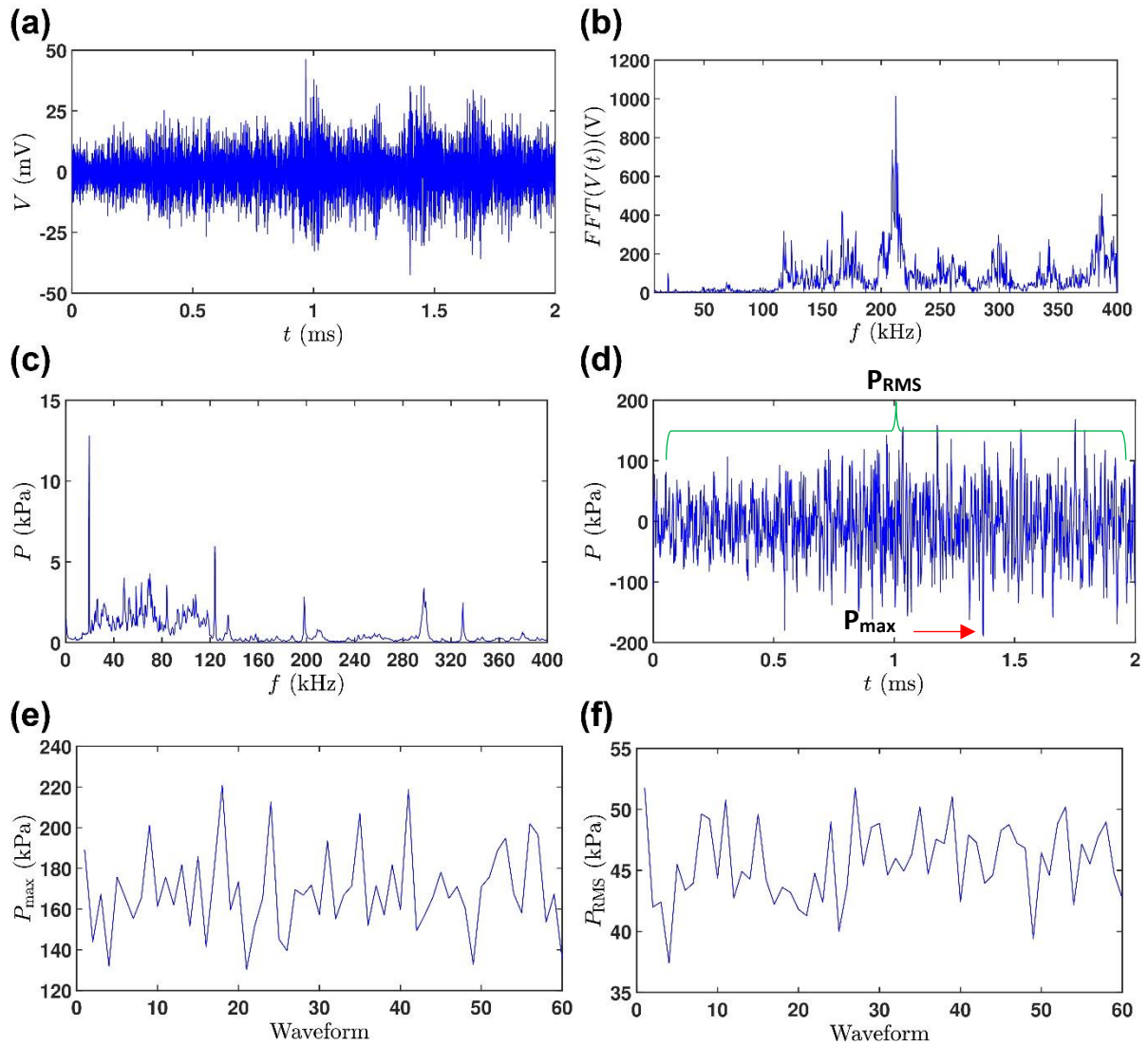


Fig. A1 The deconvolution process: a) Original voltage signal. b) Fast Fourier Transform of (a). c) Pressure vs. frequency resulting from applying the sensitivity function of the cavitometer to the signal. The pressure was averaged over 60 waveforms. d) Pressure vs. time for one sample waveform. e) P_{max} for each waveform from which the mean of maximum pressure is calculated. f) P_{RMS} for each waveform from which the mean RMS pressure is found. Results obtained for DIW with the cavitometer at position (under). Tank length was 75 mm.

A2. MATLAB Code

```
% Written by Dr. Mohammad Khavari
% NOTE: variables are defined at the end of the code
% t is in s, f is in Hz, V is in V and P is in kPa
clc;clear;close all;tic
Input_Method      = 2;           % 1: Input data via UI
                                % 2: Input data in the Code
Data_Method       = 2;           % 1: Data Acquisition by PicosCope
                                % 2: Data Acquisition by PCI Board
Multi_Method      = 1;           % 1: Single case (enter directory
of the FOLDER containing csv files) % 2: Multi cases (enter directory
of the FOLDER containing folders of all cases)
```

```

Noise_Method      = 2;          % 1: Noise subtraction in time domain
                                % 2: Noise subtraction in frequency
domain
Filter_Method     = 2;          % 1: With Applying filter
                                % 2: Without Applying filter
Save_Plots_Method = 1;          % 1: Save plots as JPEG using
export_fig
                                % 2: Do not save plots
Save_Data_Method  = 1;          % 1: Save data as MATLAB dat file
                                % 2: Do not save data
Save_Excel_Method = 2;          % 1: Save the results in an Excel
file
                                % 2: Do not save the results in an
Excel file

alpha = 0;                  % Percentage of ignored data at
beginning and end of P(t) for calculating Pmax (avoid counting peaks at
t~0)
switch Input_Method
    case 2
switch Data_Method
    case 1
        routel = 'D:\Experiments\Sample Data';
        Noise_up   = 10;          % Noise upper
value in mV (only needed if Noise_Method = 1)
        Noise_down = 10;          % Noise lower
value in mV (only needed if Noise_Method = 1)
        fs        = 500e6;        % Sampling rate
in samples per seconds
        NWF1 = 60;                % Number of
wave forms (if you don't want to analyze all)
        NoiseFileName = 'Noise_Silver_x1_y1_01'; % Noise file
name as csv (only needed if Noise_Method = 2)
    case 2
        Noise_up   = 0;          % Noise upper
value in mV (only needed if Noise_Method = 1)
        Noise_down = 0;          % Noise lower
value in mV (only needed if Noise_Method = 1)
        NWF1 = 1;                % For PCI
board, it must be 1
        NoiseFileName = 'Wat_T11_PCI_Noise'; %
Noise file name as csv (only needed if Noise_Method = 2)
        routel = cd;              % cd is current
directory: to be set where the code is
        BoardFileName = [BoardFileName '.csv'];
%        BoardFileName = uigetfile('*.csv'); % In case
want to open the csv file via UI
        fs = csvread(BoardFileName,17,2,[17,2,17,2]); % Read the
sampling rate from csv file
end
% Probe_Class = 'Cavitometer';
Probe_Class = 'Fibre-Optic Hydrophone';
% Probe_Class = 'Needle Hydrophone';

% ProbeType = 'Probe4';

% Cavitometer_position = 'Side';
% Cavitometer_position = 'Under';

```

```

% ProbeType = 'Needle Hydrophone1';

% ProbeType = '10T';

Loading_Effect = 1; % The loading effect of the
PicoScope
MATLAB_Version = 'R2018b';
% MATLAB_Version = 'Older Versions';
if (Save_Plots_Method == 1)
    Save_Plots = 'Yes';
else
    Save_Plots = 'No';
end
if (Save_Data_Method == 1)
    Save_Data = 'Yes';
else
    Save_Data = 'No';
end
if (Save_Excel_Method == 1)
    Save_Excel = 'Yes';
else
    Save_Excel = 'No';
end
if (Data_Method == 2) % For PCI board case, only
    Single Method is used
    Multi_Method = 1;
end
if (Noise_Method == 2) % Noise csv file is needed only
    for noise subtraction in frequency domain
        NoiseFileName = [NoiseFileName '.csv'];
    end
    case 1
        [Input, Button] = settingsdlg(...
            'Description' , 'Data Acquisition Device',...
            'title' , 'Choose the device',...
            'Device' , {'PicosCope','PCI Board'});
        Device_Status = Input.Device;
        if strcmpi(Button, 'Cancel')
            disp('Error! Please enter the required parameters')
            return
        end
        if strcmpi(Device_Status, 'PicosCope')
            Data_Method = 1;
        else
            Data_Method = 2;
        end
    end

    switch Data_Method
        case 1 % Data Acquisition by PicosCope
            [Input, Button] = settingsdlg(...
                'Description' , 'Input Data',...
                'title' , 'Choose the desired cases',...
                'Cases' , {'Single','Multiple'},...
                'Probe' , {'Cavitometer','Fibre-Optic
Hydrophone','Needle Hydrophone'},...
                'Noise Subtraction' , {'Time Domain','Frequency Domain'},...
                'Apply Filter' , {'Yes','No'},...

```



```

'Save Plots'          , {'Yes','No'},...
'Save Data'           , {'Yes','No'},...
'Save in Excel'       , {'Yes','No'},...
'Data Source'         , 'D:\...');
Case_Status           = Input.Cases;
route1                = Input.DataSource;
Probe_Class           = Input.Probe;
NoiseMethod1          = Input.NoiseSubtraction;
FilterMethod1         = Input.ApplyFilter;
Save_Plots            = Input.SavePlots;
Save_Data             = Input.SaveData;
Save_Excel            = Input.SaveInExcel;
if strcmpi(Button, 'Cancel')
    disp('Error! Please enter the required parameters')
    return
end
if strcmpi(Case_Status, 'Single')
    Multi_Method = 1;
else
    Multi_Method = 2;
end
if strcmpi(NoiseMethod1, 'Time Domain')
    Noise_Method = 1;
else
    Noise_Method = 2;
end
if strcmpi(FilterMethod1, 'Yes')
    Filter_Method = 1;
else
    Filter_Method = 2;
end
switch Noise_Method
    case 1
        if strcmpi(Probe_Class, 'Cavitometer')
            [Input, Button] = settingsdlg(...
                'Description',          'Input all the required
parameters/variables',...
                'title',                'CAVITOMETER',...
                'Cavitometer Position', {'Under','Side'},...
                'Probe' ,                {'Probe4'},...
                'Pre Amplifier Type' ,    {'B','A'},...
                'MATLAB Version' ,        {'R2018b','Older
Versions'},...
                'Sampling Rate Mega Sample per sec',500,...
                'Upper threshold of noise in mV',    0.5,...
                'Lower threshold of noise in mV',    0.5,...
                'Loading Effect of Picoscope',       1,...
                {'Use all the waveforms?'; 'Check'}, [true, true],...
                'Number of Waveforms',              1);
            if strcmpi(Button, 'Cancel')
                disp('Error! Please enter the required parameters')
                return
            end
            Cavitometer_position = Input.CavitometerPosition;
            ProbeType = Input.Probe;
            PreAmpType = Input.PreAmplifierType;
            Loading_Effect = Input.LoadingEffectOfPicoscope;
            fs = (Input.SamplingRateMegaSamplePerSec)*1e6;

```

```

        Noise_up      = Input.UpperThresholdOfNoiseInMV;
        Noise_down    = Input.LowerThresholdOfNoiseInMV;
        MATLAB_Version = Input.MATLABVersion;
    elseif strcmpi(Probe_Class, 'Fibre-Optic Hydrophone')
        [Input, Button] = settingsdlg(...
            'Description',          'Input all the required
parameters/variables',...
            'title'                ,          'FIBRE-OPTIC
HYDROPHONE',...
            'Probe'                ,          {'10T',}
            'Sampling Rate Mega Sample per sec', 500,...
            'Upper threshold of noise in mV',    10,...
            'Lower threshold of noise in mV',    10,...
            'Loading Effect of Picoscope',      1,...
            'MATLAB Version' ,                {'R2018b','Older
Versions'},...
            {'Use all the waveforms?'; 'Check'}, [true, true],...
            'Number of Waveforms',              1);
        if strcmpi(Button, 'Cancel')
            disp('Error! Please enter the required parameters')
            return
        end
        Loading_Effect = Input.LoadingEffectOfPicoscope;
        fs             = (Input.SamplingRateMegaSamplePerSec)*1e6;
        Noise_up       = Input.UpperThresholdOfNoiseInMV;
        Noise_down     = Input.LowerThresholdOfNoiseInMV;
        MATLAB_Version = Input.MATLABVersion;
        ProbeType      = Input.Probe;
    elseif strcmpi(Probe_Class, 'Needle Hydrophone')
        [Input, Button] = settingsdlg(...
            'Description',          'Input all the required
parameters/variables',...
            'title'                ,          'NEEDLE HYDROPHONE',...
            'Probe'                ,          {'Needle
Hydrophone1','Needle Hydrophone2','Needle Hydrophone3','Needle
Hydrophone4'},...
            'Sampling Rate Mega Sample per sec', 500,...
            'Upper threshold of noise in mV',    10,...
            'Lower threshold of noise in mV',    10,...
            'Loading Effect of Picoscope',      1,...
            'MATLAB Version' ,                {'R2018b','Older
Versions'},...
            {'Use all the waveforms?'; 'Check'}, [true, true],...
            'Number of Waveforms',              1);
        if strcmpi(Button, 'Cancel')
            disp('Error! Please enter the required parameters')
            return
        end
        Loading_Effect = Input.LoadingEffectOfPicoscope;
        fs             = (Input.SamplingRateMegaSamplePerSec)*1e6;
        Noise_up       = Input.UpperThresholdOfNoiseInMV;
        Noise_down     = Input.LowerThresholdOfNoiseInMV;
        MATLAB_Version = Input.MATLABVersion;
        ProbeType      = Input.Probe;
    end
    case 2
    if strcmpi(Probe_Class, 'Cavitometer')
        [Input, ~] = settingsdlg(...

```

```

        'Description',                                'Input all the required
parameters/variables',...
        'title' ,                                     'CAVITOMETER',...
        'Cavitometer Position',                       {'Under','Side'},...
        'Probe' ,                                     {'Probe4'},...
        'Pre Amplifier Type' ,                         {'B','A'},...
        'MATLAB Version' ,                             {'R2018b','Older
Versions'},...
        'Sampling Rate Mega Sample per sec',500,...
        'Noise File Name in csv',                     'Noise',...
        'Loading Effect of Picoscope',                 1,...
        {'Use all the waveforms?'; 'Check'}, [true, true],...
        'Number of Waveforms',                        1);
    if strcmpi(Button, 'Cancel')
        disp('Error! Please enter the required parameters')
        return
    end
    Cavitometer_position = Input.CavitometerPosition;
    ProbeType = Input.Probe;
    PreAmpType = Input.PreAmplifierType;
    Loading_Effect = Input.LoadingEffectOfPicoscope;
    fs = (Input.SamplingRateMegaSamplePerSec)*1e6;
    NoiseFileName = [Input.NoiseFileNameInCsv '.csv'];
    MATLAB_Version = Input.MATLABVersion;
elseif strcmpi(Probe_Class, 'Fibre-Optic Hydrophone')
    [Input, Button] = settingsdlg(...
        'Description',                                'Input all the required
parameters/variables',...
        'title' ,                                     'FIBRE-OPTIC
HYDROPHONE',...
        'Probe' ,                                     {'10T'},...
        'Sampling Rate Mega Sample per sec', 500,...
        'Noise File Name in csv',                     'Noise',...
        'Loading Effect of Picoscope',                 1,...
        'MATLAB Version' ,                             {'R2018b','Older
Versions'},...
        {'Use all the waveforms?'; 'Check'}, [true, true],...
        'Number of Waveforms',                        1);
    if strcmpi(Button, 'Cancel')
        disp('Error! Please enter the required parameters')
        return
    end
    Loading_Effect = Input.LoadingEffectOfPicoscope;
    fs = (Input.SamplingRateMegaSamplePerSec)*1e6;
    NoiseFileName = [Input.NoiseFileNameInCsv '.csv'];
    MATLAB_Version = Input.MATLABVersion;
    ProbeType = Input.Probe;
elseif strcmpi(Probe_Class, 'Needle Hydrophone')
    [Input, Button] = settingsdlg(...
        'Description',                                'Input all the required
parameters/variables',...
        'title' ,                                     'NEEDLE HYDROPHONE',...
        'Probe' ,                                     {'Needle
Hydrophone1'},...
        'Sampling Rate Mega Sample per sec', 500,...
        'Noise File Name in csv',                     'Noise',...
        'Loading Effect of Picoscope',                 1,...

```

```

        'MATLAB Version' ,                {'R2018b','Older
Versions'},...
        {'Use all the waveforms?'; 'Check'}, [true, true],...
        'Number of Waveforms',            1);
    if strcmpi(Button, 'Cancel')
        disp('Error! Please enter the required parameters')
        return
    end
    Loading_Effect = Input.LoadingEffectOfPicoscope;
    fs              = (Input.SamplingRateMegaSamplePerSec)*1e6;
    NoiseFileName = [Input.NoiseFileNameInCsv '.csv'];
    MATLAB_Version = Input.MATLABVersion;
    ProbeType      = Input.Probe;
end
end

    case 2 % Data Acquisition by PCI Board
[Input, Button] = settingsdlg(...
'Description'      , 'Input Data',...
'title'            , 'Choose the desired cases',...
'Probe'            , {'Cavitometer','Fibre-Optic
Hydrophone','Needle Hydrophone'},...
'Noise Subtraction' , {'Time Domain','Frequency Domain'},...
'Apply Filter'      , {'Yes','No'},...
'Save Plots'        , {'Yes','No'},...
'Save Data'         , {'Yes','No'},...
'Save in Excel'     , {'Yes','No'});
routel              = cd;
Probe_Class         = Input.Probe;
NoiseMethod1        = Input.NoiseSubtraction;
FilterMethod1       = Input.ApplyFilter;
Save_Plots          = Input.SavePlots;
Save_Data           = Input.SaveData;
Save_Excel          = Input.SaveInExcel;
NWF1 = 1;                                                    % For PCI board, it
must be 1
    if strcmpi(Button, 'Cancel')
        disp('Error! Please enter the required parameters')
        return
    end
    Multi Method = 1;                                        % For PCI board,
only Single Method is used
    if strcmpi(NoiseMethod1, 'Time Domain')
        Noise_Method = 1;
    else
        Noise_Method = 2;
    end
    if strcmpi(FilterMethod1, 'Yes')
        Filter_Method = 1;
    else
        Filter_Method = 2;
    end
    BoardFileName = uigetfile('*.csv');                    % Open the csv file
of PCI board via UI
    switch Noise_Method
        case 1
            if strcmpi(Probe_Class, 'Cavitometer')
                [Input, Button] = settingsdlg(...

```

```

        'Description',                    'Input all the required
parameters/variables',...
        'title'                        ,    'CAVITOMETER',...
        'Cavitometer Position',        {'Under','Side'},...
        'Probe' ,                      {'Probe4'},...
        'Pre Amplifier Type' ,          {'B','A'},...
        'Upper threshold of noise in mV', 0.5,...
        'Lower threshold of noise in mV', 0.5,...
        'MATLAB Version' ,              {'R2018b','Older
Versions'}});
    if strcmpi(Button, 'Cancel')
        disp('Error! Please enter the required parameters')
        return
    end
    Cavitometer_position = Input.CavitometerPosition;
    ProbeType = Input.Probe;
    PreAmpType = Input.PreAmplifierType;
    Loading_Effect = 1;
    fs =
csvread(BoardFileName,17,2,[17,2,17,2]);           % Read the
sampling rate from csv file
    Noise_up      = Input.UpperThresholdOfNoiseInMV;
    Noise_down    = Input.LowerThresholdOfNoiseInMV;
    MATLAB_Version = Input.MATLABVersion;
    elseif strcmpi(Probe_Class, 'Fibre-Optic Hydrophone')
        [Input, Button] = settingsdlg(...
        'Description',                    'Input all the required
parameters/variables',...
        'title'                        ,    'FIBRE-OPTIC
HYDROPHONE',...
        'Probe' ,                      {'10T','11T','12T','14T','15T','16T','17T','11T_2021','15T_2021','19T_2
021','20T_2021','23T_2021'},...
        'Upper threshold of noise in mV', 10,...
        'Lower threshold of noise in mV', 10,...
        'MATLAB Version' ,              {'R2018b','Older
Versions'}});
    if strcmpi(Button, 'Cancel')
        disp('Error! Please enter the required parameters')
        return
    end
    Loading_Effect = 1;
    fs =
csvread(BoardFileName,17,2,[17,2,17,2]);           % Read the
sampling rate from csv file
    Noise_up      = Input.UpperThresholdOfNoiseInMV;
    Noise_down    = Input.LowerThresholdOfNoiseInMV;
    MATLAB_Version = Input.MATLABVersion;
    ProbeType     = Input.Probe;
    elseif strcmpi(Probe_Class, 'Needle Hydrophone')
        [Input, Button] = settingsdlg(...
        'Description',                    'Input all the required
parameters/variables',...
        'title'                        ,    'NEEDLE HYDROPHONE',...
        'Probe' ,                      {'Needle Hydrophone1'},...
        'Upper threshold of noise in mV', 10,...
        'Lower threshold of noise in mV', 10,...

