

Quench Sensitivity of 7xxx Series Aluminium Alloys

A Thesis Submitted for the Degree of
Doctor of Philosophy

by
Yong Zhang

Department of Materials Engineering
Monash University
Clayton, Victoria
Australia

June 2014

Copyright Notices

Notice 1

Under the Copyright Act 1968, this thesis must be used only under the normal conditions of scholarly fair dealing. In particular no results or conclusions should be extracted from it, nor should it be copied or closely paraphrased in whole or in part without the written consent of the author. Proper written acknowledgement should be made for any assistance obtained from this thesis.

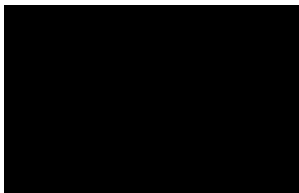
Notice 2

I certify that I have made all reasonable efforts to secure copyright permissions for third-party content included in this thesis and have not knowingly added copyright content to my work without the owner's permission.

Statement of originality

The work submitted does not contain any material that has been accepted previously for the award of any other degree or diploma at Monash University or any other institution. To the best of my knowledge and belief, it does not contain any materials previously published or written by any other person, except where due reference is made in the text of the thesis.

Yong Zhang



Melbourne, June 2014

Acknowledgements

I wish to acknowledge the Aluminium Corporation of China Ltd (Chalco) for the scholarships provided to undertake this PhD degree in Australia in the Department of Materials Engineering at Monash University.

Firstly, I would like to thank my supervisors, Prof. B.C Muddle of the Department of Materials Engineering for his support and inspiration, Dr. Paul Rometsch for his tireless discussion, availability to meet with me and correct my work without delay, Prof. Nick Birbilis for his fruitful suggestion, especially in the later stages of the project. I would also like to thank Dr. Colleen Bettles for her generous help with the journal publication.

I am indebted to all the technical staff and the administrative staff, of the Department of Materials Engineering, especially to Prof. Jianfeng Nie and Mr. Sam Gao for their tireless help in the familiarisation with transmission electron microscopy techniques and analysis, Mr. Daniel Curtis for his help in preparing samples, Ms. Tara Schiller for her generous help to operate the new DSC equipment at Monash, and Dr. Steve Knight for his help and discussion.

I would also like to thank all the staff at the Monash Centre for Electron Microscopy (MCEM), for their patience and promptness with all the help provided. I would also like to thank Dr. Matthew Weyland for helping me with the high resolution imaging, Dr. Xiya Fang, Dr. Yu Chen, Dr. Russel King, Mr. Renji Pan, Dr. Flame Burgmann and Ms Ellen Lavoie for providing patient training in operating the world-class equipment at MCEM.

There are a number of people from Rostock University in Germany who helped me with the specialised DSC devices. In particular, I thank Dr. Benjamin Milkereit,

Prof. Olaf Kessler, Prof. Christoph Schick, Dr. Davit Zohrobyan, Ms. Lydia Giersberg, Dr. Julia Osten, Mr. Philipp Schumacher, Mr. Matthias Krawutschke and Mr. Rudolf Amelang for their contributions to the completion of my research.

Many friends who have made life enjoyable at Monash University: Dr. Zhou Xu, Mr. Hao Zhong, Dr. Lingfei Cao, Dr. Suming Zhu, Dr. Yuman Zhu, Dr. Hoipeng Ng and Dr. Liwei Quan are also acknowledged for their encouragement and support during my study.

A special thanks to my parents for their encouragement in my whole life. Thanks also to the contribution from my old brother Bin Zhang, and to my mother and sister in law.

Finally, I would like to express my gratitude to my wife, Liu Yang for her patience and support throughout my study, and also to my son, Boao Zhang for the joy he brings to our family life.

Abstract

The quench sensitivity of high strength 7xxx series aluminium alloys becomes an increasingly important issue as the product thickness increases. Due to the nature of thermal conduction, the centre layer of a thick aluminium plate experiences a slower cooling rate than the surface. This can lead to variations in properties such as strength, corrosion resistance and fracture toughness across the thickness of a plate. The objective of this work was to study the quench-induced precipitation behaviour in different 7xxx alloys with systematic changes of alloy composition and processing history. Detailed microstructural analysis has been carried out using SEM, EBSD, TEM and HAADF-HRTEM. Vickers hardness values, electrical conductivities and the precipitation heats determined from differential scanning calorimetry (DSC) were measured for a wide range of different cooling rate conditions to evaluate the different quench sensitivity behaviours. The main findings from this work are as follows:

1. The results show that the Al_3Zr dispersoids in recrystallised grains can become preferential nucleation sites for quench-induced precipitates in air cooling condition. The microstructural characterisation shows that the Al_3Zr dispersoids tend to maintain their metastable structure and orientation when recrystallisation occurs. This causes them to lose coherency with the matrix after recrystallisation and thereby causes them to become more

potent heterogeneous nucleation sites for quench-induced precipitation. It should be noted that incoherent Al_3Zr dispersoids are not the only preferential sites for quench-induced precipitates. They can precipitate out at grain/subgrain boundaries in air cooling condition. However, the current research still demonstrates that materials containing a higher fraction of recrystallisation will lead to a significant increase of quench sensitivity.

2. The precipitation heats for quench-induced precipitates have been studied using a specialised DSC technique over a wide range of cooling rate conditions. A continuous cooling precipitation (CCP) diagram for commercially produced alloy 7150 has been developed based on a combination of DSC measurements, microstructure analysis and hardness testing. The results show that there are three main quench-induced precipitation located in different temperature ranges. It is demonstrated that the high temperature reaction from about 350 to 470 °C corresponds to S-phase (Al_2CuMg), the medium temperature reaction from about 200 to 400 °C corresponds to M-phase (MgZn_2) and the low temperature reaction from about 250 to 150 °C corresponds to a unique platelet phase containing both Cu and Zn. The critical cooling rates were determined to be 3 K/s for the S-phase, 10 K/s for the M-phase, and 300 K/s for the unique platelet phase in alloy 7150. The platelet phase has not been previously reported for alloy 7150. The platelets precipitate with a high aspect ratio and have a hexagonal structure ($a=0.429$ nm, $c=1.385$ nm) according to HAADF-STEM images. It is shown that this platelet phase can contribute to strengthening.
3. It was shown that the surface layer of a 7150 thick plate is more sensitive to cooling rate than the centre layer. This can be ascribed to a relatively higher degree of recrystallisation in the surface layer. Therefore there are more nucleation sites for quench-induced precipitates in the same cooling condition. It was confirmed with DSC analysis that the precipitation heat

values for the surface layer are higher than for the centre layer, demonstrating that there is more quench-induced precipitation occurring in the surface layer.

4. A number of CCP diagrams were developed for alloys 7085, 7037, 7020 and 7055 with systematic changes in alloy composition. It is demonstrated that the quench sensitivity generally increases with increasing total alloy content. Therefore alloy 7020 exhibits the lowest quench sensitivity when compared with the other studied alloys. It is noted that the amount of M-phase increases with increasing Zn content. Therefore alloys 7085, 7037 and 7055 can precipitate more M-phase during slow cooling than alloys 7150 and 7020. However, the precipitation of S-phase during continuous cooling was found to be significantly suppressed with increasing Zn/Mg ratio. Quench factor analysis (QFA) also indicates that higher k_3 values can be found for the higher Zn/Mg ratio alloys 7085 and 7037, suggesting that the energy required to form a nucleus is higher in these two alloys. This is in agreement with experimental observations that these two alloys contained less S-phase and exhibited relatively low quench sensitivities.

It was shown that the CCP diagrams provide a useful method of quantifying the quench sensitivities of different alloys. The CCP diagrams can also facilitate engineers to design and optimise industrial cooling process more effectively. However, it requires a deep understating of the quench-induced precipitation to develop a reliable CCP diagram for a given alloy, i.e. what types of quench-induced precipitation reactions happen, where they preferentially nucleate and how many much precipitation occurs during the cooling process. The current research therefore shows that the quench sensitivity of a 7xxx alloy can be decreased by decreasing the degree of deformation, decreasing the fraction of recrystallisation, decreasing the total grain boundary area, decreasing the number

of incoherent dispersoids, decreasing the total alloying content, increasing the Zn/Mg ratio and decreasing the Cu content.

Table of contents

Acknowledgements.....	I
Abstract	III
Table of contents.....	VII
Chapter 1. Introduction.....	1
Chapter 2. Literature review	5
2.1. Development of 7xxx alloys for aerospace applications	5
2.2. Quench sensitivity of 7xxx alloys	12
2.3. Effect of alloy composition on quench sensitivity	15
2.4. Characterisation of quench sensitivity	30
2.4.1. Time-temperature-transformation (TTT) diagrams.....	30
2.4.2. Time-temperature-property (TTP) diagrams.....	34
2.5. Continuous-cooling-transformation (CCT) diagrams	39
2.6. Modelling approaches for non-isothermal transformations.....	42
2.6.1. Quench factor analysis	42

2.6.2. Other modeling approaches	48
2.7. Research aims.....	49
Chapter 3. Materials and methods	51
3.1. Materials casting and processing	51
3.2. Heat treatment	53
3.2.1. Heat treatments for solution treatment work in chapter 4	53
3.2.2. Heat treatments and DSC work in chapter 5 and Chapter 6.....	53
3.2.3. Step quenching experiments	62
3.3. Self-designed Jominy quenching Rig.....	64
3.4. Hardness testing	65
3.5. Scanning electron microscopy (SEM).....	65
3.6. Electron backscattered diffraction (EBSD)	65
3.7. Transmission electron microscopy (TEM)	66
3.8. High angle annular dark-field imaging - scanning transmission electron microscopy (HAADF-STEM).....	66
Chapter 4. Effect of thermo-mechanical processing	67
4.1. Introduction	67
4.2. Microstructure evolution before and after homogenisation	68
4.3. Different quench sensitivity behaviour before/after deformation.....	74
4.4. Quench sensitivity behaviour of 7150 thick plate.....	79
4.5. Different quench sensitivity behaviour after further deformation	91
4.6. Discussion	94
4.7. Conclusions	97
Chapter 5. CCP diagram for alloy 7150 thick plate	99

5.1. Introduction	99
5.2. Jominy end quench	100
5.3. Constructing CCP diagrams for alloy 7150 plate.....	103
5.3.1. DSC curves and CCP diagrams	103
5.3.2. SEM characterisation	109
5.3.3. TEM characterisations	113
5.3.4. CCP diagram for alloy 7150.....	123
5.4. DSC analysis for plate surface and centre	125
5.5. Discussion	130
5.6. Conclusions	134
Chapter 6. CCP diagrams for other studied 7xxx alloys.....	137
6.1. Introduction	137
6.2. CCP diagram for alloy 7020	138
6.3. CCP diagram for alloy 7085	146
6.4. CCP diagram for alloy 7037	150
6.5. CCP diagram for alloy 7055	155
6.6. Quench factor analysis for studied alloys.....	158
6.7. Discussion of quench sensitivity of studied 7xxx series alloys	167
6.8. Conclusions	176
Chapter 7. Conclusions and future work.....	179
7.1. Conclusions	179
7.2. Recommendations for future work.....	182
Publications and Presentations	184
References	187

Chapter 1. Introduction

The aerospace industry is now showing a shift from a defense-driven condition that pushed technology to its limits, to one that is dictated more by commercial interests [1]. This has led to an increased emphasis on issues like cost effectiveness, damage tolerance, durability, uniformity, and high life-cycle designs as primary considerations in aeronautical material development and selection [2, 3]. This has provided the necessary impetus to materials scientists and engineers to make material refinements while concurrently engineering new alloys and innovative processing techniques to effectively meet the increased demands set by the newer generation of aircraft.

Among the candidate materials available to meet the challenges of modern airframe design are aluminium 7xxx series alloys. In fact, 7xxx series alloys have been widely used in the aerospace industry for over 80 years, but until now, the aerospace industry still heavily relies on these alloys due to their desirable strength-to-weight-to-cost ratios. The addition of Cu to the ternary Al-Zn-Mg system, together with small amounts of Cr, Mn and/or Zr, has resulted in the highest strength aluminium alloys available, with the yield strengths of some 7xxx alloys reaching more than 600 MPa [4].

High strength 7xxx series alloys have been widely used in the aerospace industry since the 1940s [5, 6]. Due to their high strength, they are normally used for load bearing structures such as beams or spars in airplane wings. For this purpose, high strength 7xxx series alloys tend to be produced as thick plates. It is thus expected that the surface and centre layers of these thick plates will experience different cooling paths during quenching after solution treatment. As a result, the strength in the centre layer decreases dramatically with increasing thickness of the plates. In order to achieve a high strength at the centre, the plates must be cooled as fast as possible to avoid the precipitation of equilibrium phases. However, the argument for faster quenching rates is not entirely practical since both the magnitude of residual stresses and of the distortion that develops in the products tend to increase with increasing cooling rate [4]. It is therefore the purpose of the current research to discover ways of decreasing the quench sensitivity so that adequate combinations of properties can be achieved over a wider range of cooling rates. This will be achieved by investigating the underlying mechanisms and degrees of quench sensitivity for several 7xxx series alloys, with alloy AA7150 as the benchmark. The following main aspects are included in this work:

1. To clarify and explain the underlying mechanisms of why an alloy is sensitive to slow cooling conditions. The corresponding microstructural features such as recrystallisation, dispersoid particles and quench-induced precipitation are investigated. A series of 7xxx alloys with systematic changes in major alloying additions are studied for the purpose of improving the combined properties of aluminium thick plates by careful design and control of the chemical composition and heat treatment process.
2. To describe the quench sensitivity by means of the development of continuous cooling precipitation (CCP) diagrams for the studied 7xxx aluminium alloys. This method utilises different techniques that include specialised DSC measurements, dilatometer quenching and microstructure analysis. The quench sensitivity is

evaluated based on a detailed analysis of each precipitation reaction peak during continuous cooling.

3. To describe the CCP diagrams of the studied 7xxx alloys using the quench factor analysis method. This numerical process is developed further to illustrate the effect of quench rate on the precipitation reactions of 7xxx alloys and to model the C-curves for overall precipitation reactions.

Chapter 2. Literature review

2.1. Development of 7xxx alloys for aerospace applications

The development of aluminium alloys has greatly influenced the history of world aviation. It is believed that the more durable and reliable aluminium alloys became, the higher, faster and safer airplanes flew. But, before it became the essential and most important material for aircraft manufacturers, aluminium navigated a long route from pure metal to high-strength alloys.

It has been more than 100 years, since the Wright brothers' first use of an aluminium-copper casting for their aircraft crankcase in 1903. Alfred Wilm and his assistant Jablonski, two German metallurgists, discovered age hardening precipitation in the Al-Cu-Mg system (known as Duralumin) system in 1906 [7, 8]. Nicholson *et. al* in 1958 pointed out that the strengthening may be attributed to the elastic strains near coherent G.P. zones or submicroscopic particles (Al_2Cu) [9]. This outstanding discovery has unveiled an important strengthening method for aluminium alloys. Consequently, a series of aluminium alloys were developed with reasonable strength during the Second World War, and they have been widely applied to airplane manufacturing since then.

The first aluminium alloy designed for airplanes is alloy 2017 (Al-4Cu-1.5Mg-0.5Mn. wt%) with a yield strength of about 250 MPa [10]. This alloy has been

applied to Junker F-13 airplanes (as shown in **Fig 2.1**). Alloy 2024 (Al-4Cu-1.5Mg-0.5Mn, wt%) was used for the commercial airplane DC-3 in the T3 temper with a yield strength of about 325 MPa (as shown in **Fig 2.1**).

In 1923, Sander and Meissner in Germany found that the ternary Al-Zn-Mg alloys exhibited a more outstanding age hardening behaviour than any other compositions at that time [6, 10]. Based on this ternary system, several 7xxx series aluminium alloys have been developed. An AA7075-T6 material (Al-5.6Zn-2.5Mg-1.6Cu-0.23Cr-0.3Mn, in wt%) was developed in 1943 with a yield strength of about 500 MPa [11]. The Cu and Cr were included to benefit the stress corrosion cracking (SCC) resistance [12, 13]. As a results, the high strength alloy AA7075-T6 has been widely used in aircraft applications. However, due to the loss of strength in heavy gauge sections, application of this alloy are limited plates with thicknesses of 75 mm or less [14]. But due to its high static strength, this alloy is still used in modern aircraft applications today.

In 1954, a general awareness of lifetime design for aluminium alloys was aroused due to the famous DeHavilland Comet aircraft crashes [15] (the Comet aircraft has been shown in **Fig 2.1**). The investigation showed that the failure started with fatigue cracking at the aft lower corner of the forward escape hatch. Therefore, the fatigue lifetime has been taken into account in aircraft design as well as other properties such as static strength, formability and resistance to SCC. It has been found that the resistance to SCC in moderately thick products (especially in the short transverse direction) in T6 temper was inadequate, but the alloys were found to have a highly favourable SCC resistance in the overaged T7X type temper. As a result, AA7075-T73 and AA7075-T76 type alloy and temper combinations were developed with increased resistance to SCC and exfoliation corrosion. These types of alloys have been successfully applied to aircraft since 1940s [5].

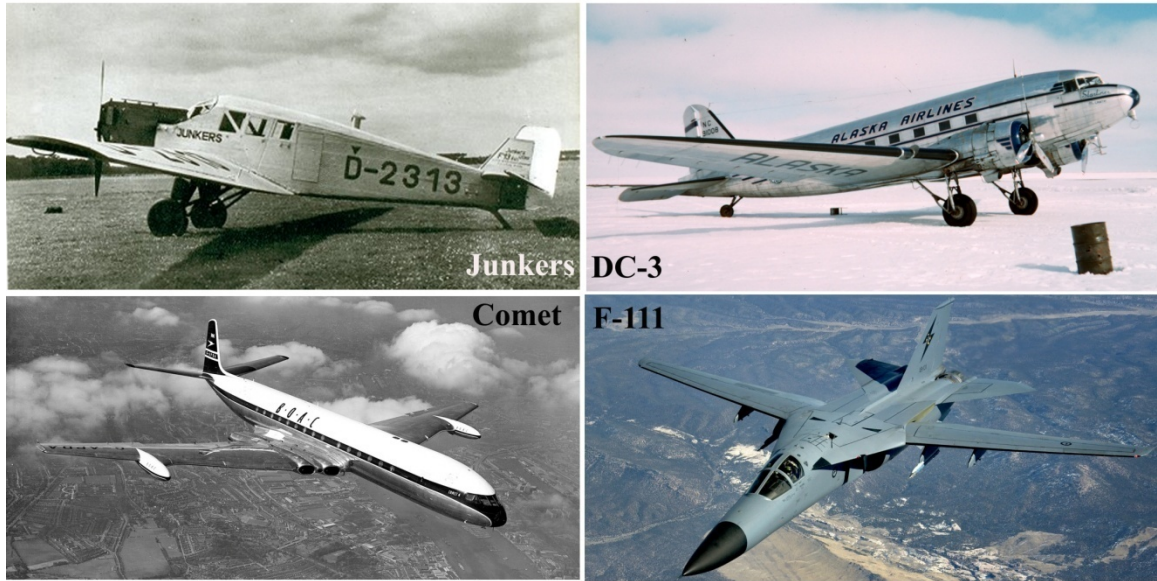


Figure 2.1: Four classical aircrafts that are often cited as milestones in relation to aluminium property design in the aircraft industry's approach to structural integrity [15].

In 1967, a new military aircraft F-111, entered service with two variable-sweep wings (aircraft F-111 has been shown in **Fig 2.1**) [16]. The design ideal was to enable changes to the angle of the sweep wings to fulfill different flying modes. However, it was only two years later that one of the planes lost one of the wings during a training flight. It took years to find out that the tragedy was caused by an undetected flaw that was later discovered in the lower plate of the let-hand wing pivot fitting [15]. The United States Air Force (USAF) then provided a mandated new guideline (MIL-A-008866) to ensure the safety of aircraft with damage tolerance requirements [17]. According to these guidelines, the aluminium alloys are allowed a certain damage tolerance so that a crack can be detected before catastrophic failure. Therefore the aircraft structure will continue to withstand a high proportion of its design load even after damage has occurred. The instability of the crack is associated with the critical stress intensity factor called K_{Ic} , with units expressed in $MPa\sqrt{m}$.

In 1971, Alcoa developed a Zr-containing alloy AA7050 (Al-6.0Zn-2.0Mg-2.0Cu-0.15Zr, in wt%). The aim was to produce an alloy with higher strength and high SCC resistance in the T6 temper. The material AA7050-T76 was found to exhibit an optimum combination of strength and SCC resistance. Most importantly, the alloy exhibited lower quench sensitivity with decreasing Cr content. Therefore alloy AA7050-T76 has been used in various geographic scale components including some thick gauge sections. Until now, alloy AA7050 is known as the most widely used commercial 7xxx alloys [6, 18-20].

Later in 1978, the alloy AA7150 (Al-5.6Zn-2.2Mg-2.0Cu-0.15Zr, in wt%) with lower impurity contents was designed to achieve a better fracture toughness compared with alloy AA7050. But this alloy was not widely used until a better temper was developed in 1993 by Alcoa, called the T77 temper. It has been shown that alloy AA7150-T77 has a higher damage tolerance as well as a reasonable SCC resistance without sacrifice in strength when compared with AA7050-T76 [21-25]. Since this temper is still under patent, the exact details and mechanisms are still unclear yet. But it is generally believed that the T77 temper is based on a three step ageing treatment that Cina has developed in 1973 [26]. The Cina process involves short time exposure to a relatively high temperature in the range from 200-280 °C (known as retrogression). This T77 temper can also be applied to other 7xxx series alloys, including the alloy AA7055 (Al-8.0Zn-2.0Mg-2.0Cu-0.12Zr) that was developed in 1991 to achieve a desirable combined properties.

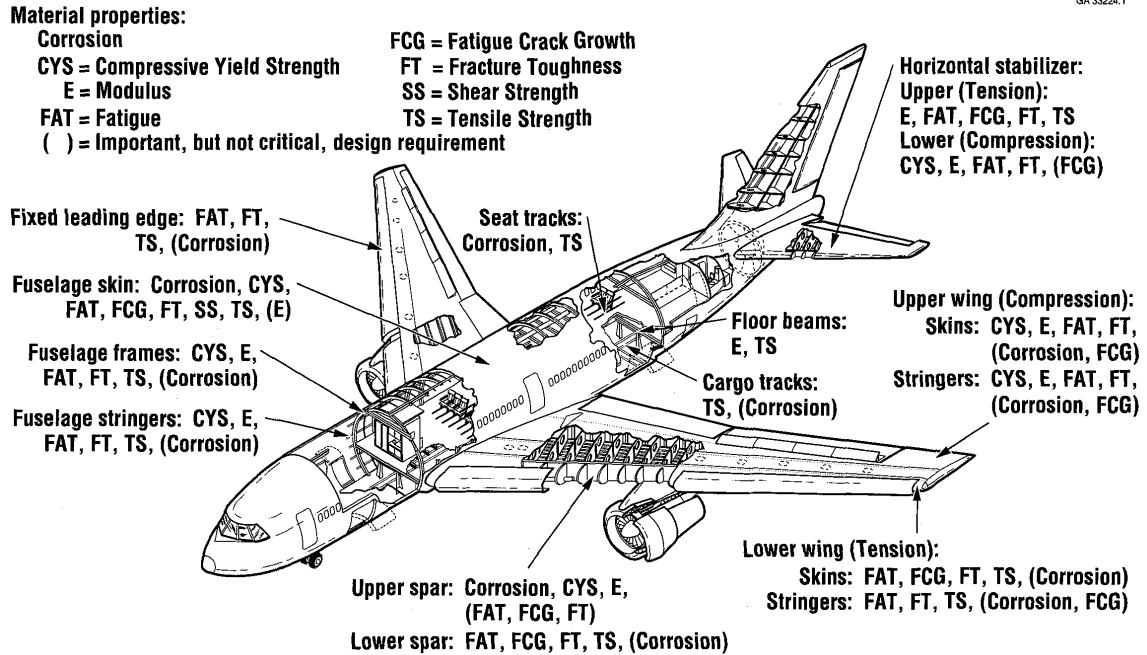


Figure 2.2: Critical requirements of modern airframe components [5]

Today, the aircraft designers are more likely to choose alloys for different components according to their unique combinations of properties (as shown in **Fig 2.2**). For example, the upper wing skins of most of today's large aircraft are typically made from high strength 7xxx series aluminium alloys such as AA7150, AA7055 or AA7056 due to the upper wing structures being compressively loaded [16, 20]. However, since the lower wing structures of these same aircraft wings are under tension during flight, they will require a higher damage tolerance than their upper wing counterparts [20]. Although one might desire to design lower wings using a higher strength alloy to maximise weight efficiency, the damage tolerance characteristics of such alloys often fall short of design expectations. As such, most commercial jetliner manufacturers today specify a more damage-tolerant 2xxx series alloy, such as 2324 or 2524 aluminum, for their lower wing applications. Other load bearing structures (for extensive application in heavy-duty structures)

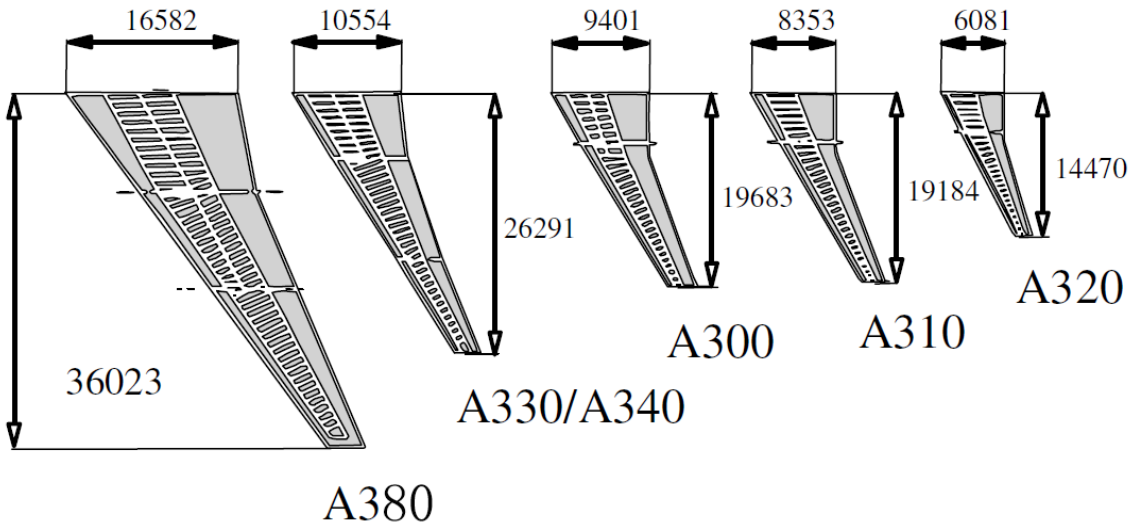


Figure 2.3 Wing sizes for modern large-bodied aircraft, with dimensions in mm [1].

such as beams, body stringers, integral spar members and landing gear parts are also made of 7xxx alloys [1].

As the size of new jet aircraft gets larger, or as current jetliner models grow to accommodate heavier payloads and/or longer flight ranges to improve performance and economy, the demand for weight saving of structural components, such as fuselage, wing and spar parts continues to increase. To meet the future requirements of airframe manufacturers, the aluminium alloy material suppliers are being asked to extend their capabilities in relation to casting volumes, rolling mill sizes (length, width and thickness), stretching capabilities, static material properties, durability, damage tolerance and corrosion resistance. Such consideration of multiple material attributes for aircraft applications eventually led to today's damage tolerant designs, which combine the principles of fail-safe design with periodic inspection techniques.

Fig 2.3 illustrates that the increased wing size requirements for modern large-bodied aircraft. It is shown that the length of the Airbus A330 wing is almost doubled when compared to the Airbus A320 wing. The Airbus A380 is known as

the world's largest commercial airliner. It is capable of carrying more than 500 passengers and has a total wingspan of more than 72 m. It is reported that the Airbus A380 still heavily relies on aluminium-based alloys that 61% of the structure is made of aluminum alloys, especially the wing structural parts such as the panels, stringers, spars and ribs [18-20].

A large jet aircraft requires very large wing box components. From the designer's perspective, it would be good if an upper spar, web and lower spar of a wing box could be produced from a thick simple section such as a thick plate of aluminium alloy products so that both welding and rivet-jointing can be avoided. This machining operation is known as 'hogging out' the part from its plate products. From a metallurgical point of view, any welding or riveting could potentially deteriorate the properties by introducing unexpected defects. Moreover, it is known that 7xxx series alloys exhibit poor weldability due to the fact that the dendritic structure formed in the fusion zone can seriously compromise the mechanical properties of the welded product [12]. Therefore a special welding technique named Friction Stir Welding has been developed for these types of alloys [27]. Nevertheless the high strength 7xxx series alloys are still tend to be produced as thick plates, including some fuselage structures [19].

Making integral parts for such wings would require products as thick as 6 to 8 inches (152 to 203 mm) or more. Alloy 7050-T74 is often used for thick sections. The industry standard for 6 inch (152 mm) thick 7050-T7451 plate, as listed in Aerospace Materials Specification AMS 4050H, specifies a minimum yield strength in longitudinal (L) direction of 414 MPa and a plane-strain fracture toughness, or K_{IC} , (L-T), of $26 \text{ MPa}\sqrt{\text{m}}$ [28]. For that same alloy temper and thickness, specified values in the transverse direction (L-T and T-L) are 414 MPa and $24 \text{ MPa}\sqrt{\text{m}}$, respectively [28]. By comparison, the more recently developed upper wing alloy, 7055-T7751 aluminium, about 0.375 to 1.5 inches (9.5 to 38.1 mm) thick, can meet a minimum yield strength of 593 MPa. If an integral spar of

7050-T74, with a 414 MPa minimum yield strength is used with the aforesaid 7055 alloy, then the overall strength capabilities of that upper wing skin would not be taken full advantage of for maximum weight efficiencies [22]. Hence, higher strength, thick aluminium alloys with sufficient fracture toughness are needed for manufacturing the integral spar configurations now desired for new jetliner designs. This is but one specific example of the benefits of an aluminium alloy with high strength and toughness in thick sections. Many other examples exist in modern aircraft, such as the wing ribs, webs or stringers, wing panels or skins, the fuselage frame, floor beams or bulkheads, and even landing gear beams or various combinations of these aircraft structural components.

2.2. Quench sensitivity of 7xxx alloys

Quenching is a critical step in the sequence of an industrial processing line. The objective of quenching is to preserve the solid solution formed at the solution treatment temperature by rapidly cooling to a lower temperature so the solute atoms can contribute to the precipitation hardening during subsequent ageing. The solution treatment temperature for 7xxx alloys is generally within the range of 460-490 °C [29]. The purpose of this solution treatment process is to maximise the concentration of soluble alloying elements (including copper, zinc, magnesium and/or silicon) in solution without overheating.

However, seeking improved properties in thick sections results in quench sensitivity issues. As a product shape thickens, the quench rate experienced at the interior cross section of that product naturally decreases. That decrease results in a loss of strength and fracture toughness for thicker products, especially in inner regions across the thickness. The quench sensitivity phenomenon is normally interpreted as a 'loss of solute' mechanism due to the formation of quench-induced precipitates during the cooling process. This depletes the matrix of solute atoms for subsequent ageing, causing a remarkable decrease of age hardening capability

[30]. There is also a well known, inverse relationship between strength and SCC resistance and exfoliation corrosion behaviour, so that the properties vary a lot across the thickness section [4].

In heavy sections, the quench rate is limited principally by the thermal conductivity of the metal, which is essentially uncontrollable. However, one can expect different cooling profiles across the thickness section from different quenchants. According to Hatch [31], the average cooling rate varies with the plate thickness in a manner that can be approximately expressed by the following equation:

$$\text{Log} r_1 = \log r_2 - k \log t \quad \text{Eqn 2.1}$$

Where: r_1 is the average cooling rate at a thickness t , r_2 is the average cooling rate at a 1 cm (0.4 in.) thickness, and k is a constant.

Fig. 2.4 shows the average cooling rates of aluminium plates with thicknesses ranging from 1.6 mm (0.06 in.) to 250 mm (8 in), achieved by immersion in water at five different temperatures and by cooling in still air. The dashed line indicates the theoretical maximum cooling rate that can be obtained at the mid-planes of plates with different thicknesses. It can be seen that the cooling rate at the mid-plane of a typical 75 mm thick plate is about 10 °C/s (between 290 - 400 °C) when immersing this plate into 24 °C water. It should also be pointed out that modern industrial manufacturing plants are equipped with tandem roller hearth furnace systems which use high pressure water spray quenching systems designed specifically for 7xxx series thick plates quenching processes. Thus, the real cooling curves of thick plate could be slightly higher than those indicated by the solid lines in **Fig. 2.4**.

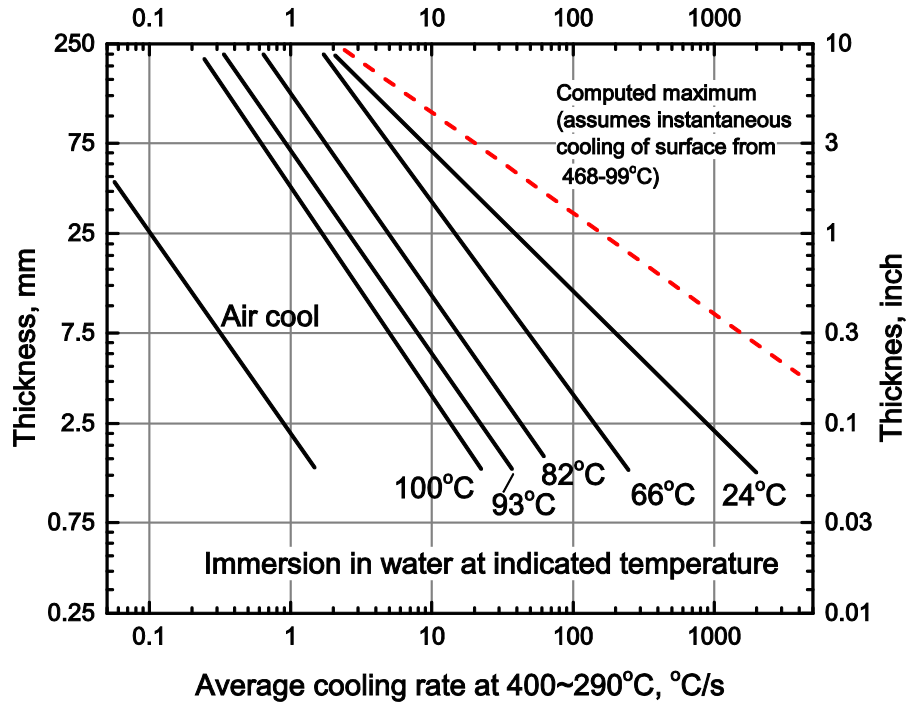


Figure 2.4: Effects of thickness and quenching medium on average cooling rates at mid-planes of aluminium alloy sheet and plate quenched from solution temperatures [31].

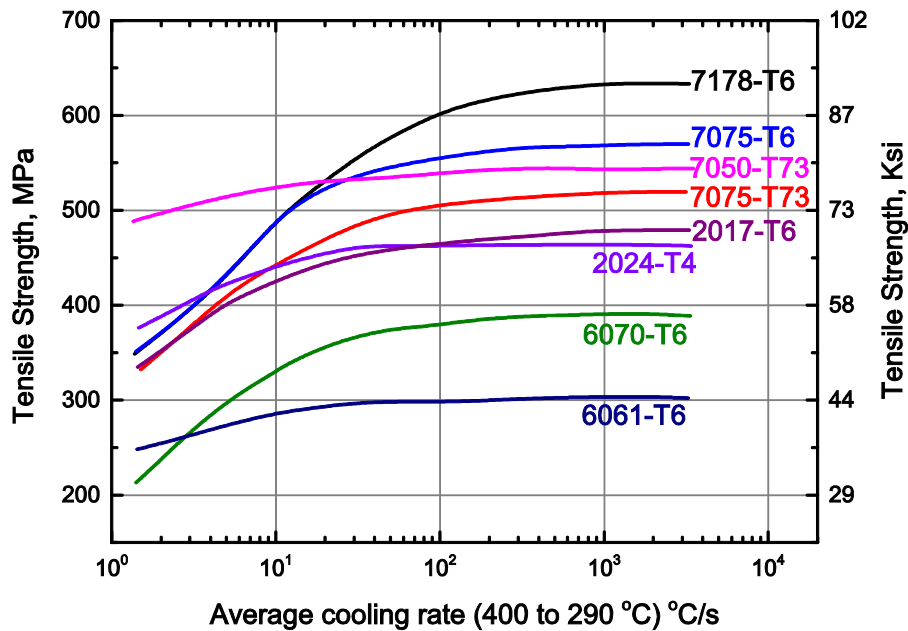


Figure 2.5: Tensile strengths of eight aluminium alloys as a function of average cooling rate during cooling [31].

Fig. 2.5 shows the tensile strengths of eight aluminium alloys as a function of average cooling rate during cooling. Different cooling rates were achieved by quenching sheet and plate panels of various thicknesses in different quenchants. It is shown the strengths of all the aluminium alloys, including 2xxx series alloys and 6xxx series alloys are decreasing with decreasing cooling rates. The alloys 7178-T6 and 7075-T6 are more distinguished than other alloys. According to this diagram, 7178-T6 and 7075-T6 are among the most quench sensitive products.

2.3. Effect of alloy composition on quench sensitivity

It is believed that the quench sensitivity is greatly affected by the alloy composition. An increased alloying content generally makes the alloy more quench sensitive [32-34]. However, higher alloying contents do not necessarily increase the quench sensitivity of an alloy [35]. Some research work also shows that the quench sensitivity can be changed by means of thermo-mechanical processing. Suzuki demonstrated that the quench sensitivity increases with increasing cold reduction and zirconium content for 7xxx alloys [36]. Liu proposed that controlling the rolling reduction at 67% and lowering deformation rate would be desirable for the quench sensitivity of alloy 7050 [37]. This section discusses the effect of alloy composition on quench sensitivity while the effect of deformation on quench sensitivity will be discussed in Chapter 4 in more detail.

The compositions of traditional high strength 7xxx series aluminium alloys range from about: 6 to 10 wt. % Zn, 1.2 to 1.9 wt.% Mg, 1.2 to 2.2 wt % Cu, and 0.05 to 0.4 wt % Zr, with the balance being Al and incidental elements and impurities. The term "incidental elements" can include relatively small amounts of Ti, B and others elements added for a particular purpose. For example, Ti with either B or C serves as a grain refiner during direct chill casting [38]. Incidental elements can also be present in significant amounts and add desirable or other characteristics on

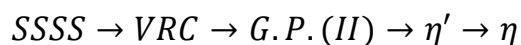
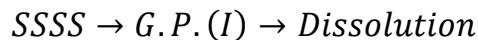
their own without departing from the scope of the invention, including reduced quench sensitivity and improved property combinations.

Fe and Si

Fe and Si are impurities in 7xxx alloys. Their contents should be strictly kept at a very low level [20, 39, 40]. The iron is normally tied up with copper during solidification, causing the $\text{Al}_7\text{Cu}_2\text{Fe}$ phase to be formed. As a result, the effective copper content has to be considered [39]. In some instances, it is necessary to adjust the actual Cu and Mg contents to account for the levels of Fe and Si content in the alloy. It is known that Si will tie up with Mg during solidification to form the Mg_2Si phase. It should be noted that the Mn acts in a similar manner to Cu with Fe present promoting the formation of $\text{Al}_{15}(\text{FeMn})_3\text{Si}_2$ [41]. These primary intermetallic phases are insoluble coarse particles which may become crack initiation sites and lead to failure [42]. The effect of Fe and Si content on the quench sensitivity is not yet known, but it is believed that the addition of Fe and Si will increase the quench sensitivity due to the formation of these intermetallic phases [43].

Zn and Mg

Zn and Mg are the two main alloying elements in Al-Zn-Mg-Cu alloys. Many compositions are now available which may contain 5-8 wt% Zn and 1-3 wt% Mg (Zn+Mg in the range of 6-11 wt%). For good weldability, the Zn+Mg content should be less than 6 wt%. The main alloying elements of Zn and Mg control the basic features of the structure and the properties of commercial alloys largely by controlling the ageing response of 7xxx series alloys [33, 44, 45]. The normal precipitation sequences of Al-Zn-Mg-Cu alloys can be presented as [46-48]:



Here, SSSS refers to supersaturated solid solution and VRC refers to vacancy rich clusters.

After quenching from solution treatment to room temperature, there will be a supersaturation of both vacancies and solute atoms within the matrix. There are two types of zones or clusters formed at room temperature: GP(I)-zones and vacancy-rich-clusters (VRC). The VRC are thought to be formed right after or during the quench to room temperature and to be quite stable at this temperature. The GP(I) zones formed at an early stage of ageing have a significantly higher Cu content than those formed during later stages of ageing [49, 50]. They are assumed to constitute the main formation route to η' , with GP(II) zones as an intermediate phase [51]. At higher aging temperatures, above the GP zone solvus, GP(II) zones transform into η' while GP(I) zones either dissolve or transform into η' if they have reached some critical size [52, 53].

Metastable η' is the main strengthening phase for 7xxx series alloys. It is believed that the η' precipitates are thin platelets phase that are fully coherent with the aluminium matrix in their habit plane. It is generally accepted that η' has a hexagonal crystal structure ($a=0.496\text{nm}$, $c=1.402\text{nm}$) [54, 55]. Gjønnes and Yan have reported an orthorhombic structure for η' precipitates with lattice parameters $a=0.496$, $c=0.868\text{ nm}$ [56, 57]. The orientation relationship between the η' precipitates and the aluminium matrix is believed to be:

$$(0001)_{\eta'} // \{111\}_{\alpha} \text{ and } \langle 11\bar{2}0 \rangle_{\eta'} // \langle 112 \rangle_{\alpha}$$

According to Dumont, the composition of the η' phases changes with increasing ageing time [55]. In the T6 state, the probable composition of the metastable η' phase was estimated to be 20% Al, 55%Zn and 25% Mg, with a Zn/Mg ratio of about 2.2 [55]. In the T7 state, these precipitates transform to the stable η phases

with a Zn/Mg ratio of 2. Sha and Cerezo showed that the η' precipitates have the Zn/Mg ratio of about 1.2 based on 3D atom probe analysis [49].

The equilibrium phase η , also known as M-phase with stoichiometry MgZn_2 is the equilibrium state for η' precipitates. The η phase has a hexagonal structure (space group $P6_3/mmc$, $a=0.5221$ nm, $c=0.8567$ nm). It is reported that there are nine different orientation relationships between the η phase and aluminium matrix [58]. Xu recently reported that the Zn atoms of the η phase can be replaced by Cu and Al atoms, the new stoichiometry for η phase has been propose to be $\text{Mg}_3\text{Zn}_3\text{Cu}_3\text{Al}$ [59].

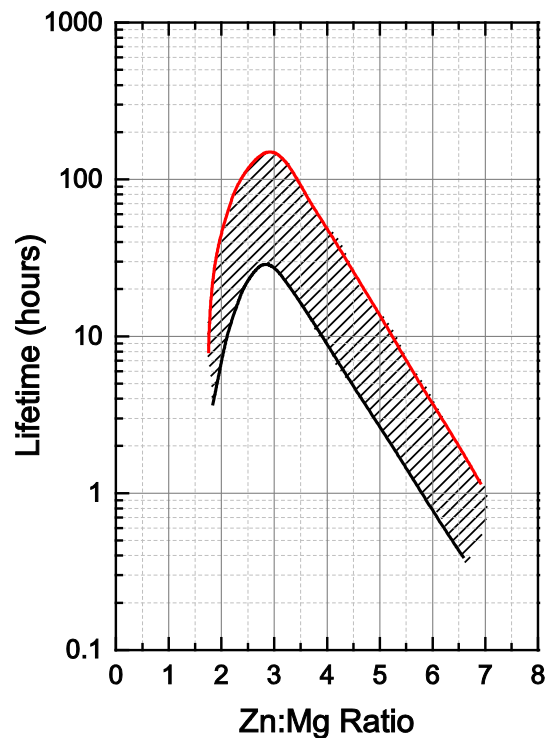


Figure 2.6: Effect of Zn/Mg ratio on the susceptibility of Al-Zn-Mg alloys to stress corrosion cracking (the alloy state has not been labeled) [4].

It is believed that different mechanical properties could be obtained by adjusting the Zn/Mg ratio of 7xxx series alloys. According to Lim *et al*, alloys with a higher

Zn/Mg ratio are less quench-sensitive compared to the conventional Al-Zn-Mg alloys [60]. For most existing commercially produced 7xxx series alloys, such as AA7050, AA7150, AA7055, a Zn/Mg ratio (by wt %) of between 2.0 and 4.0 is applied to achieve maximum resistance to stress corrosion cracking (as shown in **Fig. 2.6**).

Other alloys such as 7020 and 7085, with higher Zn/Mg ratios of up to 4-5 by wt%, are known to have reduced quench sensitivities. Alloy 7085 displays a uniquely attractive combination of strength and toughness for thick and ultra-thick (up to 300 mm) section products [61]. The mechanism by which the lower quench sensitivity is achieved by the high Zn/Mg ratios is not yet clear. A possible explanation may be that the higher Zn/Mg ratio tends to decelerate the decomposition rate to form more stable phases that result in a lower strength and a higher electrical conductivity [62]. Lim proposed that the excess magnesium in the lower Zn/Mg ratio alloys enhances the kinetics of precipitation, so that an alloy with a low quench sensitivity can be achieved with a low Cu+Mg content and with a high Zn/Mg ratio [32]. Boselli *et al* found that the solvus temperatures for S-phase (Al_2CuMg) and M-phase (MgZn_2) are lower in alloys 7085 than that in alloy 7050 [61]. This means that alloy 7085 can be thermally processed with fewer constraints than 7050, and the lower solvus temperature decrease heterogeneous precipitation during slow cooling. Lim also showed that the Zn/Mg ratio (iso-ratio line) increases from 2.0 to 4.0 for a constant Cu level of 2.0 wt%, the alloys move from a two-phase (M+S) to a single phase field [32]. As a result, an exploration of the effect of Zn/Mg ratio on the quench sensitivity of Al-Zn-Mg-Cu alloys is one of the tasks in this research.

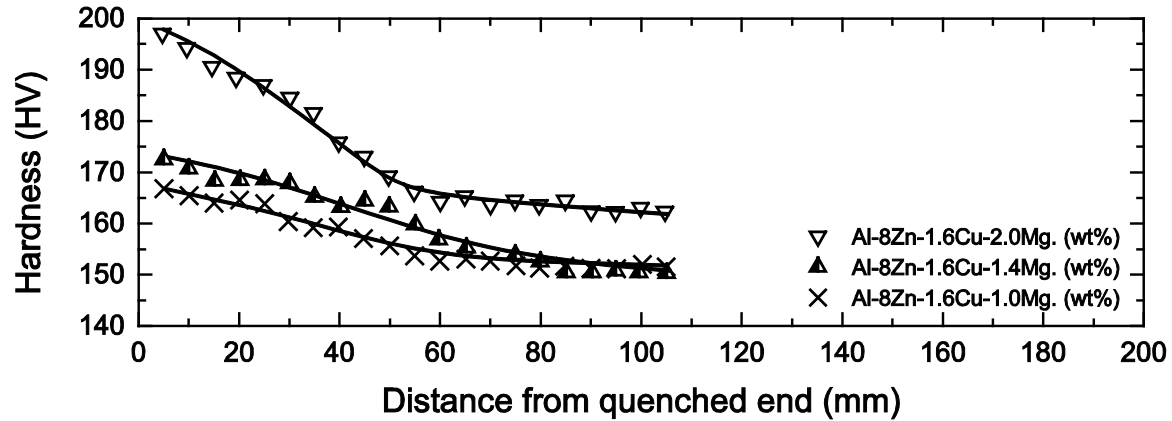


Figure 2.7: Ageing hardness curves of the Jominy-end-quenched samples for 3 different alloys with different Mg content, the figure has been adjusted in comparison with the other Jominy-End quench results in Figure 2.10 [63].

The strong impact of increasing Mg concentration on strength (beneficial) and on toughness (detrimental) is well known. The basis of the Zn/Mg ratio adjustments is the observation that a partial replacement of Mg with Zn (a slightly less effective hardener per wt%) enables an increase in toughness while maintaining adequate strength. Deng *et al* have studied the effect of Mg content on quench sensitivity of 7xxx alloys using the Jominy end quench experiment (as shown in **Fig. 2.7**). They found that the quench sensitivity increases with increasing Mg content, even though the alloy seems to be more strengthened with higher Mg content [63]. This result is in agreement with the work of Bryant in 1966 [64]. Chakrabarti *et al* also pointed out that the Zn content does not necessarily increase quench sensitivity if the alloy is properly formulated [65]. They recommended that, in order to decreasing quench sensitivity with balanced fracture toughness, the Mg content should be below about 1.68 or 1.7 wt% and preferably below the level of Cu content.

Cu

Minor additions of Cu are added to some alloys but the amount is normally kept below 3 wt% [66]. The effect of Cu on the resistance to fatigue also depends on the concentrations of Zn and Mg. At 4 wt% Zn and 2 wt% Mg, an increase in the Cu content causes an increase in the strength and a decrease in the number of cycles before failure during repeated cyclic tensile testing. This could be because Cu does not participate in the formation of any hardening phases (but Cu can form intermetallic phases such as S-phase and Fe-phase) in a typical concentration range of 1-3 wt% and increases the plasticity by fully residing in the supersaturated solid solution [58]. In this case, an increase in the content of Cu causes parallel increases in the strength, plasticity, low-cycle fatigue and corrosion resistance. This fundamental conclusion was made in the doctoral thesis of I. N. Fridlyander in 1958 [66].

Sarkar *et al* demonstrated that the stress corrosion crack velocity tended to decrease with increasing Cu content at higher stress intensities, shown in **Fig. 2.8** [67]. They also stated that the resistance of 7xxx series alloys to S.C.C alloys varies with Cu content. The Cu-bearing materials demonstrated a superior stress corrosion cracking resistance in slow cooling condition because the Cu atoms participate in copper-rich reactions in slow cooling conditions.

Deschamps *et al* found that the addition of Cu may affect the precipitation kinetics of 7xxx series alloys. They proposed that the Cu addition could increase the strengthening ability of the precipitates. Moreover, they found different size distributions of GP zones within Cu-bearing alloys [64, 68]. Xu *et al* emphasised that only Cu additions of <3 wt% are beneficial to strengthening of 7xxx series alloys [69].

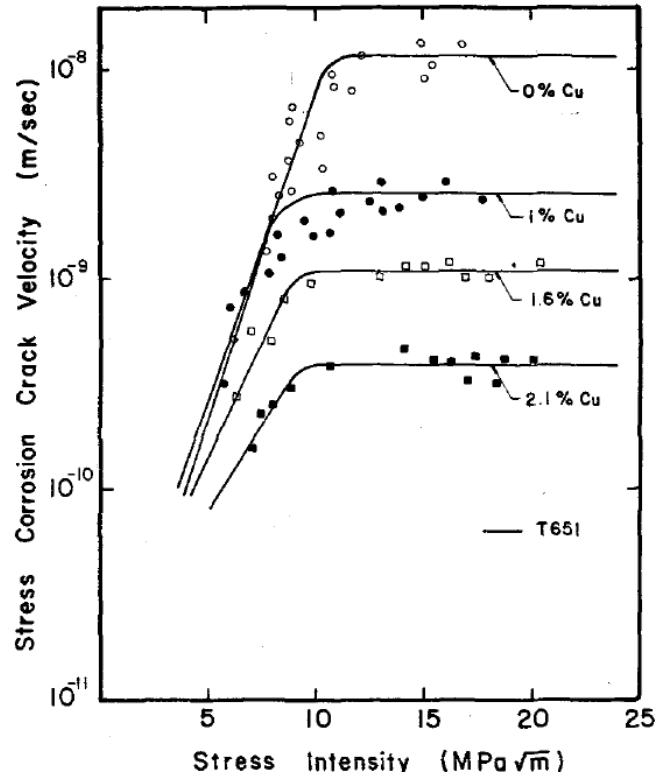


Figure 2.8: Stress corrosion crack velocity vs. stress intensity for modified 7050 alloys with various copper contents [67].

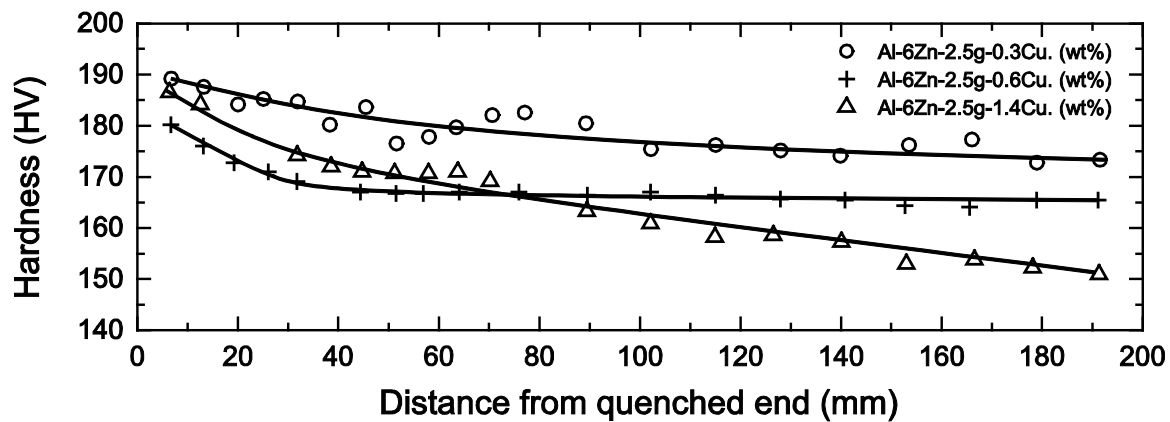


Figure 2.9: Effect of Cu contents between 0.3 and 1.4 wt% on the Jominy curves for alloys containing 6 wt% Zn and 2.5 wt% Mg. The Jominy bars were solution-treated for 1h at 465°C and artificially aged for 12 h at 135°C [64].

The effect of Cu content on quench sensitivity in terms of hardness values has been presented by Bryant, as illustrated in **Fig 2.9** [64]. It is shown that the hardness along the Jominy bar is decreasing, suggesting that the materials is quench sensitive. The alloy with higher Cu content is more quench sensitive than the lower Cu content alloy. Deschamps *et al* also stated that the copper addition could increase the quench sensitivity of the 7xxx series alloys, as the overall supersaturation of the alloy is increased [68]. Livak and Papazian, however, demonstrated that a small addition of Cu to Al-Zn-Mg alloy could decrease the quench sensitivity by promoting the formation of solute-vacancy complexes for the subsequent ageing process [70].

A possible explanation for the effect of Cu on the quench sensitivity may be that the addition of Cu can increase the total supersaturation in the Al-Zn-Mg-Cu alloys and thus shift the nose of the precipitation C-curve to lower times. Thus, a great tolerance in lower cooling rates is acceptable in these alloys with lower Cu contents [68]. However, the literature remains vague about the exact mechanisms by which Cu can influence the quench sensitivity.

Additional elements

There are three types of alloying elements in Al-Zn-Mg-Cu alloys: (i) the major alloying elements, including Zn, Mg and Cu, (ii) the impurities such as iron and silicon, and (iii) deliberate minor additions such as Cr, Mn, Ti and/or Zr. There are more than 30 elements, including rare earth elements, that can be added to Al-Zn-Mg-Cu alloys with specific alloy design intentions. Even though the total addition of those trace elements is normally less than 1 wt%, the effects on modifying the relevant properties are so remarkable that extensive studies have been carried out. The most well known replacement of the dispersoid forming elements Cr and Mn with Zr in the late 1960s reduced the quench sensitivity of Al-Zn-Mg-Cu alloys and led to the transition from the old version Al-Zn-Mg-Cu alloy 7075 to the new

Al-Zn-Mg-Cu alloy 7050. **Fig 2.10** shows a systematic work on the quench sensitivity of several 7xxx alloys has been conducted by Holl [43]. This figure presents the effect of small additions of dispersoid-forming elements on the hardness of alloys experiencing different cooling paths. It is shown that Cr and V have significant effects on quench sensitivity. A small amount of such elements could cause a remarkable reduction of hardness over a given cooling rate range.

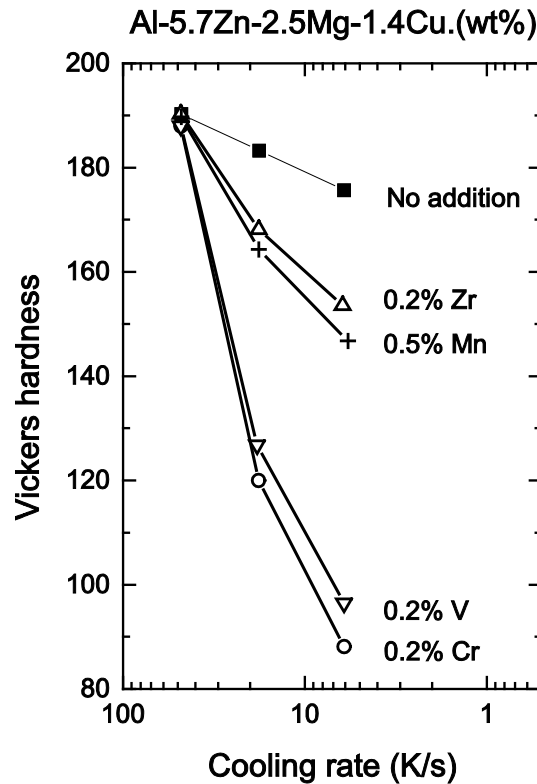


Figure 2.10: The effects of various dispersoid-forming elements on the hardness of an Al-5.7wt%Zn-2.5wt%Mg-1.4wt%Cu alloy, plotted for different average cooling rates (calculated over the critical temperature range) to quantify the quench sensitivities of the various alloys, alloys are aged at 120 °C for 100 hours [43].

However, a small amount of such dispersoid-forming elements is necessary in 7xxx series alloy. It is believed that the addition of small amounts of Cr, Mn and also Zr definitely reduces the susceptibility to SCC in 7xxx alloys by suppressing the recrystallisation through the formation of fine dispersoid particles at a

relatively high temperature [38]. Research has show that by forming these large non-coherent particles, the stress concentration has been relieved, which results in a higher resistance to SCC [71]. These dispersoids are also reported to be heterogeneous nucleation sites for quench-induced phases [36, 72-75]. It is also shown that a Cr addition is the most efficient for precipitating quench-induced phases, causing Cr-bearing alloys to exhibit higher quench sensitivity [12, 76, 77].

In the 1980s, 7xxx alloys with Zr-additions were found to exhibit a relatively lower quench sensitivity when compared with previous generations of alloys that contained Cr and Mn as minor element additions [78-80]. Detailed work has shown that unlike Cr- and Mn-bearing dispersoids, Zr-containing dispersoids can reduce the possibility of quench-induced precipitate nucleation on the dispersoids by forming coherent dispersoids with a lower interfacial energy [36, 43, 74]. However, it was found that some Zr-bearing dispersoids can also promote precipitation within certain grains during quenching [81]. The exact nature and mechanisms for such precipitation behaviour are not yet fully understood. One of the explanations would be that there are two forms of Al_3Zr dispersoids existing in 7xxx aluminium alloys, with the same stoichiometry but a different structure: a stable equilibrium form with a tetragonal D_{023} structure and a metastable form with a cubic L_{12} structure [53, 82]. Only the metastable dispersoids can inhibit recrystallisation and grain growth by pinning the grain boundary movement. The equilibrium dispersoids, on the other hand, act as nucleation sites for quench-induced precipitates during cooling. There is another hypothesis that the metastable Al_3Zr dispersoids lose their coherency with the matrix after recrystallisation [36, 73, 74, 81]. The increased interfacial energy due to incoherency with the matrix will then increase the likelihood for heterogeneous quench-induced precipitation on these dispersoids. However, both of these hypotheses lack supporting experimental evidence. It is also one of the topics that will be discussed thoroughly in later chapters.

As mentioned before, more than 30 elements can be added to aluminium alloys for specific property design. Besides scandium, some other additional elements have been studied as well particularly in Japan and Russia in the 1960s.

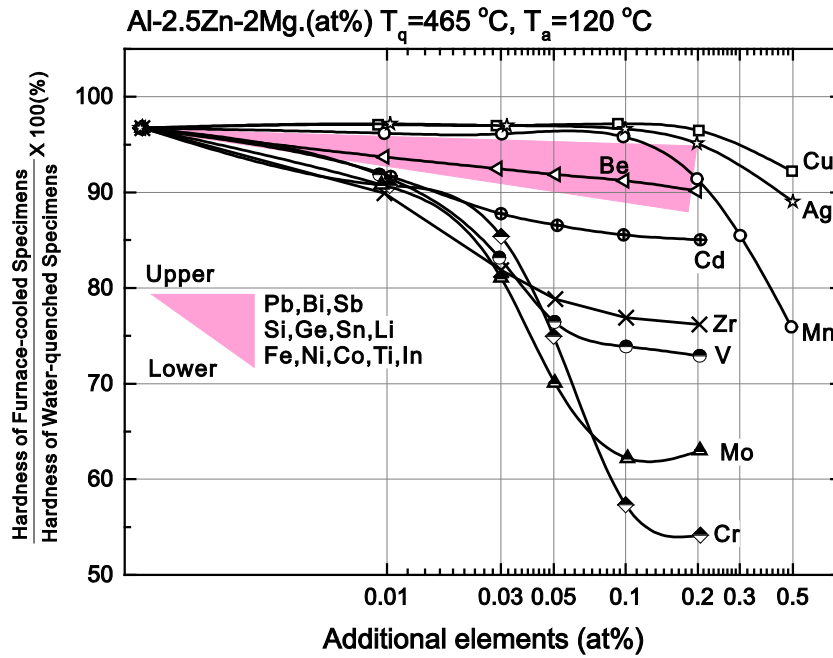


Figure 2.11: Influence of minor element additions on the quench-sensitivity of Al-2.5 Zn-2 Mg (in at%) alloys. Specimens were aged at 120°C to the maximum hardness after the water-quenching or the furnace-cooling ($15^\circ\text{C}/\text{min}$) [77]

Baba has studied the influence of additional elements on the quench sensitivity and nucleation of precipitates in Al-Zn-Mg-Cu alloys [77]. He has added Li, Be, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ge, Zr Mo, Ag, Cd, In, Sn, Sb, Pb and Bi in quantities of less than 0.5 at% to Al-2.5Zn-2Mg (at%) alloys. The purpose of this research was to study the effects of additional elements on the quench sensitivity by means of hardness or electrical resistivity variations. He then ranked all the 22 elements into three groups according to their effect on quench sensitivity. The quench sensitivity was described by the ratio of the hardness in the furnace cooled conditions to that in the water quenched condition. The results are shown in **Fig.**

2.11. It can be seen that Cr causes the most significant increase of quench sensitivity and is therefore ranked as a group C element. The elements Mo, V, Zr, Mn have a moderate effect on changing the quench sensitivity and are ranked as group B, followed by Cd, Ag, Be and Cu (group A), which have the least effect on quench sensitivity.

A series of papers have been published by Polmear *et al* to describe the effects of small additions of Ag to Al-Zn-Mg alloys on ageing characteristics and microstructures [83-92]. The preliminary studies have shown that the optimum Ag addition to Al-Zn-Mg alloys is 0.3 wt% [86, 87]. The most pronounced effect of adding Ag is that it can stimulate precipitation when these alloys are aged in a temperature range of about 120 to 220°C, and thus enable the precipitates, particularly along the grain boundaries, to become more evenly dispersed. Moreover, Ag atoms are found to have a high binding energy with Zn and Mg atoms and vacancies. As a result, both general solute depletion and solute depletion adjacent to grain boundaries can be minimised, resulting in narrower precipitation free zones in Ag-bearing alloys than in Ag-free alloys [84, 93, 94]. The presence of dispersed precipitates on grain boundaries and narrower precipitation free zones leads to a remarkable improvement in the SCC resistance of Ag-bearing alloys.

Elkington and Turner have studied the effect of Ag on the SCC of high-strength Al-Zn-Mg-Cu alloys at different cooling rates [95]. It is shown that the quench sensitivity increases with silver addition. The results also demonstrated that the silver addition led to a marked improvement in the SCC resistance of 7xxx alloys.