```

```

        'MATLAB Version' ,                {'R2018b','Older
Versions'}});
        if strcmpi(Button, 'Cancel')
            disp('Error! Please enter the required parameters')
            return
        end
        Loading_Effect = 1;
        fs =
csvread(BoardFileName,17,2,[17,2,17,2]);           % Read the
sampling rate from csv file
        Noise_up       = Input.UpperThresholdOfNoiseInMV;
        Noise_down     = Input.LowerThresholdOfNoiseInMV;
        MATLAB_Version = Input.MATLABVersion;
        ProbeType      = Input.Probe;
    end
    case 2
        if strcmpi(Probe_Class, 'Cavitometer')
            [Input, ~] = settingsdlg(...
                'Description',                'Input all the required
parameters/variables',...
                'title',                    'CAVITOMETER',...
                'Cavitometer Position',     {'Under','Side'},...
                'Probe' ,                   {'Probe4'},...
                'Pre Amplifier Type' ,       {'B','A'},...
                'Noise File Name in csv',    'Noise',...
                'MATLAB Version' ,          {'R2018b','Older
Versions'}});
            if strcmpi(Button, 'Cancel')
                disp('Error! Please enter the required parameters')
                return
            end
            Cavitometer_position = Input.CavitometerPosition;
            ProbeType = Input.Probe;
            PreAmpType = Input.PreAmplifierType;
            Loading_Effect = 1;
            fs =
csvread(BoardFileName,17,2,[17,2,17,2]);           % Read the
sampling rate from csv file
            NoiseFileName = [Input.NoiseFileNameInCsv '.csv'];
            MATLAB_Version = Input.MATLABVersion;
            elseif strcmpi(Probe_Class, 'Fibre-Optic Hydrophone')
                [Input, Button] = settingsdlg(...
                    'Description',                'Input all the required
parameters/variables',...
                    'title',                    'FIBRE-OPTIC
HYDROPHONE',...
                    'Probe' ,                   {'10T'},...
                    'Noise File Name in csv',    'Noise',...
                    'MATLAB Version' ,          {'R2018b','Older
Versions'}});
                if strcmpi(Button, 'Cancel')
                    disp('Error! Please enter the required parameters')
                    return
                end
                Loading_Effect = 1;
                fs =
csvread(BoardFileName,17,2,[17,2,17,2]);           % Read the
sampling rate from csv file

```

```

        NoiseFileName = [Input.NoiseFileNameInCsv '.csv'];
        MATLAB_Version = Input.MATLABVersion;
        ProbeType = Input.Probe;
    elseif strcmpi(Probe_Class, 'Needle Hydrophone')
        [Input, Button] = settingsdlg(...
            'Description', 'Input all the required
parameters/variables',...
            'title', 'NEEDLE HYDROPHONE',...
            'Probe', {'Needle Hydrophone1'},...
            'Noise File Name in csv', 'Noise',...
            'MATLAB Version', {'R2018b', 'Older
Versions'});
        if strcmpi(Button, 'Cancel')
            disp('Error! Please enter the required parameters')
            return
        end
        Loading_Effect = 1;
        fs =
csvread(BoardFileName,17,2,[17,2,17,2]); % Read the
sampling rate from csv file
        NoiseFileName = [Input.NoiseFileNameInCsv '.csv'];
        MATLAB_Version = Input.MATLABVersion;
        ProbeType = Input.Probe;
    end
end
end

end
switch Multi_Method
    case 1 % Single Case
        NFiles = 1; % Number of cases
    case 2 % Multi Case
        main_route = routel;
        File_Pattern1 = fullfile(main_route);All_Files1 =
dir(File_Pattern1);
        NFiles = length(All_Files1)-2;
    end
warning off
marker_font = 24;font_size = 20;font_size2 = 24;box_thickness =
3;Line thickness = 1;
save Input Data
for u = 1:NFiles
    load Input Data
    switch Multi_Method
        case 1 % Single Case
            route = routel;
        case 2 % Multi Cases
            disp(NFiles-u)
            route = [File_Pattern1 '\ ' All_Files1(u+2).name]
    end
%% Find the calibration range for each probe class and type
switch Probe_Class
    case 'Cavitometer'
        switch ProbeType
            case 'Probe4'
                fmin = 8e3; % in Hz
                fmax = 400e3; % in Hz
        end
end
end

```

```

case 'Fibre-Optic Hydrophone'
switch Data_Method
case 1 % Data Acquisition by PicosCope
switch ProbeType
case '10T'
fmin = 1e6; % in Hz
fmax = 30e6; % in Hz

end
if (floor(fs/2)<fmax)
fmax = floor(fs/2); % in Hz
end
case 2 % Data Acquisition by PCI Board
switch ProbeType
case '10T'
fmin = 1e6; % in Hz
fmax = floor(fs/2); % in Hz

end

end
case 'Needle Hydrophone'
switch ProbeType
case 'Needle Hydrophone1'
fmin = 8e3; % in Hz
fmax = 400e3; % in Hz

end

end
%% Filter Design
% Each probe with different calibration needs a different filter.
% If the filter becomes unstable, play with values of Wdiff (and so Ws)
and Rs
switch Filter_Method
case 1
Fn = fs/2;
switch Probe_Class
case 'Cavitometer'
switch ProbeType
case 'Probe4'
switch Data_Method
case 1 % Data Acquisition by PicosCope
Wp = fmax/Fn; % Normalised Passband

Frequency (in Hz)
Wdiff = 100e3; % Length of transition
region of the filter (in Hz)
Ws = (Wdiff+fmax)/Fn; % Normalised Stopband
Rp = 1; % Passband Ripple
Rs = 20; % Stopband Ripple
(Rs>Rp)

case 2 % Data Acquisition by PCI Board
Wp = fmax/Fn; % Normalised Passband

Frequency (in Hz)
Wdiff = 50e3; % Length of transition
region of the filter (in Hz)
Ws = (Wdiff+fmax)/Fn; % Normalised Stopband
Rp = 1; % Passband Ripple

```



```

Rs = 20; % Stopband Ripple
(Rs>Rp)
end
end
% case 'Fibre-Optic Hydrophone' % Unused (filter is
directly applied later)
% switch Data_Method
% case 1 % Data Acquisition by PicosCope
% Wp = [fmin 0.95*fmax]/Fn; % Normalised
Passband
% Ws = [0.09 Wp(2)+0.02]; % Normalised
Stopband
% Rp = 1; % Passband
Ripple/Attenuation
% Rs = 20; % Stopband
Ripple/Attenuation
% Wp = [fmin fmax]/Fn; % Normalised
Passband
% Ws = [0.9e6 35e6]/Fn; % Normalised
Stopband
% case 2 % Data Acquisition by PCI Board
% Wp = [fmin 0.95*fmax]/Fn; % Normalised
Passband
% Ws = [0.09 Wp(2)+0.02]; % Normalised
Stopband
% Rp = 1; % Passband
Ripple/Attenuation
% Rs = 20; % Stopband
Ripple/Attenuation
% end
case 'Needle Hydrophone'
switch Data_Method
case 1 % Data Acquisition by PicosCope
Wp = fmax/Fn; % Normalised Passband
Frequency
Wdiff = 100e3; % Length of transition
region of the filter (in Hz)
Ws = (Wdiff+fmax)/Fn; % Normalised Stopband
Rp = 1; % Passband Ripple
Rs = 20; % Stopband Ripple
(Rs>Rp)
case 2 % Data Acquisition by PCI Board
Wp = fmax/Fn; % Normalised Passband
Frequency
Wdiff = 50e3; % Length of transition
region of the filter (in Hz)
Ws = (Wdiff+fmax)/Fn; % Normalised Stopband
Rp = 1; % Passband Ripple
Rs = 20; % Stopband Ripple
(Rs>Rp)
end
end
if (strcmpi(Probe_Class, 'Fibre-Optic Hydrophone')) % use
bandpass filter for FOH and low pass for other probes
%%%% This is not used for FOH. I use bandpass function
directly for FOH
%
```

```

% [n,Wn] = ellipord(Wp,Ws,Rp,Rs); %
Calculate Elliptic Filter Optimum Order
% disp('Filter order');disp(n);
% [z,p,k] = ellip(n,Rp,Rs,Wn,'bandpass'); %
Elliptic Filter
% [sos,g] = zp2sos(z,p,k); % Second-
Order-Section For Stability
else
    [n,Wn] = buttord(Wp,Ws,Rp,Rs); % Find
filter order and cutoff frequency
    disp('Filter order');disp(n);
    [z,p,k] = butter(n,Wn,'low'); % Design
butterworth filter (unstable)
    [sos,g] = zp2sos(z,p,k); % Convert
to second-order section form (stable)
end
end
%% Read Noise
switch Noise_Method
    case 2
        switch Data_Method
            case 1 % Read data from PicosCope
                M1 = csvread(NoiseFileName,3,0);
                fileID = fopen(NoiseFileName);
                C1 =
textscan(fileID,'%s %s','Delimiter',' ');fclose(fileID);
                if (strcmpi(C1{2}{2}, '(V)'))
                    disp(['Unit of Noise is ' C1{2}{2}]);
                    Noise = M1(:,2); % Noise
in V
                    elseif(strcmpi(C1{2}{2}, '(mV)'))
                        Noise = 0.001.*M1(:,2); % Noise
in V
                        end
                    case 2 % Read data from PCI Board
                        M1 = csvread(NoiseFileName,24,0); % Noise
should be in volt. t from Noise file is not read
                        Noise = M1(:,4);
                    end
                clear M1
                switch Filter_Method
                    case 1
                        if (strcmpi(Probe Class, 'Fibre-Optic Hydrophone')) % use
bandpass filter for FOH and low pass for other probes
                            Noise2 = bandpass(Noise,[fmin fmax],fs); % Noise
after filtering (band pass for FOH)
                        else
                            Noise2 = filtfilt(sos, g, Noise); % Noise
after filtering (low pass for other probes)
                        end
                            FT_Noise = fft(Noise2); % The
next few lines will be used for Noise subtraction in freq domain
                            SS_FT_Noise = DS2SS(FT_Noise);
                            FT_NF_Noise = fft(Noise); % Even
with filter, we calculate fft of noise for without filter case
                            SS_FT_NF_Noise = DS2SS(FT_NF_Noise);
                            case 2
Without Applying Filter

```

```

        FT_NF_Noise      = fft(Noise);
        SS_FT_NF_Noise   = DS2SS(FT_NF_Noise);
    end
end
disp('Reading Signals')
%% Read V-t data from csv
switch Data_Method
case 1                % Data Acquisition by PicosCope
format long
dt=1/fs;
start_counter = 1;
switch MATLAB_Version
    case 'R2018b'                % If using
MATLAB R2018b or newer versions (5x faster)
        File_Pattern = fullfile(route, '*.csv');
        All_Files = dir(File_Pattern); FileRouteName = fullfile(route,
All_Files(start_counter).name);
        fileID = fopen(FileRouteName);
        C = textscan(fileID, '%s %s', 'Delimiter', ',', '');
        fclose(fileID);
        if isempty(C{1}{3}))                % Check if the
empty (third) row in first csv file is ignored or not
            L0 = length(C{1})-1;                % Size of
original data (if the empty row is not automatically ignored)
        else
            L0 = length(C{1});                % Size of
original data (if the empty row is automatically ignored)
        end
        switch Input_Method
        case 1
            if (Input.Check == 1)                % Check whether
to use all the number of waveforms or the ones specified by user
                NWF = length(All_Files);
            elseif (Input.Check ~= 1)
                NWF = Input.NumberOfWaveforms;
            end
        case 2
            NWF = min ([length(All_Files) NWF1]);
        end
        if (length(All_Files)<10)                % check if
there is less than 10 waveforms (to keep the original name intact)
            format1 = All_Files(start_counter).name(1:end-6);
        else
            format1 = All_Files(start_counter).name(1:end-7);
        end
        if (length(All_Files)==1)                % check if
there is less than 10 waveforms (to keep the original name intact)
            format1 = All_Files(start_counter).name(1:end-4);
        end
        L1 = L0-2;                % Size of rows
containing data (without two first non-numeric rows)
        tV = zeros(1,L0);                % Preallocation
to L0
        M = zeros(1,L0);                % Preallocation
to L0
        Vt1 = zeros(L1,NWF);                % Preallocation
to L1 (because first two rows are already removed in M)
        for i = start_counter:NWF

```

```

disp(i)
FileRouteName = fullfile(route, All_Files(i).name);
opts = delimitedTextImportOptions("NumVariables", 2);
opts.VariableTypes(:) = {'double'};opts.Delimiter =
",";opts.ExtraColumnsRule = "ignore";
opts.EmptyLineRule = "read";D = readtable(FileRouteName, opts);
D = D{:, :};
fileID = fopen(FileRouteName);
C = textscan(fileID, '%s %s', 'Delimiter', ',', '');
fclose(fileID);
if (strcmpi(C{2}{2}, '(V)'))
    disp(['Unit is ' C{2}{2}]);
    M = D(:,2); % no need to
convert to V
    M(isnan(M))=0; % convert NaN
values to zero
    M(1:3) = []; % remove first
three rows (no data)
elseif (strcmpi(C{2}{2}, '(mV)'))
    M = 0.001.*D(:,2); % convert to V
    M(isnan(M))=0; % convert NaN
values to zero
    M(1:3) = []; % remove first
three rows (no data)
end
Vt1(:,i) = M; % Assign to
main Voltage Matrix
if (i==1)
    tV = 0.001.*D(:,1); % READ TIME
data (only once)
end
clear D M
M = zeros(1,L0); % Preallocation
to L0
end
tV(1:3) = []; % remove first
three rows (no data)
case 'Older Versions' % If using
MATLAB versions older than R2018b (5x slower)
    File_Pattern = fullfile(route, '*.csv');
    All_Files = dir(File_Pattern);FileRouteName = fullfile(route,
All_Files(start_counter).name);
    fileID = fopen(FileRouteName);
    C = textscan(fileID, '%s %s', 'Delimiter', ',', '');
    fclose(fileID);
    if isempty(C{1}{3})) % Check if the
empty (third) row in first csv file is ignored or not
        L0 = length(C{1})-1; % Size of
original data (if the empty row is not automatically ignored)
    else
        L0 = length(C{1}); % Size of
original data (if the empty row is automatically ignored)
    end
    switch Input_Method
    case 1
        if(Input.Check == 1) % Check whether
to use all number of waveforms or the ones specified by user
            NWF = length(All_Files);

```

```

elseif (Input.Check ~= 1)
    NWF = Input.NumberOfWaveforms;
end
case 2
    NWF = length(All_Files);
end
if (length(All_Files)<10) % check if
there is less than 10 waveforms (to keep the original name intact)
    format1 = All_Files(start_counter).name(1:end-6);
else
    format1 = All_Files(start_counter).name(1:end-7);
end
if (length(All_Files)==1) % check if
there is less than 10 waveforms (to keep the original name intact)
    format1 = All_Files(start_counter).name(1:end-4);
end
L1 = L0-2; % Size of rows
containing data (without two first non-numeric rows)
tV = zeros(1,L0); % Preallocation
to L0
M = zeros(1,L0); % Preallocation
to L0
Vt1 = zeros(L1,NWF); % Preallocation
to L1 (because first two rows are already removed in M)
%%% READ TIME
for j = 3:L0
    tV(j) = 0.001.*sscanf(C{1}{j},'%f'); % convert to
seconds
end
tV(1:2) = []; % remove first
two rows (no data)
%%% READ VOLTAGE
for i = start_counter:NWF
    disp(i)
    FileRouteName = fullfile(route, All_Files(i).name);
    fileID = fopen(FileRouteName);
    C = textscan(fileID,'%s %s','Delimiter',' ','');
    fclose(fileID);
    if (strcmpi(C{2}{2}, '(V)')) % if length is
3 it means original voltage is in V, if it is 4 it means voltage is in
mV
        disp(['Unit is ' C{2}{2}]);
        for j = 1:length(C{1})
            so = sscanf(C{2}{j},'%f');
            if ~isempty(so)
                M(j) = so;
            end
        end
        M(isnan(M))=0; % convert NaN
values to Zero
M(1:2) = []; % remove first
two rows (no data)
elseif (strcmpi(C{2}{2}, '(mV)'))
    for j = 1:length(C{1})
        so = 0.001.*sscanf(C{2}{j},'%f');
        if ~isempty(so)
            M(j) = so;
        end
    end
end

```

```

                end
                M(isnan(M))=0; % convert NaN
values to Zero
                M(1:2) = []; % remove first
two rows (no data)
                end
                Vt1(:,i) = M;
                clear M
                M = zeros(1,L0); % Preallocation
to L0
                end
end
% Check if the number of original data points is odd, if yes, ignore
the last data for tV and Vt
if (mod(L1,2)~=0)
    L1 = L1-1; % if number of
data point is odd
    tV(end) = []; % ignore the
last data point
    y1_temp = zeros(L1,NWF);
    for i=1:NWF
        y1 = Vt1(:,i);
        y1(end) = [];
        y1_temp(:,i) = y1;
        clear y1
    end
    clear Vt1
    Vt1 = y1_temp;
end
clear y1_temp
L2 = L1/2+1; % Size of
single sided spectrum
bin_vals = (0 : L1-1);
fV = bin_vals*(fs/L1); % in Hz
ind_min = find(fV>fmin,1,'first')-1; % First index
of calibration range
ind_max = find(fV<fmax,1, 'last'); % Last index of
calibration range

case 2 % Data Acquisition by PCI Board
format1 = BoardFileName(1:end-4);
M2 = csvread(BoardFileName,24,0);
fs = csvread(BoardFileName,17,2,[17,2,17,2]);
FR = csvread(BoardFileName,8,2,[8,2,8,2]);
tV = M2(:,1)-M2(1);
dt = 1/fs;
tV(1) = 0;
for i = 2:size(M2(:,1))
    tV(i) = tV(i-1)+dt;
end
Vt1 = M2(:,4);
if mod(length(Vt1),2)~=0
    Vt1 = Vt1(1:end-1);
    tV = tV(1:end-1);
end
NWF = NWF1;
L1 = length(M2);

```

```

L2 = L1/2+1; % Size of
single sided spectrum
bin_vals = (0 : L1-1);
fV = bin_vals*(fs/L1); % in Hz
f1 = fmin:1e6:fmax; % in Hz
ind_min = find(fV>fmin,1,'first')-1; % First index
of calibration range
ind_max = find(fV<fmax,1, 'last'); % Last index of
calibration range
end
%% Sensitivity Interpolation
switch Probe_Class
    case 'Cavitometer'
        switch ProbeType

            case 'Probe4'
                [f1,S_Original] =
Sensitivity_CAV(Cavitometer_position,ProbeType);
                S1 = zeros(L2,1); % create the
sensitivity vector
                S1(1:ind_min-1) = S_Original(1); % assign all values
before fmin to the mean value
                S1(ind_max+1:end) = S_Original(end); % assign all values
after fmax to the mean value
                for i = ind_min:1:ind_max
                    S1(i) = interp1(f1,S_Original,fV(i),'PCHIP');
                end
                % S1(1:ind_min-1) = mean(S_Original); % assign all
values before fmin to the mean value
                % S1(ind_max+1:end) = mean(S_Original); % assign all
values after fmax to the mean value
                % for i = ind_min:1:ind_max
                % S1(i) = interp1(f1,S_Original,fV(i),'PCHIP');
                % end
                % writetable(table(S1),'MyS11.csv');
                S = S1./Loading_Effect;
            end

        case 'Fibre-Optic Hydrophone'
            switch ProbeType

                case '10T'
                    f1 = fmin:1e6:fmax; % in Hz
                    S_Original = 1e-9.*[256.307 282.425 309.992 353.795
398.284 428.797 464.433 499.977 558.636 649.384 597.184 623.976
690.781 711.75 780.066 778.891 686.172 487.769 563.25 1120.55
1010.68 756.805 640.464 666.229 683.299 699.514 735.52 733.858
558.253 572.352];

                    end
                    if
length(f1)<length(S_Original) % if
sampling rate is lower than calibration range (30MHz), smaller range of
calibration function should be used
                        S_Original = S_Original(1:length(f1));
                    end
                    switch Data_Method
                        case 1 % Data Acquisition by PicosCope

```

```

        S1 =
zeros(L2,1); % Preallocate
the sensitivity vector
        S1(1:ind_min-1) =
S_Original(1); % assign all values before fmin
to the mean value
        S1(ind_max+1:end) =
S_Original(end); % assign all values after fmax
to the mean value
        for i = ind_min:1:ind_max
            S1(i) = interp1(f1,S_Original,fV(i),'PCHIP');
        end
        S = S1./Loading_Effect;

    case 2 % Data Acquisition by PCI Board

        S1 =
zeros(L2,1); % Preallocate
the sensitivity vector
        S_Original_Selected =
S_Original(1:fmax/1e6); % Since the sampling rate is less
than the calibration range, we use a selected range of S upto fs/2
        S1(1:ind_min-1) =
S_Original_Selected(1); % assign all values before fmin
to the mean value
        S1(ind_max+1:end) =
S_Original_Selected(end); % assign all values after fmax
to the mean value
        for i = ind_min:1:ind_max
            S1(i) = interp1(f1,S_Original_Selected,fV(i),'PCHIP');
        end
        S = S1./Loading_Effect;
    end

    case 'Needle Hydrophone'
        switch ProbeType

            case 'Needle Hydrophone1'
                f1 =
1000.*[8      8.5      9      9.5      10      12      14      16      18
20      22      24      26      28      30      32      34      36
38      40      45      50      55      60      65      70      75
80      85      90      95      100      105      110      115      120
125      130      135      140      145      150      155      160      165
170      175      180      185      190      195      200      205      210
215      220      225      230      235      240      245      250      255
260      265      270      275      280      285      290      295      300
305      310      315      320      325      330      335      340      345
350      360      370      380      390      400];
                SdB_NeedleHyd = [-244.9616 -248.9885 -249.4009 -
250.082 -252.0194 -253.9786 -254.5181 -257.8421 -
260.3204 -253.8374 -256.2626 -253.3638 -
251.6654 -249.5458 -247.6 -246.2 -245.3 -245.6 -245.2 -
246.2 -246.2 -245.9 -245.7 -243.0 -240.8 -240.4 -240.4 -239.5 -
238.7 -238.0 -237.2 -236.8 -237.3 -236.1 -234.4 -234.3 -234.8 -
235.3 -234.9 -234.2 -233.5 -232.5 -232.2 -232.3 -232.4 -232.8 -
233.7 -234.1 -233.9 -232.9 -232.1 -232.1 -232.4 -232.7 -232.7 -