Fig 2.12 shows how the quench sensitivity varies with additions of Cr and Mn. It also may be noted that the quench sensitivity of the alloys is further increased by the addition of Ag. However, it seems that the proof stress of alloys with Ag only is much more stable than when combined with additions of Mn and Cr. There are

no results for combined additions of Ag and Zr, since most of this work was done in the 1960s when Mn and Cr were conventionally added to inhibit recrystallisation in these alloys. After the substitution of Mn and Cr with Zr, no research has been carried out on 7xxx alloys containing both Ag and Zr in terms of quench sensitivity. However, it is of interest to find out that 7xxx alloys containing both Ag and Mn exhibit moderate quench sensitivity, as illustrate in **Fig. 2.12**. As mentioned before, Mn additions show a similar effect on quench sensitivity for Al-Zn-Mg-Cu alloys as Zr additions do. Thus it may be expected that the addition of Ag to Zr-containing alloys could improve the quench sensitivity of the Zr-bearing alloys.

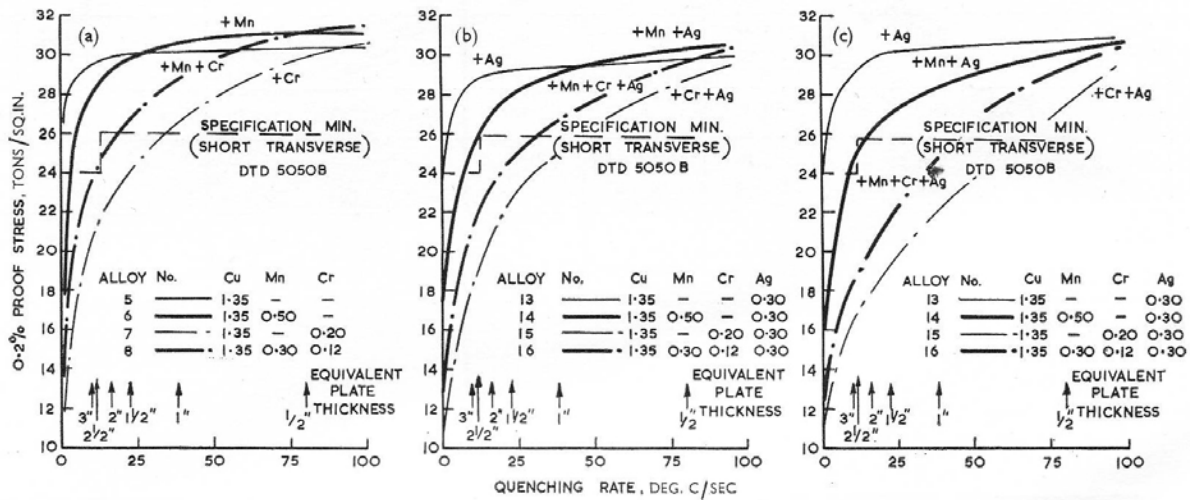


Figure 2.12: Variation in 0.2% proof stress with quenching rate of Al-Zn-Mg-Cu alloys, (a) without Ag, aged 12 h at 135°C; (b) with Ag, aged 12 h at 135°C; (c) with Ag, aged 6 h at 165°C. The alloys contain about 6 Zn-2.5 Mg-1.5Cu (in wt%) together with small additions of Mn or Cr, as indicated [95].

Another interesting addition is Co. Unlike Ag additions, Co additions to Al-Zn-Mg-Cu alloys are thought to be supplementary to Zr [96]. It is expected that fully coherent Co-bearing dispersoids will inhibit both recrystallisation of grains and precipitation of $MgZn_2$ phases during quenching.

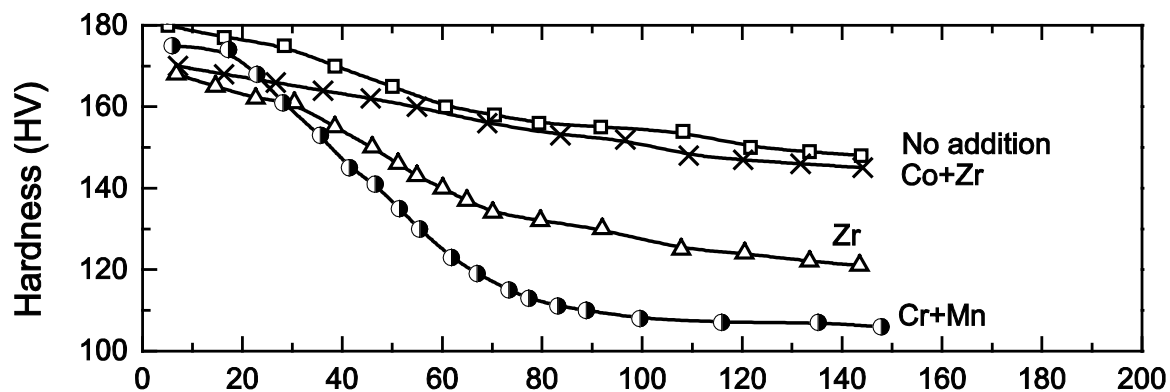


Figure 2.13: Trace addition effects on quench sensitivity of Al-Zn-Mg-Cu alloys, represented in terms of hardness along the length of a Jominy bar after ageing. The figure has been adjusted for ease of comparison with other Jominy end quench results in this chapter [97].

According to Menon, a stable phase Al_3Co_2 with monoclinic structure can be detected at relatively low cooling rates after the rapid solidification of Al-Co powders [98]. However, the Co-bearing particles in polycrystalline aluminium alloys is unclear as of yet. Since the Al_3Co_2 particles are quite stable at elevated temperatures, it is assumed that they can retard the movement of grain boundaries and thus inhibit recrystallisation and grain growth.

More curiously, one translated paper from Russia has shown that the Russian scientists have already tried to add Co to Al-Zn-Mg-Cu alloys for the purpose of improving the quench sensitivity [97]. Their research shows that the Co addition effect on the quench sensitivity is very positive when Zr is also present, as illustrated in **Fig 2.13**. The addition of Cr and Mn still present the highest quench sensitivity among all their studied alloys.

2.4. Characterisation of quench sensitivity

2.4.1. Time-temperature-transformation (TTT) diagrams

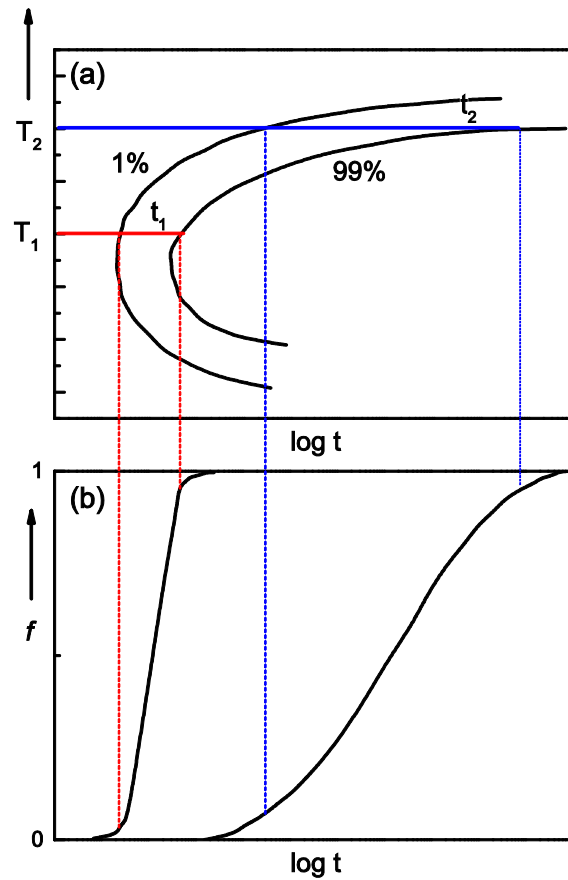


Figure 2.14: The percentage transformation versus time for different transformation temperatures; the two curves indicate the attainment of $f=1\%$ and 99% , respectively [99].

There are two types of diagrams can help to describe phase transformation as a function of time or temperature. One is the TTT diagram that describes the isothermal phase transformation by plotting the fraction transformationed as a function of time and temperature, as shown in **Fig 2.14**. It is derived from classic nucleation theory applied to diffusion controlled solid state reactions. It is shown how, at a given temperature T_1 for a precipitation of β from an α matrix, the volume fraction of β phase increases from 1 to 99% over a time period of t_1 . However, at a lower temperature T_2 , it will take a time period of t_2 for β to be

transformed to 99%. It is shown that $t_2 < t_1$, suggesting that the alloy experiences a fast phase transformation rate at an intermediate temperature range. This is because there is less supersaturation at the T_1 temperature. However, the diffusion rate is greater at elevated temperatures. On the other hand, there is greater supersaturation at the lower temperature ($< T_2$), but the diffusion rate is lower. As a result the fastest precipitation rate happens at an intermediate temperature (close to T_2) where both the amount of supersaturation and the diffusion rate are relatively high.

This causes the typical C-shaped behavior under isothermal conditions, as shown in **Fig. 2.15**. A TTT diagram can be obtained by cooling samples quickly to a fixed intermediate temperature and then observing the resulting isothermal transformation (known as interrupted quenching experiments) in terms of fraction transformed, mechanical properties or other properties caused by the phase transformation. Then the terminology would be different corresponding to the different properties at given conditions, such as TTY diagrams for time-temperature-yield strength or TTP for time-temperature-property diagrams. Tiryakioğlu *et al* used the term 'nucleation diagram' and hence referred to time-temperature-nucleation (TTN) diagrams [100].

The TTT curves are difficult to be established as a lot of interrupted quenching experiments are needed. Furthermore the composition of the solid solution is continuously changing with time. Archambault and Godard used a differential resistivity method to measure resistivity changes at different cooling rates (0.017 K/s, 0.083 K/s and 0.17 K/s) [101]. They normalised the experimental resistivity curves and considered the characteristic time during interrupted quenching experiments. A TTT curve for the precipitation of the M- phase (MgZn_2) was then obtained. It was shown that the TTT curve for the MgZn_2 phase is also C-shaped with the 'nose' temperature being within the range of 350-375 °C. They also

pointed out that there might be another low temperature reaction at a temperature close of 200 °C.

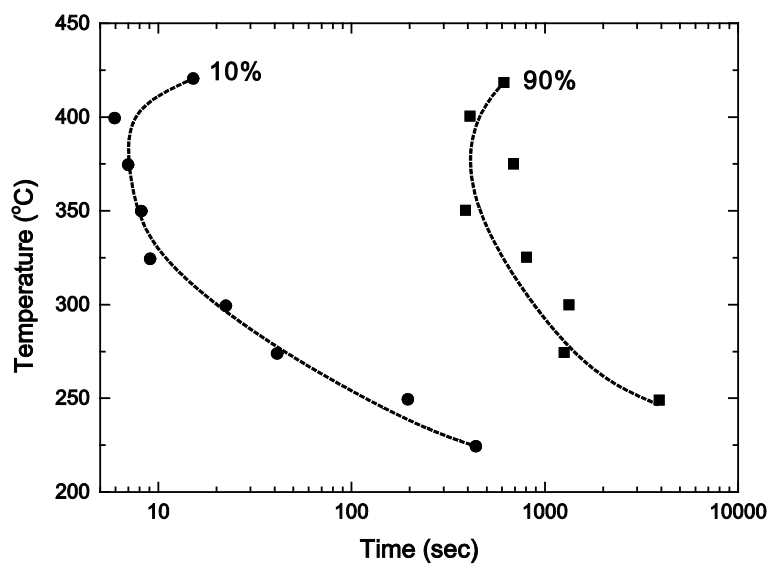


Figure 2.15: TTT curves for the M-phase precipitation in alloy 7010 (Al-5.99Zn-2.33Mg-1.73Cu-0.11Zr, in wt%) [101].

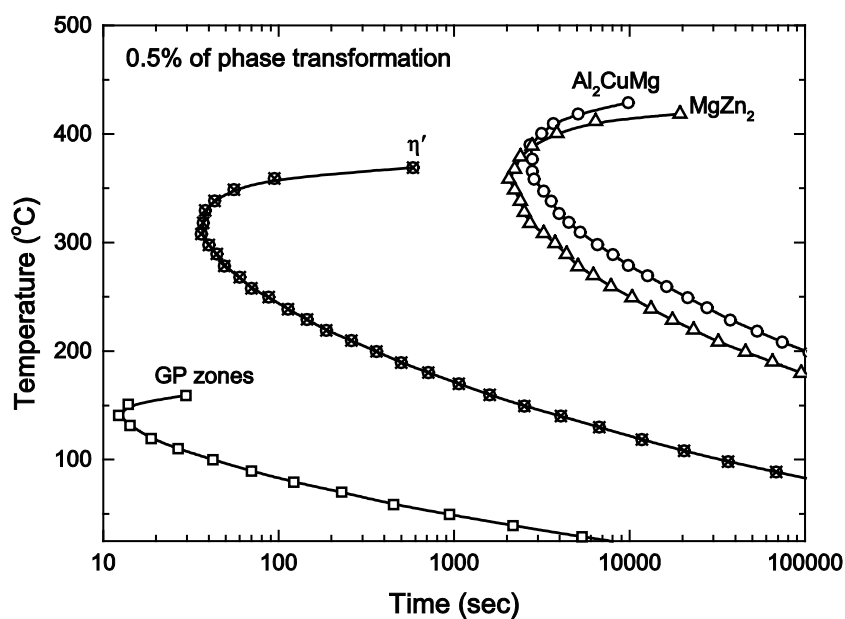


Figure 2.16: Calculated TTT diagrams for AA7075 [102].

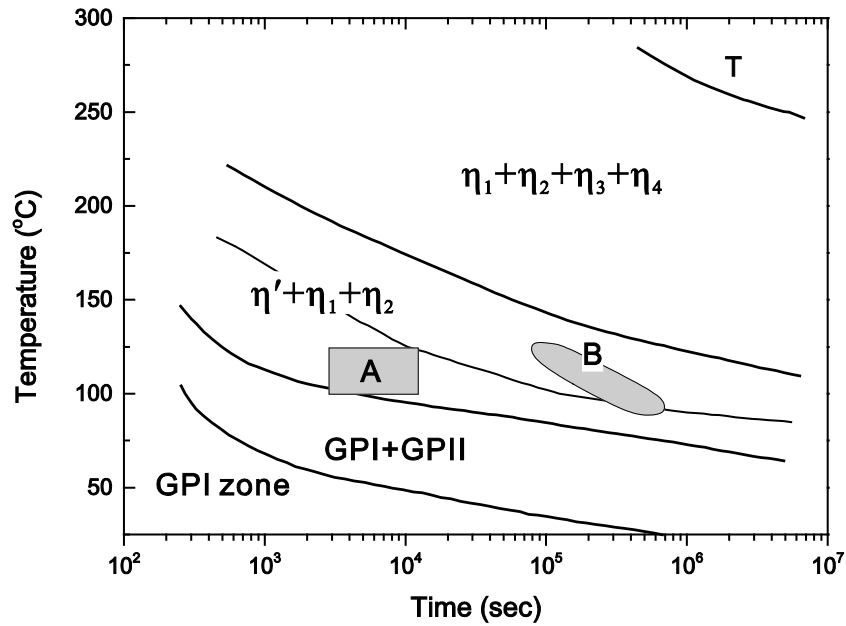


Figure 2.17: TTT diagram for ageing of Al-6.1Zn-2.4Mg-1.6Cu (wt.%) alloy. The area A corresponds to single stage ageing regimes with minimum duration, while the area B corresponds to the maximum yield strength [103, 104].

Saunders showed that the CALPHAD method can be used to calculate the metastable phase present in a quasi-equilibrium state while some stable phases were excluded [102]. His calculation is based on the assumption that the equilibrium concentration of vacancies present at the solution treatment temperature is retained after quenching to low temperature. The software program JMatPro was then used to calculate the TTT diagrams for alloy AA7075. It is shown that the 'nose' temperature for MgZn_2 phase is with the temperature range of 350- 400 °C. However, the transformation time is different to the measured results in **Fig 2.15**. There are also some low temperature reactions in this diagram, such as the transformation of GP zones, and η' precipitation. However, it seems that the 'nose' temperatures for GP zones and η' are higher than in measured results [45, 105-107].

Russian scientists have plotted a series of TTT diagrams for different aluminium alloys (to assist with artificial ageing regime design) by using the X-ray investigations and TEM observation on monocrystals [103, 104]. By applying these TTT diagrams, they discovered that the peak ageing temper for 7xxx series alloys can be achieved by two-stage ageing regimes comprised of a low temperature step followed by a shorter duration higher temperature step (rather than single step ageing for a relatively long exposure). However, many of the results are published in Russian. **Fig 2.17** shows one example of such TTT diagrams presented by Ber in 2000 [103, 104].

It is noted that the TTT diagrams are very helpful for heat treatment design. However, it is very hard for metallurgists to find a suitable technique to get a conclusive and industrially useful TTT diagram, especially for commercially produced alloys that may contain multiple phase transformations at a given temperature. Therefore a more sophisticated method is needed to measure the TTT diagrams for aluminium alloys.

2.4.2. Time-temperature-property (TTP) diagrams

Instead of isothermally measured amounts of phase transformation, it is more feasible for people to detect specific properties that are affected by isothermal phase transformations. Fink and Willey pioneered attempts to describe the effects of quenching on the properties of aluminium alloys [108]. Using an interrupted quenching technique, they developed C-curves for the strength and corrosion behaviour of alloy AA7075-T6 [108]. Their interrupted quenching technique involved transferring the specimens from the solution treatment temperature to oil baths at predetermined temperatures for a designed matrix of times and temperatures. The specimens were then quenched using room temperature (RT) water for relevant property testing, such as yield strength (YTS), tensile strength

(TS) or corrosion resistance (CR). **Fig 2.18** shows the typical C-curves of alloy AA7075 that were measured by Fink and Willey in 1947. It is shown that the C-curve shifts to the right when more holding time at a given temperature, indicating that both YTS and TS are decreasing with decreasing cooling rate. Their research also showed that the YTS is more sensitive to cooling rate than other properties. The TTP diagrams also show that the C-shaped curves for YTS are broader than those for TS, indicating that the YTS changes more significantly at a given cooling rate than TS. It is also noted that the noses of the C-curves are between 290-400 °C.

Liu has compared C-curves for typical Al-Zn-Mg-Cu alloys 7075, 7050 and 7085 [19]. He found that the most significant change for these three different curves is that the 'noses' of the curves (i.e. the critical temperatures and times) shift to lower temperatures and longer times when progressing from alloy AA7075 to AA7085 (as shown in **Fig. 2.19**). This means that solute can remain in solution for longer times and to relatively lower temperatures in alloy AA7085. Consequently, a slower cooling rate can be tolerated in the critical temperature range for a given drop in properties. They found that there are relatively coarse S-phase and M-phase precipitates on high angle grain boundaries in alloy AA7050 while only M phase is present in alloy AA7085. It is believed that the absence of S-phase on grain boundaries in alloy AA7085 can benefit the strength-toughness balance of alloy AA7085.

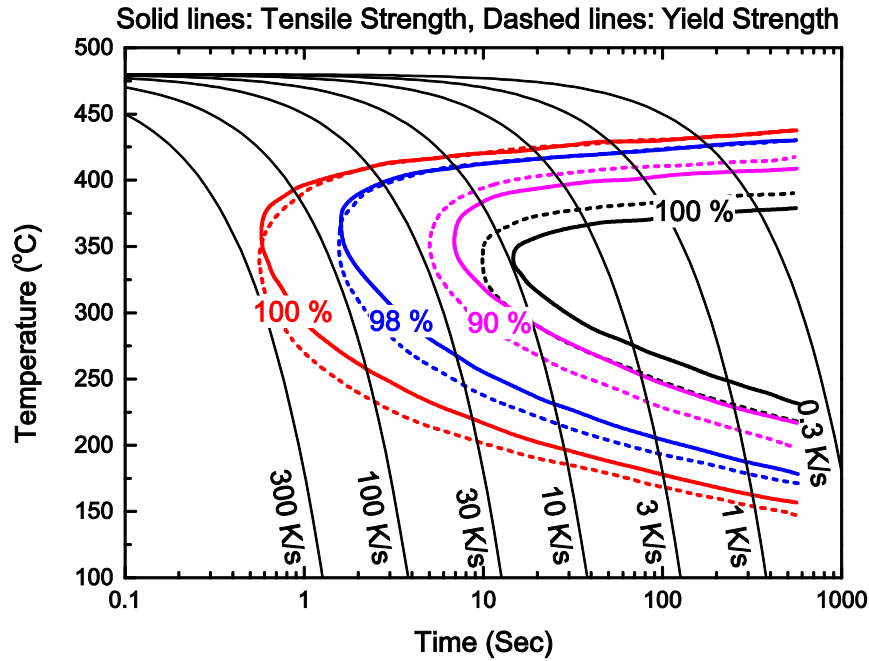


Figure 2.18: Detected TTP diagrams for alloy AA7075-T6, after ageing for 24 h at 121 °C [108].

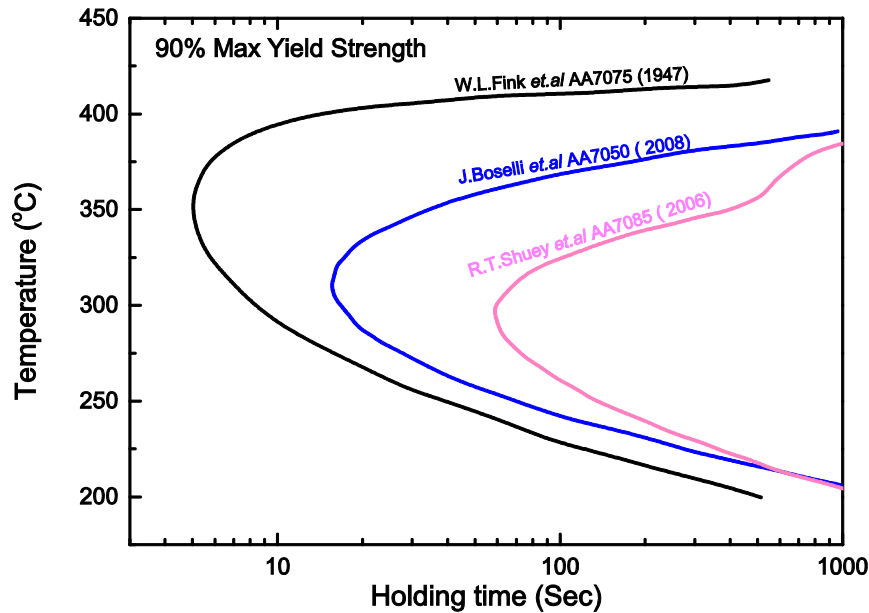


Figure 2.19: A comparison of published TTP curves corresponding to 90% of maximum yield strength [61, 108-110].

The C-curve can also be applied to demonstrate the corrosion behaviour. **Fig. 2.20** shows the corrosion resistance behaviour of alloy AA7075 in different cooling conditions. It is shown that, for both unstressed and stressed samples, only the pitting type of attack can be found in fast cooling conditions of >80 K/s. Within the cooling rate range of 50-80 K/s, some intergranular corrosion can be found along with pitting attack. At the lower cooling rates of 5-50 K/s, the intergranular type of corrosion predominates the corrosion behaviour while some pitting still exists. At very low cooling rates of <5 K/s, pitting attack predominates again.

A similar corrosion behaviour can be found in alloy AA2024-T4 [111]. According to Willey, only innocuous pitting type can be found when cooling rate was above a critical level [31]. Below this level, both pitting and intergranular corrosion co-exist. Unlike for alloy AA7075, alloy AA2024 shows entirely intergranular corrosion in very slow cooling rate range. The author attributes the corrosion behaviour to the precipitation of Al_2CuMg at grain boundaries during slow cooling.

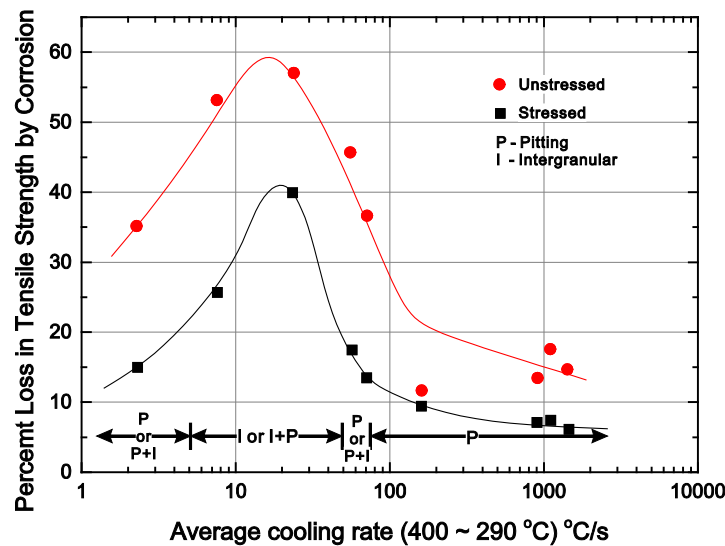


Figure 2.20: Effect of quenching rate on resistance to corrosion of alloy AA7075 [108]

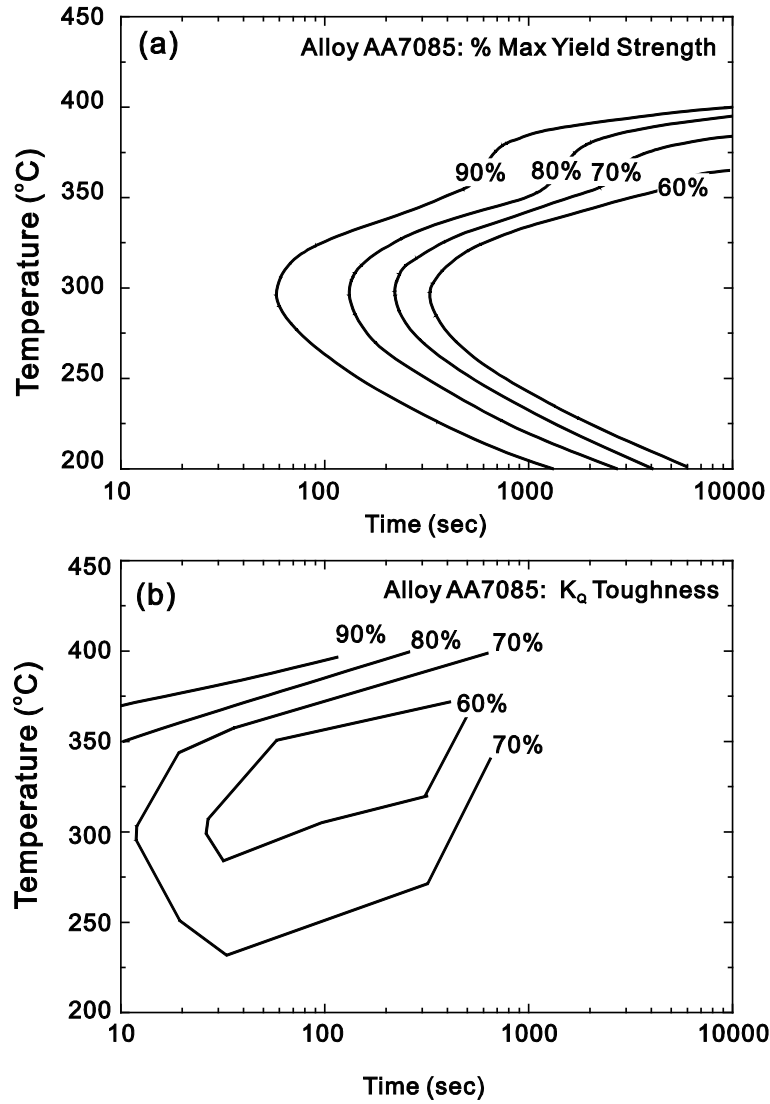


Figure 2.21: TTP diagrams for (a) yield strength and (b) toughness for alloy AA7085-T6 [110].

The Kahn tear test has been used to determine the toughness of samples after interrupt quenching experiments [112-114]. The results can also be plotted as TTP diagrams for toughness. Dumont *et al* found that the effect of quenching rate on fracture toughness is more dramatic than the effect on yield stress in alloy AA7050 [114]. They believed that the toughness is related to the coarse grain boundary precipitates that form during slow cooling. By contrast, the yield stress is more related to the matrix and work hardening rate, and these two factors are

more weakly dependent on the quenching rate. Shuey also demonstrated that ,for a AA7085 plate, the $MgZn_2$ phase can only be found on grain boundaries at the higher holding temperature of interrupt quenching experiments [110]. This is an indication that the $MgZn_2$ phase preferentially nucleates at grain boundaries in slow cooling rate conditions. At medium and low holding temperatures, more sub-grain boundary precipitates can be found compared to grain boundaries precipitates.

Fig 2.21 (a) shows the TTP diagrams for the yield strength of alloy AA7085 [110]. It is evident that the C-curves shift to longer times when more strength has been lost. However, the contour plot of the toughness behaviour at different holding times is no longer C-shaped, as shown in **Fig 2.21** (b). It is shown that the quench sensitivity in relation to the fracture toughness is much more complex than that of the yield strength. This may be due to the fact that the fracture toughness is not only a function of precipitation but also a function of the grain structure. The energy dissipated per unit area during fracture may happen by intergranular or transgranular fracture modes. The two modes may be mixed according to different cooling paths or microstructures. However, the TTP diagrams corresponding to fracture toughness offer a unique way to represent the quench sensitivity.

2.5. Continuous-cooling-transformation (CCT) diagrams

Herding demonstrated a differential scanning calorimeter (DSC) method in 2002 that opens up new opportunities for the construction of continuous cooling diagrams for aluminium alloys [115]. Kessler *et al* provided a methodology to construct CCT diagrams for alloy AA7020 (Al-4.5Zn-1Mg, in wt%) by means of newly developed continuous cooling DSC technique. **Fig. 2.22** shows that a CCT diagram can be plotted by connecting the precipitation onset temperature data in temperature-time space. The critical cooling rate was found to be about 2.6 K/s (155 K/min) [116]. Deschamps *et al* also used DSC to record the precipitation

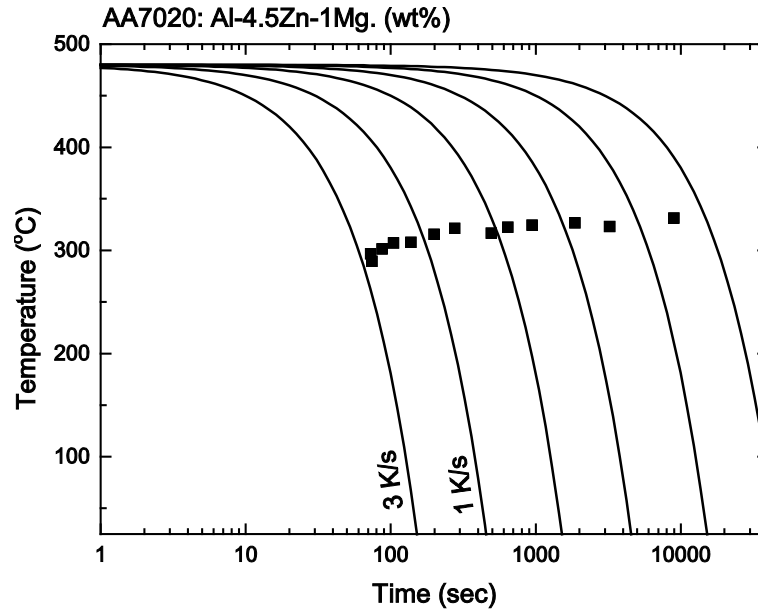


Figure 2.22: Continuous cooling transformation diagram for alloy AA7020 published by Kessler [116], Only the onset temperatures of the precipitation reaction have been marked in this figure.

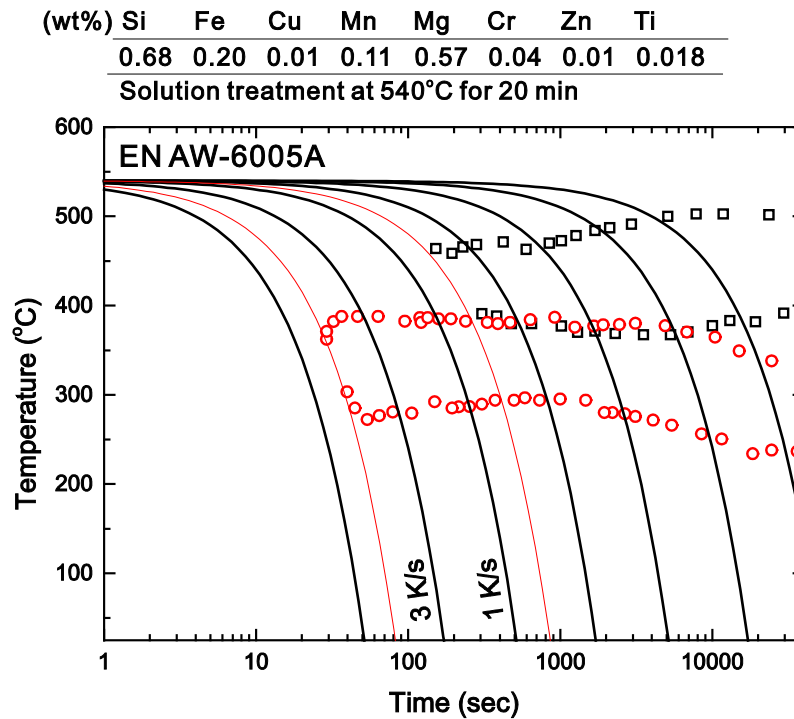


Figure 2.23: Full-range continuous cooling precipitation (CCP) diagram for alloy 6005A. The red lines represent the critical cooling rates for different reactions. Both onset temperatures and completed temperatures of the precipitation reactions have been marked in this figure.

reactions at constant cooling rates for a similar alloy, but could not detect a DSC signal at a cooling rate of 3.3 K/s (200 K/min) [117].

Milkereit *et al* developed this method significantly in order to record CCT diagrams over a wide range of cooling rates from 0.0017 K/s (0.1 K/min) to 6.25 K/s (375 K/min) by using three different types of DSC devices for alloy 6005A (as shown in **Fig 2.23**) [118]. By recording the exothermic heat capacity curves of the precipitation reactions during cooling, a full range of CCP diagrams could be obtained. In addition, the hardness values after artificial ageing were measured for the respective cooling curves. Milkereit developed CCP diagrams for wrought aluminium alloys 6060, 6063, 6005A and two batches of 6082 by means of the same technique [119]. It was found that the critical cooling rate for 6xxx series alloys increases with an increasing concentration of alloying elements: 0.5 K/s for 6060, 1.5 K/s for 6063; 6.25 K/s for 6005A; 16.7 K/s for lean 6082; 133 K/s for concentrated 6082.

It is therefore possible to apply this newly developed technique to 7xxx series aluminium alloys. However, for highly alloyed 7xxx alloys, the critical cooling rate is expected to be very high. Its value can hardly be determined by traditional DSC techniques which are limited to cooling rates of about 5 to 10 K/s. By using an indirect differential fast scanning calorimeter (DFSC) and utilising extremely small samples measuring $20\text{ }\mu\text{m} \times 90\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$, Zohrabyan *et al* found that the critical cooling rate for alloy 7049A is about 300 K/s [120]. Alloy AA7150 is nearly as highly alloyed as alloy 7049A, except that it has a lower Zn content. It is therefore reasonable to assume that the critical cooling rate for alloy AA7150 alloy is of a similar order of magnitude.

Electrical resistive is more sensitivity than the precipitation heat for monitoring the changing amount of solute in solution during continuous cooling. Li *et al* have designed an in-situ testing system that can measure the changing resistivity during

continuous cooling of 7xxx series alloys [121, 122]. **Fig. 2.24** shows the detected CCT diagram for alloy AA7475 cooled the solution treatment temperature. It should be noted that unlike the CCT diagrams constructed by the DSC technique, the resistivity measurements cannot separate multiple reactions. Therefore the onset/completed temperature are the points where the whole reaction starts/ends.

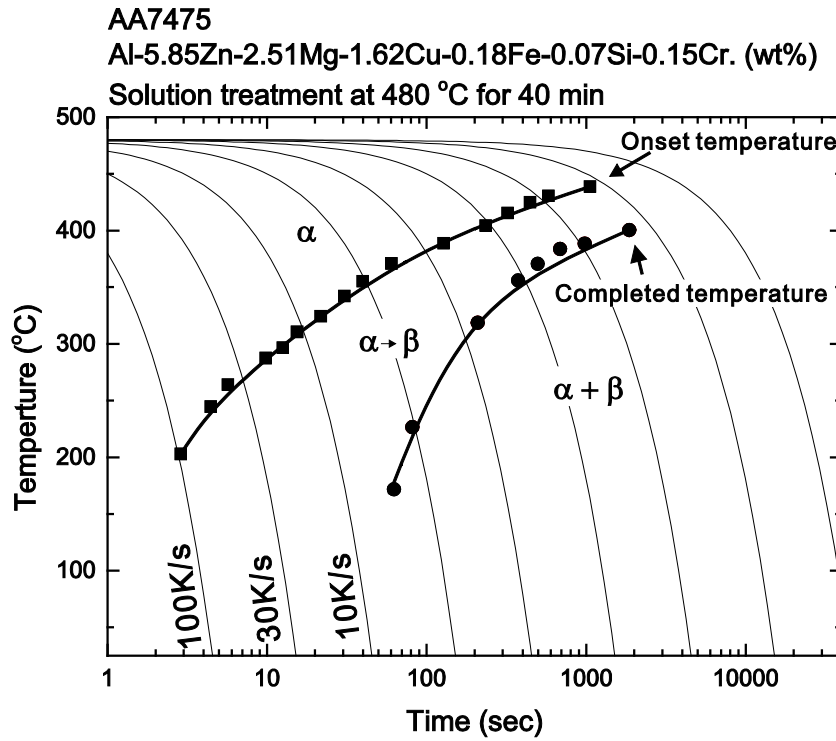


Figure 2.24: Detected CCT curve for alloy AA7475 using electrical resistivity measurements [121]. The β represents the overall reaction that happens during continuous cooling.

2.6. Modelling approaches for non-isothermal transformations

2.6.1. Quench factor analysis

The classical nucleation theory describes the nucleation rate as a function of time, t , at a given temperature as:

$$I = \beta \cdot \exp(-\Delta G_m / kt) \cdot \exp(-\Delta G^* / kt) \quad \text{Eqn 2.2}$$

where:

ΔG^* = activation energy for nucleation,

ΔG_m = activation energy for diffusion,

k = Boltzmann's constant,

β = parameter including density of potential nucleation sites.

The growth kinetics at a particular temperature can be described by an Avrami-type equation:

$$\zeta = 1 - \exp(-k(T) \cdot t^n) \quad \text{Eqn 2.3}$$

where:

$k(T)$ = temperature dependent term,

t = time at fixed temperature,

ζ = volume fraction transformed.

The numerical exponent n is independent of temperature that its value varies from ~ 1 to 4 depending on Christian [123]. However, the transformation kinetics under non-isothermal conditions are extremely complex as the nucleation rate and growth rate of the transformation are both time-dependent and temperature-dependent. However, Cahn stated that heterogeneous precipitation (which is typically observed during the quenching of aluminium alloys) tends to follow the additivity rule [124]. If the limited number of heterogeneous nucleation sites are consumed very early in the reaction then it is assumed that the transformation rate is only a function of time, and independent of the actual thermal path [125]. The additivity rule is only valid for a limited range of non-isothermal reactions. However, there is still a lot of published work that has been carried out to predict the transformation behaviour during continuous cooling using isothermal transformation kinetics (i.e. TTT and TTP diagrams) by assuming that the reactions are additive [100, 108, 111, 126-137].

Evancho and Staley developed a quench factor analysis (QFA) modelling approach for aluminium alloys in 1971, which involves an integration of cooling curves and TTP diagrams to predict the corrosion and/or mechanical property behaviour of heat-treatable aluminium alloys after cooling [138].

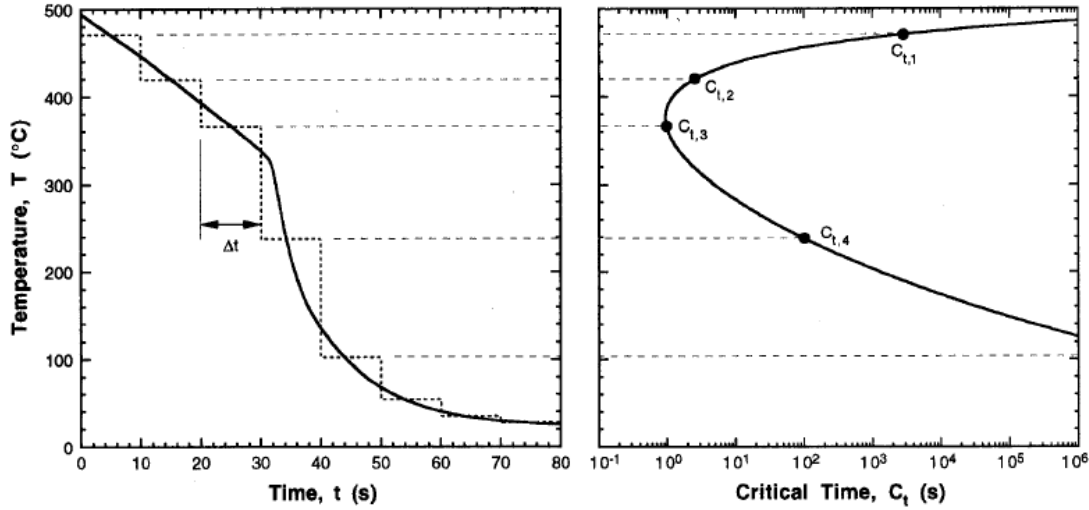


Figure 2.25: Schematic of quench factor calculation using a cooling curve and a C-curve [72].

The QFA method assumes that all nucleation occurred early in the reaction due to a limited number of nucleation sites for heterogeneous precipitation [124]. As a result, the reaction is isokinetic and the amount of precipitation during continuous cooling is given by the integral

$$\tau = \int_{t_0}^{t_f} \frac{1}{C_t} dt = \sum \frac{\Delta t}{C_t} = \frac{\Delta t_1}{C_{t,1}} + \frac{\Delta t_2}{C_{t,2}} + \dots + \frac{\Delta t_{f-1}}{C_{t,f-1}} \quad \text{Eqn 2.4}$$

Where:

τ = the quench factor,

C_t = critical time from C-curve,

t_0 = the time at start of cooling,

t_f = the time at finish of cooling.

The C_t function is defined by:

$$C_t = -k_1 k_2 \exp\left(\frac{k_3 k_4^2}{RT(k_4 - T)^2}\right) \exp\left(\frac{k_5}{RT}\right) \quad \text{Eqn 2.5}$$

where:

k_1 = constant equivalent to $\ln(\text{fraction untransformed during the quench})$,

k_2 = constant related to the reciprocal of the number of nucleation sites,

k_3 = constant related to the energy required to form a nucleus,

k_4 = constant related to the solvus temperature,

k_5 = constant related to the activation energy for diffusion,

R = gas constant = $8.3143 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$,

T = temperature in Kelvin.

Therefore the properties after continuous cooling can be calculated by an equation such as:

$$\sigma = \sigma_{\max} \cdot \exp(k_1 \tau) \quad \text{Eqn 2.6}$$

where:

σ = yield strength after ageing,

$\sigma_{\max}$ = maximum aged YT with fast quenching (normally water quench),

$k_1 = \ln(\sigma_c)$,

σ_c = fraction of $\sigma_{\max}$ represented by C-curve

There are numerous papers that have been published to evaluate quench sensitivity for various aluminium alloys. Dolan and Robinson used hardness, electrical conductivity and tensile strength to calculate the C-curves for some aluminium alloys including 7175-T73, 6061-T6 and 2017-T4 [128]. They found that the C-curves can be used to help reduce residual stresses of the alloys. They also pointed out that the C-curve is not appropriate for very slow cooling conditions. Mackenzie and Newkirk demonstrated that a Jominy end quench approach could be used for quench factor determination. A set of samples with different cooling

curves can be obtained by Jominy end quenching, so that the Jominy end quench method exhibits less scatter than other methods [127]. Rometsch *et al* have further developed the QFA by incorporating improvements such as a square root dependency of yield strength on the volume fraction of precipitates [139]. The purpose of this is to enable more physically realistic explanations for the various fitted parameters.

Table 2.1: Fitted QFA constants for various aluminium alloys and tempers from the literatures

Alloy	k_2 (s)	k_3 (J/mol)	k_4 (K)	k_5 (J/mol)	Ref
7050-T76	2.2×10^{-19}	5190	850	180 000	[138]
7075-T6	4.1×10^{-13}	1050	780	140 000	[138]
7175-T73	7.6×10^{-10}	412	750	112 200	[128]
6061-T6	5.1×10^{-8}	978	822	94 182	[128]
603-T6	1.1×10^{-10}	154	750	131 000	[35]
2017-T4	6.8×10^{-21}	5794	900	206 784	[128]
2024-T351	1.28×10^{-11}	577	760	133 888	[140]

Table 2.1 shows the calculated QFA parameters from the literature for various aluminium alloys and tempers. It is shown that the individual constants change significantly from one alloy/temper to another. Although the constants reflect a physical meaning, the exact values are fitted and therefore semi-empirical.

In most cases, the QFA equations consider only a single type of precipitate, while nearly all the alloys being studied contain several types of precipitates. Tiryakioglu and Shuey studied the quench sensitivity of a cast Al-7Si-0.6Mg (in wt%) alloy using interrupted and delayed quenching experiments [131]. They proposed that the loss of solute from solution for this alloy is mainly due to three different paths during quenching. As a result, separated C-curves have been presented to illustrate these paths that result in loss of Si from solution, as shown

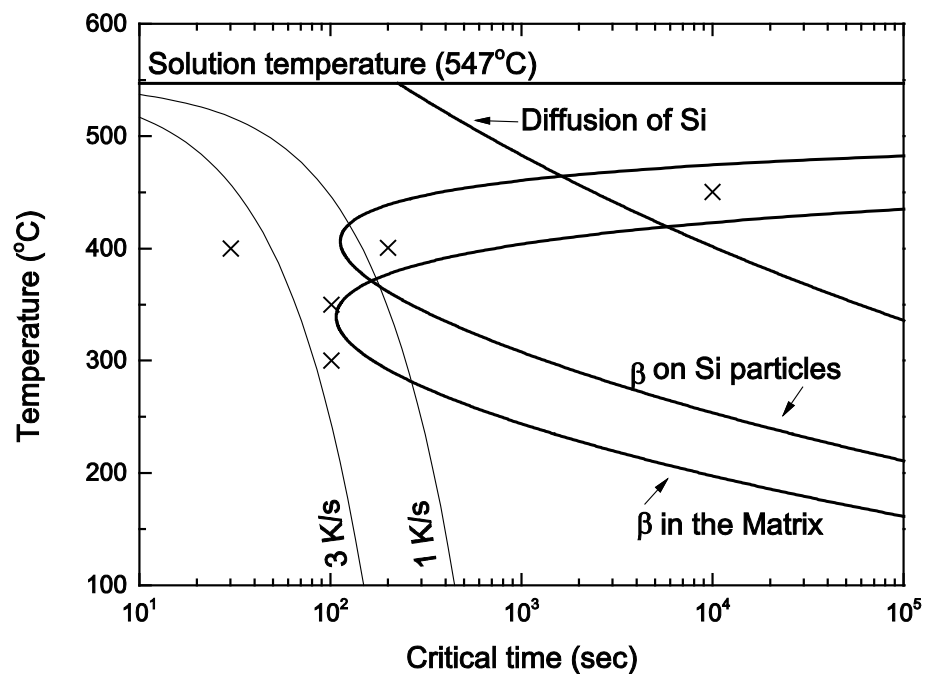


Figure 2.26: Critical times for three reactions during the quenching of an Al-7Si-0.6Mg alloy [131].

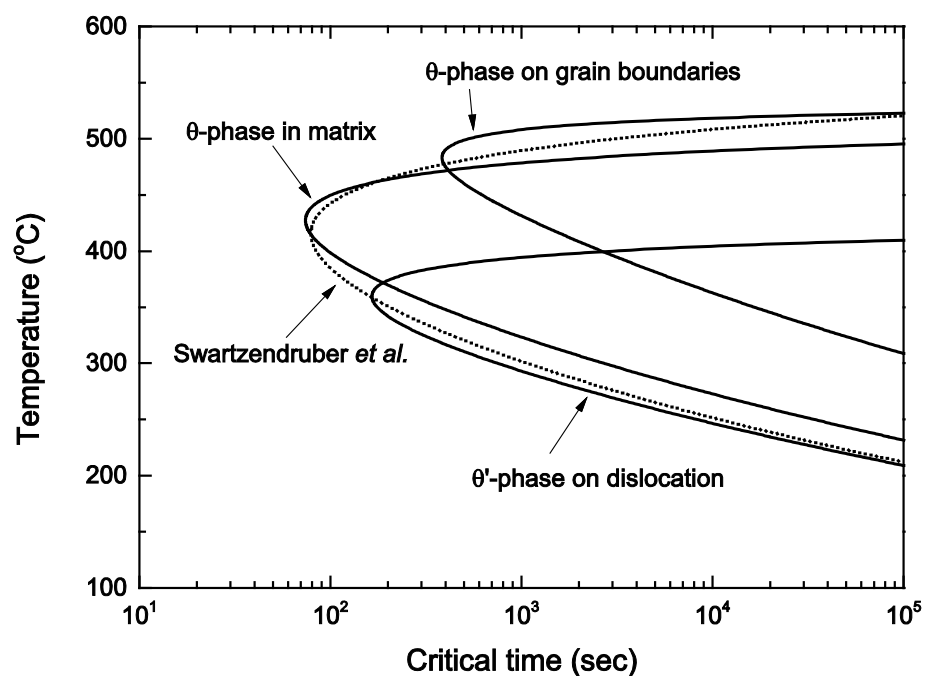


Figure 2.27: Critical time, plotted for three reactions during quenching of alloy AA2219 [100].

in **Fig 2.26**. It is shown that one of the curves represents the diffusion of Si atoms from the matrix to existing Si particles. In this case, the constant k_3 related to the nucleation of Si particles is assumed to be zero.

Tiryakioglu and Shuey also used QFA to fit multiple C-curves for data that has been measured by Swartzendruber *et al* for alloy AA2219 [100]. The results showed that a triple C-curve solution provided a better approach than a single C-curve solution (as shown in **Fig 2.27**). They also provided insights into the physical meanings of the model coefficients that can improve the original QFA method, so that an analysis of multiple precipitation reactions is feasible.

There are still some issues with the QFA modeling approach itself: (i) Due to that many constants being included, the C-curve calculations may have multiple solutions; (ii) Although the QFA constants describe physical processes, the predicted values have limited physical meanings due to the various assumptions and fitting methodologies employed during QFA; (iii) The properties and C-curves may vary for different tempers.

2.6.2. Other modeling approaches

Recently an analytical model has been proposed by Rios to describe the relationship between continuous cooling transformation (CCT) or continuous heating temperature (CHT) diagrams and other isothermal time-temperature transformation (TTT) diagrams [141]. It is a general methodology that can be used to transform an arbitrary CCT diagram into a corresponding TTT diagram. However it may not be applied to the quenching process that contains multiple quench-induced reactions.

It has been shown that the quench sensitivity of 7xxx series alloys is influenced by various factors, such as alloying elements, amount of quench-induced precipitations and nucleation sites for quench-induced precipitation. Desirable

quench sensitivities are achievable if these factors can be controlled carefully. However, in order to do this, some of the gaps outlined in this literature review need to be addressed.

2.7. Research aims

1. To clarify and explain the underlying mechanisms of why an alloy is sensitive to slow cooling conditions. The corresponding microstructural features such as recrystallisation, dispersoid particles and quench-induced precipitation are investigated. A series of 7xxx alloys with systematic changes in major alloying additions are studied for the purpose of improving the properties of thick products by careful design and control of the chemical composition and heat treatment process.
2. To describe the quench sensitivity by means of the development of continuous cooling precipitation (CCP) diagrams for the studied 7xxx aluminium alloys. This method utilises different techniques, including specialised DSC measurements, dilatometer quenching and microstructure analysis. The quench sensitivity is evaluated based on a detailed analysis of each precipitation reaction peak during continuous cooling.
3. To describe the CCP diagrams of the studied 7xxx alloys using the quench factor analysis method. This modeling approach is developed further to illustrate the effect of quench rate on the precipitation reactions of 7xxx alloys and to model the C-curves for overall precipitation reaction.

Chapter 3. Materials and methods

3.1. Materials casting and processing

A total of five different 7xxx series alloys have been included in the current study. Alloy AA7150 was received as a commercially produced 80 mm thick plate, supplied by the Aluminium Corporation of China Ltd (Chalco). This material formed the basis of the investigation, but several other alloys were designed and produced with systematic changes in Zn/Mg ratio, Cu content and Mg content. The compositions of all the studied alloys are shown in **Table 3.1**. Apart from the commercially extruded alloy AA7020 received from Germany, all the other designed alloys were cast into steel moulds at CSIRO in Melbourne, Australia. The alloys were melted at 700 °C with magnetic stirring. The liquid metals was poured into a pre-heated steel mould. The bottom of the steel mould was placed into a circulating water bath for chilling. After cooling down to room temperature, the cast ingots were placed into an air circulation furnace for a homogenisation treatment of 48 hours at 460 °C. After scalping the surfaces, the slabs were hot-rolled from 25 mm to 3 mm in thickness with a total reduction rate of 88%. The hot rolling temperature was 420 °C at the beginning. It dropped by about 50 °C after each pass, so that the final temperature for the plate was about 200 °C after 4 rolling passes.

Table 3.1 Actual measured chemical compositions of the studied 7xx series alloys

Weight %											
Alloy	Fe	Si	Zn	Mg	Cu	Cr	Mn	Zr	Al	Zn:Mg	Total
7150 ^A	0.03	0.02	6.26	2.08	2.10	<0.01	0.01	0.09	Bal	3.01	10.61
7150 ^{B,C}	0.05	0.02	6.33	2.15	2.04	< 0.01	0.04	0.12	Bal	2.91	10.74
7085 ^D	0.03	0.07	8.16	1.46	2.06	< 0.01	< 0.01	0.12	Bal	5.59	11.90
7037 ^D	0.02	0.12	7.82	1.37	0.91	< 0.01	< 0.01	0.12	Bal	5.71	10.36
7055 ^D	0.03	0.03	8.12	2.00	2.00	< 0.01	< 0.01	0.12	Bal	4.06	12.30
7020 ^E	0.17	0.11	4.37	1.19	0.04	0.11	0.15	0.14	Bal	3.67	6.17

Atomic %											
Alloy	Fe	Si	Zn	Mg	Cu	Cr	Mn	Zr	Al	Zn:Mg	Total
7150 ^A	0.03	0.02	2.74	2.51	0.91	-	-	0.04	Bal	1.09	6.25
7150 ^{B,C}	0.03	0.02	2.74	2.51	0.91	-	0.02	0.04	Bal	1.09	6.27
7085 ^D	0.02	0.07	3.58	1.72	0.93	-	-	0.04	Bal	2.08	6.36
7037 ^D	0.01	0.12	3.40	1.60	0.41	-	-	0.04	Bal	2.13	5.58
7055 ^D	0.02	0.03	3.56	2.36	0.90	-	-	0.04	Bal	1.51	6.91
7020 ^E	0.08	0.11	1.85	1.36	0.02	0.06	0.08	0.04	Bal	1.36	3.45

Notes:

^A Pilot product supplied by Chalco with ingot and hot rolled 25 mm thick plate;^B Commercial product supplied by Chalco with hot rolled 80 mm thick plate;^C Unless stated otherwise, all 7150 samples were taken from the centre layer of the thick plate;^D Designed, cast and hot rolled in the lab;^E Commercially extruded 30 mm diameter round bar.

Samples from hot rolled plates were typically solutionised by ramping slowly from 460 to 480 °C, while alloy 7020 samples were cut from a 30 mm diameter extruded rod and solutionised directly at 480 °C for 30 min. Samples were then cooled to room temperature at controlled rates and typically aged for 24 hours at 120 °C. Further details are given in the next section.

3.2. Heat treatment

3.2.1. Heat treatments for solution treatment work in chapter 4

The solution treatment work for Chapter 4 was performed by heating up samples to 460 °C for 1 hour and then slowly heating up to 480 °C and holding for another one hour in an air-circulation furnace (Carbolite Furnace). After solution treatment, the samples were immediately quenched into a bucket of water at room temperature or cooled in static air.

Ageing at 120 °C was performed in oil baths with a temperature variation of about ± 1 °C for a duration of up to 24 hours.

3.2.2. Heat treatments and DSC work in chapter 5 and Chapter 6

It is the purpose of this work to construct CCP diagrams for different alloys, based on a combination of DSC measurements, microstructure analysis and hardness testing. Several conventional DSC devices are used employing the method described by Milkereit *et al* to record the excess specific heat curves at different cooling rates ranging from very slow cooling (~ 0.005 K/s) to as fast as possible [118]. Corresponding microstructural analysis is carried out to help interpret the results. The Differential Fast-Scanning Calorimetry (DFSC) technique [120] was considered for the purpose of cooling samples at extremely fast rates. However, due to the very small size of the DFSC samples (i.e. of a similar order as the grain size), they were deemed to be too small to capture adequate information about grain boundary precipitation. Therefore such DFSC measurements are not included in this investigation. In order to

extend the range of controlled cooling rates, a quenching dilatometer was utilised to achieve cooling rates faster than 5 K/s. However, no exothermal heat can be detected with the dilatometer. Typical cooling rate ranges for the various devices and experiments in this work are shown in **Fig 3.1**.

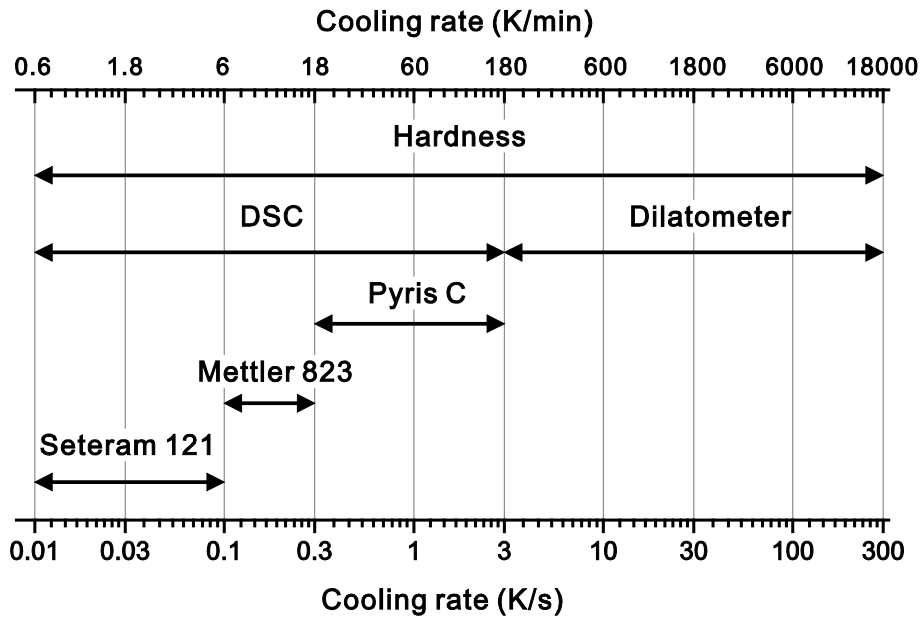


Figure 3.1 Cooling rate ranges for the different DSC devices and the quenching dilatometer employed in this work.

Table 3.2: Sample sizes and reference mass for different DSC devices

DSC devices	Sample sizes (mm)	Reference mass (mg)
Perkin Elmer Pyris C	$\varnothing 6.4 \times 1$	83.5
Mettler 823	$\varnothing 5.4 \times 1.4$	82.4
Setaram 121	$\varnothing 6.1 (5.7) \times 21.65$	1742

The DSC samples were solutionised in the different DSC devices before cooling at controlled linear cooling rates from 480 °C. However, due to the fact that a very large number of DSC measurements were required for different cooling rates and for different alloys, a pre-solution treatment was performed to heat up bulk samples to 460 °C for 1 hour and then slowly heating up to 480 °C and holding for another one hour in an air-circulation furnace before water

quenching. The small disc samples were then cut from the solutionised bulk materials for subsequent DSC measurements. The sample size and corresponding reference sample mass for each device are shown in **Table 3.2**. In order to minimise the asymmetry of the thermal lag between the measured sample and the reference sample, the DSC samples were ground manually with fine SiC paper until their weights were close to that of the pure Al reference samples.

It is generally considered that, if a bulk material is to be studied by DSC, a fixed sample size is normally used to minimise the detection variations. Moreover, in order to avoid any temperature inhomogeneity and substantial thermal lag from detected samples, a relatively smaller sample is always preferred. However, for cooling processes with a wide range of cooling rates, one fixed sample size is not appropriate any more. One reason for this is that the fast cooling reactions may differ from the slow cooling reactions. As the fast cooling reactions in Al alloys would cause relatively smaller heat flows, a higher sensitivity DSC device is needed. Although a larger sample size is preferred to detect smaller heat flows, this is not ideal for fast cooling rates due to thermal lag issues. Baseline measurements will be carried out regularly to make sure that the baseline correction procedure is repeatable. For the slow cooling rates a special CALVET-type DSC was employed. The CALVET-type Setaram 121 DSC is used in a climatised room with stable temperature. In order to detect very weak heat evolutions over extremely long durations, significantly large sample sizes were used with the Setaram 121 DSC.

The DSC samples and the reference samples were enclosed in pure aluminium pans to avoid surface radiation from the samples [118]. It is believed that the radiation losses may affect the shape of the baseline [142]. Furthermore, it is impossible to evaluate the measured DSC curves precisely without aluminium covers. The samples were sealed within the aluminium pans with standard crimper press rigs. Due to the different sample sizes, the covering pans are different, as illustrated in **Fig. 3.2**.

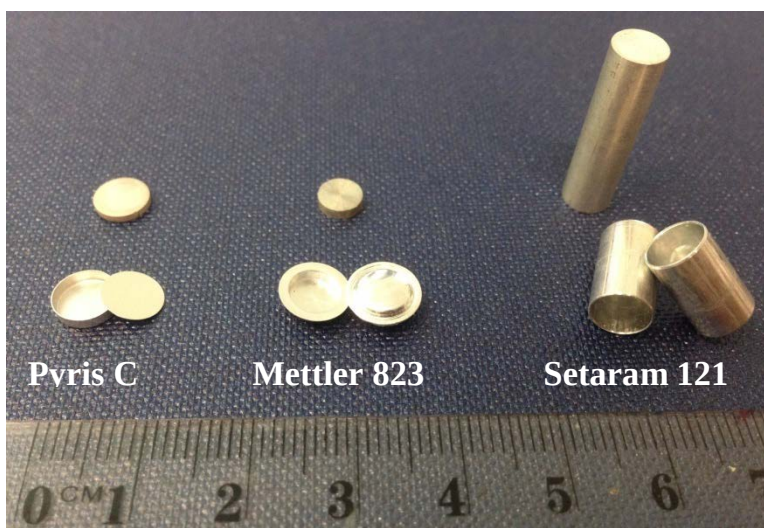


Figure:3.2. DSC samples and pure aluminium pans for the different DSC devices. The DSC samples were crimped into the aluminium pans using standard crimpers for each device.

The samples were then carefully placed into the corresponding DSC chambers for the continuous cooling experiments. The pre-solutionised samples were heated quickly to 480 °C and held for 10 min to cause the temperature to stabilise. They were then cooled according to the different continuous cooling treatments that were programmed into the different DSC devices.

One aim of this work is the detection of the critical cooling rate after which precipitation no longer occurs during cooling. In this case, any heat flow below the detect limitation of the DSC devices is considered as the critical cooling rate. However, some precipitation reactions have very small associated heat flows. The challenge is to separate the signal from the noise level in these cases. Therefore, the following criteria were used to help define the detection limit [118]:

- the reaction is detectable in at least three repeated experiments,
- the reaction is detectable also at the next slower cooling rate,
- the specific precipitation heat is at least 0.1 J/g,
- the peak-temperatures are in the same region as for next slower rate.

The measured DSC raw data contains the heat flow (mW) value of the sample as a function of time and temperature. This heat flow value could be affected by unavoidable asymmetries such as different mass of the measured sample and the reference or different locations of sample placements. Moreover, the heat flow value is affected by the thermal inertia of the measuring system (thermal lag). It is obvious that this thermal lag would become more prominent in fast cooling conditions. Consequently, the sample mass should be as small as possible in extreme fast conditions. Zohrabyan *et al* have reported a sample size of about $100 \times 100 \text{ }\mu\text{m}$ for DFSC experiments [120]. Therefore, a conversion or evaluation of the original measured heat flow curve must be performed for traditional DSC techniques if a precise analysis is needed. The purpose of this manipulation is to eliminate the disturbances and asymmetries from the real measurements [142].