```



```

232.2  -231.7 -231.4 -231.2 -231.2 -231.1 -231.1 -230.9 -230.5 -
230.1  -229.8 -229.5 -229.3 -229.0 -228.8 -228.9 -229.0 -229.1 -
229.0  -229.0 -229.0 -228.9 -228.8 -228.7 -228.7 -228.7 -228.6 -
228.6  -228.7 -228.9 -228.8 -229.2];
    S_Original = 10.^ (SdB_NeedleHyd./20).*1e6; %
result is in V/Pa
    S1 = zeros(L2,1); %
Preallocate the sensitivity vector
    S1(1:ind_min-1) = S_Original(1); %
assign all values before fmin to the mean value
    S1(ind_max+1:end) = S_Original(end); %
assign all values after fmax to the mean value
    for i = ind_min:1:ind_max
        S1(i) = interp1(f1,S_Original,fV(i),'PCHIP');
    end
    S = S1./Loading_Effect;

end
%% Main Calculations
% Preallocation of matrices and vectors (NF is for Non-filtered values)
Vt2 = zeros(L1,NWF);
Vf1 = zeros(L1,NWF);
Vf2_0 = zeros(L2,NWF);
Vf2NF_0 = zeros(L2,NWF);
Vf2 = zeros(L2,NWF);
P2 = zeros(L1,NWF);
P3 = zeros(L1,NWF);
Pt = zeros(L1,NWF);
Pmax0 = zeros(1,NWF);
Prms0 = zeros(1,NWF);
Pmax1 = zeros(1,NWF);
Prms1 = zeros(1,NWF);
P_mean = zeros(1,L1);
P_std = zeros(1,L1);
Vt2NF = zeros(L1,NWF);
Vf1NF = zeros(L1,NWF);
Vf2NF = zeros(L2,NWF);
P2NF = zeros(L1,NWF);
P3NF = zeros(L1,NWF);
PtNF = zeros(L1,NWF);
P_meanNF = zeros(1,L1);
P_stdNF = zeros(1,L1);
Pmax1NF = zeros(1,NWF);
Prms1NF = zeros(1,NWF);
switch Data_Method
    case 1 % Data Acquisition by PicosCope
        tP = linspace(0,round(tV(end)*1000,1),length(tV)); %
t vector (in ms) for plotting P(t), based on t of original data
    case 2 % Data Acquisition by PCI Board
        tP = linspace(0,round(tV(end)*1e6,1)/1000,length(tV)); %
t vector (in ms) for plotting P(t), based on t of original data
end
alpha_t = 0.01*alpha*tP(end); % time (in
ms) for ignoring P(t) values for calculating Pmax
alpha_ind = find(tP>alpha_t,1,'first'); % index of
time for ignoring P(t) values for calculating Pmax
switch Filter_Method
    case 1 % Applying Filter

```

```

switch Noise_Method
    case 1 % Noise subtraction in time domain
        for i=1:NWF
            disp(i)
            Vt2(:,i) =
Noise_Reduction(Vt1(:,i),Noise_up*0.001,Noise_down*0.001); %
Implementing Noise in time domain
            Vt2NF(:,i) =
Vt2(:,i); % NO Filter
            x = Vt2(:,i);
            if (strcmpi(Probe_Class, 'Fibre-Optic
Hydrophone')) % use bandpass filter for FOH and low pass
for other probes
                x_filtered = bandpass(x, [fmin fmax], fs);
%
                x_lp = lowpass(x, fmax,
fs); % use these two lines in case
bandpass filter becomes unstable
%
                x_filtered = highpass(x_lp, fmin, fs);
            else
                x_filtered = filtfilt(sos, g, x);
            end
            Vt2(:,i) =
x_filtered; % WITH Filter

            % With Applying Filter
            K1 =
Vt2(:,i); % Temporary array
            Vf1(:,i) = fft(K1);
            Vf2(:,i) = DS2SS(Vf1(:,i));
            P2(:,i) =
0.001.*SS2DS(Vf2(:,i)./S); % in kPa (P values in
freq domain)
            P3(:,i) =
0.001.*SS2DS2((abs(Vf2(:,i))./S)); % in kPa [positive
values for averaging (P-f)]
            K2 =
P2(:,i); % Temporary array
            Pt(:,i) =
ifft(K2); % in kPa (P values in
time domain)
            if (max(abs(Pt(:,i))) > max(abs(Pt(alpha_ind:end-
alpha_ind,i))))
                Pmax1(i) = max(abs(Pt(alpha_ind:end-
alpha_ind,i))); % Calculate rms and maximum values (ignore
alpha percent at beginning and end)
                Prms1(i) = rms(abs(Pt(alpha_ind:end-alpha_ind,i)));
            else
                Pmax1(i) =
max(abs(Pt(:,i))); % Calculate rms and
maximum values among all values
                Prms1(i) = rms(abs(Pt(:,i)));
            end
            Pmax0(i) =
max(abs(Pt(:,i))); % Calculate rms and
maximum values among all values
            Prms0(i) = rms(abs(Pt(:,i)));

            % Without Applying Filter

```

```

        K3 =
Vt2NF(:,i); % Temporary array
        Vf1NF(:,i) = fft(K3);
        Vf2NF(:,i) = DS2SS(Vf1NF(:,i));
        P2NF(:,i) =
0.001.*SS2DS(Vf2NF(:,i)./S); % in kPa (P values in
freq domain)
        P3NF(:,i) = 0.001.*SS2DS2(abs(Vf2NF(:,i))./S);
        K4 = P2NF(:,i);
        PtNF(:,i) =
ifft(K4); % in kPa (P values in
time domain)
        if (max(abs(PtNF(:,i))) > max(abs(PtNF(alpha_ind:end-
alpha_ind,i))))
            Pmax1NF(i) = max(abs(PtNF(alpha_ind:end-
alpha_ind,i))); % Calculate rms and maximum values (ignore alpha
percent at beginning and end)
            Prms1NF(i) = rms(abs(PtNF(alpha_ind:end-alpha_ind,i)));
        else
            Pmax1NF(i) =
max(abs(PtNF(:,i))); % Calculate rms and
maximum values among all values
            Prms1NF(i) = rms(abs(PtNF(:,i)));
        end
        clear K1 K2 K3 K4 x x_filtered
    end
    case 2 % Noise subtraction in frequency domain
    for i=1:NWF
        disp(i)
        Vt2(:,i) =
Vt1(:,i); % No Noise
        subtraction in time domain
        Vt2NF(:,i) =
Vt2(:,i); % NO filter
        x = Vt2(:,i);
        if (strcmpi(Probe_Class, 'Fibre-Optic
Hydrophone')) % use bandpass filter for FOH and low pass
for other probes
            x_filtered = bandpass(x, [fmin fmax], fs);
        %
            x_lp = lowpass(x, fmax,
fs); % use these two lines in case
bandpass filter becomes unstable
        %
            x_filtered = highpass(x_lp, fmin, fs);
        else
            x_filtered = filtfilt(sos, g, x);
        end
        Vt2(:,i) =
x_filtered; % WITH filter

        % With Applying Filter
        K1 =
Vt2(:,i); % Temporary array
        Vf1(:,i) = fft(K1);
        Vf2_0(:,i) = DS2SS(Vf1(:,i));
        for jj =
1:length(Vf2_0) % Noise
        subtraction in freq domain
            if (real(Vf2_0(jj,i))>=0)

```

```

        real_temp = real(Vf2_0(jj,i))-
abs(real(SS_FT_Noise(jj)));          % Reminder: S_FT_Noise =
DS2SS(FT_Noise);
        if (imag(Vf2_0(jj,i))>=0)
            imag_temp = imag(Vf2_0(jj,i))-
abs(imag(SS_FT_Noise(jj)));
        else
            imag_temp = imag(Vf2_0(jj,i))+
abs(imag(SS_FT_Noise(jj)));
        end
        Vf2(jj,i) = complex (real_temp, imag_temp);
    else
        real_temp = real(Vf2_0(jj,i))+
abs(real(SS_FT_Noise(jj)));
        if (imag(Vf2_0(jj,i))>=0)
            imag_temp = imag(Vf2_0(jj,i))-
abs(imag(SS_FT_Noise(jj)));
        else
            imag_temp = imag(Vf2_0(jj,i))+
abs(imag(SS_FT_Noise(jj)));
        end
        Vf2(jj,i) = complex (real_temp, imag_temp);
    end
end
P2(:,i) =
0.001.*SS2DS(Vf2(:,i)./S);          % in kPa (P values in
freq domain)
P3(:,i) =
0.001.*SS2DS2(abs(Vf2(:,i))./S);     % in kPa [positive
values for averaging (P-f)]
K2 =
P2(:,i);                             % Temporary array
Pt(:,i) =
ifft(K2);                             % in kPa (P values in
time domain)
    if (max(abs(Pt(:,i))) > max(abs(Pt(alpha_ind:end-
alpha_ind,i))))
        Pmax1(i) = max(abs(Pt(alpha_ind:end-
alpha_ind,i))); % Calculate rms and maximum values (ignore
alpha percent at beginning and end)
        Prms1(i) = rms(abs(Pt(alpha_ind:end-alpha_ind,i)));
    else
        Pmax1(i) =
max(abs(Pt(:,i))); % Calculate rms and
maximum values among all values
        Prms1(i) = rms(abs(Pt(:,i)));
    end
    Pmax0(i) =
max(abs(Pt(:,i))); % Calculate rms and
maximum values among all values
    Prms0(i) = rms(abs(Pt(:,i)));

    % Without Applying Filter
    K3 =
Vt2NF(:,i); % Temporary array
    Vf1NF(:,i) = fft(K3);
    Vf2NF_0(:,i) = DS2SS(Vf1NF(:,i));

```

```

        for jj =
1:length(Vf2NF_0)                                % Noise
subtraction in freq domain
        if (real(Vf2NF_0(jj,i))>=0)
%           real_temp = real(Vf2NF_0(jj,i))-
abs(real(SS_FT_NF_Noise(jj)));                % Reminder: S_FT_Noise =
DS2SS(FT_Noise);
            if real(Vf2NF_0(jj,i))>=
abs(real(SS_FT_NF_Noise(jj)))
                real_temp = real(Vf2NF_0(jj,i))-
abs(real(SS_FT_NF_Noise(jj)));                % Reminder: S_FT_Noise =
DS2SS(FT_Noise);
            else
                real_temp = 0;
            end
            if (imag(Vf2NF_0(jj,i))>=0)
%           imag_temp = imag(Vf2NF_0(jj,i))-
abs(imag(SS_FT_NF_Noise(jj)));
            if imag(Vf2NF_0(jj,i))>=
abs(imag(SS_FT_NF_Noise(jj)))
                imag_temp = imag(Vf2NF_0(jj,i))-
abs(imag(SS_FT_NF_Noise(jj)));
            else
                imag_temp = 0;
            end
        else
%           imag_temp = imag(Vf2NF_0(jj,i))+
abs(imag(SS_FT_NF_Noise(jj)));
            if abs(imag(Vf2NF_0(jj,i)))>=
abs(imag(SS_FT_NF_Noise(jj)))
                imag_temp = imag(Vf2NF_0(jj,i))+
abs(imag(SS_FT_NF_Noise(jj)));
            else
                imag_temp = 0;
            end
        end
        Vf2NF(jj,i) = complex (real_temp, imag_temp);
    else
%           real_temp = real(Vf2NF_0(jj,i))+
abs(real(SS_FT_NF_Noise(jj)));
            if abs(real(Vf2NF_0(jj,i)))>=
abs(real(SS_FT_NF_Noise(jj)))
                real_temp = real(Vf2NF_0(jj,i))+
abs(real(SS_FT_NF_Noise(jj)));
            else
                real_temp = 0;
            end
            if (imag(Vf2NF_0(jj,i))>=0)
%           imag_temp = imag(Vf2NF_0(jj,i))-
abs(imag(SS_FT_NF_Noise(jj)));
            if imag(Vf2NF_0(jj,i))>=
abs(imag(SS_FT_NF_Noise(jj)))
                imag_temp = imag(Vf2NF_0(jj,i))-
abs(imag(SS_FT_NF_Noise(jj)));
            else
                imag_temp = 0;
            end
        else

```

```

%
imag_temp = imag(Vf2NF_0(jj,i))+
abs(imag(SS_FT_NF_Noise(jj)));
if abs(imag(Vf2NF_0(jj,i))) >=
abs(imag(SS_FT_NF_Noise(jj)))
imag_temp = imag(Vf2NF_0(jj,i))+
abs(imag(SS_FT_NF_Noise(jj)));
else
imag_temp = 0;
end
end
Vf2NF(jj,i) = complex (real_temp, imag_temp);
end
end
P2NF(:,i) =
0.001.*SS2DS(Vf2NF(:,i)./S); % in kPa (P values in
freq domain)
P3NF(:,i) =
0.001.*SS2DS2(abs(Vf2NF(:,i))./S); % in kPa [positive
values for averaging (P-f)]
K4 = P2NF(:,i);
PtNF(:,i) =
ifft(K4); % in kPa (P values in
time domain)
if (max(abs(PtNF(:,i))) > max(abs(PtNF(alpha_ind:end-
alpha_ind,i))))
Pmax1NF(i) = max(abs(PtNF(alpha_ind:end-
alpha_ind,i))); % Calculate rms and maximum values (ignore alpha
percent at beginning and end)
Prms1NF(i) = rms(abs(PtNF(alpha_ind:end-alpha_ind,i)));
else
Pmax1NF(i) =
max(abs(PtNF(:,i))); % Calculate rms and
maximum values among all values
Prms1NF(i) = rms(abs(PtNF(:,i)));
end
clear K1 K2 K3 K4 x x_filtered
end
end
case 2 % Without Applying Filter
switch Noise_Method
case 1 % Noise subtraction in time domain
for i=1:NWF
disp(i)
Vt2(:,i) =
Noise_Reduction(Vt1(:,i),Noise_up*0.001,Noise_down*0.001); %
Implementing Noise in time domain
K1 =
Vt2(:,i); % Temporary array
Vf1(:,i) = fft(K1);
Vf2(:,i) = DS2SS(Vf1(:,i));
P2(:,i) =
0.001.*SS2DS(Vf2(:,i)./S); % in kPa (P values in
freq domain)
P3(:,i) =
0.001.*SS2DS2(abs(Vf2(:,i))./S); % in kPa [positive
values for averaging (P-f)]
K2 =
P2(:,i); % Temporary array

```

```

        Pt(:,i) =
ifft(K2); % in kPa (P values in
time domain)
        if (max(abs(Pt(:,i))) > max(abs(Pt(alpha_ind:end-
alpha_ind,i))))
            Pmax1(i) = max(abs(Pt(alpha_ind:end-
alpha_ind,i))); % Calculate rms and maximum values (ignore
alpha percent at beginning and end)
            Prms1(i) = rms(abs(Pt(alpha_ind:end-alpha_ind,i)));
        else
            Pmax1(i) =
max(abs(Pt(:,i))); % Calculate rms and
maximum values among all values
            Prms1(i) = rms(abs(Pt(:,i)));
        end
        Pmax0(i) =
max(abs(Pt(:,i))); % Calculate rms and
maximum values among all values
        Prms0(i) = rms(abs(Pt(:,i)));
        clear K1 K2
    end
    case 2 % Noise subtraction in frequency
domain
        for i=1:NWF
            disp(i)
            Vt2(:,i) =
Vt1(:,i); % No Noise
            subtraction in time domain
            K1 =
Vt2(:,i); % Temporary array
            Vf1(:,i) = fft(K1);
            Vf2_0(:,i) = DS2SS(Vf1(:,i));
            for jj =
1:length(Vf2_0) % Noise
subtraction in freq domain
                if (real(Vf2_0(jj,i))>=0)
                    %
                    real_temp = real(Vf2_0(jj,i))-
abs(real(SS_FT_NF_Noise(jj))); % Reminder: S_FT_Noise =
DS2SS(FT_Noise);
                    if real(Vf2_0(jj,i))>=
abs(real(SS_FT_NF_Noise(jj))) % Reminder:
S_FT_Noise = DS2SS(FT_Noise);
                        real_temp = real(Vf2_0(jj,i))-
abs(real(SS_FT_NF_Noise(jj))); % Reminder: S_FT_Noise =
DS2SS(FT_Noise);
                    else
                        real_temp = 0;
                    end
                    if (imag(Vf2_0(jj,i))>=0)
                        %
                        imag_temp = imag(Vf2_0(jj,i))-
abs(imag(SS_FT_NF_Noise(jj)));
                        if imag(Vf2_0(jj,i))>=
abs(imag(SS_FT_NF_Noise(jj)))
                            imag_temp = imag(Vf2_0(jj,i))-
abs(imag(SS_FT_NF_Noise(jj)));
                        else
                            imag_temp = 0;
                        end
                    end
                end
            end
        end
    end
end

```

```

else
%           imag_temp = imag(Vf2_0(jj,i))+
abs(imag(SS_FT_NF_Noise(jj)));
%           if abs(imag(Vf2_0(jj,i))) >=
abs(imag(SS_FT_NF_Noise(jj)))
%           imag_temp = imag(Vf2_0(jj,i))+
abs(imag(SS_FT_NF_Noise(jj)));
%           else
%           imag_temp = 0;
%           end
end
Vf2(jj,i) = complex (real_temp, imag_temp);
else
%           real_temp = real(Vf2_0(jj,i))+
abs(real(SS_FT_NF_Noise(jj)));
%           if abs(real(Vf2_0(jj,i))) >=
abs(real(SS_FT_NF_Noise(jj)))
%           real_temp = real(Vf2_0(jj,i))+
abs(real(SS_FT_NF_Noise(jj)));
%           else
%           real_temp = 0;
%           end
%           if (imag(Vf2_0(jj,i))>=0)
%           imag_temp = imag(Vf2_0(jj,i))-
abs(imag(SS_FT_NF_Noise(jj)));
%           if imag(Vf2_0(jj,i)) >=
abs(imag(SS_FT_NF_Noise(jj)))
%           imag_temp = imag(Vf2_0(jj,i))-
abs(imag(SS_FT_NF_Noise(jj)));
%           else
%           imag_temp = 0;
%           end
else
%           imag_temp = imag(Vf2_0(jj,i))+
abs(imag(SS_FT_NF_Noise(jj)));
%           if abs(imag(Vf2_0(jj,i))) >=
abs(imag(SS_FT_NF_Noise(jj)))
%           imag_temp = imag(Vf2_0(jj,i))+
abs(imag(SS_FT_NF_Noise(jj)));
%           else
%           imag_temp = 0;
%           end
end
Vf2(jj,i) = complex (real_temp, imag_temp);
end
end
P2(:,i) =
0.001.*SS2DS(Vf2(:,i)./S); % in kPa (P values in
freq domain)
P3(:,i) =
0.001.*SS2DS2(abs(Vf2(:,i))./S); % in kPa [positive
values for averaging (P-f)]
K2 =
P2(:,i); % Temporary array
Pt(:,i) =
ifft(K2); % in kPa (P values in
time domain)

```



```

        if (max(abs(Pt(:,i))) > max(abs(Pt(alpha_ind:end-
alpha_ind,i))))
            Pmax1(i) = max(abs(Pt(alpha_ind:end-
alpha_ind,i))); % Calculate rms and maximum values (ignore
alpha percent at beginning and end)
            Prms1(i) = rms(abs(Pt(alpha_ind:end-alpha_ind,i)));
        else
            Pmax1(i) =
max(abs(Pt(:,i))); % Calculate rms and
maximum values among all values
            Prms1(i) = rms(abs(Pt(:,i)));
        end
        Pmax0(i) =
max(abs(Pt(:,i))); % Calculate rms and
maximum values among all values
        Prms0(i) = rms(abs(Pt(:,i)));
        clear K1 K2
    end
end
end
%% Display the input information
switch Probe_Class
    case 'Cavitometer'
        switch ProbeType
            case 'Probe4'
                VarNames = {'Probe_Class','Probe_Type','Probe_Position'};
                DispData1 = {Probe_Class, ProbeType, Cavitometer_position};
                T = cell2table(DispData1,'VariableNames',VarNames);disp(T)
            end
        case 'Fibre-Optic Hydrophone'
            VarNames = {'Probe_Class','Probe_Type'};
            DispData1 = {Probe_Class, ProbeType};
            T = cell2table(DispData1,'VariableNames',VarNames);disp(T)
        case 'Needle Hydrophone'
            VarNames = {'Probe_Class','Probe_Type'};
            DispData1 = {Probe_Class, ProbeType};
            T = cell2table(DispData1,'VariableNames',VarNames);disp(T)
        end
    end
    clear VarNames DispData1 T
%% Finding the Max and RMS Pressure
switch Filter_Method
    case 1 % With Applying Filter
        % Replacing the first index (f=0) with the next index to remove
the peak at f=0
        P2(1,:) = P2(2,:);
        P3(1,:) = P3(2,:);
        format short g
        % P_max and RMS values with applying filter
        Pmax = mean (Pmax1); %
    P_max
        Pmax_std = std (Pmax1); %
    std of P_max
        Prms = mean (Prms1); %
    RMS
        Prms_std = std (Prms1); %
    std of RMS

```

```

        PmaxNS          = mean (Pmax0);                                %
P_max      (without ignoring alpha percent at beginning and end)
        PmaxNS_std      = std  (Pmax0);                                %
std of P_max (without ignoring alpha percent at beginning and end)
        PrmsNS          = mean (Prms0);                                %
RMS        (without ignoring alpha percent at beginning and end)
        PrmsNS_std      = std  (Prms0);                                %
std of RMS  (without ignoring alpha percent at beginning and end)
        % P_max and RMS values without applying filter
        PmaxNF          = mean (Pmax1NF);                              %
P_max without filter
        PmaxNF_std      = std  (Pmax1NF);
        PrmsNF          = mean (Prms1NF);                              %
RMS without filter
        PrmsNF_std      = std  (Prms1NF);
        disp('Units are in kPa');
        fprintf('\n')
        if(alpha~=0)
            disp('Comparing the results: with and without skipping the
peaks at two ends');
            fprintf('\n')
            VarNames =
{'Pmax','Pmax_NoSkip','RMS','RMS_NoSkip','Std_Max','Std_Max_NoSkip','Std_RMS','Std_RMS_NoSkip'};
            DispData1 = [Pmax PmaxNS Prms PrmsNS Pmax_std PmaxNS_std
Prms_std PrmsNS_std];
            T =
table(DispData1(1),DispData1(2),DispData1(3),DispData1(4),DispData1(5),
DispData1(6),DispData1(7),DispData1(8),'VariableNames',VarNames);disp(T)
        )
            clear VarNames DispData1 T
        end
        if(Filter_Method == 1)
            disp('Comparing the results: with and without filtering');
            fprintf('\n')
            VarNames =
{'Pmax','Pmax_NoFilter','RMS','RMS_NoFilter','Std_Max','Std_RMS'};
            DispData1 = [Pmax PmaxNF Prms PrmsNF Pmax_std Prms_std];
            T =
table(DispData1(1),DispData1(2),DispData1(3),DispData1(4),DispData1(5),
DispData1(6),'VariableNames',VarNames);disp(T)
            clear VarNames DispData1 T
        end
        disp('Final Results');
        fprintf('\n')
        VarNames = {'Pmax','RMS','Std_Max','Std_RMS'};
        DispData1 = [Pmax Prms Pmax_std Prms_std];
        T =
table(DispData1(1),DispData1(2),DispData1(3),DispData1(4),'VariableName
s',VarNames);disp(T)
        case 2 % Without Applying Filter
            format short g
            % P_max and RMS values with applying filter
            Pmax          = mean (Pmax1);                                %
P_max
            Pmax_std      = std  (Pmax1);                                % std
of P_max
            Prms          = mean (Prms1);                                % RMS