A set of DSC raw data that was measured using the Pyris C device was taken to demonstrate the evaluation process that was performed throughout this thesis. Only a continuous cooling process of 1 k/s has been considered in this case, although the heat flow values of other processes (including heat and isothermal holding) have been recorded. In order to help with the data evaluations, a short isothermal holding time before and after the cooling process is programmed deliberately. The purpose of this short isothermal holding segment is to check whether the heat flow value is stable during this time. Any fluctuation of the heat flow value at this time indicates that the DSC device is not yet fully stabilised. The different heat flow values between the reference sample and the measured sample should also be checked. It is reasonable to keep the difference of the measured heat flow values within $\pm 5 \text{ mW}$ based on practical experience. It should be noted that the baseline value is measured immediately after a sample run with the purpose of minimising any unexpected differences. It is also advisable to check that the heat flow values before and after the cooling process are at the same level, but it is still acceptable if the difference is within a reasonable range.

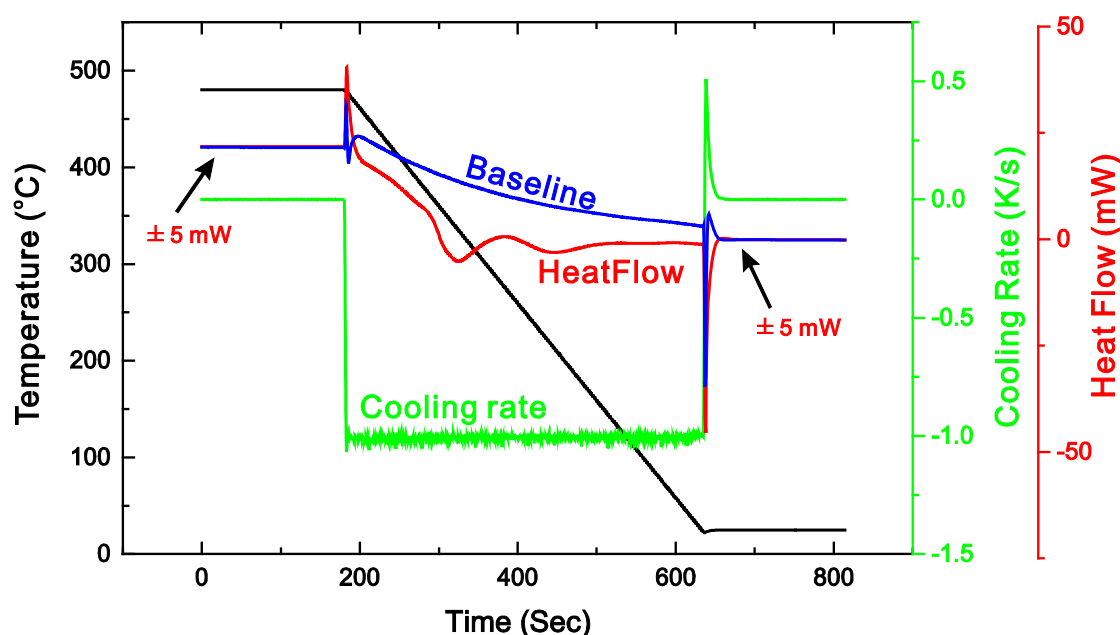


Figure 3.3 Typical DSC raw data: all these curves including temperature, cooling rate, baseline and heat flow should be examined before further evaluation.

The **Fig 3.3** illustrates an example of typical measured raw data. It is noted that the temperature profile and cooling rate have also been shown in this figure. It is very important to check whether the cooling rate is under program control before evaluation, as any significant change of the cooling rate would cause some smeared signals. It is shown that there are two distinguished peaks either at the start or at the end of the cooling process. These two peaks are corresponding to the change of the cooling rate. It is also noted that the heat flow values before and after the cooling process overlap for both the baseline measurement and the real sample measurement. This confirms that the baseline measurement and the real sample measurement start and end with matching heat flow values. Therefore, a baseline subtraction is feasible. Only if these sample measurements and baseline measurements fulfill the requirements that have been described before is any further data evaluation considered to be reliable.

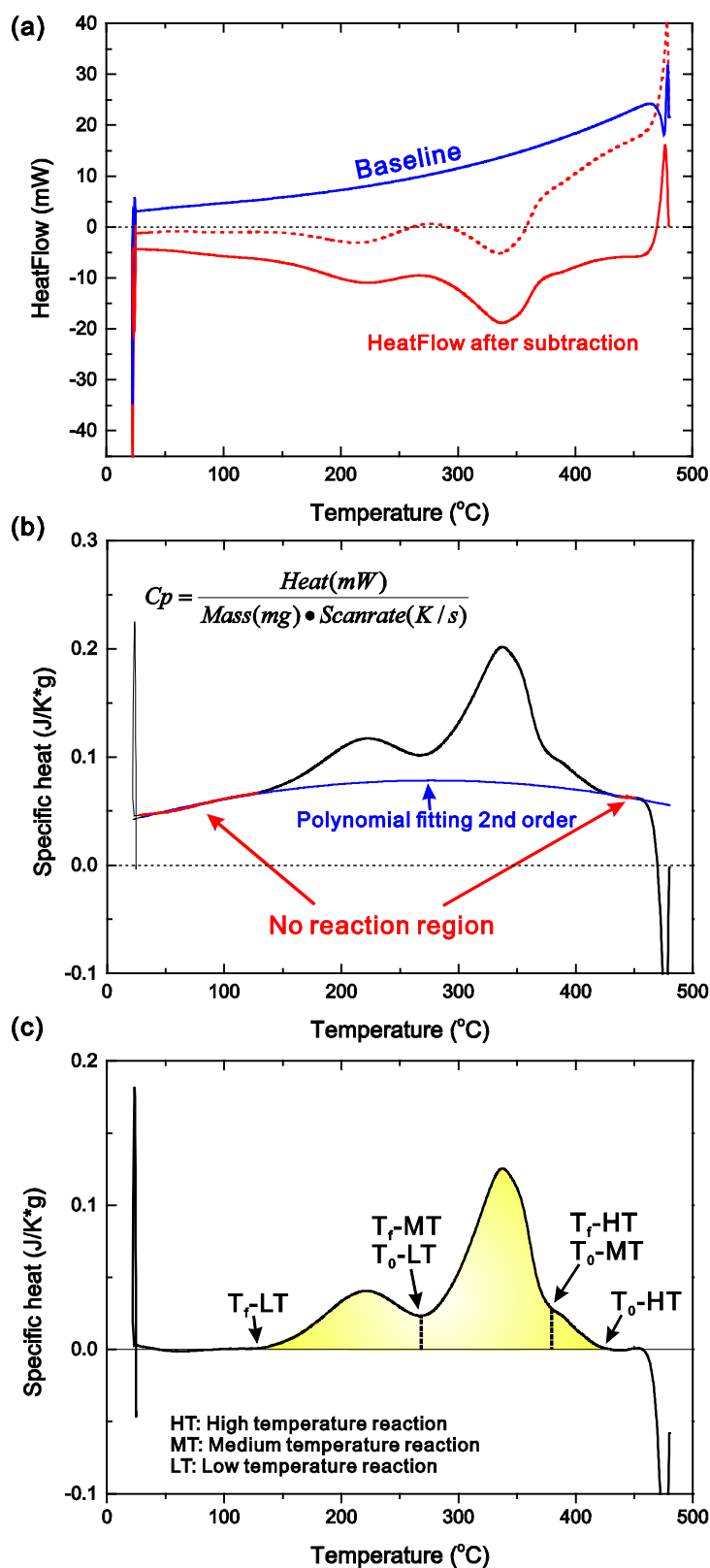


Figure. 3.4. Schematic of data evaluation for a measured DSC curve, with T_o as the onset temperature of a reaction and T_f as the finishing temperature of a reaction.

Fig 3.4 demonstrates the data evaluation of a measured DSC curve. The purpose of data evaluation is to eliminate any asymmetry from measured sample/reference or DSC devices. The data evaluation starts with a subtraction of baseline values from measured heat flow values (as shown in **Fig 3.4** (a)). The baseline curve is measured by placing reference samples (99.999% pure Al) on both the reference-furnace side and the sample-furnace side. No reaction is expected for baseline measurements. After the baseline subtraction, the zero level of the heat flow still looks curved (as shown in **Fig 3.4** (b)). This could be due to the asymmetry of the devices. A bending correction is needed at this stage. The purpose of the bending correction is to subtract the heat flow data from a polynomial fitting of the no reaction region. The no reaction region is defined as [143]:

- there is no reaction is detectable in at least three repeated experiments,
- there is no reaction is detectable also at the next slower cooling rate,
- specific precipitation heat is below 0.1 J/g,

The excess specific heat capacity ($\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$) can be calculated from the measured heat flow rate by subtracting the base-line and dividing by the sample mass and cooling rate:

$$C_p = \frac{\Phi_m - \Phi_0}{m \cdot \beta}$$

where:

C_p is the excess specific heat capacity,

Φ_m is the measured heat flow,

Φ_0 is the reference base-line,

m is the sample mass,

β is the cooling rate.

Normally the DSC runs at constant pressure, yielding the heat capacity at constant pressure $C_p(T)$. Therefore the enthalpy is determined by integration as follows [142]:

$$\Delta H = H(T_f) - H(T_o) = \int_{T_o}^{T_f} Cp(T) dT$$

Fig 3.4 (c) demonstrates the excess specific heat curve after data evaluations. It is evident that there are several heavily overlapping peaks that been heavily overlapped each other. The normal approach to separate the overlapped peaks is to use multiple Gaussian functions to fit the detected curves [118, 144]. However, there are a few problems with the Gaussian fitting. One issue is that not all the DSC peaks have a Gaussian shape. In many cases, a DSC peak increases sharply and decreases slowly. It looks more like a Gamma distribution with an asymmetric distribution. However, no fundamental theory can support this distribution so far. Another issue is that the number of reactions under a DSC curve is unclear in many situations. Therefore the Gaussian fitting method is not appropriate for such circumstances. From our experience, it is important to analyse a broad range of cooling rates from very slow rates close to equilibrium conditions to very fast cooling rates beyond the critical cooling rate to get a full understanding of the whole precipitation process in order to ensure that the peak separation process is meaningful and reliable.

Due to the overlapping issues of the detected peaks, a method described by Milkereit *et al* [145] was used to define the intersection points of the two overlapping peaks as the onset temperature for the lower temperature reaction and the finishing temperature for the high temperature reaction. The onset temperature for the high temperature reaction is defined as the onset point with respect to the zero level. **Fig 3.4 (c)** illustrates how this evaluation is performed.

Cooling rates beyond the limited range of the traditional DSC devices were achieved by utilising a Bähr DIL 805A/D quenching dilatometer device, as shown in **Fig 3.5**. The optimum sample dimensions of about 6 mm in diameter and 1 mm in height were utilized. A thermocouple was spot welded on the sample surface so that the temperature-time profile could be recorded. The

samples were then heated by an induction coil and were continuously cooled by controlled N₂ gas flow.

Finally, some of the DSC discs were aged at 120 °C in oil baths with a temperature variation of about ± 1 °C for a duration of 24 hours.

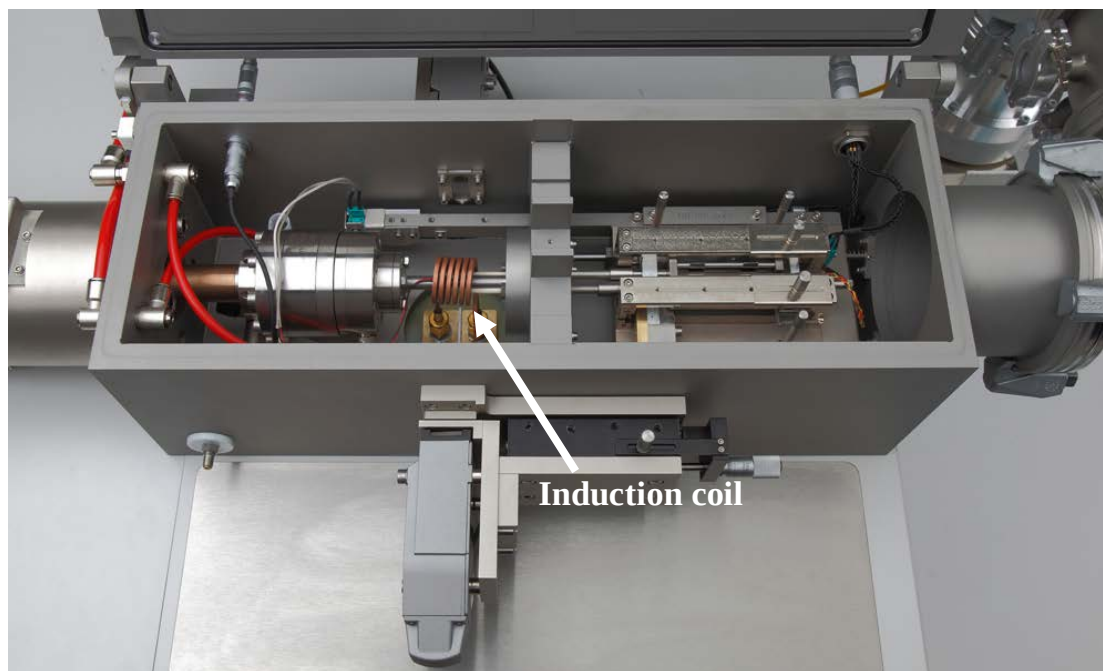


Figure 3.5: Image of the DIL 805A/D quenching dilatometer from TA instruments® website.

3.2.3. Step quenching experiments

The step quenching experiments were designed to study the precipitation behaviour during continuous cooling. This is different from interrupted quenching experiments, where samples are held isothermally at intermediate temperatures. The step quenching experiments involve cooling the samples at constant cooling rates (v) to certain intermediate temperatures and then cool rapidly to room temperature without any isothermal holding. The differences between these two types of experiments are illustrated in **Fig 3.6**. The constant cooling rate and intermediate temperature are selected according to detected DSC curves. Quenching temperature points at which given cooling rates can produce adequate amount of precipitation (for detection by electron

microscopy) are chose for the step quenching experiments. The selected cooling rates and corresponding quench temperatures are shown in **Table 3.3**.

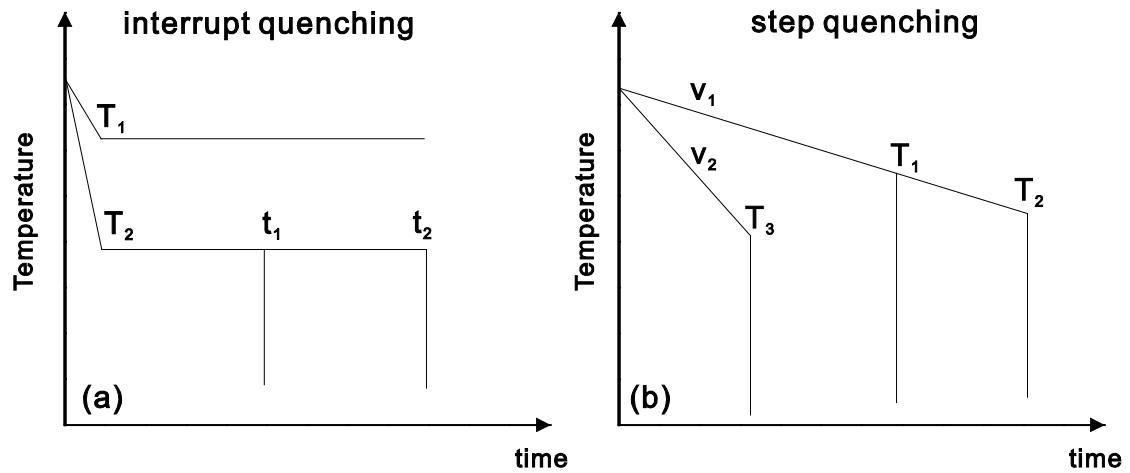


Figure 3.6: Schematic of (a): interrupted quenching and (b): step quenching methods.

Table 3.3: Selected cooling rates and corresponding quench temperatures (°C) for step quenching experiments.

Alloy	0.03 K/s		0.3 K/s		3 K/s	
7150 ^B	460	400	400	320	320	200
7085 ^D	420	340	400	340	310	180
7037 ^D	420	320	360	310	330	220
7055 ^D	460	420	450	350	320	200

The step quenching experiments were carried out using the Bähr DIL 805A/D quenching dilatometer. Corresponding microstructure characterisation work was carried out on these as-quenched (AQ) samples.

3.3. Self-designed Jominy quenching Rig

The Jominy end quench method was originally developed for the hardenability testing of steels [146]. It has been demonstrated that this end quenching experiment can also be applied to nonferrous metals researches [80, 81, 127, 134, 147, 148]. Therefore some Jominy experiments were carried out on a custom-designed Jominy end quench rig, as illustrated in **Fig 3.7**.

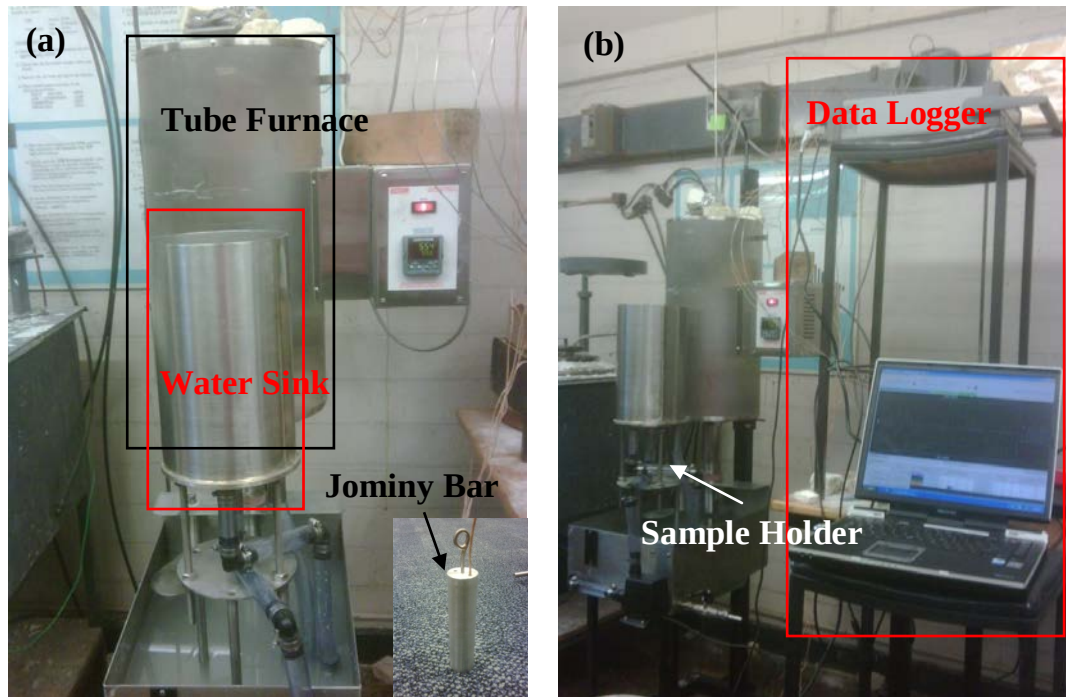


Figure 3.7 Jominy end quench rig designed for aluminium alloys showing placement of Jominy end quench rig with respect to (a) tube furnace, and (b) data logger.

Due to the good thermal conductivity of aluminium alloys, the rig needs a specially designed sample holder to avoid heat losses due to surface thermal radiation. In addition, thermocouples and a data logger system are needed for instantaneous logging of temperature-time data. The Jominy quench bar is a 110 mm long cylinder with a 25 mm diameter. Small (1.5mm diameter) vertical holes were drilled to 2 mm, 5 mm, 10 mm, 17 mm, 30 mm, 50 mm, 75 mm and 105 mm distances from the quenching end. The vertically inserted thermocouples were designed to allow the Jominy bar to drop directly into the sample holder such that every separate Jominy end quench experiment should

have the same delay time (the time gap from end of solution treatment to start of quenching).

The cylindrical bar was then solution treated at $475\pm 5^{\circ}\text{C}$ for 1 hour by suspending it in the thermally stable zone of a tube furnace. At the end of the solution treatment, the bar was released from the suspended rod, causing the sample to drop automatically into the sample holder via guides on the side. Before that, the water in the tray would be pumped to a water tank and maintained there at a constant level to give a constant water pressure for the quench spray. As soon as the sample dropped into the holder, the valve for the spray water would be released and the Jominy bar would then be quenched from one end. Instantaneous temperatures were recorded with a data logger system during the quenching process. The corresponding hardness profile was measured at the centre of the bar in 5mm intervals from the quench end before and after aging at 120°C for 24 hours.

3.4. Hardness testing

Hardness indentations were made on both as-quenched (AQ) and aged samples using a Vickers hardness testing machine with a 5 kg load. Each hardness measurement reported is the average of five different measurements made on each sample.

3.5. Scanning electron microscopy (SEM)

For microstructural analysis, samples were manually ground and polished with SiC paper, diamond paste and colloidal silica for examination with a JEOL JSM-7001F field emission gun scanning electron microscope (FEG-SEM), equipped with a Bruker Quantax EDX system.

3.6. Electron backscattered diffraction (EBSD)

EBSD mapping was performed using a JEOLTM 7001F scanning electron microscope equipped with an HKL-Channel 5TM EBSD software package

(Oxford Instruments, UK) on selected TEM foils for the purpose of measuring the misorientations of the grains observed by TEM. The step size was selected to ensure at least five mapping points across each grain width on the cross section.

3.7. Transmission electron microscopy (TEM)

For TEM analysis, samples were sliced into 0.5 mm thick sheets. Discs measuring 3 mm in diameter were punched from the sliced sheets and then ground to a thickness of $\sim 150\ \mu\text{m}$. The TEM foils were then prepared by electro-polishing the discs using a Tenupol-5 with a solution of 33% nitric acid and 67% methanol, at a temperature of -30°C . The TEM observations were undertaken using a Philips CM20 TEM and an FEI Tecnai G² T20 Twin TEM, both equipped with a Bruker Quantax 200 TEM X-ray spectrometer.

3.8. High angle annular dark-field imaging - scanning transmission electron microscopy (HAADF-STEM)

Some HAADF - STEM mode work was carried out on an FEI Titan³ 80-300 kV microscopy at 300 kV, fitted with an aberration corrector for the probing lens system, an aberration corrector for the imaging lens, a high-resolution electron energy loss spectrometer and an HAADF detector. The implementation of double aberration correctors provides atomic resolution within the precipitates.

Chapter 4. Effect of thermo-mechanical processing

4.1. Introduction

Cooling after solution treatment is not the only point in the industrial processing route where high temperature, non-isothermal precipitation can occur. There are several other cooling processes in the industrial processing route of manufacturing 7xxx products, for example cooling after solidification and cooling after homogenisation processes. However, by quench sensitivity, we normally refer to the quenching process after solution treatment, as this quenching process is designed to preserve the solutionised state from the solution temperature to room temperature. The purpose of the other cooling processes is different from the solution-quenching process.

Nevertheless, it is noted that the homogenisation process could also affect the quench sensitivity by changing the spatial distribution of dispersoids which are believed to be critical nucleation sites for quench-induced precipitates. Besides, thermo-mechanical processing such as hot rolling may also influence the quench sensitivity by changing the grain structure.

In the current work, the microstructure characterisation of alloy 7150 after solidification, homogenisation and solutionising are performed with the purpose of understanding the different quench sensitivity behaviour in different thermo mechanical processing conditions. Special attention has been given to resolve the dispersoid particle behaviour in different stages in order to unveil the mechanism of why they tend to act as preferential nucleation sites for quench-induced precipitates.

4.2. Microstructure evolution before and after homogenisation

Fig 4.1 shows the typical industrial processing line of producing a 7150 thick plate. It is a very complex process, as 7xxx products are normally provided with a high level of mechanical properties combined with other properties. Therefore each step of the processing line should be carefully controlled according to relevant standards to achieve corresponding requirements [17, 24, 25, 28, 29, 149, 150].

It is evident that there are several cooling processes included (as illustrated with blue lines in **Fig 4.1**), for example direct chilling after solidification, slow cooling after homogenization, slow cooling after hot-rolling, quenching after solution treatment and cooling after ageing. It should be noted that only the cooling process after solidification and solution treatment is forced quenching. The cooling after homogenisation is usually at very slow cooling rates. Therefore a large amount of precipitation could happen under this condition which could potentially affect the subsequent processing [151]. Moreover, the dispersoids that precipitate during the homogenisation process could affect the quench sensitivity [46, 151-157]. It is therefore of interest in the current study to illustrate the precipitation behaviour of dispersoids during the homogenisation process. It is believed that an understanding of dispersoid precipitation during the homogenisation process could help to resolve the quench sensitivity issue.

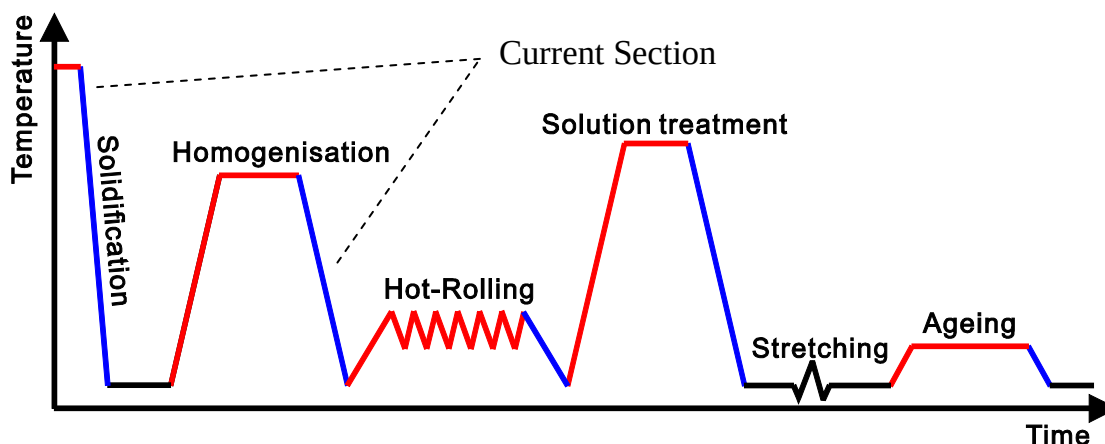


Figure 4.1: Typical industrial processing line for producing a 7xxx thick plate

The studied samples (approximately 1 cm^3 in size) were cut from a 7150^A ingot supplied by Chalco. The chemical compositions are listed in **Table 3.1**. The as-cast alloy 7150^A was homogenised at 460 °C for 48 hours. In order to avoid any precipitation during the post-homogenisation cooling process, the homogenised samples were water quenched (WQ). The as-cast microstructure has been demonstrated in **Fig. 4.2** (a) and (b), meanwhile the homogenised microstructure has been shown in **Fig 4.2** (c) and (d).

It is shown that, along with intermetallic and eutectic constituent particles along grain or dendrite boundaries there are also some elongated or irregular phases within the grains in the as-cast condition. Previous investigations have indicated that those irregularly shaped phases with bright contrast are MgZn_2 phases (due to the relatively high atomic number of Zn) while the elongated phases with grey contrast are Al_2CuMg phases [158]. It is shown that there are many white dots associated with these phase, as shown in a higher magnification image in **Fig 4.2** (b). After homogenisation at 460 °C for 48 hours, most of the intermetallic phases have been dissolved. There are still some coarse particles that can be observed within grain or at the grain boundaries. They are believed to be undissolved Fe-containing phase or S-phase (Al_2CuMg), as their dissolution temperature is above

the homogenisation temperature. It is noted in **Fig 4.2 (c)** that there are some small white particles inhomogeneously distributed with the grains. The higher magnification image in **Fig 4.2 (d)** shows that they are fine spherical particles with a diameter of approximately 50 nm. It is also noted that some of these particles tend to segregate together, leading to some relative large particles.

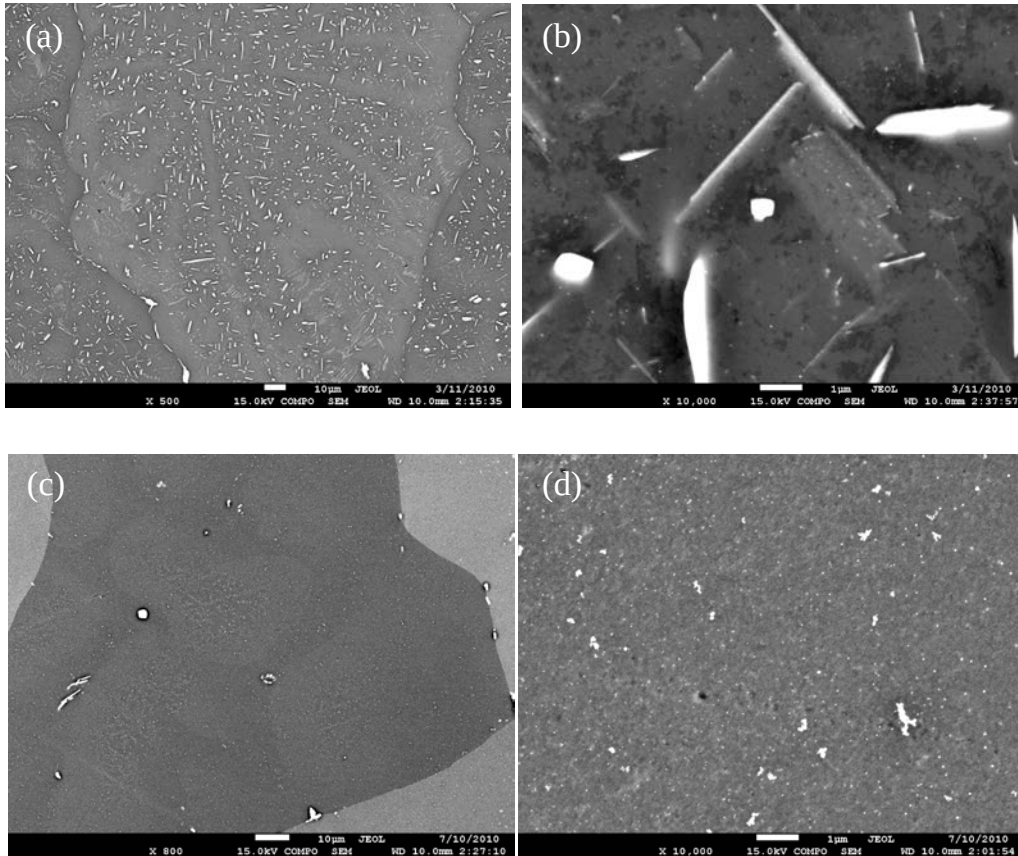


Figure 4.2: Backscattered SEM images of alloy 7150^A in the as-cast condition (a) and (b), and in the in homogenised condition (48 hours at 460 °C and water quenched) (c) and (d).

Corresponding TEM observations have been carried out to identify these white dots. The selected area diffraction (SAD) pattern in an as-cast specimen demonstrates that these spherical particles (as shown in **Fig 4.3 (a)**) are primary Al_3Zr dispersoids with *fcc* L1_2 crystal structure. They are mostly likely to form during solidification process. The diffraction pattern in **Fig 4.3 (a)** shows that

these primary dispersoids have the simple cubic/cubic orientation relationship with the Al matrix:

$$[110]Al_3Zr // [110]_{\alpha}, (010)Al_3Zr // (010)_{\alpha}$$

Fig. 4.3 (a) also shows that the size of these primary Al_3Zr dispersoids is approximately of 40-50 nm in diameter. **Fig. 4.3** (b) illustrates that the spherical particles exhibit a coffee-bean shape contrast in two beam conditions. The coffee-bean contrast is known as an Ashby-Brown contrast, which is a sign of a coherent relationship of the observed particles with the matrix. According to Woolhouse and Brown, lattice-strain effects around spherical precipitates appear as lobes of low intensity with a line of no contrast perpendicular to the reciprocal vector g [159].