```

```

        Prms_std      = std (Prms1);                                % std
of RMS
        PmaxNS        = mean (Pmax0);                                %
P_max      (without ignoring alpha percent at beginning and end)
        PmaxNS_std    = std (Pmax0);                                % std
of P_max (without ignoring alpha percent at beginning and end)
        PrmsNS        = mean (Prms0);                                % RMS
        (without ignoring alpha percent at beginning and end)
        PrmsNS_std    = std (Prms0);                                % std
of RMS      (without ignoring alpha percent at beginning and end)
        disp('Units are in kPa');
        if(alpha~=0)
            disp('Comparing with and without skipping the peaks at two
ends');
            fprintf('\n')
            VarNames =
{'Pmax','Pmax_NoSkip','RMS','RMS_NoSkip','Std_Max','Std_Max_NoSkip','Std_RMS',
'Std_RMS_NoSkip'};
            DispData1 = [Pmax PmaxNS Prms PrmsNS Pmax_std PmaxNS_std
Prms_std PrmsNS_std];
            T =
table(DispData1(1),DispData1(2),DispData1(3),DispData1(4),DispData1(5),
DispData1(6),DispData1(7),DispData1(8),'VariableNames',VarNames);disp(T
)
            end
            clear VarNames DispData1 T
            disp('Final Results');
            fprintf('\n')
            clear VarNames DispData1 T
            VarNames = {'Pmax','RMS','Std_Max','Std_RMS'};
            DispData1 = [Pmax Prms Pmax_std Prms_std];
            T =
table(DispData1(1),DispData1(2),DispData1(3),DispData1(4),'VariableName
s',VarNames);disp(T)
        end
%% Calculate mean of Voltage and Pressure to plot in Freq domain (P-f)
switch Filter_Method
    case 1 % With Applying Filter
        for i=1:L1
            % With Applying Filter
            P_mean(i) = mean ((P3(i,:)))./L1;
            P_std(i) = std ((P3(i,:)))./L1;
            % Without Applying Filter
            P_meanNF(i) = mean ((P3NF(i,:)))./L1;
            P_stdNF(i) = std ((P3NF(i,:)))./L1;
        end
    case 2 % Without Applying Filter
        for i=1:L1
            P_mean(i) = mean ((P3(i,:)))./L1;
            P_std(i) = std ((P3(i,:)))./L1;
        end
    end
end
fV_kHz = 0.001.*fV;                                % in
kHz (whole range of freq)
f_kHz = fV_kHz(ind_min:ind_max)';                    % in
kHz (only calibrated range)
P_kPa = P_mean(ind_min:ind_max)';                    %
Averaged P (kPa) values (in f domain) only in calibrated range

```

```

%% Save data
% save (['Result_' format1 ],'-v7.3','-nocompression');
Pt1 = Pt(:,1); % Save
the P(t) of the first waveform by default
if strcmpi(Save_Data, 'Yes')
    switch Filter_Method
        case 1
            save (['Result_' format1 ],'-
regexp','^(?! (Vf2_0|Vf2NF_0|Vf2|P2|P3|Vt2NF|Vf1NF|Vf2NF|P2NF|P3NF|Pt|Pt
NF|Vt1|Vt2|tV|M|))$).');
%
            save (['Result_' format1 ],'-
regexp','^(?! (Vf1|Vf2_0|Vf2NF_0|Vf2|P2|P3|Vt2NF|Vf1NF|Vf2NF|P2NF|P3NF|P
tNF|Vt1|Vt2|tV|M|))$).'); % use this one if you want to save P(t) of
all waveforms (huge data file size)
        case 2
            save (['Result_' format1 ],'-
regexp','^(?! (Vf2_0|Vf2|P2|P3|Vt1|Vt2|tV|M|))$).');
    end
end
%% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% Plots: All plots on different tabs on ONE
window without saving %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%% Plots: Sensitivity
set(0, 'DefaultFigureWindowStyle', 'docked');
if strcmpi(Probe_Class, 'Fibre-Optic Hydrophone')
    switch Data_Method
        case 1 % Data Acquisition by PicosCope
            figure('Name','S','NumberTitle','off'),plot(1e-
6.*fV(ind_min:ind_max),S(ind_min:ind_max),'-
b','linewidth',Line_thickness);box
on;set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_thi
ckness);set(gcf,'units','normalized','outerposition',[0 0 1
1]);xlabel('$ f \setminus \rm
(MHz)$','interpreter','latex','fontsize',font_size2,'fontweight','bold'
,'Color',[0 0 1]),ylabel('$ S \setminus (V \setminus \rm Pa)
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0
1]);title(format1,'interpreter','none','fontsize',font_size,'fontweight
','bold','Color',[0 0 0]);
            hold on; plot(1e-
6.*f1,S_Original,'sr','linewidth',Line_thickness,'MarkerSize',16,'Marke
rEdgeColor','red','MarkerFaceColor','red');hold off
        case 2 % Data Acquisition by PCI Board
            figure('Name','S','NumberTitle','off'),plot(1e-
6.*fV(ind_min:ind_max),S(ind_min:ind_max),'-
b','linewidth',Line_thickness);box
on;set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_thi
ckness);set(gcf,'units','normalized','outerposition',[0 0 1
1]);xlabel('$ f \setminus \rm
(MHz)$','interpreter','latex','fontsize',font_size2,'fontweight','bold'
,'Color',[0 0 1]),ylabel('$ S \setminus (V \setminus \rm Pa)
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0
1]);title(format1,'interpreter','none','fontsize',font_size,'fontweight
','bold','Color',[0 0 0]);
            hold on; plot(1e-
6.*f1,S_Original_Selected,'sr','linewidth',Line_thickness,'MarkerSize',
16,'MarkerEdgeColor','red','MarkerFaceColor','red');hold off
    end

```

```

else
    figure('Name','S','NumberTitle','off'),plot(1e-
3.*fV(ind_min:ind_max),S(ind_min:ind_max),'-
b','linewidth',Line_thickness);box
on;set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_thi
ckness);set(gcf,'units','normalized','outerposition',[0 0 1
1]);xlabel('$ f\ \rm
(kHz)$','interpreter','latex','fontsize',font_size2,'fontweight','bold'
,'Color',[0 0 1]),ylabel('$ S\ (V/\rm Pa)
$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0
1]);title(format1,'interpreter','none','fontsize',font_size,'fontweight
','bold','Color',[0 0 0]);
    hold on; plot(1e-
3.*f1,S_Original,'sr','linewidth',Line_thickness,'MarkerSize',16,'Marke
rEdgeColor','red','MarkerFaceColor','red');hold off
end

% while (1)
% answer = questdlg('Do you want to plot the
results?','Plotting','Yes','No','No');
% if strcmpi(answer, 'No')
%     break
% end
% prompt = inputdlg('Which waveform do you want to plot?');
% WF_Number = str2double(prompt{1});
WF_Number = 1;
% Plot V-t
switch Filter_Method
    case 1
        % Applying Filter
        figure('Name','V-t','NumberTitle','off'),
        subplot(2, 1, 1)
        plot(1000.*tV, 1000.*Vt1(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}
$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ V\ {\rm(mV)}
$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title('Original
Signal','fontsize',font_size,'fontweight','bold','Color',[0 0 0]);
        xlim([0 tV(end)*1000]);
        subplot(2, 1, 2)
        plot(1000.*tV, 1000.*Vt2NF(:,WF_Number),'-
b','linewidth',Line_thickness); box on
        set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}
$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ V\ {\rm(mV)}
$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title('Signal with Noise
Subtraction','fontsize',font_size,'fontweight','bold','Color',[0 0 0]);
        xlim([0 tV(end)*1000]);
        figure('Name','V-t2','NumberTitle','off'),plot(1000.*tV,
1000.*Vt2NF(:,WF_Number),'-b','linewidth',Line_thickness); box on; hold
on

```

```

        plot(1000.*tV, 1000.*Vt2(:,WF_Number) , '-
r','linewidth',Line_thickness);
        set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t \ {\rm ms})$
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ V \ {\rm mV})$
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1, ' (WF ' num2str(WF_Number),')'],
'Interpreter', 'none','Color',[0 0
0]),'fontsize',font_size,'fontweight','bold')
        xlim([0 tV(end)*1000]);
        legend ('No Filter','With Filter')
    case 2 % No Filter
        figure('Name','V-t','NumberTitle','off'),
        subplot(2, 1, 1)
        plot(1000.*tV, 1000.*Vt1(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t \ {\rm ms})$
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ V \ {\rm mV})$
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title('Original
Signal','fontsize',font_size,'fontweight','bold','Color',[0 0 0]);
        xlim([0 tV(end)*1000]);
        subplot(2, 1, 2)
        plot(1000.*tV, 1000.*Vt2(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t \ {\rm ms})$
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ V \ {\rm mV})$
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title('Signal with Noise
Subtraction','fontsize',font_size,'fontweight','bold','Color',[0 0 0]);
        xlim([0 tV(end)*1000]);
    end
    % Plots: Pmax-N, RMS-N
    if (Data_Method == 1)
        figure('Name','Pmax','NumberTitle','off'),plot(1:NWF,Pmax1,'-
sb','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ \rm Waveform$
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P_{\rm max} \ (\rm
kPa)$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold',
'Color',[0 0 1]);title(format1, 'Interpreter', 'none' , 'Color',[0 0
0]),'fontsize',font_size,'fontweight','bold')
        if(alpha~=0)
            figure('Name','Pmax2','NumberTitle','off'),plot(1:NWF,Pmax1,'-
sb','linewidth',Line_thickness); box on; hold on
            plot(1:NWF,Pmax0,'-
sr','linewidth',Line_thickness);set(gcf,'units','normalized','outerposi
tion',[0 0 1

```

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1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ \rm Waveform
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$P_{\rm max} \ (\rm
kPa)$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold',
'Color',[0 0 1]);title(format1, 'Interpreter', 'none' , 'Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
    legend ('With Skipping','No Skipping')
end

    figure('Name','RMS','NumberTitle','off'),plot(1:NWF,Prms1,'-
sb','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ \rm Waveform
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$P_{\rm RMS} \ (\rm
kPa)$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold',
'Color',[0 0 1]);title(format1, 'Interpreter', 'none' , 'Color',[0 0
0],'fontsize',font_size,'fontweight','bold')

    if(alpha~=0)
        figure('Name','RMS2','NumberTitle','off'),plot(1:NWF,Prms1,'-
sb','linewidth',Line_thickness); box on; hold on
        plot(1:NWF,Prms0,'-
sr','linewidth',Line_thickness);set(gcf,'units','normalized','outerposi
tion',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ \rm Waveform
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$P_{\rm RMS} \ (\rm
kPa)$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold',
'Color',[0 0 1]);title(format1, 'Interpreter', 'none' , 'Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
        legend ('With Skipping','No Skipping')
    end
end
% Plots: P-f
if strcmpi(Probe_Class, 'Fibre-Optic Hydrophone')
    figure('Name','P-f','NumberTitle','off'),plot(fV_kHz/1000,
P_mean,'-b','linewidth',Line_thickness);box
on;set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_thi
ckness);set(gcf,'units','normalized','outerposition',[0 0 1
1]);xlabel('$ f \ \rm
(MHz)$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold'
, 'Color',[0 0 1]),ylabel('$P_{\rm mean} \ (\rm
kPa)$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold',
'Color',[0 0 1]);title(format1, 'Interpreter', 'none', 'Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
    xlim([fmin/1e6 fmax/1e6]);
else
    figure('Name','P-f','NumberTitle','off'),plot(fV_kHz, P_mean,'-
b','linewidth',Line_thickness);box
on;set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_thi
ckness);set(gcf,'units','normalized','outerposition',[0 0 1
1]);xlabel('$ f \ \rm
(kHz)$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold'
, 'Color',[0 0 1]),ylabel('$P_{\rm mean} \ (\rm

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kPa)$','interpreter','latex','fontsize',font_size2,'fontweight','bold',
'Color',[0 0 1]);title(format1, 'Interpreter', 'none','Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
    xlim([fmin/1000 fmax/1000]);
end
% Compare P-f of filtered and non-filtered plots (without saving and
with wider x range)
switch Filter_Method
    case 1
        if strcmpi(Probe_Class, 'Fibre-Optic Hydrophone')
            figure('Name','P-f2','NumberTitle','off'),plot(fV_kHz/1000,
P_mean,'-b','linewidth',Line_thickness); box on; hold on
            plot(fV_kHz/1000, P_meanNF,'-
r','linewidth',Line_thickness);set(gca,'fontweight','bold','fontsize',f
ont_size,'LineWidth',box_thickness);set(gcf,'units','normalized','outer
position',[0 0 1 1]);xlabel('$ f \ \rm
(MHz)$','interpreter','latex','fontsize',font_size2,'fontweight','bold'
,'Color',[0 0 1]),ylabel('$P_{\rm mean} \ \rm
kPa)$','interpreter','latex','fontsize',font_size2,'fontweight','bold',
'Color',[0 0 1]);title(format1, 'Interpreter', 'none','Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
            xlim([-10 2*fmax/1e6]);legend ('With Filter','No Filter')
        else
            figure('Name','P-f2','NumberTitle','off'),plot(fV_kHz,
P_mean,'-b','linewidth',Line_thickness); box on; hold on
            plot(fV_kHz, P_meanNF,'-
r','linewidth',Line_thickness);set(gca,'fontweight','bold','fontsize',f
ont_size,'LineWidth',box_thickness);set(gcf,'units','normalized','outer
position',[0 0 1 1]);xlabel('$ f \ \rm
(kHz)$','interpreter','latex','fontsize',font_size2,'fontweight','bold'
,'Color',[0 0 1]),ylabel('$P_{\rm mean} \ \rm
kPa)$','interpreter','latex','fontsize',font_size2,'fontweight','bold',
'Color',[0 0 1]);title(format1, 'Interpreter', 'none','Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
            xlim([-10 2*fmax/1000]);legend ('With Filter','No Filter')
        end
    end
end
if (NWF >= 6)
    figure('Name','P-f3','NumberTitle','off'),hold on
    for i=1:6
        if strcmpi(Probe_Class, 'Fibre-Optic Hydrophone')
            subplot(3, 2, i)
            WF_Number= i;plot(fV_kHz./1000, P3(:,WF_Number)./L1,'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ f \ \rm
(MHz)$','interpreter','latex','fontsize',font_size2,'fontweight','bold'
,'Color',[0 0 1]),ylabel('$P \ \rm
kPa)$','interpreter','latex','fontsize',font_size2,'fontweight','bold',
'Color',[0 0 1]);title([format1, ' (WF ' num2str(WF_Number),')'],
'Interpreter', 'none','Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
            xlim([fmin/1e6 fmax/1e6]);
        else
            subplot(3, 2, i)
            WF_Number= i;plot(fV_kHz, P3(:,WF_Number)./L1,'-
b','linewidth',Line_thickness);box

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on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ f\ \rm
(kHz)$','interpreter','latex','fontsize',font_size2,'fontweight','bold'
,'Color',[0 0 1]),ylabel('$ P\ \rm
(kPa)$','interpreter','latex','fontsize',font_size2,'fontweight','bold'
,'Color',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),'')'],
'Interpreter','none','Color',[0 0
0]),'fontsize',font_size,'fontweight','bold')
    xlim([fmin/1000 fmax/1000]);
    end
    end
end
% Plots: V-f
figure('Name','V-f','NumberTitle','off'),
WF_Number = 1;
subplot(2, 1, 1)
plot(tV.*1000, 1000.*Vt2(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ \rm(ms)
$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ V\ \rm(mV)
$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),'')'],
'Interpreter','none','Color',[0 0
0]),'fontsize',font_size,'fontweight','bold')
xlim([0 tP(end)]);
subplot(2, 1, 2)
plot(fV_kHz, abs(Vf1(:,WF_Number)).*1000,'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ f\ \rm
(kHz)$','interpreter','latex','fontsize',font_size2,'fontweight','bold'
,'Color',[0 0 1]),ylabel('$ FFT
(V(t))$','interpreter','latex','fontsize',font_size2,'fontweight','bold'
,'Color',[0 0 1]);
xlim([fmin/1000 fmax/1000]);
% Plots: P-t
figure('Name','P-t','NumberTitle','off'),plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ \rm(ms)
$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P\ \rm(kPa)
$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),'')'],
'Interpreter','none','Color',[0 0
0]),'fontsize',font_size,'fontweight','bold')
% Compare P-t of filtered and non-filtered plots
switch Filter_Method
    case 1
        figure('Name','P-
t2','NumberTitle','off'),plot(tP,PtNF(:,WF_Number),'-
b','linewidth',Line_thickness); box on; hold on;

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        plot(tP,Pt(:,WF_Number),'-
r','linewidth',Line_thickness);set(gcf,'units','normalized','outerposit
ion',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P\ {\rm(kPa)}
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),')'],
'Interpreter','none','Color',[0 0
0],'fontsize',font_size,'fontweight','bold');
        legend ('No Filter','With Filter')
end
% save P-t of all waveforms in 5 subplots (4x3)
if (Data_Method == 1)
font_size = 10;font_size2 = 13;box_thickness = 3;Line_thickness = 1;
if (NWF <= 12)
    figure('Name','P-t3','NumberTitle','off'),
    for i = 1:NWF
        subplot(4, 3, i)
        WF_Number= i;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness); box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P\ {\rm(kPa)}
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),')'],
'Interpreter','none','Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
        end
    elseif (NWF > 12 && NWF <= 24)
        figure('Name','P-t3','NumberTitle','off'),
        for i = 1:12
            subplot(4, 3, i)
            WF_Number= i;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness); box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P\ {\rm(kPa)}
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),')'],
'Interpreter','none','Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
            end
        figure('Name','P-t4','NumberTitle','off'),
        for i = 1:NWF-12
            subplot(4, 3, i)
            WF_Number= i+12;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness); box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P\ {\rm(kPa)}

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$', 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold', 'Col
or', [0 0 1]);title([format1, ' (WF ' num2str(WF_Number), ')'],
'Interpreter', 'none', 'Color', [0 0
0], 'fontsize', font_size, 'fontweight', 'bold')
end
elseif (NWF > 24 && NWF <= 36)
    figure('Name', 'P-t3', 'NumberTitle', 'off'),
    for i = 1:12
        subplot(4, 3, i)
        WF_Number= i;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness); box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}$ ', 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold', 'Col
or', [0 0 1]),ylabel('$ P\ {\rm(kPa)}$ ', 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold', 'Col
or', [0 0 1]);title([format1, ' (WF ' num2str(WF_Number), ')'],
'Interpreter', 'none', 'Color', [0 0
0], 'fontsize', font_size, 'fontweight', 'bold')
end
    figure('Name', 'P-t4', 'NumberTitle', 'off'),
    for i = 1:12
        subplot(4, 3, i)
        WF_Number= i+12;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness); box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}$ ', 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold', 'Col
or', [0 0 1]),ylabel('$ P\ {\rm(kPa)}$ ', 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold', 'Col
or', [0 0 1]);title([format1, ' (WF ' num2str(WF_Number), ')'],
'Interpreter', 'none', 'Color', [0 0
0], 'fontsize', font_size, 'fontweight', 'bold')
end
    figure('Name', 'P-t5', 'NumberTitle', 'off'),
    for i = 1:NWF-24
        subplot(4, 3, i)
        WF_Number= i+24;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}$ ', 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold', 'Col
or', [0 0 1]),ylabel('$ P\ {\rm(kPa)}$ ', 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold', 'Col
or', [0 0 1]);title([format1, ' (WF ' num2str(WF_Number), ')'],
'Interpreter', 'none', 'Color', [0 0
0], 'fontsize', font_size, 'fontweight', 'bold')
end
elseif (NWF > 36 && NWF <= 48)
    figure('Name', 'P-t3', 'NumberTitle', 'off'),
    for i = 1:12
        subplot(4, 3, i)
        WF_Number= i;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1

```

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1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P\ {\rm(kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),'')'],
'Interpreter','none','Color',[0 0
0]),'fontsize',font_size,'fontweight','bold')
end
figure('Name','P-t4','NumberTitle','off'),
for i = 1:12
    subplot(4, 3, i)
    WF_Number= i+12;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P\ {\rm(kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),'')'],
'Interpreter','none','Color',[0 0
0]),'fontsize',font_size,'fontweight','bold')
end
figure('Name','P-t5','NumberTitle','off'),
for i = 1:12
    subplot(4, 3, i)
    WF_Number= i+24;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P\ {\rm(kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),'')'],
'Interpreter','none','Color',[0 0
0]),'fontsize',font_size,'fontweight','bold')
end
figure('Name','P-t6','NumberTitle','off'),
for i = 1:NWF-36
    subplot(4, 3, i)
    WF_Number= i+36;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P\ {\rm(kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),'')'],
'Interpreter','none','Color',[0 0
0]),'fontsize',font_size,'fontweight','bold')
end
elseif (NWF > 48 && NWF <= 60)
    figure('Name','P-t3','NumberTitle','off'),
    for i = 1:12
        subplot(4, 3, i)