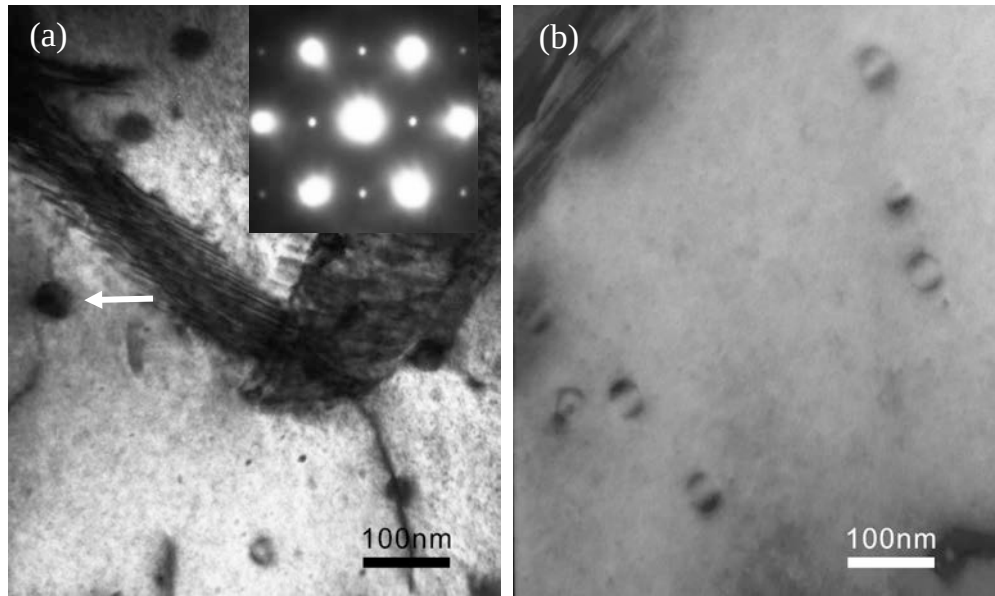


Figure 4.3: TEM observation of primary Al_3Zr dispersoids in as-cast alloy 7150. Corresponding SAD pattern shows that the primary Al_3Zr dispersoids exhibit fcc $L1_2$ crystal structure

Fig. 4.4 (a) shows the morphology of Al_3Zr dispersoids after homogenisation at 460 °C for 48 hours. It can be found that the large Al_3Zr dispersoids are existing

along with some smaller Al_3Zr dispersoids (as arrows indicate). **Fig 4.4** (b) illustrates a relatively uniformly distributed region of these dispersoids. It appears that the number density of Al_3Zr dispersoids has been changed by homogenisation. A statistical analysis of the size distribution of Al_3Zr dispersoids has been carried out relying on backscattered SEM images and TEM images with representative high dispersoids density regions in different grains in both as-cast and homogenised samples. More than 1000 dispersoids were counted in different images to minimise statistical errors.

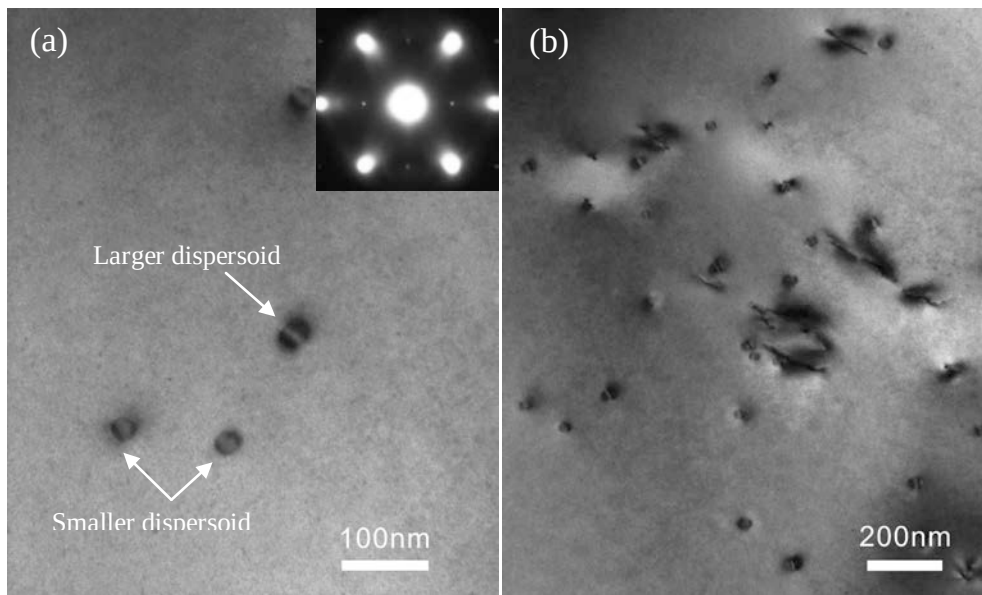


Figure 4.4: Bright field TEM images of alloy 7150 (a and b) after homogenisation at 460 °C for 48 hours followed by water quenching.

Fig. 4.5 (a) and (b) illustrate the size distribution of Al_3Zr dispersoids in alloy 7150^A in as-cast and homogenised conditions. It is demonstrated that there are two different size distributions of dispersoid particles after homogenisation while there is only one size distribution in the as-cast condition. The result indicates that a large number of small Al_3Zr dispersoids precipitated out during homogenisation. Compared with primary Al_3Zr dispersoids in the as-cast condition, the secondary Al_3Zr dispersoids exhibit a smaller size distribution. Furthermore, the TEM

analysis shows that both primary Al_3Zr dispersoids and secondary Al_3Zr dispersoids exhibit the same metastable L1_2 crystal structure.

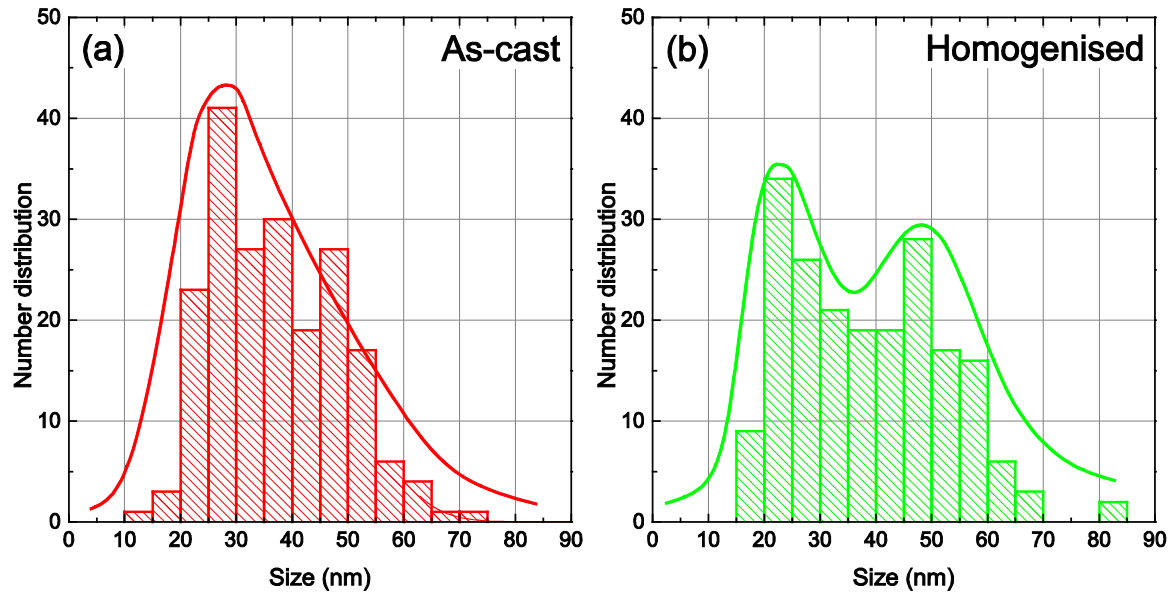


Figure 4.5: Statistical analysis of the size distribution of Al_3Zr dispersoids in as-cast (a) and homogenised (b) conditions based on image analysis of SEM and TEM images.

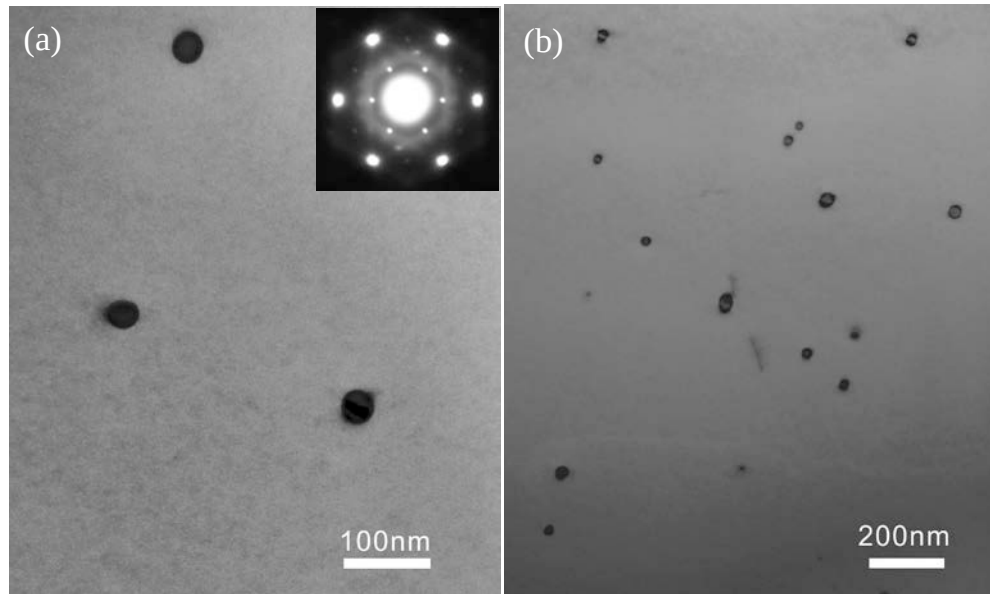


Figure 4.6: Bright field TEM observation of alloy 7150^A ((a) and (b) in different magnifications) after homogenisation at 460 °C for 200 hours.

In order to better understand the evolution of Al_3Zr dispersoids during homogenisation, a 200 hours homogenisation treatment was carried out at 460 °C. The purpose of this study was to give the Al_3Zr dispersoids adequate time to grow/transform, as the evolution of dispersoid particles is very slow due to the extremely low diffusion rate of Zr in the Al matrix [160, 161]. The TEM results have been presented in **Fig. 4.6**. It is shown that neither the size nor the number density of Al_3Zr dispersoids has been changed much compared to the 48 hour homogenisation treatment (as shown in **Fig 4.4**). The SAD pattern in **Fig. 4.6** (a) demonstrates that the Al_3Zr dispersoids retain their metastable crystal structure even after 200 hours of homogenisation. The result here is in agreement with the finding of Nes that the metastable Al_3Zr dispersoids do not change their structure until 500 hours in a binary Al-Zr system [162].

4.3. Different quench sensitivity behaviour before/after deformation

The previous section has discussed the precipitation of dispersoids during homogenisation. All this microstructure characterisation was carried out in the WQ condition, as the WQ process inhibits the unwanted quench-induced precipitation. However, the post-homogenisation cooling process is usually very slow, leading to a large amount of precipitation. Considering that these coarse particles will be broken up during rolling or re-dissolved during solutionising, there is actually less attention being paid to the post-homogenisation cooling process than to the post-solutionising cooling process. Such coarse particles may have an influence on the evolution of the microstructure in the intervening processing steps, for example, by acting as sites for particle stimulated nucleation (PSN) of recrystallisation [112]. They may also have a direct detrimental effect on the final plate if they become large enough during slow cooling that they remain after solution treatment. As a result, the quench sensitivity behaviour is expected to vary accordingly.

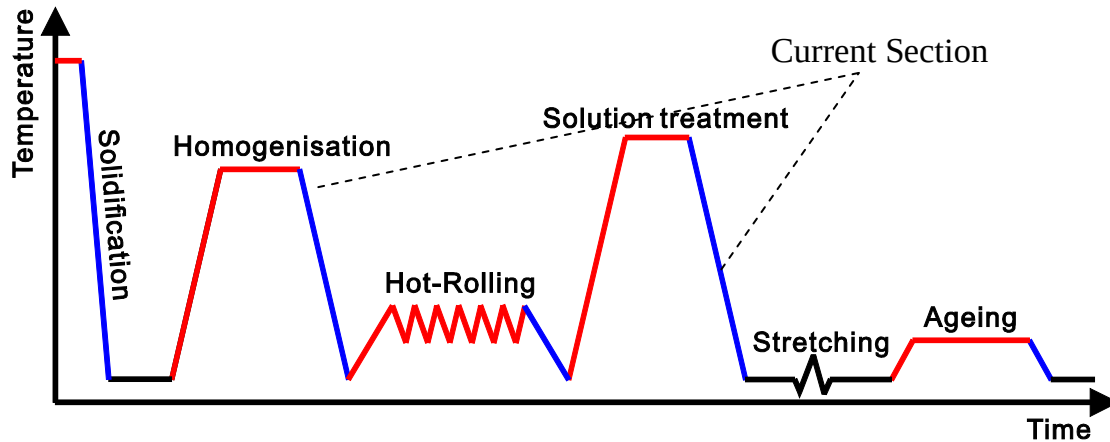


Figure 4.7: Typical industrial processing line of producing a 7xxx thick plate

The experiments were designed to solutionise as-cast alloy 7150^A at 460 °C for 48 hours and quench in room temperature water (WQ) or static air (AC). In order to make a comparison, the hot-rolled alloy 7150^A was solution treated at 475 °C for 1 hour and quenched under the same conditions (as shown in **Fig 4.7**). All samples, approximately 1 cm³ in size, were then aged at 120 °C for up to 24 hours (i.e. peak ageing for alloy 7150). The age hardening curves are plotted against ageing time in **Fig. 4.8**.

In **Fig 4.8**, the homogenised samples cooled under different conditions are represented by red lines. It is shown that there is not much difference between the two red lines with increasing ageing time, suggesting that homogenised samples exhibit low quench sensitivity. The solutionised samples cooled with different conditions are represented by black lines, as shown in **Fig 4.8**. It is demonstrated that the hardness of WQ samples increases dramatically with increasing ageing time. The WQ hardness value is almost doubled after ageing at 120 °C for 24 hours compared with the as-quenched condition. The hardness value of the AC sample after solution treatment, however, is significantly lower than that of the WQ sample in the peak aged condition, although it is still slightly higher than the hardness of the WQ sample in the as-quenched condition. It is noted that the homogenised samples have higher as-quenched hardness values. This is can be

ascribed to that more solute has been retained in homogenised samples than that in solutionised samples. Therefore a stronger solute strengthening can be found within homogenised samples.

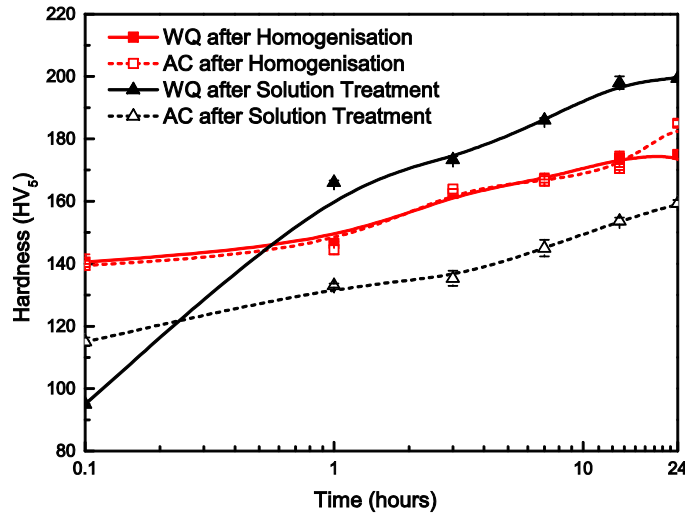


Figure 4.8: Ageing curves at 120 °C for alloy 7150^A quenched in different quenchants after homogenisation and solution treatment, respectively

The results here imply that alloy 7150^A exhibits less quench sensitivity before deformation (i.e. after homogenisation) than after deformation (i.e. after solution). Therefore it is concluded from these results that the quench sensitivity behaviour of alloy 7150^A can be changed by thermo mechanical processing.

Microstructure characterisation has been carried out on both AC samples in the as-quenched condition. The representative TEM images have been shown in **Fig 4.9**. It is demonstrated that no quench-induced precipitates can be found along with Al₃Zr dispersoids in **Fig 4.9 (a)**. By contrast, many large quench induced precipitates can be found along with Al₃Zr dispersoids after AC from solution treatment temperature (as shown in **Fig 4.9 (b)**). The results here demonstrate that the metastable L1₂ Al₃Zr dispersoids could potentially become nucleation sites for

quench induced precipitates. It seems that the likelihood for this to occur has been greatly increased after solution treatment.

It is noted in **Fig 4.8** that the age hardening curve is used to describe the quench sensitivity phenomenon. This is due to the precipitation of undesired quench-induced phases during slow cooling that depleted the matrix of solute available for subsequent ageing, thereby causing a marked decrease of hardening capability of the alloy [30]. According to this 'loss of solute' mechanism, the relationship between the age hardening curves and quench-induced precipitates can be explained as:

- Higher increment of hardness during artificial ageing after WQ indicates more solute remaining for ageing treatment.
- Lower hardness increment during ageing after AC indicates less solute remaining for ageing treatment.

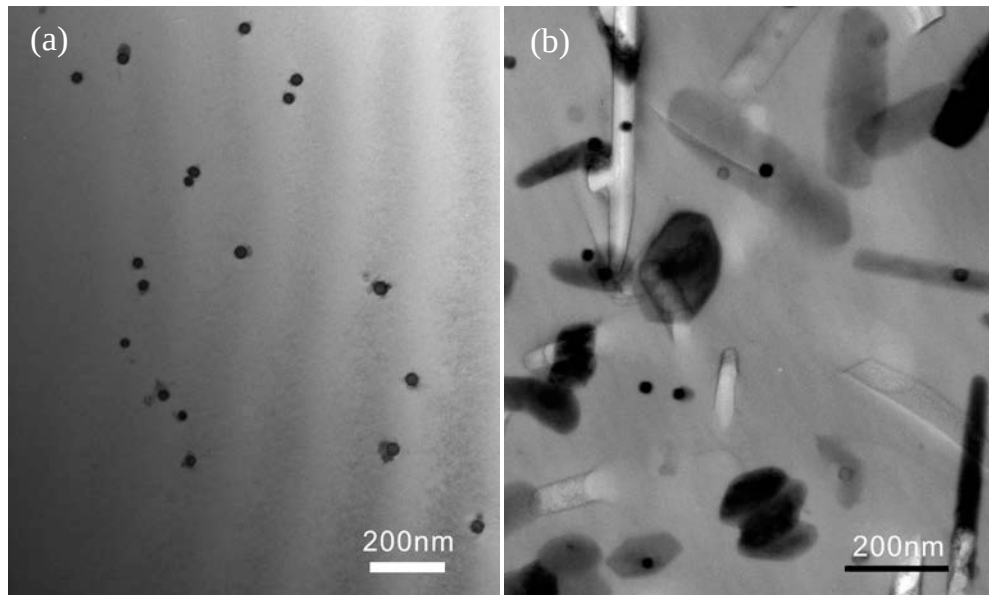


Figure 4.9: Typical TEM images of AC samples after homogenisation (a) and after solution (b) in as-quench samples.

The hardness value of WQ or AC samples at peaking ageing time (24 hours at 120 °C for alloy 7150) then can be used to illustrate whether the alloy is sensitive to different cooling conditions or not. Consequently, the R-value is introduced to represent how sensitive the material is to cooling rate. The R-value is defined as:

$$R = \frac{HV_{WQ} - HV_{AC}}{HV_{WQ}} \times 100\%$$

where:

HV_{WQ} is the peak aged hardness achieved in the WQ sample;

HV_{AC} is the peak aged hardness achieved in the AC sample.

The R-value then can be used to correlate different quench sensitivity behaviour, with higher R-values indicating relatively higher quench sensitivity and lower R-values indicating less quench sensitivity. An R-value of 0 indicates that the alloy is insensitive to cooling rate, as there is no difference in hardness between WQ samples and AC samples after ageing. **Fig 4.10** illustrates the calculated R-value for homogenised and solutionised samples. It is shown that the calculated R-value for homogenised samples is approaching zero, suggesting that this material is less quench sensitive. The calculated R-value for solutionised samples is significantly higher than that of homogenised samples, indicating that solutionised samples are more sensitive to cooling rate.

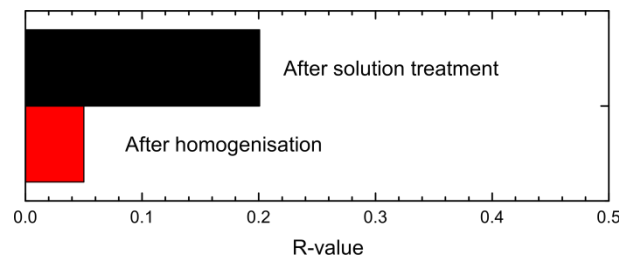


Figure 4.10: Calculated R-value for samples cooled differently after solution treatment and after homogenisation.

The R-value offers a simple and feasible way to evaluate quench sensitivity behaviour of alloys in WQ and AC conditions. It should be noted that the R-value calculation relies on the fact that specimens are cooled in two traditional cooling conditions (i.e. water quench and air cooling). It is assumed that with a given samples size (1 cm^3 in this case), the specimens can achieve the same cooling profiles. If there was any significant change of sample size, a different R-value may be obtained due to different cooling conditions. Moreover, not all the remaining solute atoms are attributed to increasing the hardness value after ageing. Some of the solute may participate to form grain boundaries precipitates and some may remain in the matrix. But for a given alloy that was cooled consistently by room temperature water or static air, the R-value can still be presented to evaluate the quench sensitivity behaviour. A more sophisticate description of quench sensitivity that covers a larger range of cooling rates will be discussed later.

4.4. Quench sensitivity behaviour of 7150 thick plate

As mentioned before, homogenisation and solution treatment have different purpose. Homogenisation is essential to remove the alloy element segregation and constituent eutectic structures that form during large direct-chill casting processes. The solution treatment, on the other hand, is to dissolve all the unwanted particles so that a supersaturate solid solution (SSSS) can be achieved after post-solution quenching. In order to preserve the solute atoms as much as possible in solution, a rapid quench is always preferred (as shown in **Fig 4.11**).

However, rapid quenching distorts thinner products such as sheet and introduces internal residual stresses into thicker products. These stresses are normally compressive at the surface and tensile in the core [128, 129, 163, 164]. Residual stresses may cause dimensional instability, particularly when components have an irregular shape or when subsequent machining operations expose the underlying tensile stresses [4]. What is also serious is that the level of residual stresses may

approach the yield stress in some high-strength alloys which, when superimposed upon normal assembly and service stresses, can cause premature failure [128, 129, 165]. For products of regular shapes such as sheet and plate, quenching stresses will be reduced if slower rates of cooling are used [65, 166]. Some alloys may be quenched with hot or boiling water, or even air-cooled after solution treatment [31, 167]. The products still show an acceptable response to subsequent age hardening. For thick plates, the level of residual quenching stresses can be counteracted by stretching (1%~5%) after quenching [150, 168]. However, this stretching process needs to be carefully controlled to avoid any further damage on products [168-170].

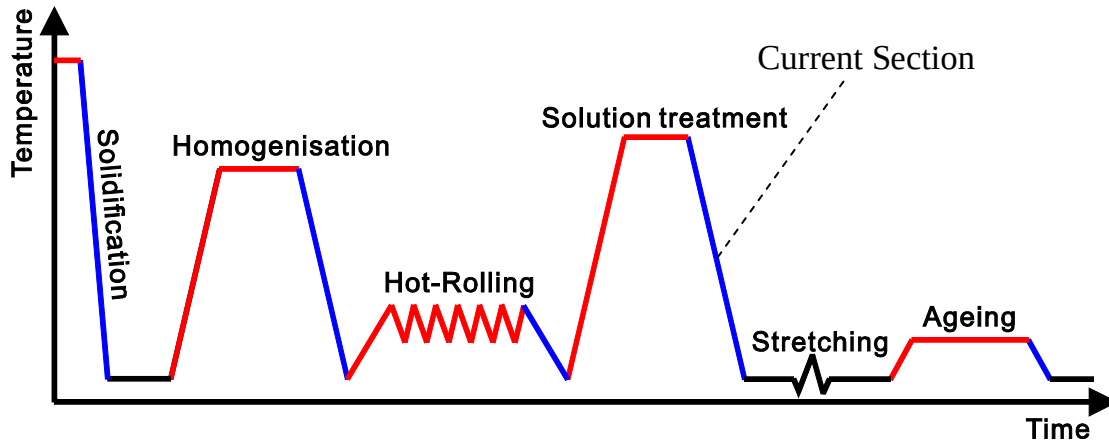


Figure 4.11: Typical industrial processing line of producing a 7xxx thick plate

When we consider the quench sensitivity of an aluminium thick plate, we normally think of the entire plate. The cooling rate at the mid-plane of a thick plate is naturally slower than that of the surface layer. However, the surface layer and centre layer also experience different degrees of thermo-mechanical processing as the full deformation cannot penetrate the whole thickness. It is believed that the surface layer is normally more deformed than the centre layer. Therefore the quench sensitivity behaviour of the surface and centre layers of a thick plate is expected to be different according to previous discussion. Therefore it is important

to illustrate the quench sensitivity behaviour of the surface layer and centre layer of an aluminium thick plate separately.

Some small pieces, approximately 1 cm^3 in size, were cut from either the surface layer or centre layer of a commercially produced 7150^B hot-rolled 80 mm thick plate, supplied also by Chalco. These samples were solutionised in a salt bath by heating up to 460 °C, holding at 460 °C for 1 hour, and then slowly heating up to 480 °C and also holding for one hour at 480 °C, followed by quenching using room temperature water or static air. The purpose of the stepped solution treatment is to get more solute in solution without overheating. Previous work on the same alloy has shown that any equilibrium M (MgZn_2) or T ($\text{Al}_2\text{Mg}_3\text{Zn}_3$) phase particles will be completely dissolved, while some S-phase (Al_2CuMg) particles may still remain after solution treatment [171]. Vickers hardness indentations were made both immediately after quenching and after artificial ageing at 120 °C.

Fig. 4.12 (a) shows aged hardness values at plate surface and centre locations after quenching into room temperature water or cooling in still air from 480 °C. It can be seen that the hardness value after 24 hours of ageing at 120 °C for the surface layer and the centre layer in the WQ condition are very close to each other. The centre layer shows slightly lower hardness values than the surface layer in the peak ageing condition, but the difference is close to the degree of scatter in the measurement results. By contrast, the surface layer and the centre layer exhibit very different hardness value after 24 hours of ageing at 120 °C in the AC condition. It is noted that the centre layer is significantly harder than the surface layer in the AC condition after ageing for 24 hours at 120°C. It is also evident that the hardness values for both layers after ageing are much lower in the AC condition than in the WQ condition.

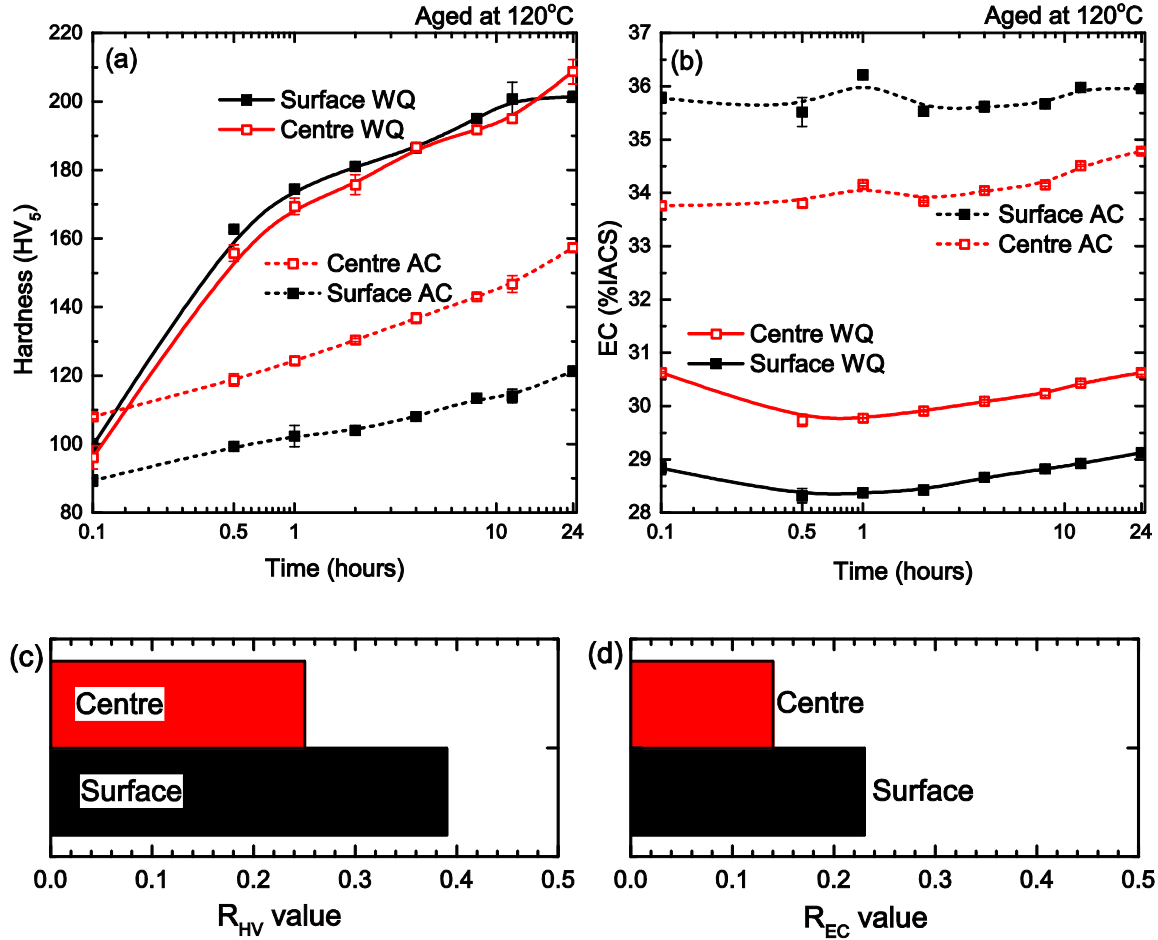


Figure 4.12: Aged hardness values (a) and electrical conductivity values (b) of samples from different layers of a thick plate after solution treatment, followed by WQ or AC. The corresponding R-values are shown in (c) and (d) respectively.

Fig. 4.12 (b) demonstrates the changes of electrical conductivity (EC) versus ageing time for those surface and centre samples cooled separately. The electrical conductivity is the measure of a material's ability to accommodate the transport of an electric charge. It is essentially related to the average time between electron scattering events. So in bulk materials, any mechanisms that can cause scattering of electrons would decrease EC value, such as lattice vibrations, impurities, lattice defects such as dislocations, grain boundaries, vacancies, or any other deviation from a perfectly periodic lattice [27, 172]. All these scattering processes decrease

the overall EC value of the alloy by reducing the mean scattering time. It is noted that the EC values of both the surface and centre layers are larger for the AC condition than for the WQ condition (**Fig 4.12 (b)**). This is an indication that more quench induced precipitation occurs during AC, thereby increasing the EC by depleting the matrix of solute. Comparing the surface layer and centre layer in the AC condition, it is shown that the surface EC value is larger than that of the centre layer, suggesting that there are more quench induced precipitation in surface layer. It is also shown in Fig 4.12 (b) that the surface EC value is lower than of the centre layer in WQ condition. This can be ascribed that the microstructures of surface layer is more in favor of electron transmission, i.e. the surface layer contains less impurities and/or grain boundaries. Moreover, the four EC curves also show that, for all conditions, there is little change of the EC values with increasing ageing time. The result shows that the age hardening precipitates have little effect on changing the EC values.

It is shown that the R-value evaluation method is also feasible for EC curves. The corresponding R-values for hardness and EC values were calculated and the results have been shown in **Fig. 4.12 (c) and (d)**, respectively. Both the hardness and EC measurements show that the surface layer exhibits relatively larger R-values, suggesting that the surface is more sensitive to cooling rate. The result here is also in agreement with the previous discussion that the thermo-mechanical process history could change the quench sensitivity behaviour of an alloy.

Figs 4.13 (a) and (b) show the WQ microstructures for both the surface layer and the centre layer. It demonstrates that both layers contain subgrains and recrystallised grains after solution treatment. The deformed structure can hardly be found within either surface layer or centre layer. It is believed that the deformed structure has been removed during solution treatment. Intermetallic particles have also been dissolved. The surface layer in **Fig. 4.13 (a)** shows a significantly higher volume fraction of recrystallised grains than the centre layer in **Fig. 4.13 (b)**. This

is mainly due to the fact that the surface layer experienced a relatively more severe deformation than the centre layer during the hot rolling process. Thus the surface layer contained more stored energy for recrystallisation.