```

```

        WF_Number= i;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t \ {\rm (ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P \ {\rm (kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),')'],
'Interpreter','none','Color',[0 0
0]),'fontsize',font_size,'fontweight','bold')
    end
    figure('Name','P-t4','NumberTitle','off'),
    for i = 1:12
        subplot(4, 3, i)
        WF_Number= i+12;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t \ {\rm (ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P \ {\rm (kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),')'],
'Interpreter','none','Color',[0 0
0]),'fontsize',font_size,'fontweight','bold')
    end
    figure('Name','P-t5','NumberTitle','off'),
    for i = 1:12
        subplot(4, 3, i)
        WF_Number= i+24;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t \ {\rm (ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P \ {\rm (kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),')'],
'Interpreter','none','Color',[0 0
0]),'fontsize',font_size,'fontweight','bold')
    end
    figure('Name','P-t6','NumberTitle','off'),
    for i = 1:12
        subplot(4, 3, i)
        WF_Number= i+36;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t \ {\rm (ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P \ {\rm (kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),')'],
'Interpreter','none','Color',[0 0
0]),'fontsize',font_size,'fontweight','bold')
    end
    figure('Name','P-t7','NumberTitle','off'),

```

```

        for i = 1:NWF-48
            subplot(4, 3, i)
            WF_Number= i+48;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P\ {\rm(kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),')'],
'Interpreter','none','Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
        end
    end
end
marker_font = 24;font_size = 20;font_size2 = 24;box_thickness =
3;Line_thickness = 1;
%% %%%%%%%%% Plots: All plots on separate windows FOR
saving %%%%%%%%%
% set(0, 'DefaultFigureWindowStyle', 'normal');
if strcmpi(Save_Plots, 'Yes')
% while (1)
% answer = questdlg('Do you want to plot the
results?','Plotting','Yes','No','No');
% if strcmpi(answer, 'No')
%     break
% end
% prompt = inputdlg('Which waveform do you want to plot?');
% WF_Number = str2double(prompt{1});
WF_Number = 1;
% Plot V-t
switch Filter_Method
    case 1
        % Applying Filter
        figure,
        plot(1000.*tV, 1000.*Vt2NF(:,WF_Number),'-
b','linewidth',Line_thickness);box on; hold on
        plot(1000.*tV, 1000.*Vt2(:,WF_Number) ,'-
r','linewidth',Line_thickness);set(gcf,'units','normalized','outerposit
ion',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ V\ {\rm(mV)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),')'],
'Interpreter','none','Color',[0 0
0],'fontsize',font_size,'fontweight','bold');legend ('No Filter','With
Filter');
        xlim([0 tV(end)*1000]);
        export_fig(sprintf(['V-t_',format1]),'-jpg','-transparent','-
m3');
    case 2
        % Without Applying Filter
        figure,
end
% Plots: Pmax-N, RMS-N
hold off
if (Data_Method == 1)

```

```

        plot(1:NWF,Pmax1,'-sb','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ \rm Waveform
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$P_{\rm max} \ (\rm
kPa)$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold',
'Color',[0 0 1]);title(format1, 'Interpreter', 'none' , 'Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
        export_fig(sprintf(['Pmax-N_',format1]),'-jpg','-transparent','-
m3')
        hold off,
        if(alpha~=0)
            plot(1:NWF,Pmax1,'-sb','linewidth',Line_thickness); box on;
hold on
            plot(1:NWF,Pmax0,'-
sr','linewidth',Line_thickness);set(gcf,'units','normalized','outerposi
tion',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ \rm Waveform
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$P_{\rm max} \ (\rm
kPa)$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold',
'Color',[0 0 1]);title(format1, 'Interpreter', 'none' , 'Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
            legend ('With Skipping','No Skipping')
            export_fig(sprintf(['Pmax-N_',format1,'_2']),'-jpg','-
transparent','-m3')
            hold off,
            end
            plot(1:NWF,Prms1,'-sb','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ \rm Waveform
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$P_{\rm RMS} \ (\rm
kPa)$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold',
'Color',[0 0 1]);title(format1, 'Interpreter', 'none' , 'Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
            export_fig(sprintf(['Prms-N_',format1]),'-jpg','-transparent','-
m3')
            hold off,
            if(alpha~=0)
                plot(1:NWF,Prms1,'-sb','linewidth',Line_thickness); box on;
hold on
                plot(1:NWF,Prms0,'-
sr','linewidth',Line_thickness);set(gcf,'units','normalized','outerposi
tion',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ \rm Waveform
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$P_{\rm RMS} \ (\rm
kPa)$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold',
'Color',[0 0 1]);title(format1, 'Interpreter', 'none' , 'Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
                legend ('With Skipping','No Skipping')
                export_fig(sprintf(['Prms-N_',format1,'_2']),'-jpg','-
transparent','-m3')

```

```

        hold off,
    end
end
% Plots: P-f
if strcmpi(Probe_Class, 'Fibre-Optic Hydrophone')
    hold off,
    plot(fV_kHz/1000, P_mean, '-b', 'linewidth', Line_thickness); box
on; set(gca, 'fontweight', 'bold', 'fontsize', font_size, 'LineWidth', box_thi
ckness); set(gcf, 'units', 'normalized', 'outerposition', [0 0 1
1]); xlabel('$ f \ \rm
(MHz)$', 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold'
, 'Color', [0 0 1]), ylabel('$P_{\rm mean} \ \ (\rm
kPa)$', 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold',
'Color', [0 0 1]); title(format1, 'Interpreter', 'none', 'Color', [0 0
0], 'fontsize', font_size, 'fontweight', 'bold')
    xlim([fmin/1e6 fmax/1e6]);
    export_fig(sprintf(['P-f_', format1]), '-jpg', '-transparent', '-m3')
else
    hold off,
    plot(fV_kHz, P_mean, '-b', 'linewidth', Line_thickness); box
on; set(gca, 'fontweight', 'bold', 'fontsize', font_size, 'LineWidth', box_thi
ckness); set(gcf, 'units', 'normalized', 'outerposition', [0 0 1
1]); xlabel('$ f \ \rm
(kHz)$', 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold'
, 'Color', [0 0 1]), ylabel('$P_{\rm mean} \ \ (\rm
kPa)$', 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold',
'Color', [0 0 1]); title(format1, 'Interpreter', 'none', 'Color', [0 0
0], 'fontsize', font_size, 'fontweight', 'bold')
    xlim([fmin/1000 fmax/1000]);
    export_fig(sprintf(['P-f_', format1]), '-jpg', '-transparent', '-m3')
end
% if (NWF >= 6)
%     hold off,
%     for i=1:6
%         if strcmpi(Probe_Class, 'Fibre-Optic Hydrophone')
%             subplot(3,2,i)
%             WF_Number= i; plot(fV_kHz./1000, P3(:,WF_Number)./L1, '-
b', 'linewidth', Line_thickness); box
on; set(gcf, 'units', 'normalized', 'outerposition', [0 0 1
1]); set(gca, 'fontweight', 'bold', 'fontsize', font_size, 'LineWidth', box_thi
ckness); xlabel('$ f \ \rm
(MHz)$', 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold'
, 'Color', [0 0 1]), ylabel('$P \ \ (\rm
kPa)$', 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold',
'Color', [0 0 1]); title([format1, ' (WF ' num2str(WF_Number), ')'],
'Interpreter', 'none', 'Color', [0 0
0], 'fontsize', font_size, 'fontweight', 'bold')
%             xlim([fmin/1e6 fmax/1e6]);
%         else
%             subplot(3,2,i)
%             WF_Number= i; plot(fV_kHz, P3(:,WF_Number)./L1, '-
b', 'linewidth', Line_thickness); box
on; set(gcf, 'units', 'normalized', 'outerposition', [0 0 1
1]); set(gca, 'fontweight', 'bold', 'fontsize', font_size, 'LineWidth', box_thi
ckness); xlabel('$ f \ \rm
(kHz)$', 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold'
, 'Color', [0 0 1]), ylabel('$P \ \ (\rm
kPa)$', 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold',

```



```

'Color',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),' )'],
'Interpreter','none','Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
%       xlim([fmin/1000 fmax/1000]);
%       end
%       end
%       export_fig(sprintf(['P-f_',format1,'_1']),'-jpg','-
transparent','-m3');close
% end
% Plots: P-t
WF_Number = 1;
% figure,
plot(tP,Pt(:,WF_Number),'-b','linewidth',Line_thickness); box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t \ {\rm(ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P \ {\rm(kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),' )'],
'Interpreter','none','Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
export_fig(sprintf(['P-t_',format1]),'-jpg','-transparent','-m3')

% Compare P-t of filtered and non-filtered plots
switch Filter_Method
case 1
hold off,
plot(tP,PtNF(:,WF_Number),'-b','linewidth',Line_thickness);box on;
hold on;
plot(tP,Pt(:,WF_Number),'-
r','linewidth',Line_thickness);set(gcf,'units','normalized','outerposit
ion',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t \ {\rm(ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P \ {\rm(kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),' )'],
'Interpreter','none','Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
legend('No Filter','With Filter')
export_fig(sprintf(['P-t_',format1,'_0']),'-jpg','-transparent','-m3')
end
% save P-t of all waveforms in 5 subplots (4x3)
if (Data_Method == 1)
font_size = 10;font_size2 = 13;box_thickness = 3;Line_thickness = 1;
if (NWF <= 12)
    hold off,
    for i = 1:NWF
        subplot(4,3,i)
        WF_Number=i;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t \ {\rm(ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P \ {\rm(kPa)}$')

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```

$, 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold', 'Col
or', [0 0 1]);title([format1, ' (WF ' num2str(WF_Number), ')'],
'Interpreter', 'none', 'Color', [0 0
0], 'fontsize', font_size, 'fontweight', 'bold')
end
export_fig(sprintf(['P-t_', format1, '_1']), '-jpg', '-transparent', '-
m3');close
elseif (NWF > 12 && NWF <= 24)
    hold off,
    for i = 1:12
        subplot(4,3,i)
        WF_Number= i;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t \ {\rm(ms)}')
$, 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold', 'Col
or', [0 0 1]),ylabel('$ P \ {\rm(kPa)}')
$, 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold', 'Col
or', [0 0 1]);title([format1, ' (WF ' num2str(WF_Number), ')'],
'Interpreter', 'none', 'Color', [0 0
0], 'fontsize', font_size, 'fontweight', 'bold')
end
export_fig(sprintf(['P-t_', format1, '_1']), '-jpg', '-transparent', '-
m3');close
figure,
for i = 1:NWF-12
    subplot(4,3,i)
    WF_Number= i+12;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t \ {\rm(ms)}')
$, 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold', 'Col
or', [0 0 1]),ylabel('$ P \ {\rm(kPa)}')
$, 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold', 'Col
or', [0 0 1]);title([format1, ' (WF ' num2str(WF_Number), ')'],
'Interpreter', 'none', 'Color', [0 0
0], 'fontsize', font_size, 'fontweight', 'bold')
end
export_fig(sprintf(['P-t_', format1, '_2']), '-jpg', '-transparent', '-
m3');close
elseif (NWF > 24 && NWF <= 36)
    hold off,
    for i = 1:12
        subplot(4,3,i)
        WF_Number= i;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t \ {\rm(ms)}')
$, 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold', 'Col
or', [0 0 1]),ylabel('$ P \ {\rm(kPa)}')
$, 'interpreter', 'latex', 'fontsize', font_size2, 'fontweight', 'bold', 'Col
or', [0 0 1]);title([format1, ' (WF ' num2str(WF_Number), ')'],
'Interpreter', 'none', 'Color', [0 0
0], 'fontsize', font_size, 'fontweight', 'bold')
end

```

```

    export_fig(sprintf(['P-t_',format1,'_1']),'-jpg','-transparent','-
m3')
    hold off,
    for i = 1:12
        subplot(4,3,i)
        WF_Number= i+12;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P\ {\rm(kPa)}
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),'')'],
'Interpreter','none','Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
    end
    export_fig(sprintf(['P-t_',format1,'_2']),'-jpg','-transparent','-
m3');close
    figure,
    for i = 1:NWF-24
        subplot(4,3,i)
        WF_Number= i+24;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P\ {\rm(kPa)}
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),'')'],
'Interpreter','none','Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
    end
    export_fig(sprintf(['P-t_',format1,'_3']),'-jpg','-transparent','-
m3');close
elseif (NWF > 36 && NWF <= 48)
    hold off,
    for i = 1:12
        subplot(4,3,i)
        WF_Number= i;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P\ {\rm(kPa)}
$', 'interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),'')'],
'Interpreter','none','Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
    end
    export_fig(sprintf(['P-t_',format1,'_1']),'-jpg','-transparent','-
m3')
    hold off,
    for i = 1:12
        subplot(4,3,i)

```

```

        WF_Number= i+12;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t \ {\rm(ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P \ {\rm(kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),')'],
'Interpreter','none','Color',[0 0
0]),'fontsize',font_size,'fontweight','bold')
    end
    export_fig(sprintf(['P-t_',format1,'_2']),'-jpg','-transparent','-
m3')
    hold off,
    for i = 1:12
        subplot(4,3,i)
        WF_Number= i+24;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t \ {\rm(ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P \ {\rm(kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),')'],
'Interpreter','none','Color',[0 0
0]),'fontsize',font_size,'fontweight','bold')
    end
    export_fig(sprintf(['P-t_',format1,'_3']),'-jpg','-transparent','-
m3');close
    figure,
    for i = 1:NWF-36
        subplot(4,3,i)
        WF_Number= i+36;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t \ {\rm(ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P \ {\rm(kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),')'],
'Interpreter','none','Color',[0 0
0]),'fontsize',font_size,'fontweight','bold')
    end
    export_fig(sprintf(['P-t_',format1,'_4']),'-jpg','-transparent','-
m3');close
elseif (NWF > 48 && NWF <= 60)
    hold off,
    for i = 1:12
        subplot(4,3,i)
        WF_Number= i;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t \ {\rm(ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col

```

```

or',[0 0 1]),ylabel('$ P\ {\rm(kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Color',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),'')'],
'Interpreter','none','Color',[0 0 1]),'fontsize',font_size,'fontweight','bold')
end
export_fig(sprintf(['P-t_',format1,'_1']),'-jpg','-transparent','-m3')
hold off,
for i = 1:12
    subplot(4,3,i)
    WF_Number= i+12;plot(tP,Pt(:,WF_Number),'-b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1 1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_thickness);xlabel('$ t\ {\rm(ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Color',[0 0 1]),ylabel('$ P\ {\rm(kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Color',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),'')'],
'Interpreter','none','Color',[0 0 1]),'fontsize',font_size,'fontweight','bold')
end
export_fig(sprintf(['P-t_',format1,'_2']),'-jpg','-transparent','-m3')
hold off,
for i = 1:12
    subplot(4,3,i)
    WF_Number= i+24;plot(tP,Pt(:,WF_Number),'-b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1 1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_thickness);xlabel('$ t\ {\rm(ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Color',[0 0 1]),ylabel('$ P\ {\rm(kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Color',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),'')'],
'Interpreter','none','Color',[0 0 1]),'fontsize',font_size,'fontweight','bold')
end
export_fig(sprintf(['P-t_',format1,'_3']),'-jpg','-transparent','-m3')
hold off,
for i = 1:12
    subplot(4,3,i)
    WF_Number= i+36;plot(tP,Pt(:,WF_Number),'-b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1 1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_thickness);xlabel('$ t\ {\rm(ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Color',[0 0 1]),ylabel('$ P\ {\rm(kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Color',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),'')'],
'Interpreter','none','Color',[0 0 1]),'fontsize',font_size,'fontweight','bold')
end

```

```

        export_fig(sprintf(['P-t_',format1,'_4']),'-jpg','-transparent','-
m3');close
        figure,
        for i = 1:NWF-48
            subplot(4,3,i)
            WF_Number= i+48;plot(tP,Pt(:,WF_Number),'-
b','linewidth',Line_thickness);box
on;set(gcf,'units','normalized','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size,'LineWidth',box_th
ickness);xlabel('$ t\ {\rm(ms)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]),ylabel('$ P\ {\rm(kPa)}$','interpreter','latex','fontsize',font_size2,'fontweight','bold','Col
or',[0 0 1]);title([format1,' (WF ' num2str(WF_Number),')'],
'Interpreter','none','Color',[0 0
0],'fontsize',font_size,'fontweight','bold')
        end
        export_fig(sprintf(['P-t_',format1,'_5']),'-jpg','-transparent','-
m3');close
    end
end
end
marker_font = 24;font_size = 20;font_size2 = 24;box_thickness =
3;Line_thickness = 1;
set(0,'DefaultFigureWindowStyle','normal');
%% WRITING to EXCEL: P and V data in freq domain from fmin to fmax and
their average
% answer = questdlg('Do you want to save the results in an Excel
file?','Write to Excel','Yes','No','No');% answer = 'No';% answer =
'Yes';
switch Filter_Method
    case 1
        switch Save_Excel
            % case 'No'
            % return
            case 'Yes'
                ExcelFile= ['Output_' format1 '.xlsx'];
                for i = 1:NWF
                    temp = ['WaveForm' num2str(i)];
                    WF_Vector{i} = temp;
                end
                WaveForms =
WF_Vector';
                Vector for number of Waveforms
                Maximum_P = Pmax1';RMS_P = Prms1';
                warning('off','MATLAB:xlswrite:AddSheet');

                writetable(table(WaveForms,Maximum_P,RMS_P),ExcelFile,'Sheet',1)
                writetable(table(f_kHz,P_kPa),
ExcelFile,'Sheet',4)
                xlswrite(ExcelFile,cellstr('Mean(kPa)'), 'Sheet1', ['A'
num2str(NWF+3)]); % Write Headline for Mean
                xlswrite(ExcelFile,cellstr('Std (kPa)'), 'Sheet1', ['A'
num2str(NWF+4)]); % Write Headline for Std
                xlswrite(ExcelFile,Pmax, 'Sheet1', ['B'
num2str(NWF+3)]); % Write Mean of P_max
                xlswrite(ExcelFile,Prms, 'Sheet1', ['C'
num2str(NWF+3)]); % Write Mean of P_RMS

```

```

        xlswrite(ExcelFile,Pmax_std,'Sheet1',['B'
num2str(NWF+4)]); % Write Std of P_max
        xlswrite(ExcelFile,Prms_std,'Sheet1',['C'
num2str(NWF+4)]); % Write Std of P_RMS
        xlswrite(ExcelFile,cellstr('Max'),'Sheet1',['B'
num2str(NWF+5)]); % Write Headline for Max
        xlswrite(ExcelFile,cellstr('RMS'),'Sheet1',['C'
num2str(NWF+5)]); % Write Headline for RMS

        % Write Pmax and RMS of non-filtered values
        Maximum_P = Pmax1NF';RMS_P = Prms1NF';

writetable(table(WaveForms,Maximum_P,RMS_P),ExcelFile,'Sheet',2)
        xlswrite(ExcelFile,cellstr('Mean(kPa)'),'Sheet2',['A'
num2str(NWF+3)]); % Write Headline for Mean
        xlswrite(ExcelFile,cellstr('Std (kPa)'),'Sheet2',['A'
num2str(NWF+4)]); % Write Headline for Std
        xlswrite(ExcelFile,PmaxNF,'Sheet2',['B'
num2str(NWF+3)]); % Write Mean of P_max
        xlswrite(ExcelFile,PrmsNF,'Sheet2',['C'
num2str(NWF+3)]); % Write Mean of P_RMS
        xlswrite(ExcelFile,PmaxNF_std,'Sheet2',['B'
num2str(NWF+4)]); % Write Std of P_max
        xlswrite(ExcelFile,PrmsNF_std,'Sheet2',['C'
num2str(NWF+4)]); % Write Std of P_RMS
        xlswrite(ExcelFile,cellstr('Max (No Filter)'),'Sheet2',['B'
num2str(NWF+5)]); % Write Headline for Max
        xlswrite(ExcelFile,cellstr('RMS (No Filter)'),'Sheet2',['C'
num2str(NWF+5)]); % Write Headline for RMS

        % Write Pmax and RMS of No skipping values (original Pmax
and RMS without skipping the two ends)
        Maximum_P = Pmax0';RMS_P = Prms0';

writetable(table(WaveForms,Maximum_P,RMS_P),ExcelFile,'Sheet',3)
        xlswrite(ExcelFile,cellstr('Mean(kPa)'),'Sheet3',['A'
num2str(NWF+3)]); % Write Headline for Mean
        xlswrite(ExcelFile,cellstr('Std (kPa)'),'Sheet3',['A'
num2str(NWF+4)]); % Write Headline for Std
        xlswrite(ExcelFile,PmaxNS,'Sheet3',['B'
num2str(NWF+3)]); % Write Mean of P_max
        xlswrite(ExcelFile,PrmsNS,'Sheet3',['C'
num2str(NWF+3)]); % Write Mean of P_RMS
        xlswrite(ExcelFile,PmaxNS_std,'Sheet3',['B'
num2str(NWF+4)]); % Write Std of P_max
        xlswrite(ExcelFile,PrmsNS_std,'Sheet3',['C'
num2str(NWF+4)]); % Write Std of P_RMS
        xlswrite(ExcelFile,cellstr('Max (No
Skipping)'),'Sheet3',['B' num2str(NWF+5)]); % Write Headline for Max
        xlswrite(ExcelFile,cellstr('RMS (No
Skipping)'),'Sheet3',['C' num2str(NWF+5)]); % Write Headline for RMS
    end
    case 2
        switch Save_Excel
            % case 'No'
            % return
            case 'Yes'
                ExcelFile= ['Output_' format1 '.xlsx'];