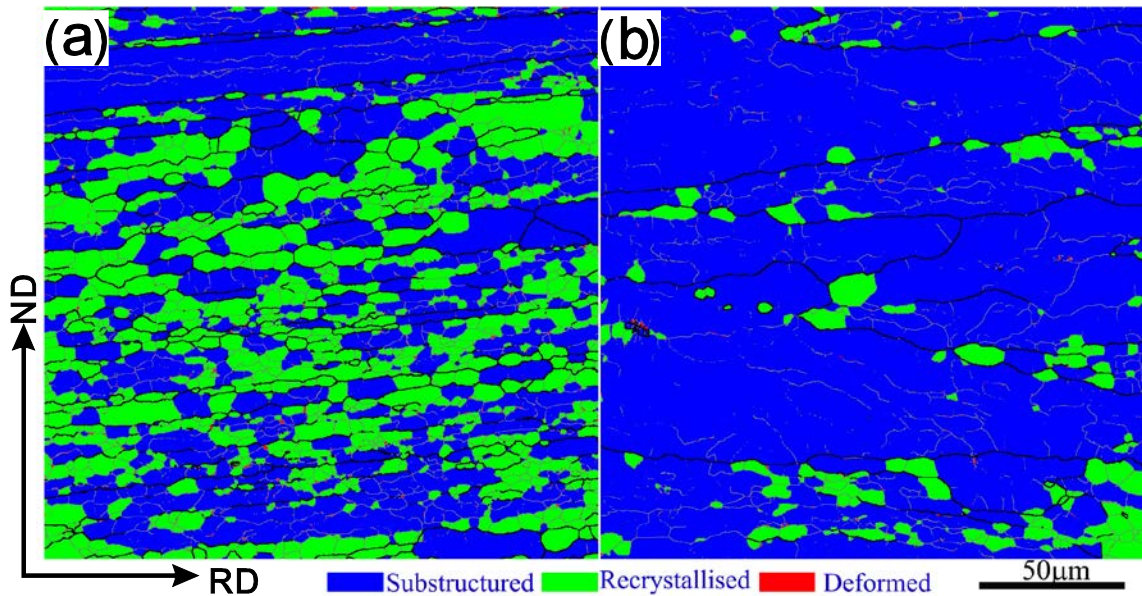


Figure 4.13: Typical water-quenched microstructures of (a) surface layer and (b) centre layer, with recrystallised grains here representing misorientation angles of $>15^\circ$

The respective AC grain structures are assumed to be similar to those shown in **Figs. 4.13** (a) and (b) since the grain structure is influenced by the solution treatment rather than by the quenching conditions. The main microstructural difference between WQ and AC will be that the latter results in more quench-induced precipitation.

More detailed microstructural information is revealed by TEM for the WQ and AC conditions, as shown in **Figs. 4.14** (a) and (c), respectively. A similar region containing both subgrains and recrystallised grains has been chosen to provide a good comparison between both cooling conditions. The main criterion to distinguish a recrystallised grain from others by TEM is to check whether the misorientation angles between adjacent grains are $>10-15^\circ$. All the misorientation

information described in angle/axis notation for observed grains is listed in **Table 4.1**. For this purpose, the TEM foils were examined first by TEM. A few TEM foils were then selected for EBSD mapping with the purpose of recording the exact misorientations of the observed grains. Only those foils containing both subgrains and recrystallised grains were then chosen for further detailed TEM analysis. By this method it was possible to obtain the EBSD results in **Figs. 4.14** (b) and (d) for areas that correspond with the TEM results in **Figs. 4.14** (a) and (c), respectively.

Table 4.1 shows that, within the observed area, the misorientation angles between the smaller grains are around 5° , which is much smaller than the 15° criterion in this case. Therefore all the smaller grains in **Fig 4.14** (grains 1-3 and 5-6) are assumed to be subgrains. **Table 4.1** also shows that the misorientation angles between every small grain and the adjacent large grain are quite large (around 40°). Therefore the two observed large grains in **Fig 4.14** (grains 4 and 7) are classified as recrystallised grains. On average, these recrystallised grains (around $20\text{ }\mu\text{m}$ in size) are much bigger than the subgrains ($\sim 2\text{-}5\text{ }\mu\text{m}$ in size). More importantly, the recrystallised grains give more uniform image contrast than the subgrains. This is mainly due to the reduced amount of dislocations and stacking faults that are caused by deformation.

From the microstructure characterisation in **Figs. 4.13** to **Fig. 4.14**, it is evident that the recrystallised grain structure is a critical factor that can influence the hardness values in slow cooling conditions.

It is evident that the quench-induced phases precipitate preferentially within the recrystallised grains at a slow cooling rate (as illustrated in **Fig. 4.14** (c)). Due to the different degree of recrystallisation between the surface layer and the centre layer, the respective age hardening curves are significantly different in the air-cooled condition. Nevertheless, the age hardening curves for WQ samples are

similar to each other mainly due to the fact that all quench-induced precipitation has been suppressed in both the surface and centre layers due to the fast cooling rate, leaving similar amounts of solute in solution and therefore resulting in similar hardening increments after artificial ageing.

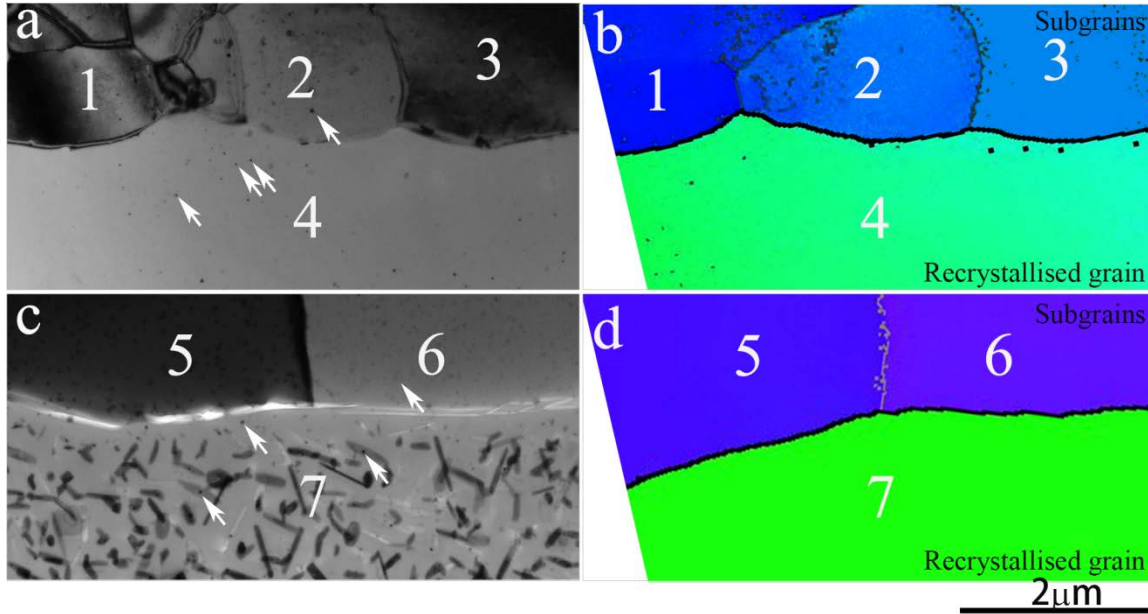


Figure 4.14: As-quenched microstructures for (a) water-quenched and (c) air-cooled samples from the plate centre layer (dispersoids are identified with arrows). Corresponding EBSD mapping for these areas is shown in (b) and (d), respectively. The grains observed by both TEM and EBSD mapping are numbered from 1 to 4 for the water-quenched condition and from 5 to 7 for the air-cooled condition

Table 4.1: Orientation relationships between the observed grains in Fig. 2 to distinguish between low angle grain boundaries (LAGB) and high angle grain boundaries (HAGB)

LAGB (0-15°)		HAGB (>15°)	
$\angle_{1-2}$	5.4° about $\langle 14\bar{1} \rangle$	$\angle_{1-4}$	40.4° about $\langle 34\bar{1} \rangle$
$\angle_{2-3}$	5.3° about $\langle 01\bar{3} \rangle$	$\angle_{2-4}$	41.7° about $\langle 3\bar{1}3 \rangle$
$\angle_{5-6}$	3.4° about $\langle 034 \rangle$	$\angle_{3-4}$	46.1° about $\langle 43\bar{1} \rangle$
		$\angle_{5-7}$	35.2° about $\langle \bar{3}2\bar{2} \rangle$
		$\angle_{6-7}$	35.4° about $\langle \bar{4}3\bar{2} \rangle$

It is also evident that there are no quench-induced precipitates in either the subgrains or the recrystallised grain in **Fig. 4.14** (a). However, many scattered spherical particles can be found inhomogeneously distributed within each grain with wide variations in the particle size and spacing. Previous discussion has shown that these spherical particles are metastable $L1_2$ Al_3Zr dispersoids that have precipitated during the homogenisation process. These fine dispersoids do not dissolve during solution treatment at $480^\circ C$ and are therefore observed after WQ.

Furthermore, **Fig. 4.14** (c) shows that a large number of quench-induced precipitates are found to coexist with Al_3Zr dispersoids in recrystallised grains and are also found on grain boundaries after air-cooling. While subgrains also contain Al_3Zr dispersoids but no quench-induced precipitates, it is generally accepted that equilibrium precipitates nucleate preferentially on defects such as dislocations, grain boundaries and free surfaces that can reduce the activation energy barrier. **Fig. 4.14** (c) indicates that Al_3Zr dispersoids in recrystallised grains are preferred nucleation sites for quench-induced precipitates compared to Al_3Zr dispersoids in subgrains.

As discussed before that there are two possible hypothesis can be used to explain the quench-induced precipitation preferentially nucleate on Al_3Zr dispersoids. One of the explanations would be that there are two forms of Al_3Zr dispersoids existing in 7xxx aluminium alloys, with the same stoichiometry but a different structure: a stable equilibrium form with a tetragonal $D0_{23}$ structure and a metastable form with a cubic $L1_2$ structure [53, 82]. Only the metastable dispersoids can inhibit recrystallisation and grain growth by pinning the grain boundary movement. The equilibrium dispersoids, on the other hand, act as nucleation sites for quench-induced precipitates during cooling. There is another hypothesis that the metastable Al_3Zr dispersoids lose their coherency with the matrix after recrystallisation [36, 73, 74, 81]. The increased interfacial energy due to incoherency with the matrix will then increase the likelihood for heterogeneous

quench-induced precipitation on these dispersoids. However, both of these hypotheses lack supporting experimental evidence. It is also one of the topics that will be discussed thoroughly in later chapters.

In order to evaluate these two hypotheses, two different TEM observation methods have been designed. Given that a new grain orientation has formed during recrystallisation, then it is expected that a new orientation relationship between the matrix and the dispersoids will form. Therefore the recrystallised grains are tilted to a low index crystal direction (normally [110] and [100]) for TEM observation, since both the crystal structure and the orientation of the Al_3Zr dispersoids within the recrystallised grain will be clearly revealed together with the matrix simultaneously. On the other hand, if the orientation relationship between dispersoids and the matrix has been changed after recrystallisation, then it is expected that the Al_3Zr dispersoids in the recrystallised grain should maintain their original orientation when a new recrystallised grain is formed. In other words, since the recrystallisation process involves the migration of high angle grain boundaries, the associated movement of Al atoms between adjacent grains may be expected to change the orientation relationship and the degree of coherency between the dispersoids and the matrix.

Figs. 4.15 (c) and (d) present a detailed MBDP analysis of Al_3Zr dispersoids in subgrain 1 and recrystallised grain 4 from **Fig. 4.14** (a) in the WQ condition. Both BF and DF images of the same region are shown in **Figs. 4.15** (a) and (b) respectively. The DF image in **Fig. 4.14** (b) uses the specific diffraction spot (100) from the Al_3Zr dispersoids so that only the scattered electrons from the same type/orientation of Al_3Zr dispersoids are visible. It is therefore possible to see the distribution of those dispersoids in the subgrain in **Fig. 4.15** (b), while they are only faintly visible in the BF image in **Fig. 4.15** (a). Compared with the spatial distribution of Al_3Zr dispersoids in the BF image shown in **Fig 4.15** (a), it is interesting to discover that there are some scattered Al_3Zr dispersoids showing up

as white dots in the DF image of the recrystallised grain (identified with arrows) in **Figs. 4.15** (a) and (b). This is evidence to show that the Al_3Zr dispersoids existing in a recrystallised grain can maintain their original orientations when a new recrystallised grain is formed. A similar result has been published recently for AA7010 alloy with combined Sc and Zr additions as dispersoid forming elements [173]. It is noted that there are also some other dispersoids that do not show up as white dots in the recrystallised grain. This is because these dispersoids existing in different subgrains previously. Therefore they exhibit different orientations after recrystallisation happens.

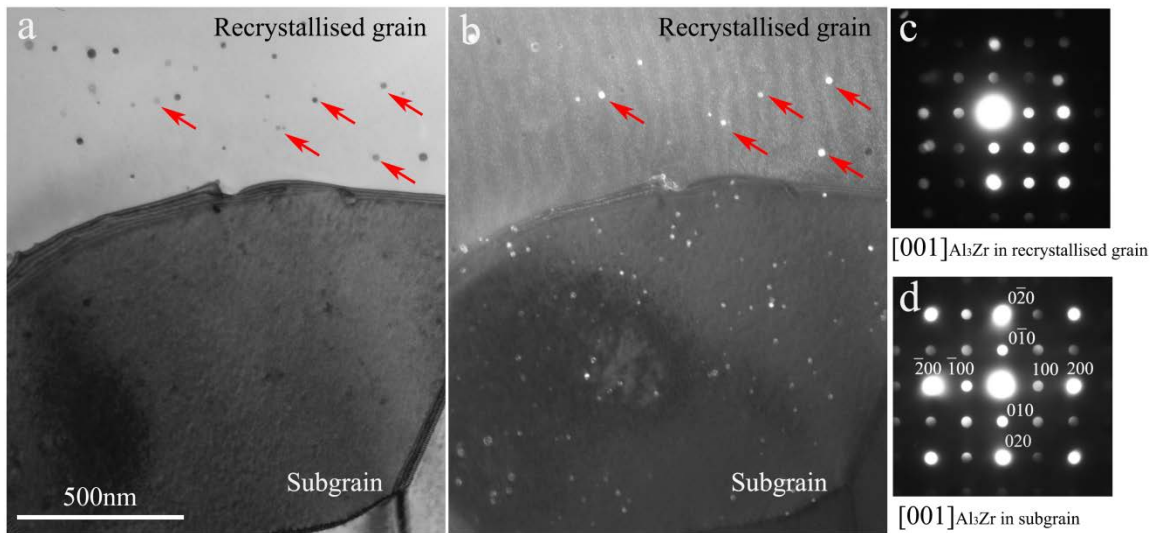


Figure 4.15: (a) bright field (BF) image and (b) dark field (DF) image showing the distribution of Al_3Zr dispersoids in the water-quenched condition. The DF image uses the diffraction spots from Al_3Zr dispersoids appearing at (100) positions, which are prohibited reflection position for the face-centred cubic matrix. Corresponding micro-beam diffraction patterns (MBDP) with the same incident electron-beam parallel to $[001]_{\text{Al}_3\text{Zr}}$ are shown in (c) and (d).

Furthermore, the crystal structure of Al_3Zr dispersoids in both the recrystallised grain and the subgrain has been examined. From the results shown in **Figs. 4.15** (c) and (d), it appears that the Al_3Zr dispersoids in the subgrains exhibit the L1_2

metastable crystal structure. The dispersoids have the simple cubic/cubic orientation relationship with the Al matrix:

$$[100]Al_3Zr // [100]_{\alpha}, (010)Al_3Zr // (010)_{\alpha}$$

It is also evident that the Al matrix has contributed to the brightness of the MBDP, which makes the {200} planes appear brighter in **Fig. 4.15** (d). When shifting the incident beam directly to the Al_3Zr dispersoids in the recrystallised grain, the $L1_2$ metastable crystal structure spots can still be viewed but the symmetry of the diffraction spots from the Al matrix has been lost. It is likely that the Al_3Zr dispersoids in the recrystallised grain have no particular orientation relationship with the Al matrix. This supports the view that $L1_2$ Al_3Zr dispersoids maintain their original structure/orientation when recrystallisation happens, although their orientation relationship and coherency with the matrix changes.

Fig 4.16 shows a similar TEM observation and MBDPs for the AC condition. A BF image and a DF image of the same region are shown in **Figs. 4.16** (a) and (b), respectively, while the corresponding MBDPs are shown in **Figs. 4.16** (c) and (d). It can be seen that a large amount of quench-induced precipitates are associated with Al_3Zr dispersoids in the recrystallised grain (identified with arrows). However, **Figs. 4.16** (a) and (b) show that there are no such quench-induced precipitates in the subgrain. The MBDP of the $L1_2$ [011] Al_3Zr dispersoids from the subgrain in **Fig. 4.16** (d) reveals a cubic/cubic orientation relationship between the dispersoids and the Al matrix. When shifting the incident beam directly to the Al_3Zr dispersoids in the recrystallised grain, only the diffraction spots from the $L1_2$ metastable crystal structure can be observed. These results indicate that the metastable Al_3Zr dispersoids not only maintain their original structure/orientation when recrystallisation happens, but are also likely to have lost their coherency with the matrix. The resulting significant increase in interfacial energy between the dispersoids and the Al matrix in the recrystallised grain causes the incoherent

L_{12} Al_3Zr in recrystallised grains to act as preferential nucleation sites for quench-induced precipitation during slow cooling. By contrast, the coherent L_{12} Al_3Zr dispersoids in unrecrystallised subgrains do not act as preferential nucleation sites for quench-induced precipitation during slow cooling. The material is therefore expected to become more quench sensitive with an increasing degree of recrystallisation. This is in agreement with the observation in **Figs 4.12-4.13** that the more recrystallised plate surface is more quench sensitive than the less recrystallised plate centre.

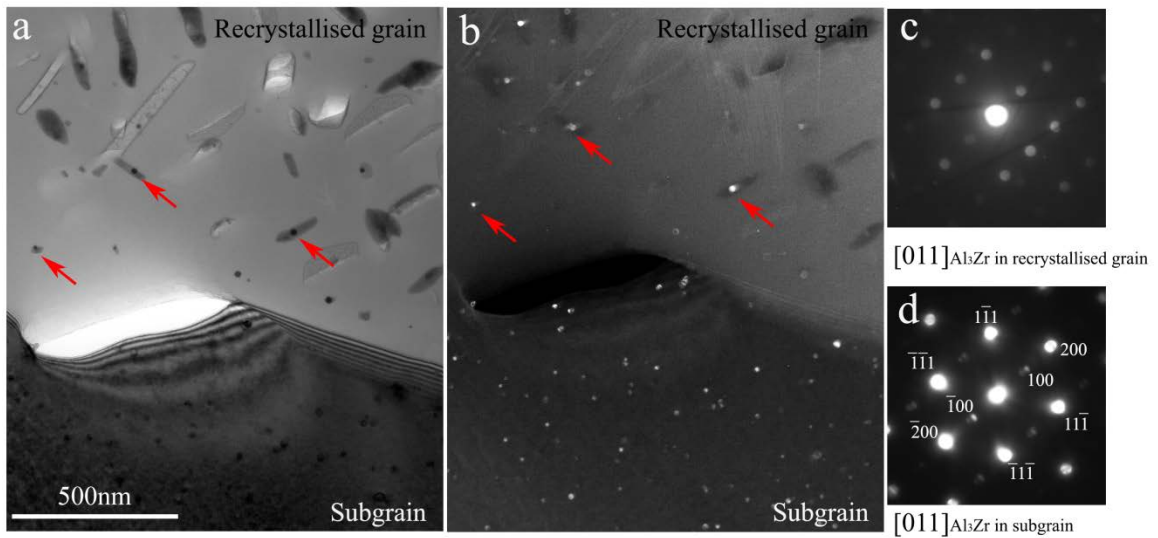


Figure 4.16: (a) BF image and (b) DF image showing the distribution of Al_3Zr dispersoids in the air cooled condition. The DF image uses the diffraction spot from Al_3Zr dispersoids appearing at (100) positions, which are prohibited reflection positions for the face-centred cubic matrix. Corresponding MBDPs in different grains are shown in (c) and (d), with the incident electron-beam parallel to $[011]_{Al_3Zr}$.

4.5. Different quench sensitivity behaviour after further deformation

It was noted that the quench sensitivity will increase with an increasing degree of recrystallisation. The incoherent Al_3Zr dispersoids in recrystallised grains act as nucleation sites for quench induced precipitates. If this theory stands, then one can

expect that the alloy should become more quench sensitive with more recrystallisation.

Therefore an experiment was designed to apply further rolling reductions to 5 mm thick slices cut from the centre layer of an 80 mm 7150 thick plate. Two different reductions were applied: 20% reduction to 4 mm with one pass, and 50% reduction to 2.5 mm with one pass, respectively. The hot rolling temperature was 420 °C at the beginning. The deformed specimens are solutionised with same temperature regimes as before. Small samples were then WQ and AC to room temperature, followed by ageing at 120 °C for up to 24 hours.

Fig. 4.17 (a) shows age hardening curves for the original centre layer, centre layer + 20% reduction and centre layer + 50% reduction samples. The corresponding EC curves have been shown in **Fig 4.17** (b). It is shown that the curves are close to each other in the WQ conditions. It is demonstrated in **Fig. 4.17** (a) that the AC hardness curves are shifting to lower hardness values with increasing deformation. Meanwhile, the WQ hardness curves for the three conditions are almost the same. **Fig 4.17** (b) shows that the WQ EC curves are almost overlapped, but that the AC EC curves become higher with increasing deformation. The results indicate that the amount of quench induced precipitation is increasing with increasing deformation. Therefore the AC EC curves are shifting to higher values and the AC hardness curves are shifting to lower values after ageing.

It is noted in **Fig 4.17** (b) that there is a significant drop in the WQ EC curves within the first half hour of ageing at 120 °C. A similar trend can be found in **Fig 4.12** (b). This is ascribed to the formation of a high number density of fine age hardening precipitates at the beginning of ageing. It is shown in **Fig 4.17** (a) that the hardness values increased dramatically at the beginning of ageing. With increasing ageing time, more solute is consumed from solution and the age hardening precipitates become bigger and more widely spaced, thereby causing

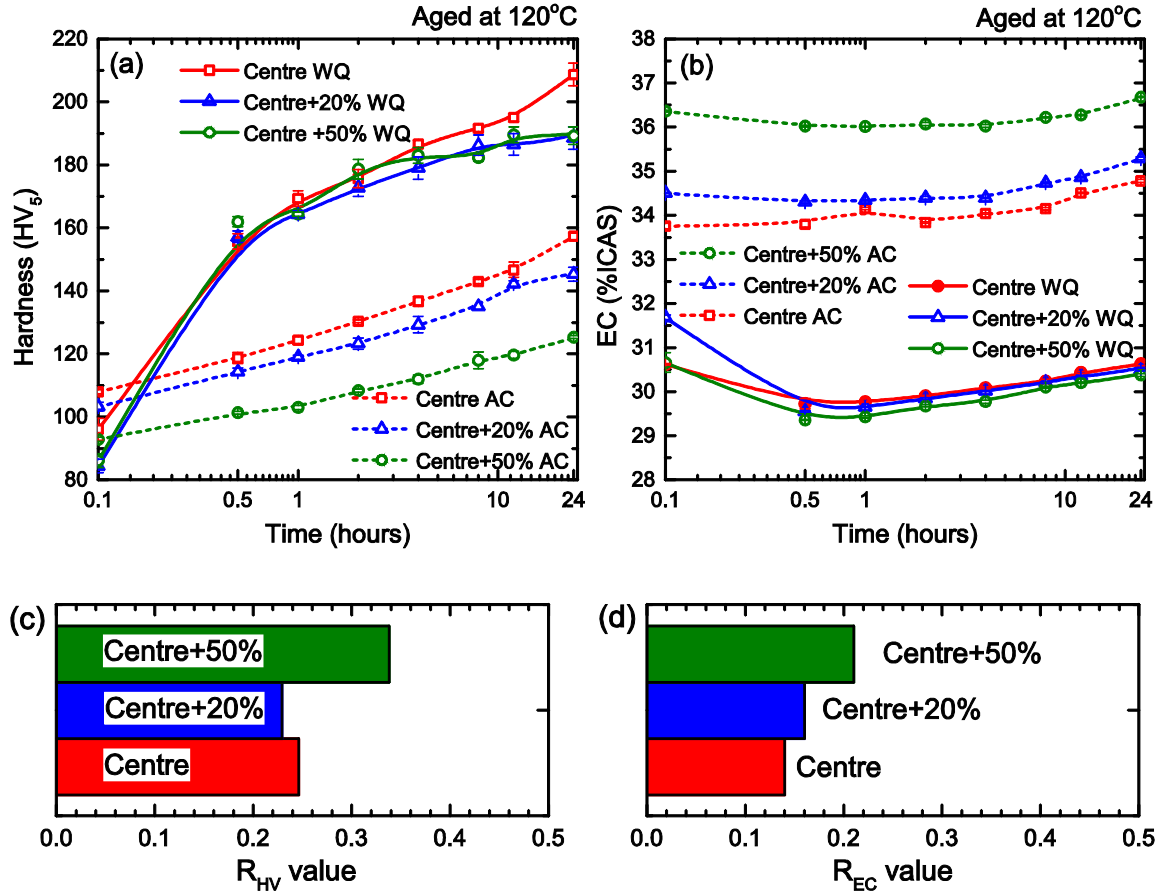


Figure 4.17: Age hardening curves (a) and electric conductivity values (b) of deformed samples after solution treatment followed by WQ or AC. The corresponding R-values based on 24 h at 120 °C are shown in (c) and (d), respectively.

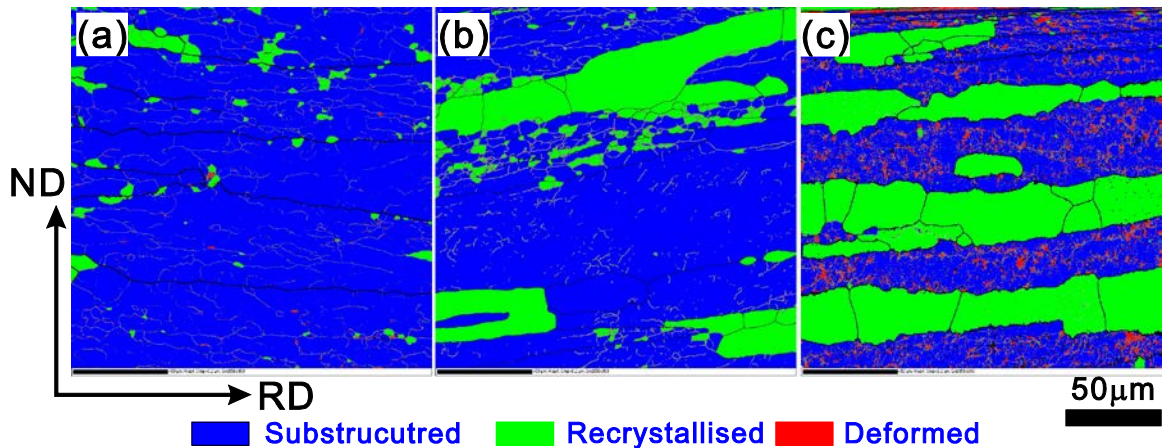


Figure 4.18: WQ microstructures of (a) centre layer, (b) centre layer + 20% reduction and (c) centre layer + 50% reduction after solution treatment, with recrystallised grains here representing misorientation angles of $>15^\circ$

less scattering of electrons. As a result, the EC values slowly increase with increasing ageing time after the first half hour of ageing at 120 °C. The R-values corresponding to hardness and EC are also calculated separately (as shown in **Fig 4.17** (c) and (d)). The results are consistent with the previous discussion that the quench sensitivity increases with increasing deformation.

The corresponding microstructures in **Fig 4.18** demonstrate that the degree of recrystallisation increases with an increasing amount of deformation. As discussed earlier, that the quench-induced precipitates tend to preferentially nucleate on Al_3Zr dispersoids in recrystallised grains, causing a higher degree of recrystallisation to result in a more severe quench sensitivity.

4.6. Discussion

Microstructured characterisation has been carried out to identify the critical nucleation sites for quench-induced precipitation in this chapter. Metastable Al_3Zr dispersoids precipitate during the homogenisation treatment. Due to the very low diffusion rate of Zr in Al matrix, it takes a long time for such dispersoids to be transformed into the equilibrium structure. The result is in consistent with some previous publications [153, 162, 174-177]. However, there are still some publications proposed that the equilibrium Al_3Zr dispersoids with a tetragonal D_{023} structure can be found with 7xxx series alloys [53, 82]. They believed that the quench-induced precipitates can be preferentially nucleate on these equilibrium Al_3Zr dispersoids. The current study shows that it is unlikely for this metastable Al_3Zr dispersoids to transform to equilibrium structure within a relatively short homogenisation treatment or solution treatment. The microstructure characterisations demonstrate that the metastable Al_3Zr dispersoids become incoherent with the Al matrix after recrystallisation happens. Because the metastable Al_3Zr dispersoids maintained their crystal structure and original orientations when recrystallised boundaries passed by. Therefore the significantly

increased interfacial energy between the dispersoids and the Al matrix in the recrystallised grain causes the incoherent Al_3Zr dispersoids to act as preferential nucleation sites for quench-induced precipitation during slow cooling. Therefore the quench sensitivity of an alloy can be manipulated by controlling the degree of recrystallisation. Robson showed that introducing a step homogenisation treatment can change the spatial distribution of Al_3Zr dispersoids and decrease the amount of recrystallisation in alloy AA7050 [151].

However, it should be noted that incoherent Al_3Zr dispersoids are not the only preferential sites for quench-induced precipitates. **Fig 4.19** demonstrates that there are plenty of quench-induced precipitates at grain/subgrain boundaries. The morphologies of these precipitates indicate that they may represent different types of quench-induced particles. They are unlikely to be the same quench-induced precipitates in recrystallised grains (as shown in **Fig 4.9** and **Fig 4.14**). It is reasonable to assume that different quench-induced phases are associated with different preferential nucleation sites. Fink and Willey also pointed out that the materials exhibit different corrosion behaviour in different cooling conditions for alloy 7075 [108]. They found that only the pitting type of attack in fast cooling conditions of above 80 K/s. Within the cooling rate range of 50-80 K/s, some intergranular corrosion can be found along with pitting attack. At the lower cooling rates of 5-50 K/s, the intergranular type of corrosion predominates the corrosion behaviour while some pitting still exists. At very low cooling rates of below 5 K/s, pitting attack predominates again. This is an indication that there are different types of quench induced precipitates on grain boundaries or within grains in different cooling conditions.

Therefore the hypothesis of decreasing the quench sensitivity by minimising the recrystallisation fraction is not entirely correct. Qi *et al* demonstrated that the quench sensitivity increased for alloy 7085 with a very limited fraction of

recrystallisation [178]. They believe that grain/subgrain boundary precipitation is dominating the quench-induced reactions in this case.

Nevertheless, the current research still demonstrates that the materials containing a higher fraction of recrystallisation will lead to a significant increase of quench sensitivity. The calculated R-values can be used to quantify the quench sensitivity behaviour of WQ and AC samples with 1 cm^3 in size. The microstructure characterisation in **Fig 4.12** and **Fig 4.18** also shows that the higher degree of recrystallisation is also accompanied by a smaller subgrains and deformed microstructures. Therefore the grain boundary precipitates is negligible for such circumstance.