```

```

        for i = 1:NWF
            temp = ['WaveForm' num2str(i)];
            WF_Vector{i} = temp;
        end
        WaveForms =
WF_Vector';
Vector for number of Waveforms
        Maximum_P = Pmax1';RMS_P = Prms1';
        warning('off','MATLAB:xlswrite:AddSheet');

writetable(table(WaveForms,Maximum_P,RMS_P),ExcelFile,'Sheet',1)
        writetable(table(f_kHz,P_kPa),
ExcelFile,'Sheet',3)
        xlswrite(ExcelFile,cellstr('Mean(kPa)'), 'Sheet1', ['A'
num2str(NWF+3)]); % Write Headline for Mean
        xlswrite(ExcelFile,cellstr('Std (kPa)'), 'Sheet1', ['A'
num2str(NWF+4)]); % Write Headline for Std
        xlswrite(ExcelFile,Pmax, 'Sheet1', ['B'
num2str(NWF+3)]); % Write Mean of P_max
        xlswrite(ExcelFile,Prms, 'Sheet1', ['C'
num2str(NWF+3)]); % Write Mean of P_RMS
        xlswrite(ExcelFile,Pmax_std, 'Sheet1', ['B'
num2str(NWF+4)]); % Write Std of P_max
        xlswrite(ExcelFile,Prms_std, 'Sheet1', ['C'
num2str(NWF+4)]); % Write Std of P_RMS
        xlswrite(ExcelFile,cellstr('Max'), 'Sheet1', ['B'
num2str(NWF+5)]); % Write Headline for Max
        xlswrite(ExcelFile,cellstr('RMS'), 'Sheet1', ['C'
num2str(NWF+5)]); % Write Headline for RMS

        % Write Pmax and RMS of No skipping values (original Pmax
and RMS without skipping the two ends)
        Maximum_P = Pmax0';RMS_P = Prms0';

writetable(table(WaveForms,Maximum_P,RMS_P),ExcelFile,'Sheet',2)
        xlswrite(ExcelFile,cellstr('Mean(kPa)'), 'Sheet2', ['A'
num2str(NWF+3)]); % Write Headline for Mean
        xlswrite(ExcelFile,cellstr('Std (kPa)'), 'Sheet2', ['A'
num2str(NWF+4)]); % Write Headline for Std
        xlswrite(ExcelFile,Pmax, 'Sheet2', ['B'
num2str(NWF+3)]); % Write Mean of P_max
        xlswrite(ExcelFile,Prms, 'Sheet2', ['C'
num2str(NWF+3)]); % Write Mean of P_RMS
        xlswrite(ExcelFile,Pmax_std, 'Sheet2', ['B'
num2str(NWF+4)]); % Write Std of P_max
        xlswrite(ExcelFile,Prms_std, 'Sheet2', ['C'
num2str(NWF+4)]); % Write Std of P_RMS
        xlswrite(ExcelFile,cellstr('Max (No
Skipping)'), 'Sheet2', ['B' num2str(NWF+5)]); % Write
Headline for Max
        xlswrite(ExcelFile,cellstr('RMS (No
Skipping)'), 'Sheet2', ['C' num2str(NWF+5)]); % Write
Headline for RMS
        end
    end
    switch Multi_Method
        case 2
            if (u ~= NFiles)

```



```

        close all;clear
    end
end
end
toc
%% Internal Functions (DO NOT CHANGE)
% Function to subtract the noise from a signal
function [y1] = Noise_Reduction (y1,upper_limit,lower_limit)
    for i = 1:length(y1)
        if (y1(i) >= upper_limit)
            y1(i) = y1(i) - upper_limit;
        elseif (y1(i) <= -lower_limit)
            y1(i) = y1(i) + lower_limit;
        else
            y1(i) = y1(i);
        end
    end
end
end
%% Function to convert from double-sided spectrum to single-sided
spectrum
function [SS] = DS2SS (DS)
    N1 = length(DS);
    N2 = N1/2+1;
    SS = zeros(N2,1);
    SS (1) = DS (1);
    for i=2:N2-1
        SS(i) = 2.*DS(i);
    end
    SS (N2) = DS(N2);
end
%% Function to convert from single-sided spectrum to double-sided
spectrum
function [DS] = SS2DS (SS)
    N1 = length(SS);
    N2 = 2*(N1-1);
    DS = zeros(N2,1);
    DS (1) = SS (1);
    for i=2:N2/2
        DS(i) = 0.5.*SS(i);
    end
    DS (N2/2+1) = SS (N2/2+1);
    for i=1:N2/2-1
        DS_real      = 0.5.*real(SS (N2/2+1-i));           % real
        DS_imag      = -0.5.*imag(SS (N2/2+1-i));           % imag
        DS (N2/2+1+i) = complex (DS_real, DS_imag);         % create
    end
    DS (N2/2+1+i) = 0.5.*SS (N2/2+1-i);                     %
    % Original form (for abs or real values)
end
end
function [DS] = SS2DS2 (SS)
    N1 = length(SS);
    N2 = 2*(N1-1);
    DS = zeros(N2,1);
    DS (1) = SS (1);
    for i=2:N2/2

```

```

        DS(i) = 0.5.*SS(i);
    end
    DS (N2/2+1) = SS (N2/2+1);
    for i=1:N2/2-1
        DS(N2/2+1+i) = 0.5.*SS(N2/2+1-i);           % Original
    end
end
form (for abs or real values)
end
%% Function for computing the sensitivity of Cavitometers
function [f1,S_Original,S_1MHz] =
Sensitivity_CAV(Cavitometer_position,ProbeType)
%%% Probe 3_Attenuator and Probe 4 use the new calibration from 8-400
kHz
SdB_Side_Probe4 = [-273      -276      -277      -275      -270      -274      -
271      -271      -274      -271      -270      -270      -269      -268      -267      -
268      -268      -270      -271      -271      -270      -269      -267      -268      -
268      -269      -270      -272      -274      -275      -278      -281      -284      -
286      -289      -289      -285      -288      -290      -288      -290      -290      -
292      -289      -285      -279      -276      -272      -271      -269      -269      -
270      -272      -279      -283      -285      -282      -278      -280      -277      -
277      -274      -270      -267      -265      -264      -263      -262      -261      -
260      -259      -259      -259      -259      -260      -261      -259      -257      -
255      -255      -255      -255      -254      -252      -251      -250      -249      -
249      -249      -249      -249      -248      -247      -247      -246      -246      -
247      -248      -249      -251      -253      -254      -255      -256      -258      -
259      -261      -262      -263      -262      -261      -260      -248      -249      -
249      -249      -248      -248      -247      -247      -247      -247      -248      -
249      -251      -251      -252      -252      -251      -251      -250      -250      -
250      -250      -250      -251      -252      -254      -255      -257      -258      -
259      -259      -256      -253      -251      -248      -247      -246      -245      -
245      -244      -244      -243      -243      -242      -242      -243      -243      -
243      -244      -245      -245      -246      -246      -246      -246      -245      -
245      -245      -244      -244      -244      -243      -243      -243      -242      -
242      -242      -241      -241      -241      -241      -241      -242      -242      -
243      -244      -245      -246      -247      -248      -250      -251      -254      -
257      -260      -265      -274      -284      -272      -269      -267      -266      -
264      -263      -261      -259      -257      -256      -255      -255      -254      -
254      -255      -256      -256      -258      -259      -262      -267      -278      -
268      -261      -258      -255      -254      -253      -252      -252      -251      -
251      -251      -251      -252      -252      -253      -254      -256      -258      -
261      -265      -273      -277      -265      -260      -257      -254      -253      -
251      -250      -249      -249      -248      -248      -247      -247      -248      -
248      -248      -249      -250      -251      -252      -254      -256      -259      -
262      -264      -262      -260      -258      -257      -256      -255      -254      -
254      -254      -255      -255      -256      -256      -256      -256      -255      -
254      -254      -253      -251      -250      -249      -247      -246      -245      -
244      -243      -243      -243      -243      -243      -243      -244      -245      -
247      -250      -252      -251      -247      -244      -242      -240      -238      -
237      -236      -235      -234      -234      -233      -233      -233      -234      -
234      -235      -236      -238      -239      -241      -241      -240      -239      -
237      -235      -233      -231      -229      -228      -227      -225      -225      -
224      -223      -223      -223      -223      -223      -223      -224      -225      -
225      -226      -227      -227      -228      -228      -228      -229      -229      -
229      -230      -231      -233      -235      -238      -242      -242      -238      -
235      -232      -230      -229      -228      -228      -228      -228      -228      -
228      -229      -230      -231      -232      -234      -235      -236      -236      -
235      -234      -234      -233      -233      -233      -233      -234      -235      -
236      -238      -239      -239      -239      -239      -238      -238      -237      -

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237	-237	-237	-237	-237	-238	-239	-239	-240	-
242	-243	-245	-247	-249	-251	-252	-253	-252	-
251	-250	-249	-248	-247	-247	-246	-246	-245	-
245	-245	-245	-245	-245	-245	-245	-245	-245	-
244	-244	-243	-243	-242	-242	-241	-241	-240	-
240	-240	-241	-241	-241	-242	-243	-244	-245	-
247	-247	-247	-247	-246	-245	-244	-243	-242	-
242	-242	-241	-241	-241	-242	-242	-242	-241	-
241	-240	-240	-239	-239	-238	-238	-238	-238	-
238	-238	-239	-239	-240	-241	-242	-243	-244	-
245	-246	-247	-248	-248	-248	-247	-245	-244	-
242	-242	-241	-241	-241	-242	-242	-244	-245	-
246	-247	-247	-247	-247	-246	-245	-244	-243	-
242	-242	-242	-242	-243	-244	-246	-248	-251	-
255	-263	-272	-262	-258	-256	-255	-254	-253	-
251	-249	-246	-245	-243	-242	-240	-240	-239	-
239	-238	-238	-238	-239	-239	-240	-240	-241	-
242	-243	-245	-247	-249	-251	-253	-256	-258	-
259	-259	-259	-259	-259	-260	-261	-263	-265	-
266	-265	-263	-262	-260	-257	-255	-253	-251	-
250	-249	-248	-247	-247	-246	-247	-247	-247	-
248	-248	-249	-249	-250	-250	-251	-252	-253	-
254	-255	-255	-256	-255	-255	-254	-253	-253	-
252	-251	-251	-250	-250	-249	-248	-248	-247	-
247	-247	-246	-246	-246	-247	-247	-248	-248	-
249	-250	-251	-253	-254	-256	-257	-259	-260	-
262	-263	-263	-264	-265	-265	-265	-264	-262	-
260	-258	-256	-255	-253	-252	-251	-251	-250	-
250	-250	-250	-250	-250	-250	-250	-250	-250	-
250	-251	-253	-255	-259	-268	-266	-259	-255];	-
SdB_Under_Probe4 = [-270	-271	-273	-273	-272	-273	-272	-273	-273	-
276	-279	-279	-279	-282	-276	-279	-280	-282	-
280	-278	-280	-280	-278	-280	-284	-288	-285	-
283	-281	-279	-279	-279	-278	-280	-284	-288	-
295	-295	-291	-290	-294	-291	-291	-293	-287	-
296	-289	-282	-281	-277	-274	-272	-271	-271	-
272	-272	-276	-276	-281	-278	-275	-274	-271	-
273	-275	-276	-275	-269	-267	-265	-266	-267	-
267	-267	-266	-265	-266	-268	-270	-270	-265	-
263	-261	-260	-259	-260	-260	-259	-258	-257	-
258	-261	-269	-260	-253	-250	-247	-246	-246	-
247	-249	-254	-263	-258	-254	-253	-254	-260	-
272	-262	-257	-256	-257	-256	-254	-252	-251	-
249	-247	-246	-245	-243	-242	-240	-240	-239	-
239	-238	-239	-239	-239	-239	-239	-239	-239	-
239	-239	-239	-240	-240	-241	-241	-242	-243	-
244	-245	-246	-248	-250	-251	-250	-248	-246	-
245	-244	-244	-243	-243	-243	-243	-242	-242	-
242	-242	-242	-241	-241	-241	-241	-241	-241	-
241	-241	-242	-242	-242	-243	-244	-246	-247	-
249	-252	-254	-257	-259	-261	-260	-260	-260	-
261	-262	-263	-261	-258	-255	-253	-252	-251	-
250	-249	-248	-248	-247	-247	-246	-246	-246	-
245	-245	-244	-243	-243	-242	-241	-241	-240	-
240	-239	-239	-239	-238	-238	-238	-238	-238	-
239	-239	-239	-240	-241	-241	-242	-243	-244	-
245	-246	-247	-248	-249	-249	-250	-251	-252	-
252	-253	-252	-252	-251	-250	-249	-248	-247	-

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246    -245    -244    -243    -242    -241    -241    -240    -240    -
240    -240    -239    -239    -240    -240    -240    -241    -241    -
242    -243    -244    -245    -247    -249    -251    -253    -256    -
258    -259    -258    -257    -256    -256    -255    -255    -255    -
255    -254    -254    -253    -252    -251    -251    -250    -250    -
250    -250    -251    -252    -254    -256    -256    -253    -250    -
247    -245    -243    -241    -240    -239    -238    -237    -236    -
236    -235    -235    -235    -236    -236    -236    -236    -235    -
234    -233    -231    -230    -229    -228    -227    -227    -227    -
227    -228    -228    -229    -229    -228    -228    -227    -226    -
225    -225    -225    -225    -225    -225    -226    -227    -228    -
229    -230    -232    -235    -238    -246    -250    -239    -234    -
231    -228    -227    -226    -225    -224    -224    -224    -225    -
225    -226    -226    -227    -228    -229    -230    -231    -232    -
233    -235    -236    -236    -237    -237    -236    -235    -233    -
232    -230    -229    -228    -227    -226    -226    -226    -226    -
226    -226    -227    -228    -228    -230    -231    -232    -234    -
236    -238    -239    -240    -240    -240    -240    -240    -242    -
244    -248    -263    -250    -243    -238    -235    -233    -231    -
229    -228    -228    -227    -227    -227    -227    -228    -229    -
230    -231    -232    -233    -235    -235    -235    -235    -235    -
235    -235    -235    -235    -235    -234    -234    -235    -235    -
235    -236    -237    -238    -240    -241    -243    -243    -243    -
241    -239    -237    -235    -234    -233    -232    -231    -230    -
229    -229    -228    -228    -228    -227    -227    -227    -227    -
226    -226    -226    -226    -226    -226    -226    -226    -226    -
226    -227    -227    -228    -228    -229    -230    -231    -231    -
232    -233    -234    -235    -236    -236    -237    -237    -237    -
238    -238    -238    -239    -239    -239    -239    -239    -239    -
238    -238    -237    -237    -237    -236    -237    -237    -237    -
238    -238    -239    -239    -240    -240    -241    -241    -242    -
242    -242    -243    -243    -244    -246    -247    -249    -251    -
252    -251    -250    -249    -249    -249    -248    -248    -247    -
247    -246    -245    -245    -245    -245    -245    -246    -247    -
249    -251    -253    -255    -256    -256    -255    -253    -252    -
250    -249    -249    -248    -248    -248    -248    -249    -249    -
250    -251    -252    -253    -254    -256    -259    -261    -264    -
264    -261    -259    -258    -256    -255    -254    -252    -251    -
250    -249    -248    -247    -246    -245    -244    -244    -243    -
243    -244    -244    -245    -246    -247    -248    -249    -250    -
250    -250    -250    -250    -249    -248    -246    -245    -244    -
244    -243    -243    -243    -244    -244    -245    -246    -247    -
248    -249    -250    -250    -251    -251    -252    -252    -253    -
254    -255    -256    -256    -256    -255    -253    -252    -251    -
250    -249    -249    -249    -250    -251    -252    -254    -255    -
256    -256    -255    -254    -253    -252    -252    -251    -251    -
251    -251    -250    -250    -249    -249    -249    -249    -249];
switch Cavitometer_position
    case 'Side'
%%% f1 is in Hz and
    switch ProbeType

        case 'Probe4'
            f1 =
[8000  9000  10000  11000  12000  13000  14000  15000  16000  17000
 18000  19000  20000  21000  22000  23000  24000  25000  26000
 27000  28000  29000  30000  31000  32000  33000  34000  35000
 36000  37000  38000  39000  40000  41000  42000  43000  44000

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45000	46000	47000	48000	49000	50000	51000	52000	53000
54000	55000	56000	57000	58000	59000	60000	61000	62000
63000	64000	65000	66000	67000	68000	69000	70000	71000
72000	73000	74000	75000	76000	77000	78000	79000	80000
81000	82000	83000	84000	85000	86000	87000	88000	89000
90000	91000	92000	93000	94000	95000	96000	97000	98000
99000	100000	101000	102000	103000	104000	105000	106000	107000
108000	109000	110000	111000	112000	113000	114000	115000	116000
117000	118000	119000	120000.0034	120500.0034	121000.0034			
121500.0034	122000.0035	122500.0035	123000.0035					
123500.0035	124000.0035	124500.0035	125000.0035					
125500.0035	126000.0036	126500.0036	127000.0036					
127500.0036	128000.0036	128500.0036	129000.0036					
129500.0037	130000.0037	130500.0037	131000.0037					
131500.0037	132000.0037	132500.0037	133000.0038					
133500.0038	134000.0038	134500.0038	135000.0038					
135500.0038	136000.0038	136500.0039	137000.0039					
137500.0039	138000.0039	138500.0039	139000.0039					
139500.0039	140000.004	140500.004	141000.004					
141500.004	142000.004	142500.004	143000.004					
143500.0041	144000.0041	144500.0041	145000.0041					
145500.0041	146000.0041	146500.0041	147000.0042					
147500.0042	148000.0042	148500.0042	149000.0042					
149500.0042	150000.0042	150500.0043	151000.0043					
151500.0043	152000.0043	152500.0043	153000.0043					
153500.0043	154000.0044	154500.0044	155000.0044					
155500.0044	156000.0044	156500.0044	157000.0044					
157500.0045	158000.0045	158500.0045	159000.0045					
159500.0045	160000.0045	160500.0045	161000.0046					
161500.0046	162000.0046	162500.0046	163000.0046					
163500.0046	164000.0046	164500.0047	165000.0047					
165500.0047	166000.0047	166500.0047	167000.0047					
167500.0047	168000.0048	168500.0048	169000.0048					
169500.0048	170000.0048	170500.0048	171000.0048					
171500.0049	172000.0049	172500.0049	173000.0049					
173500.0049	174000.0049	174500.0049	175000.0049					
175500.005	176000.005	176500.005	177000.005					
177500.005	178000.005	178500.005	179000.0051					
179500.0051	180000.0051	180500.0051	181000.0051					
181500.0051	182000.0051	182500.0052	183000.0052					
183500.0052	184000.0052	184500.0052	185000.0052					
185500.0052	186000.0053	186500.0053	187000.0053					
187500.0053	188000.0053	188500.0053	189000.0053					
189500.0054	190000.0054	190500.0054	191000.0054					
191500.0054	192000.0054	192500.0054	193000.0055					
193500.0055	194000.0055	194500.0055	195000.0055					
195500.0055	196000.0055	196500.0056	197000.0056					
197500.0056	198000.0056	198500.0056	199000.0056					
199500.0056	200000.0057	200500.0057	201000.0057					
201500.0057	202000.0057	202500.0057	203000.0057					
203500.0058	204000.0058	204500.0058	205000.0058					
205500.0058	206000.0058	206500.0058	207000.0059					
207500.0059	208000.0059	208500.0059	209000.0059					
209500.0059	210000.0059	210500.006	211000.006					
211500.006	212000.006	212500.006	213000.006					
213500.006	214000.0061	214500.0061	215000.0061					
215500.0061	216000.0061	216500.0061	217000.0061					
217500.0062	218000.0062	218500.0062	219000.0062					

219500.0062	220000.0062	220500.0062	221000.0063
221500.0063	222000.0063	222500.0063	223000.0063
223500.0063	224000.0063	224500.0063	225000.0064
225500.0064	226000.0064	226500.0064	227000.0064
227500.0064	228000.0064	228500.0065	229000.0065
229500.0065	230000.0065	230500.0065	231000.0065
231500.0065	232000.0066	232500.0066	233000.0066
233500.0066	234000.0066	234500.0066	235000.0066
235500.0067	236000.0067	236500.0067	237000.0067
237500.0067	238000.0067	238500.0067	239000.0068
239500.0068	240000.0068	240500.0068	241000.0068
241500.0068	242000.0068	242500.0069	243000.0069
243500.0069	244000.0069	244500.0069	245000.0069
245500.0069	246000.007	246500.007	247000.007
247500.007	248000.007	248500.007	249000.007
249500.0071	250000.0071	250500.0071	251000.0071
251500.0071	252000.0071	252500.0071	253000.0072
253500.0072	254000.0072	254500.0072	255000.0072
255500.0072	256000.0072	256500.0073	257000.0073
257500.0073	258000.0073	258500.0073	259000.0073
259500.0073	260000.0074	260500.0074	261000.0074
261500.0074	262000.0074	262500.0074	263000.0074
263500.0075	264000.0075	264500.0075	265000.0075
265500.0075	266000.0075	266500.0075	267000.0076
267500.0076	268000.0076	268500.0076	269000.0076
269500.0076	270000.0076	270500.0077	271000.0077
271500.0077	272000.0077	272500.0077	273000.0077
273500.0077	274000.0077	274500.0078	275000.0078
275500.0078	276000.0078	276500.0078	277000.0078
277500.0078	278000.0079	278500.0079	279000.0079
279500.0079	280000.0079	280500.0079	281000.0079
281500.008	282000.008	282500.008	283000.008
283500.008	284000.008	284500.008	285000.0081
285500.0081	286000.0081	286500.0081	287000.0081
287500.0081	288000.0081	288500.0082	289000.0082
289500.0082	290000.0082	290500.0082	291000.0082
291500.0082	292000.0083	292500.0083	293000.0083
293500.0083	294000.0083	294500.0083	295000.0083
295500.0084	296000.0084	296500.0084	297000.0084
297500.0084	298000.0084	298500.0084	299000.0085
299500.0085	300000.0085	300500.0085	301000.0085
301500.0085	302000.0085	302500.0086	303000.0086
303500.0086	304000.0086	304500.0086	305000.0086
305500.0086	306000.0087	306500.0087	307000.0087
307500.0087	308000.0087	308500.0087	309000.0087
309500.0088	310000.0088	310500.0088	311000.0088
311500.0088	312000.0088	312500.0088	313000.0089
313500.0089	314000.0089	314500.0089	315000.0089
315500.0089	316000.0089	316500.009	317000.009
317500.009	318000.009	318500.009	319000.009
319500.009	320000.0091	320500.0091	321000.0091
321500.0091	322000.0091	322500.0091	323000.0091
323500.0091	324000.0092	324500.0092	325000.0092
325500.0092	326000.0092	326500.0092	327000.0092
327500.0093	328000.0093	328500.0093	329000.0093
329500.0093	330000.0093	330500.0093	331000.0094
331500.0094	332000.0094	332500.0094	333000.0094
333500.0094	334000.0094	334500.0095	335000.0095

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335500.0095    336000.0095    336500.0095    337000.0095
337500.0095    338000.0096    338500.0096    339000.0096
339500.0096    340000.0096    340500.0096    341000.0096
341500.0097    342000.0097    342500.0097    343000.0097
343500.0097    344000.0097    344500.0097    345000.0098
345500.0098    346000.0098    346500.0098    347000.0098
347500.0098    348000.0098    348500.0099    349000.0099
349500.0099    350000.0099    350500.0099    351000.0099
351500.0099    352000.01    352500.01    353000.01
353500.01    354000.01    354500.01    355000.01
355500.0101    356000.0101    356500.0101    357000.0101
357500.0101    358000.0101    358500.0101    359000.0102
359500.0102    360000.0102    360500.0102    361000.0102
361500.0102    362000.0102    362500.0103    363000.0103
363500.0103    364000.0103    364500.0103    365000.0103
365500.0103    366000.0104    366500.0104    367000.0104
367500.0104    368000.0104    368500.0104    369000.0104
369500.0105    370000.0105    370500.0105    371000.0105
371500.0105    372000.0105    372500.0105    373000.0105
373500.0106    374000.0106    374500.0106    375000.0106
375500.0106    376000.0106    376500.0106    377000.0107
377500.0107    378000.0107    378500.0107    379000.0107
379500.0107    380000.0107    380500.0108    381000.0108
381500.0108    382000.0108    382500.0108    383000.0108
383500.0108    384000.0109    384500.0109    385000.0109
385500.0109    386000.0109    386500.0109    387000.0109
387500.011    388000.011    388500.011    389000.011
389500.011    390000.011    390500.011    391000.0111
391500.0111    392000.0111    392500.0111    393000.0111
393500.0111    394000.0111    394500.0112    395000.0112
395500.0112    396000.0112    396500.0112    397000.0112
397500.0112    398000.0113    398500.0113    399000.0113
399500.0113];
    SdB_Side = SdB_Side_Probe4;
end
TF_Side = 10.^ (SdB_Side./20).*1e6;    % result is in
V/Pa    % work with Standard SI units
S_Original = TF_Side;
case 'Under'
switch ProbeType

    case 'Probe4'
        f1 =
[8000    9000    10000    11000    12000    13000    14000    15000    16000    17000
18000    19000    20000    21000    22000    23000    24000    25000    26000
27000    28000    29000    30000    31000    32000    33000    34000    35000
36000    37000    38000    39000    40000    41000    42000    43000    44000
45000    46000    47000    48000    49000    50000    51000    52000    53000
54000    55000    56000    57000    58000    59000    60000    61000    62000
63000    64000    65000    66000    67000    68000    69000    70000    71000
72000    73000    74000    75000    76000    77000    78000    79000    80000
81000    82000    83000    84000    85000    86000    87000    88000    89000
90000    91000    92000    93000    94000    95000    96000    97000    98000
99000    100000    101000    102000    103000    104000    105000    106000    107000
108000    109000    110000    111000    112000    113000    114000    115000    116000
117000    118000    119000    120000.0034    120500.0034    121000.0034
121500.0034    122000.0035    122500.0035    123000.0035
123500.0035    124000.0035    124500.0035    125000.0035

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125500.0035	126000.0036	126500.0036	127000.0036
127500.0036	128000.0036	128500.0036	129000.0036
129500.0037	130000.0037	130500.0037	131000.0037
131500.0037	132000.0037	132500.0037	133000.0038
133500.0038	134000.0038	134500.0038	135000.0038
135500.0038	136000.0038	136500.0039	137000.0039
137500.0039	138000.0039	138500.0039	139000.0039
139500.0039	140000.004	140500.004	141000.004
141500.004	142000.004	142500.004	143000.004
143500.0041	144000.0041	144500.0041	145000.0041
145500.0041	146000.0041	146500.0041	147000.0042
147500.0042	148000.0042	148500.0042	149000.0042
149500.0042	150000.0042	150500.0043	151000.0043
151500.0043	152000.0043	152500.0043	153000.0043
153500.0043	154000.0044	154500.0044	155000.0044
155500.0044	156000.0044	156500.0044	157000.0044
157500.0045	158000.0045	158500.0045	159000.0045
159500.0045	160000.0045	160500.0045	161000.0046
161500.0046	162000.0046	162500.0046	163000.0046
163500.0046	164000.0046	164500.0047	165000.0047
165500.0047	166000.0047	166500.0047	167000.0047
167500.0047	168000.0048	168500.0048	169000.0048
169500.0048	170000.0048	170500.0048	171000.0048
171500.0049	172000.0049	172500.0049	173000.0049
173500.0049	174000.0049	174500.0049	175000.0049
175500.005	176000.005	176500.005	177000.005
177500.005	178000.005	178500.005	179000.0051
179500.0051	180000.0051	180500.0051	181000.0051
181500.0051	182000.0051	182500.0052	183000.0052
183500.0052	184000.0052	184500.0052	185000.0052
185500.0052	186000.0053	186500.0053	187000.0053
187500.0053	188000.0053	188500.0053	189000.0053
189500.0054	190000.0054	190500.0054	191000.0054
191500.0054	192000.0054	192500.0054	193000.0055
193500.0055	194000.0055	194500.0055	195000.0055
195500.0055	196000.0055	196500.0056	197000.0056
197500.0056	198000.0056	198500.0056	199000.0056
199500.0056	200000.0057	200500.0057	201000.0057
201500.0057	202000.0057	202500.0057	203000.0057
203500.0058	204000.0058	204500.0058	205000.0058
205500.0058	206000.0058	206500.0058	207000.0059
207500.0059	208000.0059	208500.0059	209000.0059
209500.0059	210000.0059	210500.006	211000.006
211500.006	212000.006	212500.006	213000.006
213500.006	214000.0061	214500.0061	215000.0061
215500.0061	216000.0061	216500.0061	217000.0061
217500.0062	218000.0062	218500.0062	219000.0062
219500.0062	220000.0062	220500.0062	221000.0063
221500.0063	222000.0063	222500.0063	223000.0063
223500.0063	224000.0063	224500.0063	225000.0064
225500.0064	226000.0064	226500.0064	227000.0064
227500.0064	228000.0064	228500.0065	229000.0065
229500.0065	230000.0065	230500.0065	231000.0065
231500.0065	232000.0066	232500.0066	233000.0066
233500.0066	234000.0066	234500.0066	235000.0066
235500.0067	236000.0067	236500.0067	237000.0067
237500.0067	238000.0067	238500.0067	239000.0068
239500.0068	240000.0068	240500.0068	241000.0068

241500.0068	242000.0068	242500.0069	243000.0069
243500.0069	244000.0069	244500.0069	245000.0069
245500.0069	246000.007	246500.007	247000.007
247500.007	248000.007	248500.007	249000.007
249500.0071	250000.0071	250500.0071	251000.0071
251500.0071	252000.0071	252500.0071	253000.0072
253500.0072	254000.0072	254500.0072	255000.0072
255500.0072	256000.0072	256500.0073	257000.0073
257500.0073	258000.0073	258500.0073	259000.0073
259500.0073	260000.0074	260500.0074	261000.0074
261500.0074	262000.0074	262500.0074	263000.0074
263500.0075	264000.0075	264500.0075	265000.0075
265500.0075	266000.0075	266500.0075	267000.0076
267500.0076	268000.0076	268500.0076	269000.0076
269500.0076	270000.0076	270500.0077	271000.0077
271500.0077	272000.0077	272500.0077	273000.0077
273500.0077	274000.0077	274500.0078	275000.0078
275500.0078	276000.0078	276500.0078	277000.0078
277500.0078	278000.0079	278500.0079	279000.0079
279500.0079	280000.0079	280500.0079	281000.0079
281500.008	282000.008	282500.008	283000.008
283500.008	284000.008	284500.008	285000.0081
285500.0081	286000.0081	286500.0081	287000.0081
287500.0081	288000.0081	288500.0082	289000.0082
289500.0082	290000.0082	290500.0082	291000.0082
291500.0082	292000.0083	292500.0083	293000.0083
293500.0083	294000.0083	294500.0083	295000.0083
295500.0084	296000.0084	296500.0084	297000.0084
297500.0084	298000.0084	298500.0084	299000.0085
299500.0085	300000.0085	300500.0085	301000.0085
301500.0085	302000.0085	302500.0086	303000.0086
303500.0086	304000.0086	304500.0086	305000.0086
305500.0086	306000.0087	306500.0087	307000.0087
307500.0087	308000.0087	308500.0087	309000.0087
309500.0088	310000.0088	310500.0088	311000.0088
311500.0088	312000.0088	312500.0088	313000.0089
313500.0089	314000.0089	314500.0089	315000.0089
315500.0089	316000.0089	316500.009	317000.009
317500.009	318000.009	318500.009	319000.009
319500.009	320000.0091	320500.0091	321000.0091
321500.0091	322000.0091	322500.0091	323000.0091
323500.0091	324000.0092	324500.0092	325000.0092
325500.0092	326000.0092	326500.0092	327000.0092
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333500.0094	334000.0094	334500.0095	335000.0095
335500.0095	336000.0095	336500.0095	337000.0095
337500.0095	338000.0096	338500.0096	339000.0096
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345500.0098	346000.0098	346500.0098	347000.0098
347500.0098	348000.0098	348500.0099	349000.0099
349500.0099	350000.0099	350500.0099	351000.0099
351500.0099	352000.01	352500.01	353000.01
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383500.0108    384000.0109    384500.0109    385000.0109
385500.0109    386000.0109    386500.0109    387000.0109
387500.011    388000.011    388500.011    389000.011
389500.011    390000.011    390500.011    391000.0111
391500.0111    392000.0111    392500.0111    393000.0111
393500.0111    394000.0111    394500.0112    395000.0112
395500.0112    396000.0112    396500.0112    397000.0112
397500.0112    398000.0113    398500.0113    399000.0113
399500.0113];
    SdB_Under = SdB_Under_Probe4;
end
TF_Under = 10.^(SdB_Under./20).*1e6;          % result is in V/Pa
S_Original = TF_Under;
end
% font_size = 14;marker_size = 12;
% figure,plot(f1,S_Original,'-
ob','linewidth',1,'markersize',marker_size); hold on
% xlabel('f (kHz)','fontsize',font_size,'fontweight','bold','Color',[0
0 1]);ylabel('Sensitivity
(mV/kPa)','fontsize',font_size,'fontweight','bold','Color',[0 0 1])
% title('Sensitivity','Color',[0 0
1],'fontsize',font_size,'fontweight','bold'),set(gcf,'units','normalize
d','outerposition',[0 0 1
1]);set(gca,'fontweight','bold','fontsize',font_size);
% f_desired = f1(1):1:f1(end);
% S_Final_All = interp1(f1,S_Original,f_desired,'PCHIP');
%
plot(f_desired,S_Final_All,'sr','linewidth',1,'markersize',marker_size-
4)
% %
set(gca,'XTick',(f1(1):1:f1(end)),'fontweight','bold','fontsize',12);
% legend('Measured','Interpolated','Location','NorthEast')
% xlim([14e3 31e3])
end

%% Variables
% S:   Sensitivity vector (contains the interpolation)
% tV:  t from CVS file (in s)
% fV:  freq (from fs or tV)
% Vt1: V matrix (Voltage) from CSV (in V)
% Vt2: new V matrix (after noise subtraction)
% Vf1: fft(Vt2) --> Fast Fourier Transform of Vt1
% Vf2: Single-sided form of Vf1 (Vf1 is double-sided)
% P1:  real(Vf2)/S
% P2:  Double-sided form of P1 (P1 is single-sided)

```

```
% Pt:  P in time domain = ifft(P2) --> Inverse Fast Fourier Transform
of P2
% tP:  time vector of P (in s)
% P4:  Double-sided form of abs(Vf2)/S --> for averaging the pressure
for all waveforms (for averaging we use positive values)
%%%% Main outputs: Pf and P4
```

A3. Upscaling studies of ultrasonic melt processing upon direct-chill (DC) casting[§]

The final step in the UltraMelt2 project was to conduct pilot-scale studies to determine the UST efficiency and its scaling up potential. The studies were conducted at Advanced Metal Casting Centre (AMCC) of the BCAST in collaboration with our project partners (BRU, GRE, and Constellium). This study aimed at optimising and upscaling the UST process during DC casting of liquid Al alloy through proper flow management techniques using the knowledge gained from Chapter 8.

UST of Al alloys for microstructural refinement in DC casting setup can be performed either conventionally by immersing the vibrating sonotrode in a hot top melt pool or alternatively by submerging the sonotrode in a launder with or without the use of baffles. The latter way offers more opportunities for upscaling. Effective ultrasonic treatment of liquid metal depends essentially on the generated acoustic field intensity and treatment time of the melt within the cavitation zone. While the former is judged mainly on the basis of pressure amplification within the treatment volume that in turn relies on the achievement of resonance cavitation conditions, the latter is interpreted in terms of residence time of grain refining particles or substrates within the melt. This chapter first talks about the estimation of residence time for both UST approaches using numerical simulations (performed in the University of Greenwich) and then comparing their effect in maximising the treatment efficiency upon pilot-scale casting.

Based on the results from the resonance length studies (Chapter 8) and the residence time estimation (revealed that the mean residence time of grain refining particles during UST in a launder increases by almost 120% when compared with the UST in a DC casting hot top), pilot-scale experiments were designed and performed with and without strategically placed baffles separated by a distance of 1λ in a launder during DC casting. The influence of partitions (baffles) on the UST efficiency through in-situ acoustic pressure measurements and ex-situ macro- and microstructural observations is highlighted. The presence of partitions in launder has a strong positive effect of grain refinement of an AA6XXX aluminium alloy.

[§] Contents of this section is taken from C. Beckwith, et al., Metals (Basel). 11, 674 (2021) and T. Subroto, et al., Light Metals 2022, 649 (2022). – Reproduced after permission.

A3.1 Introduction

Microstructural refinement through grain size reduction is important in casting to improve mechanical properties and reduce defects such as hot tearing in aluminium alloys [436]. Various methods have been tried and tested for grain refinement during casting, for example, adding an inoculant (grain refiner) [437], ultrasonic refinement using a vibrating sonotrode [1], alternating current (AC) induction coil treatment [438] coupled with direct current (DC) field [439]. The main mechanisms through which the refinement occurs have been reviewed in Chapter 2. Just to recap, the refinement can take place through, (a) activation of non-metallic inclusions in the form of indigenous oxides such as Al_2O_3 present within the melt and exogenous grain refiners, like TiB_2 , that promote heterogeneous nucleation, or (b) fragmentation of dendrites and intermetallics/dispersoids such as Al_3Zr . In relation to the ultrasonic processing, a conventional approach is to apply ultrasonic treatment in the mould or hot top, which inevitably limits the processed volume to the area directly below the sonotrode and the spread of the effects to larger volumes required the use of several sonotrodes. An alternative approach is to process the flowing melt in a launder that feeds one or more moulds. A challenge here is to increase the residence time of the melt in an active cavitation zone as the melt is constantly flowing in and out. The addition of partitions can help in managing the flow thereby providing higher residence time for the melt to be processed continuously. Subroto et al. [366] have previously tested this approach in pilot-scale experiments, however without partitions, and observed the grain refining effect through primary intermetallic fragmentation, with the refined crystals then acting as active sites for Al grain nucleation.

The research presented here goes a step further by comparing the effectiveness of the two treatment approaches in terms of residence time through numerical simulations. A coupled numerical method was developed based on the finite element solver for the nonlinear Helmholtz cavitation model [440] and was validated by comparing the frequency domain results obtained upon applying FFT to the pressure in the time domain acquired from a Calfisch equation solver [286]. Based on the results of the process effectiveness, pilot-scale experiments were performed aimed at improving the melt residence time and acoustic pressure distribution that maximises the UST efficiency. The effect of partitions and UST on the grain refinement upon DC casting of an AA6XXX aluminium alloy with Zr additions (a hypothesis is that primary Al_3Zr crystals fragmented upon UST will act as substrate for Al grain nucleation) was revealed through microstructural observations of the cast billets. It should be noted that the

billets were cast both with and without partitions and with and without UST to understand the UST effectiveness.

A3.2 Materials and methods

A3.2.1 DC casting experiments

An AA6XXX series Al alloy with an addition of 0.254 wt% Zr but without any AlTiB grain refiner was used. Zr acted as an indicator for assessing the UST efficiency as it is well known that its additions significantly improve (through the formation and fragmentation of primary Al_3Zr particles) the grain refinement in alloys processed with ultrasound [1,441]. The chemical composition of the alloy was measured using optical emission spectroscopy (OES) as shown in Table A1. Two 1 m long billets with a diameter of 152 mm were cast using a hot top mould at a casting speed of 140 mm/min. DC casting was carried out at AMCC, BCAST, Brunel University London. One billet was cast with partition added onto the launder, and the other one acted as a reference for comparison and was cast without partitions. The first half of the billet was cast without UST but with immersed idle sonotrode and once it reached about 0.5 m in length, UST was applied by switching on the transducer that powered the sonotrode. The schematic of the experimental setup is shown in Fig. A2a.

Table A1 Average chemical composition (wt%) of the alloy obtained through optical emission spectroscopy (OES).

Al	Si	Fe	Cu	Mn	Mg	Zr	Cr	Ti
Balance	0.75	0.24	0.76	0.49	0.63	0.25	0.1	0.05

The billets were cast at a pouring temperature of 730°C. The sonotrode was powered using a water cooled 5-kW magnetostrictive transducer (Realtec) operating at a frequency of 17.3 kHz. The ultrasound within the melt was introduced using a cylindrical Nb sonotrode with a diameter of 40 mm. The sonotrode was immersed approximately 12 mm below the surface of the melt and was positioned in-between a pair of refractory partitions (when those were used) separated by a distance of 266 mm (corresponding to 1λ of the ultrasound wave at the transducer frequency). The hot top was further 200 mm away from downstream partition (see Fig. A2b). The partitions were designed and deployed in a way that allowed for the melt to flow both from top and bottom of the partitions in order to avoid overflowing and entrapment of melt in the launder.

The cavitation activity in terms of acoustic pressure intensity was measured using a high temperature cavitometer calibrated in the frequency range of 8 – 400 kHz. The details of the cavitometer can be found elsewhere [297]. The cavitometer probe tip was submerged about 30 mm below the melt surface at a distance of approximately 15 mm from the downstream partition towards the sonotrode. 60 waveforms obtained at a sampling of 5×10^6 samples per second were deconvoluted using the process presented in Section A1.

Fig. A2 (a) Illustration of UST-DC-casting setup with the UST sonotrode positioned in the middle between the partitions before hot top, (b) Zoomed side view of sonotrode and partitions.

A3.2.2 Numerical methods

computing the acoustic pressure field that accounted for the cavitation activity within the melt. The cavitation bubble activity was modelled via Keller-Miksis approach [442]. Discretised single bubble simulations were conducted at varying pressures, and the numerically computed coefficients were regarded as a function of local pressure in the Helmholtz equation.

Melt flow simulations were performed using combined algorithms in an OpenFOAM solver. A single continuum approach was implemented to model the solidification behaviour, where a solid region accounted for a momentum sink configuration. A brief overview of the numerical methods is presented in this section with more details can be found in [384]. The acoustic pressure was calculated using Helmholtz model with an assumption that the pressure field can be approximated through a time harmonic solution. To verify this assumption of considering the sufficiency of driving frequency in the model, a full time-dependent modelling was carried out for the launder system based on Calflich model of acoustic cavitation [440]. The implementation of this time efficient computational model was done with an assumption related to the effect of cavitation bubble dynamics on the induced ultrasonic field [429]. An FFT analysis of this time-dependent result is shown in Fig. A3a and the computed raw pressure signals in Fig. A3b. From the FFT analysis, the driving frequency was seen to dominate over higher harmonics, validating the use of a harmonic model. While it is possible that application of UST could lead to visible surface vibrations, the effect is minimal when compared to the main acoustic field. Also, no noticeable surface vibrations were encountered during the experiments. For this reason, the free surface is assumed to be a fixed sound-soft boundary.

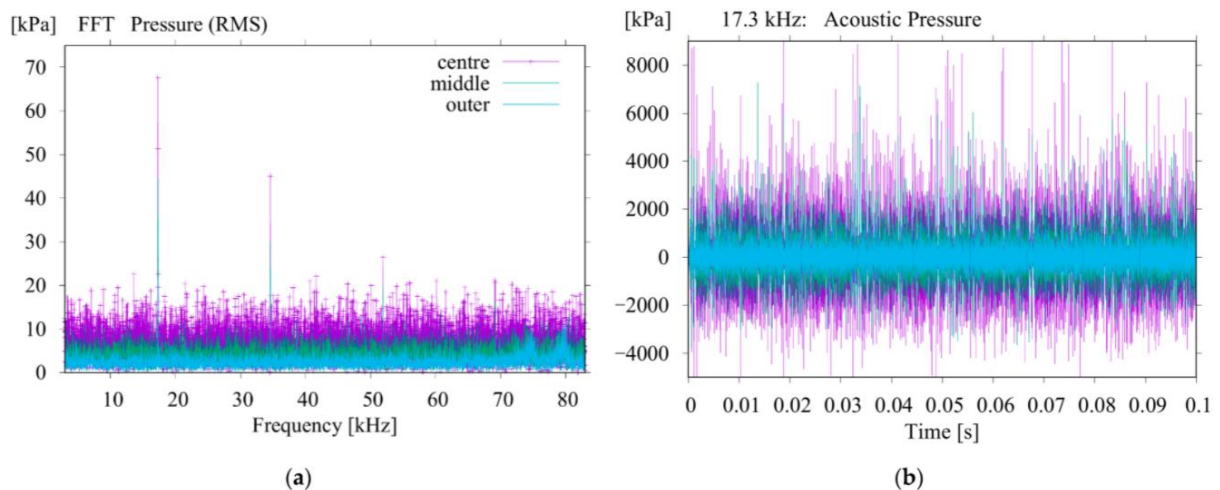


Fig. A3 (a) FFT frequency response from a Calflich cavitation model with the sonotrode positioned in the launder, and (b) the time series data at three nodal locations.

It is understood that the nucleating particles such as Al_3Zr or TiB_2 are although very small, prone to sediment and do not flow continuously within the bulk liquid, which means that the massless particle cannot be used for simulations. In addition to their higher density, these particles also exhibit plate-like morphology. Therefore, to take into account all of these crucial factors, a non-spherical drag model [443] was used for modelling the particle flow and distribution both in hot top and in launder with partitions. The fragmentation of these particles has not been modelled yet and can be opted as a potential future work. In this study, the density of the nucleating particles was taken as 4140 kg/m^3 [444] with a non-spherical drag model coefficient as 0.512. Lagrangian particle tracking via discrete element method (DEM) was used to determine the location of nucleating particles in the final billet. Previously, it was shown that different launder configurations have only a slight influence on the total processing time [423]. Therefore, in this work, only one partition configuration has been considered and tested, and the residence time of particles were compared those processed in the hot-top.

A3.3 Results and discussion

A3.3.1 Casting simulation

The efficiency of UST relies on several factors, but more specifically on the developed acoustic pressure field within the melt and the melt residence time within the active cavitation zone.. The cavitation zone is not limited only to regions below the ultrasonic horn but also spread to the areas nearby where the cavitation bubbles are transported by induced acoustic streaming, and where they can still vigorously pulsate and collapse. The melt/particle residence time can be increased by either using multiple ultrasonic sources that process a larger melt volume, or by involving melt recirculation around the cavitation zone for continuous treatment. The latter is obviously more economically and technologically viable and sustainable. So, here we shall look into the both numerically estimated pressure and residence time factors and their variation in DC casting hot top and launder.

Details of the numerical estimation technique of the acoustic pressure field has been briefly described in Appendix. The acoustic pressure distribution for processing the melt in launder and hot top is shown in Fig. A4a and Fig. A4b, respectively. Peak pressures under the sonotrode were observed to be comparable in both cases, however, the processing in launder encompassed a larger region with the pressure above the Blake threshold of liquid aluminium ($\sim 217 \text{ kPa}$) [366]. The comparison of pressure amplitudes vertically below the sonotrode is shown in Fig.

A4c. It can be seen that the acoustic waves attenuate rapidly in the region just below the source, forming the primary cavitation region. This decay of the acoustic waves away from the ultrasonic source follows a similar trend of the reduction of shock wave pressure as $1/r$ (see Fig. 5.18) though the shock pressure decay much faster in shorter distances away from the horn owing to shorter wavelength as discussed in Chapter 5 than the incident acoustic wave or harmonics. The acoustic energy is dissipated in the form of thermal and viscous losses, as well as acoustic radiation [445]. It is in this region that large bubble structures develop and contribute to the effect known as acoustic shielding [350] as also previously discussed in Chapter 2,4,5 and 6.

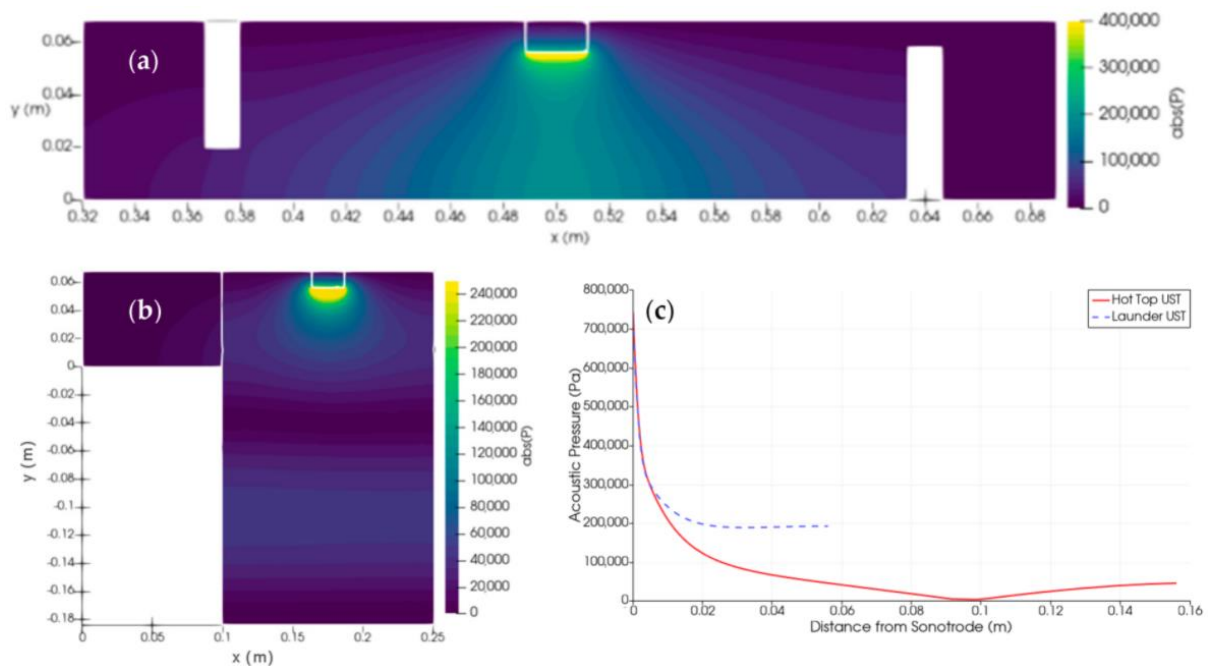


Fig. A4 Acoustic pressure distribution in (a) the launder and (b) the hot-top, and (c) a comparison of the pressure observed as a function of the vertical distance from the sonotrode tip.

Atamanenko et al. [174] previously established the relationship between processing time and the grain size. It was demonstrated experimentally that without UST, no grain refinement was observed in an Al-0.18 wt% Zr-0.07 wt% Ti alloy. However, with UST the grain size reduced from 285 μm to almost 180 μm just after 3 s of processing, and longer treatment times of 7s and 10 s further reduced the grain size to 107 μm to 67 μm , respectively. Even though the importance of active cavitation zone was clearly established, only the total processing time was measured and not the residence time in the active zone. The simulation results presented in Fig. A5 demonstrate the difference in particle residence time within the active cavitation zone when

applying UST in the launder and in hot top. A total of 10000 particles were released over a 5 s interval once the fluid simulation reached a steady state. Here, the residence time is defined simply as the time a refining particle of size similar to that of actual inoculants like TiB₂ spends being suspended in the liquid region, where the acoustic pressure is above the Blake threshold pressure (217 kPa). Upon moving the processing into the launder, particle recirculation allows for much higher average particle residence time when compared to processing in the hot top. The mean particle residence time in the launder was about 67 ± 45 ms, while the average time in case of hot top was around 30 ± 17 ms. In contrast to Ref. [174], the time found here relates to the active zone residence time, rather than the total processing time (or the operational time of transducer), hence the time scale may be different. However, it should be noted that it is this active zone residence time, which is an important criterion for the efficiency of processing.

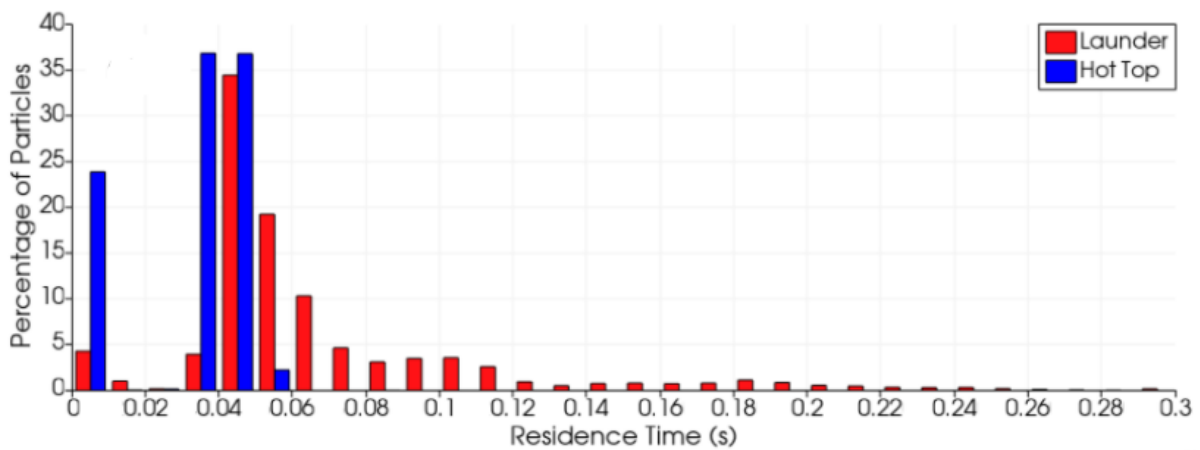


Fig. A5 Computed particle residence time in the billet through processing in the hot-top and in the launder.

A3.3.2 Pilot-scale DC casting

Acoustic pressure measurements during pilot scale trials in the DC caster launder showed that the presence of partitions generally improves the pressure field in terms of the maximum pressure ($P_{\max}$) and the average pressure (P_{RMS}) distribution. P_{Max} and P_{RMS} with partitions were measured to be approximately 1086 ± 731 kPa, and 57 ± 20 kPa, respectively, while without partitions, P_{Max} and P_{RMS} were around 507 ± 499 kPa and 37 ± 13 kPa, respectively. The results are in line with the experiments conducted in Chapter 8 (see Fig. 8.7). This means that there was an approximately 50% increase in RMS acoustic pressure, the maximum pressure increased by 2 times. This indicated more intense cavitation activity when partitions were employed. Subroto et al. [366] previously also observed this effect of partitions through numerical simulations, where it was shown that the presence of partitions significantly

enhances the pressure distribution almost by two fold that could potentially improve the efficiency of UST.

Figure A6 shows the effect of UST on grain structure of the billet on a macroscopic level. It can be seen in Figs. A6a and A6c that without UST, feathery or columnar grain structure developed in the billet. This type of structure typically points towards a poor grain refinement [446] and is not desired in industrial alloy production as it lead to inferior mechanical properties, such as susceptibility to solidification cracking, lack of ductility and homogeneous deformability [8]. However, when UST was applied, the feathery region in the billet was suppressed and fine equiaxed grains occupied most of the billet cross-section (see Figs. A6b and A6d). The effect of UST seems to be more pronounced in the case of partitions in the launder, promoting further grain refinement in the as cast billets. McCartney [9] suggested that two conditions must be fulfilled for the grain refinement to be effective; (a) there should be numerous potent substrates introduced in the melt, and (b) those substrates need to be activated for Al grains to nucleate. Since the amount of Zr added in this alloy is beyond the solubility limit of Zr in liquid Al (~ 0.11 wt%), Al_3Zr particles form in the melt as primary intermetallics. Such particles are potent nucleants for Al grains [447] owing to their minimum crystallographic mismatch with the Al phase [171] but only when they are below a certain size ($\sim 3 - 5 \mu\text{m}$) [174]. One of the main structure refinement mechanisms using UST above the liquidus of aluminium is the refinement of primary intermetallics through enhanced nucleation and fragmentation [1], leading to multiplication of potent substrates in the melt. Thus understanding the fragmentation mechanism (see Chapter 4 and 6) of these intermetallics becomes necessary. In our experiments, the temperature of the melt during UST was between 707°C and 715°C , which is about 10°C below the liquidus of Al_3Zr phase and 50°C above the liquidus of the matrix aluminium alloy. Therefore, the fragmentation of the primary intermetallics and nucleation of Al on them is the most likely reason for the observed grain refinement.

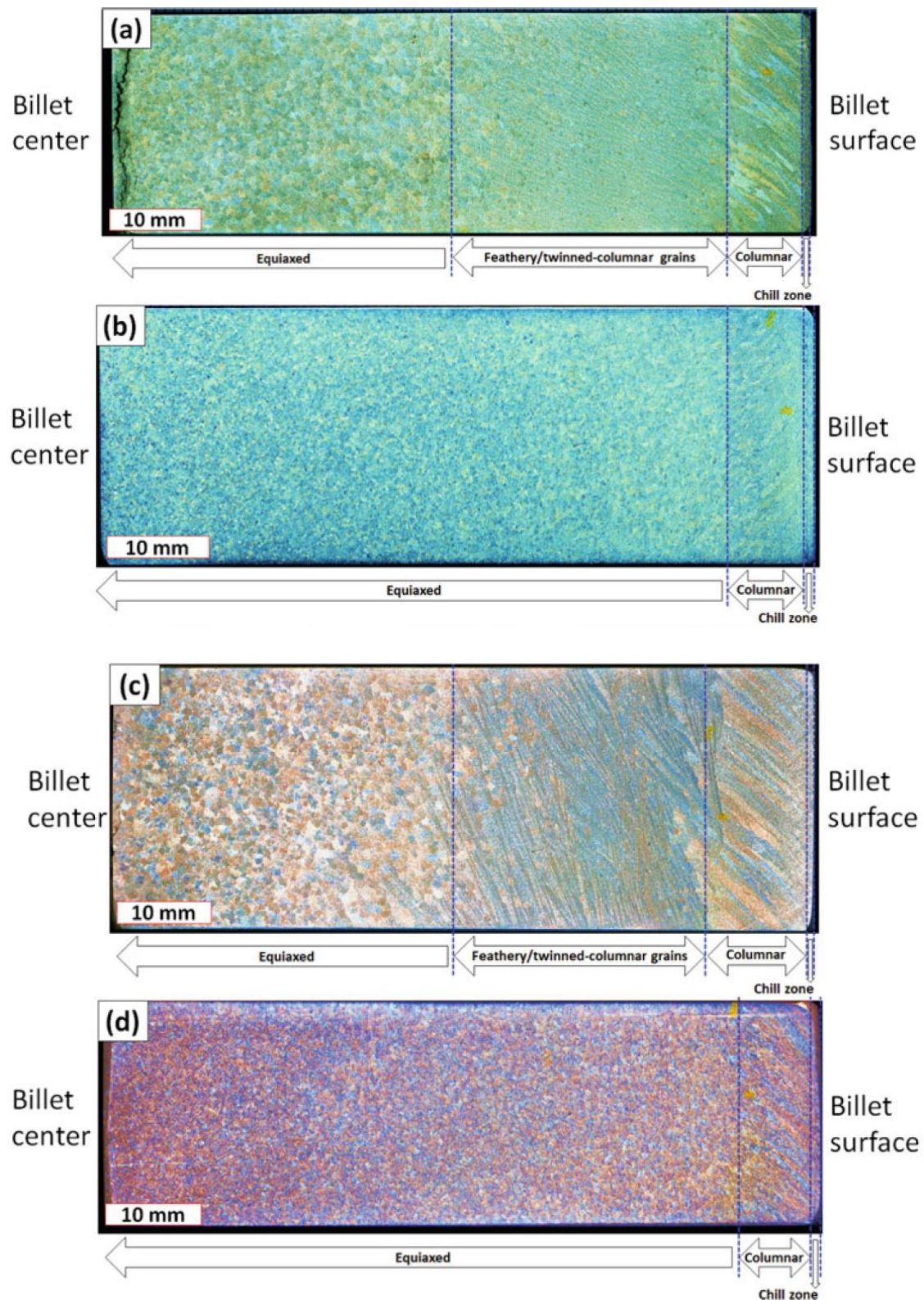


Fig. A6 Etched macrostructures revealed the effect of UST and partitions at different processing conditions. (a) Without partitions and without UST, (b) without partitions but with UST, (c) with partitions but without UST, and (d) with both partitions and UST.

In order to properly assess the effectiveness of UST on structure refinement, we performed microscopic analysis of the grain structure from the central part of the billet, where the grain structure from both parts of the billets (with and without UST) are equiaxed. In general, Fig. A7 shows that the application of UST significantly reduced the grain size in both billets, i.e., cast without (Fig. A7a – No UST to Fig. A7b – with UST) and with partitions (Fig. A7c – No UST to Fig. A7d – with UST).

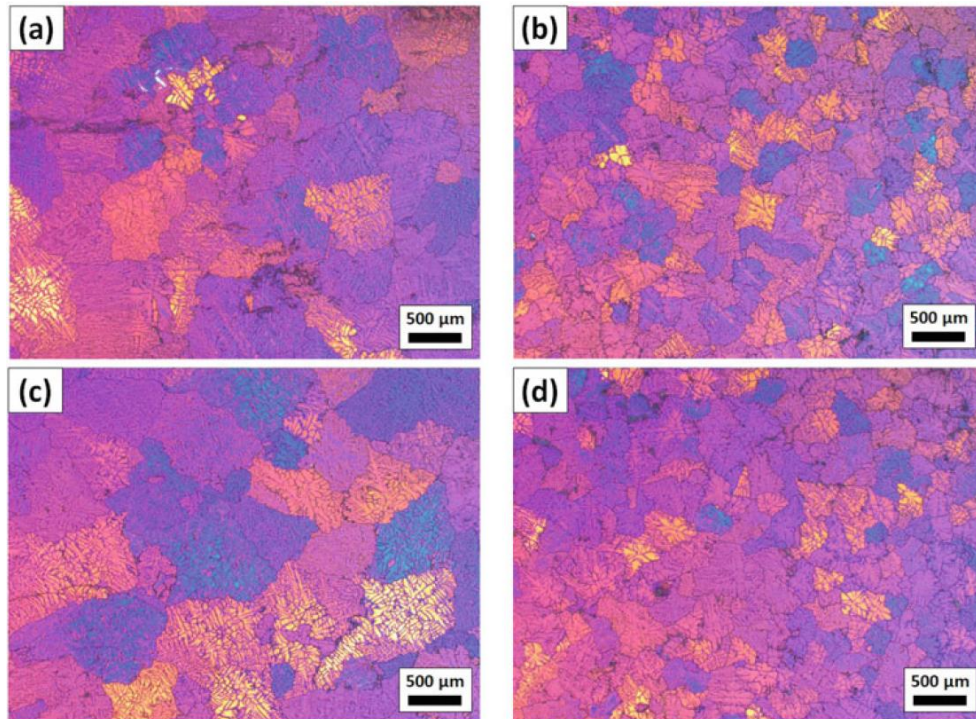


Fig. A7 Typical microstructure at the center of the billet at different processing conditions (a) without partitions and without UST, (b) without partitions but with UST, (c) with partitions but without UST, and (d) with both partitions and UST.

The quantitative grain size analysis (Table A2) suggests that the presence of partitions did not alter the average grain size for casting without UST. But when the UST was activated, the presence of partitions assisted in improving the UST efficiency by an additional 10% refinement. This could be explained by the increase of cavitation activity caused by the resonance due to presence of partitions as also indicated from the acoustic pressure measurements (see Chapter 8). This also verifies the numerical simulation results in our previous work [366] that partitions may provide a positive impact on structure refinement using UST.

Table A2 Quantitative grain size analysis under different processing conditions.

Avg. grain size on centre of billets (μm)	With partitions	No partitions
No UST	455 ± 50	450 ± 40
With UST	220 ± 10	240 ± 10

The results obtained in this work demonstrate a proof of concept that the presence of partitions can help in improving the efficiency of UST in the melt flow in a launder during DC casting. Moreover, these results on grain refinement upon DC casting demonstrate that in refinement in industrial casting can be achieved via UST without using any inoculants. This is especially important for a range of alloy systems such as Al-Zr, where the addition of grain refiners such as TiB_2 results in Zr poisoning leading to detrimental effects caused by agglomeration and low mixing efficiency. Therefore, future strategies for commercial implementation should be focussed on suppressing the use of costly, wasteful and hazardous grain refiners and replace them with UST that can offer rapid and effective alternative solutions that is economical and environment friendly with significantly less or even without the use of inoculants. This opens the possibility for further improvement of treatment efficiency by optimising the design and placement of the partitions in the DC casting launder with the aim of attaining maximum acoustic pressure and optimum residence time. Treating the melt in the melt flow allows potential upscaling of UST to treating larger volumes upon casting in a number of moulds simultaneously, using fewer ultrasonic sources. Some of the possible parameters to be examined in the future are the effect of sonotrode positioning with respect to partitions [422] during UST-DC casting, inclination of the sonotrode with respect to the flow, and also geometry and positioning of the partitions [423]. The use of numerical simulations to obtain the best geometry and positioning of the partitions will be beneficial to minimise the trials and improve the efficiency of resource and time.

A3.4 Conclusions

This work focused on the numerical simulation estimation and comparison of UST effects on processing liquid Al in the DC casting hot top and in launder in terms of generated acoustic pressure field and residence time of grain-refining particles within the active cavitation zone. This was further complemented by pilot-scale experiments to demonstrate the potential benefits

of applying UST during DC casting of an AA6XXX Al alloy with added Zr in a launder. The effect of partitions (placed in the launder) on the efficiency of UST was investigated through both acoustic pressure measurements and macro- and micro structure analysis. Following conclusions were drawn from these studies:

1. The acoustic pressure field extends to a larger region with pressures close to Blake threshold in the case of UST in a launder when compared to that in a hot top.
2. Ultrasonic melt processing in a launder exhibits an increase in residence time of grain refining particles by 120% as compared to the UST in the hot top upon DC casting.
3. Pilot-scale studies in an industrial DC casting facility reveal that UST successfully suppresses the formation of feathery/columnar grains and refines the microstructure of as-cast billets by decreasing the grain size by almost 50% as compared to those obtained without UST.
4. The presence of partitions spaced at a distance 1λ in the launder during UST-DC casting positively impacts the structure refinement with generated maximum acoustic pressure being almost twice as high and up to 600 kPa to that of pressures measured without partitions.
5. Microstructure observations show an additional 10% grain size reduction when using partitions during UST-DC casting.

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