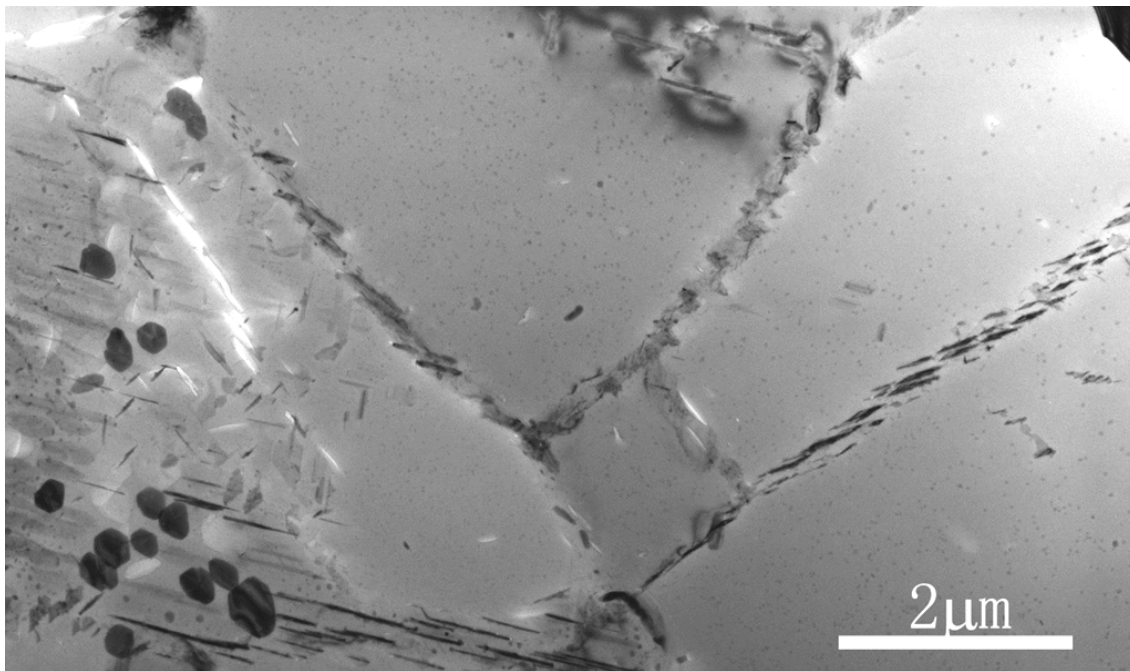


Figure 4.19: TEM image of AC samples after solution treatment, noticing that the quenched-induced precipitates are tend to preferentially nucleate at grain/subgrain boundaries, the different morphology of the particles may refer to different type of quench-induced precipitates.

4.7. Conclusions

The key results are summarised as follows:

1. Primary large Al_3Zr dispersoids can be found along with smaller secondary Al_3Zr dispersoids after homogenisation. Both types of Al_3Zr dispersoids are coherent with the Al matrix and have the metastable L_{12} crystal structure. The experiments show that the Al_3Zr dispersoids retain this metastable crystal structure even after 200 hours of homogenisation at 460 °C.
2. Alloy 7150 is more sensitive to cooling rate after solution treatment compared with after homogenisation. It was found that increased hot-rolling deformation increases the quench sensitivity by increasing the degree of recrystallisation. An R-value has been introduced to quantify the quench sensitivity of an alloy cooled by WQ and AC.
3. Different layers of an aluminium thick plate exhibit different quench sensitivity behaviour. It was demonstrated that there is a significantly higher volume fraction of recrystallised grains in the surface layer of this thick plate, which makes the surface layer more quench sensitive than the centre layer. Quench-induced precipitates were found to nucleate preferentially on Al_3Zr dispersoids in recrystallised grains in AC conditions. MBDP of Al_3Zr dispersoids in different grains and subgrains were recorded to examine their crystal structure and orientation relationship with the matrix. The results show that the Al_3Zr dispersoids have the same L_{12} metastable crystal structure in both recrystallised grains and in unrecrystallised grains. The Al_3Zr dispersoids maintain their original structure and tend to maintain their original orientation when recrystallisation occurs. This would cause the dispersoids to become incoherent after recrystallisation, making them to be preferential nucleation sites for quench-induced precipitation in slow cooling conditions.

Chapter 5. CCP diagram for alloy 7150 thick plate

5.1. Introduction

Chapter 4 has discussed the quench sensitivity of alloy 7150 at different processing stages. It was concluded that the quench sensitivity of alloy 7150 is influenced by the different thermo-mechanical processing history. Therefore the surface layer and the centre layer of an aluminium thick plate exhibit different quench sensitivities. The microstructure analysis demonstrates that Al_3Zr dispersoids in recrystallised grains act as preferential nucleation sites for quench induced precipitates. As a result, the quench sensitivity increases with increasing degree of recrystallisation.

It was also noted that an R-value could be used to evaluate the quench sensitivity behaviour. This method can be used for WQ and AC samples of a given sample size. It was noted that when cooling a thick plate from the solution temperature, the cooling profile changes gradually from the surface to the centre layer. The cooling rate range can become wider if a plate becoming thicker. It is thus necessary to expand the current study to a broader range of cooling rates. There are several methods that have been demonstrated in Chapter 2 that can be used for multiple cooling studies. The current chapter is trying to explore a feasible

quenching method that can be used for quench sensitivity studies. As a result, the Jominy end quench method has been introduced to simulate the real cooling process of a thick plate. Later on, a DSC method has been employed to cooling samples continuously within different DSC devices with a wide range of cooling rates. The purpose of this was to construct a continuous cooling precipitation (CCP) diagram for alloy 7150 based on a combination of DSC measurements, microstructure analysis and hardness testing. Furthermore, interrupted quenching experiments have been carried out to identify different types of quench-induced precipitates during continuous cooling.

5.2. Jominy end quench

The Jominy end quench method was originally developed for the hardenability testing of steel [146]. The Jominy end quench method offers a set of specimens with different cooling rates by a single quench. In order to simulate the real cooling process of an aluminium thick plate, the Jominy end quench rig was designed to cool a Jominy bar from one end. In this case, the Jominy quench bar is a 110 mm long cylinder with a 25 mm diameter, cut from a thick plate that was supplied by Chalco. The rig contains a vertical tube furnace, a cooling system and a data logger system that has been shown in **Fig 3.7**.

The logged cooling curves are shown in **Fig. 5.1**. It is demonstrated that the cooling rate varies along the length of the Jominy bar from very rapid at the fast quench end to very slow at the other end. It takes about 600 sec for the whole Jominy bar to be cooled down to room temperature. It is shown that the Jominy bar is cooled non-linearly, with the temperature dropping quickly at first and then leveling off dramatically for all the locations. However, there is a relatively linear cooling rate range from 450 °C to 200 °C. The temperature at different locations is slowly tapering off below 200 °C. The dashed black lines indicate the referenced linear cooling rates (100 K/s, 10 K/s and 3 K/s) in this figure. It is shown that the

average cooling rate at a 2 mm distance from the quenched end is approaching 100 K/s. The average cooling rate at 50 mm distances from the fast quenching end is about 10 K/s. It is estimated that the cooling rate at the other end of the Jominy bar is about ~ 3 K/s. Therefore the average cooling rate range for the entire Jominy bar is estimated to be between about 100 K/s and 3 K/s. It should be noted that this is still a limited range for a quench sensitivity study. For typical aluminium alloy 7150, produced as 80 mm thick plates, the cooling rate at the mid-plane is < 10 K/s between 400 °C and 290 °C (as shown in **Fig 2.4**). However, for a real industrial application, the cooling conditions for the centre layer may not be comparable to the Jominy quench conditions, as the centre layer of a thick plate experiences effectively one-dimensional heat conduction during real industrial quenching process, i.e with temperature depending on the plate thickness [31, 179]. This is relying on the assumption that the centre layer is insulated, with no heat transfer from other directions. However, for a small Jominy bar where one end is cooled by spray water while the other surfaces are experiencing air cooling at the same time, the cooling conditions may no longer be approximated by one-dimensional conduction. Therefore the Jominy quench conditions may not be directly comparable to the real situation.

The corresponding hardness profile was measured at the centre of the Jominy bar at different locations from the quenched end to another end after ageing at 120 °C for 24 hours. The results have been shown in **Fig 5.2**. It is shown that the hardness value decreases with increasing distance from the quenched end, suggesting that the alloy 7150 is quench sensitive. The hardness curve shows that its value drops from about 200 HV at the quenched end to about 175 HV at about 100 mm away from the quenched end. It is expected that the hardness values would drop further with even lower cooling rates. However, the Jominy end quench cannot offer any slower cooling rate conditions for such circumstances. The slower cooling samples are very useful for quench sensitivity studies, as the centre layer experiences

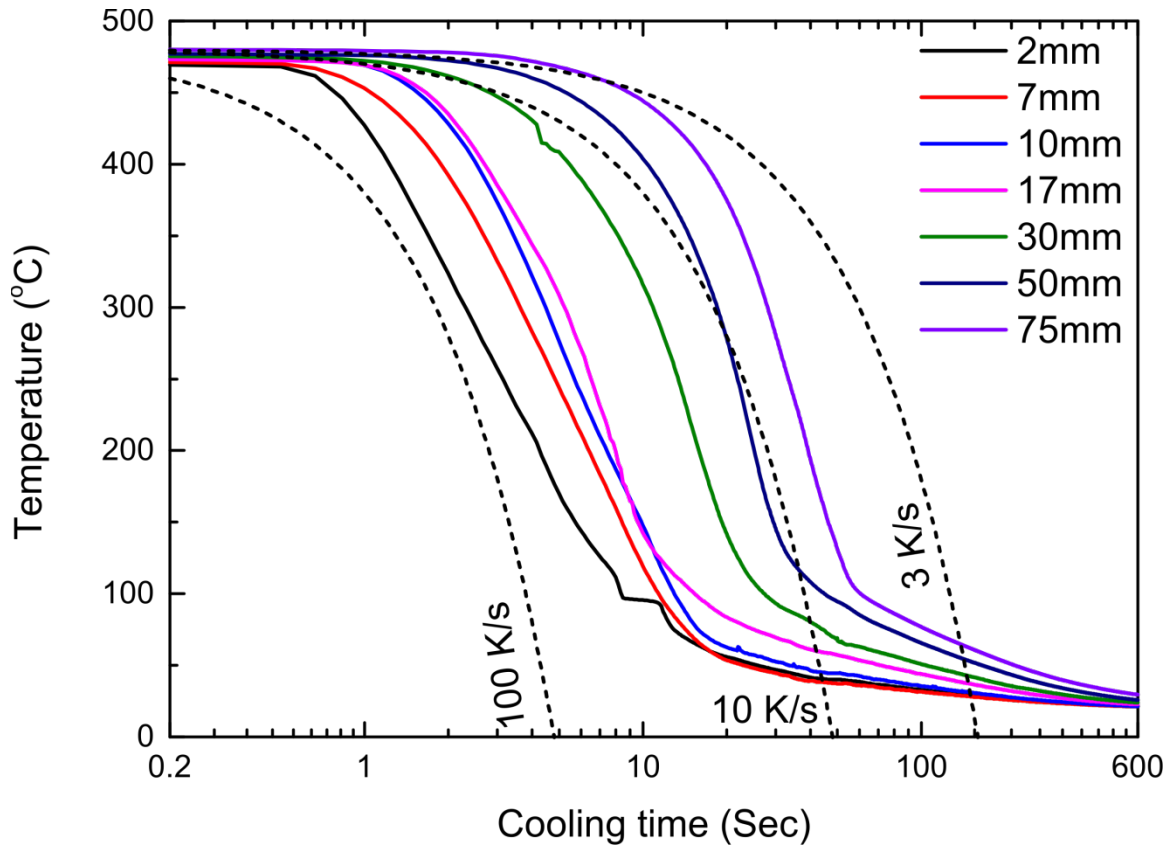


Figure 5.1: Measured cooling curves at different distances from the Jominy bar quench end (solid curves covering 2-75 mm) and three superimposed linear cooling curves (dashed curves covering 3-100 K/s).

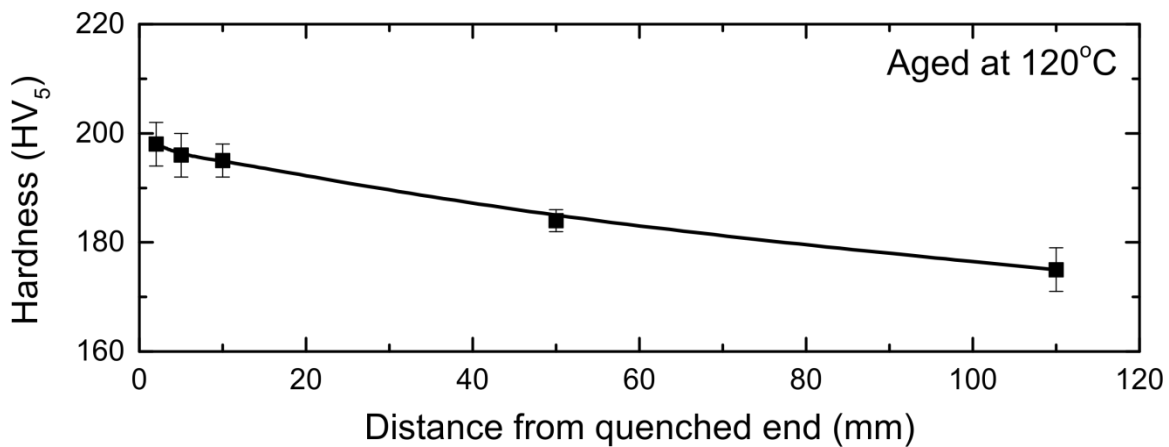


Figure 5.2: Hardness profile along the Jominy bar after ageing at 120 °C for 24 hours.

slower cooling rates as the plate thickness is increased. It is therefore of interest from both scientific and industrial view points to study the quench sensitivity over a wider range of cooling rates in a controlled manner.

5.3. Constructing CCP diagrams for alloy 7150 plate

5.3.1. DSC curves and CCP diagrams

Differential Scanning Calorimetry (DSC) is a thermoanalytical technique that can measure the exothermal heat flow of samples under continuous cooling program [142]. This method has proven to be a sensitive and reproducible technique for the study of phase transformations [180]. Most importantly, the DSC technique provides a method that can cool samples continuously over a wide range of cooling rates.

Milkereit *et al* used this method to record continuous cooling precipitation (CCP) diagrams for wrought aluminium alloys 6060, 6063, 6005A and two batches of 6082 [119, 143]. It was demonstrated that DSC curves at different cooling rates ranging from very slow cooling at ~ 0.005 K/s to 5 K/s are achievable. In order to extend the range of controlled cooling rates, a quenching dilatometer was utilised to achieve cooling rates faster than 5 K/s. However, no exothermal heat flows can be detected with the dilatometer.

Fig. 5.3 shows the bending-corrected excess specific heat curves for samples cut from the centre layer of an alloy 7150 thick plate cooled at various linear cooling rates from 0.005 K/s to 3 K/s. The original DSC-curves were obtained during cooling from solution annealing in three different types of DSC devices corresponding to different cooling rates ranges (Setaram 121 DSC: 0.005 to 0.1 K/s; Mettler-Toledo 823 DSC: 0.2 to 0.5 K/s; Perkin-Elmer Pyris 1 DSC: 0.5 to 3 K/s). In **Fig 5.3**, the curves are shifted and arranged in order of increasing cooling rate, starting with the slowest rate on top. The horizontal dashed lines represent the zero level. Deviations exceeding this level indicate exothermal reactions.

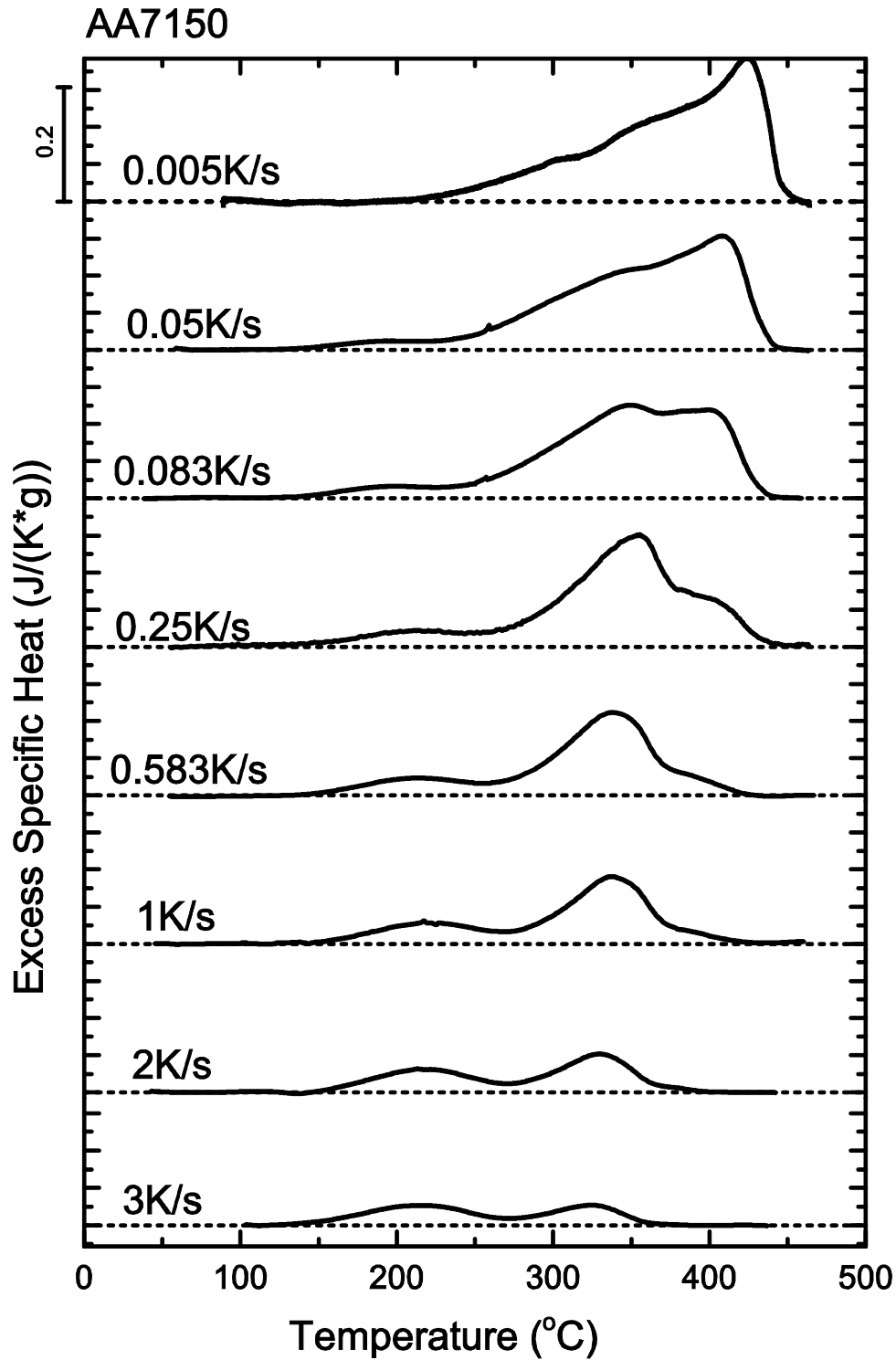


Figure 5.3: Detected DSC curves after solution annealing for alloy AA7150 with cooling rates varying from about 0.005 to 3 K/s.

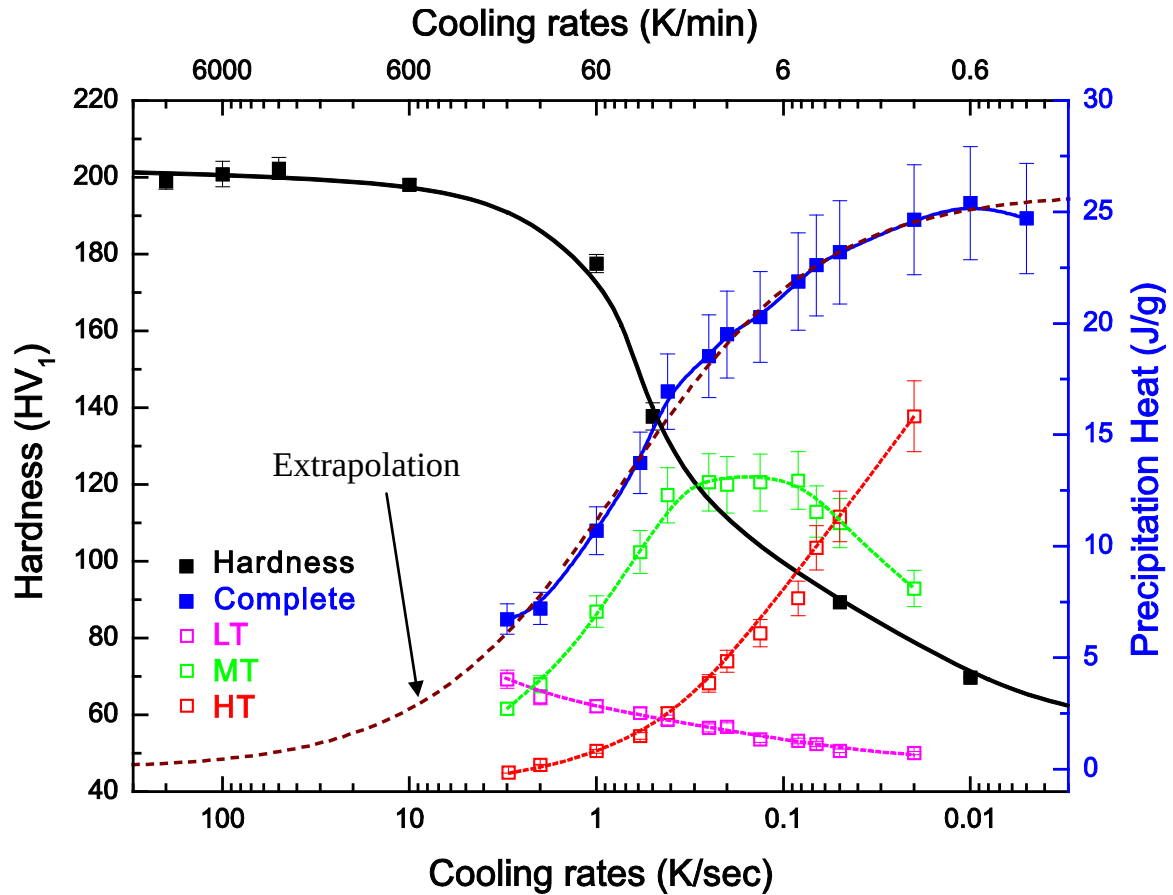


Figure 5.4: Specific precipitation heats for high-temperature (HT), medium-temperature (MT), low-temperature (LT) and the sum of all (complete) reactions after cooling to room temperature from solution annealing at 480 °C, for samples from the centre layer of alloy 7150, as a function of cooling rate. Vickers hardness values after subsequent artificial ageing for 24 h at 120 °C are also shown.

It can be seen that the investigated alloy shows a precipitation behaviour with at least three precipitation reactions. The reactions can be subdivided into high, medium and low temperature reactions according to their temperature regimes. These three reactions vary as a function of cooling rate.

An important piece of information is the intensity of the precipitation reactions. The intensities of the three reactions can be calculated by integrating the precipitation enthalpy (ΔH) for the exothermic reactions at constant pressure over the cooling process. The system's change in enthalpy equals the energy released in

the reaction, also known as the precipitation heat. This intensity can be observed from the peak areas of the DSC curves in **Fig 5.3**, and its values are displayed in **Fig 5.4** for the studied alloy, where both the specific precipitation heats during cooling to room temperature and the hardness after ageing are presented as functions of the cooling rate. The cooling rate axis uses a decreasing logarithmic scale from left to right for ease of comparison with the time scale of the CCP diagrams presented later in this chapter. For the precipitation heats, the error bars show an estimated error of 10 %, resulting from the evaluation procedure. For the hardness values, standard deviations calculated from five indentations are shown.

The complete ΔH_C curve and separate three reactions ($\Delta H_{HT} + \Delta H_{MT} + \Delta H_{LT}$) curves have been shown in **Fig. 5.4**. It is noted that the high temperature reaction is increasingly suppressed with increasing cooling rate. The intensity of the medium temperature reaction first increases with increasing cooling rate before decreasing again. It is known that the suppression of a higher temperature reaction would normally enable the intensity of a lower temperature reaction to be increased due to a higher amount of alloying elements remaining in supersaturated solid solution. Hence, the low temperature reaction intensity increases with increasing cooling rate due to a combination of both the thermodynamic and kinetic factors associated with the nucleation and growth of a higher number density of smaller precipitates. It is believed that with increasing cooling rate, the intensity of the low temperature reaction will be totally suppressed at very fast cooling rates. However the decreasing trend is beyond the detection limit of the current DSC method.

It is shown that the highest temperature reaction starts at about 450 °C. The total peak-area decreases with increasing cooling rate, starting from about 25 J/g at a cooling rate of 0.005 K/s. At the cooling rate of 0.083 K/s, the second peak can be clearly distinguished at an intermediate temperature of about 350 °C. It is believed that the medium temperature peak overlaps with the high temperature peak so that it cannot be identified easily at slower cooling rates. With increasing cooling rate,

the high temperature peak area decreases. At a cooling rate of 3 K/s the high temperature peak has virtually disappeared. It is believed that the critical cooling rate for the high temperature reaction revealed by DSC is about 3 K/s.

The medium temperature reaction peak area increases first, starting from about 8 J/g at a cooling rate of 0.02 K/s. The peak area values of the medium temperature reaction show a plateau value of about 12.5 J/g at cooling rates between 0.083 and 0.583 K/s. The peak area values of this medium temperature reaction then decrease dramatically to about 3 J/g at a cooling rate of 3 K/s, which is the fastest cooling rate that could be achieved in these DSC experiments. It is interesting to discover that there is another low temperature reaction showing up at the faster cooling rates at a lower temperature range of about 220 °C. It can be seen that the low temperature peak areas are relatively small. This indicates that the transformation amount of the low temperature reaction is quite small when compared with the high temperature and medium temperature reactions. However, this low temperature peak area increases slowly with increasing cooling rate in the cooling rate range of about 0.1 K/s to 3 K/s, while the medium temperature peak area decreases in this cooling rate range. The peak areas of the medium temperature reaction and low temperature reaction are similar in size at a cooling rate of around 2-3 K/s.

In general, the total amount transformed in these reactions tends to decrease with increasing cooling rate. This is consistent with earlier findings in some other 7xxx series alloys and 6xxx series alloys [116, 117, 119]. The cooling rate at which ΔH_C reaches 0 is defined as the critical cooling rate (CCR). It is obvious that the CCR point is not reached in this case, but by means of additional data analysis, an extrapolated CCR value for alloy 7150 can be determined to be about 300 K/s.

The CCR value can also be estimated using hardness testing. **Fig 5.4** shows demonstrates that the hardness curve for alloy 7150 after artificial ageing at

120 °C for 24 hours. Here it is assumed that all the remaining solute after the cooling process contributes to hardening. Thus, the hardness curves increase with increasing cooling rate as rapid cooling will preserve more solute in solution for the subsequent ageing process compared to slow cooling, thereby giving the alloy the potential to reach its maximum strength after ageing. Moreover, there is no further increase in hardness if samples are cooled faster than the critical cooling rate as no more solute is lost to non-hardening precipitates during faster cooling. It is noted that a hardness plateau can be found in **Fig 5.4**, where the CCR appears to be ~60 K/s. It is evident that the CCR for alloy 7150 from hardness testing occurs at much lower quenching rates than the CCR that was obtained by DSC with extrapolation. This could be due to the fact that the hardness value is not sufficiently sensitive to reflect small changes in volume fraction of precipitates.

Nevertheless, both methods result in a CCR range for alloy 7150 of 60-300 K/s, which is a relatively small range on a logarithmic scale. Both methods offer a feasible way to approximate the CCR value for the studied alloy.

A continuous cooling precipitation diagram for alloy 7150 is developed by connecting the onset/finishing temperatures for each quench-induced precipitation in a time-temperature coordinate matrix (as shown in **Fig 5.5**). It is shown that there are three quench-induced precipitation regions corresponding to HT reaction region, MT reaction region and LT reaction region. It is demonstrated that the critical cooling rate for HT reaction is 3 K/s as no precipitation heat from HT can be detected at this cooling rate. The critical cooling rates for MT and LT are beyond the detection limit of the DSC technique. It requires detailed microstructure analysis to determine the critical cooling rates for MT and LT reactions.

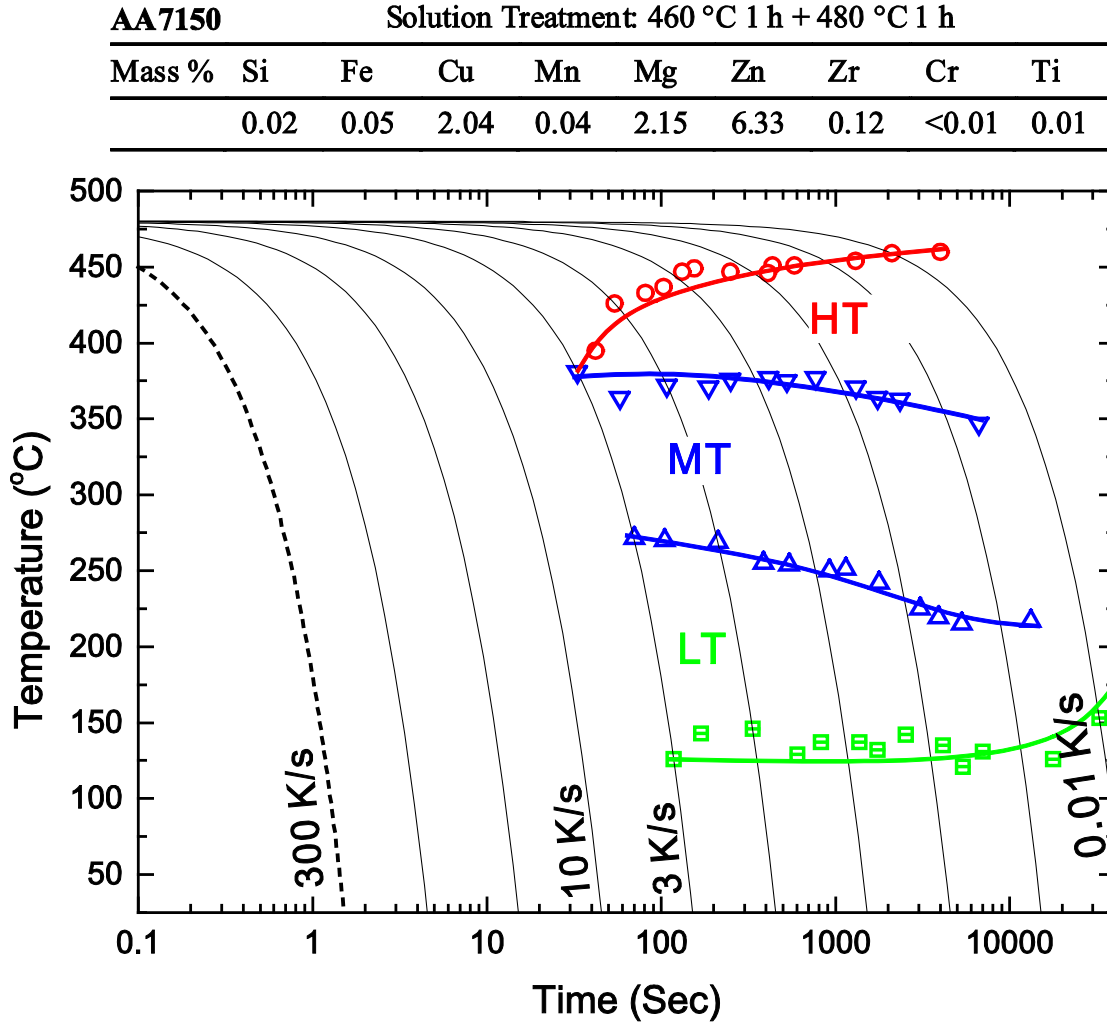


Figure 5.5: Developed continuous cooling precipitation (CCP) diagram for studied alloy 7150 after solution treatment, showing linear cooling rates ranging from 300 K/s to 0.01 K/s.

5.3.2. SEM characterisation

Fig 5.6 shows typical backscattered SEM images of alloy 7150 at different cooling rates ranging from 0.005 K/s to 100 K/s. As mentioned earlier, any samples with cooling rates beyond 3 K/s were cooled using a quenching dilatometer. The backscattered images give information about electron beam scattering interactions with different atomic species. According to phase contrast theory, phases that contain more higher atomic number elements will appear brighter in backscattered

SEM images. The left column images (at a low magnification) clearly show that the total amount of precipitation increases with decreasing cooling rate, while the right column shows these phases in more detail at a higher magnification.

It is evident from **Fig 5.6** (a) and (c) that at extremely slow cooling rates, quench-induced phases exhibit both a larger volume fraction and a significantly larger size than in any other conditions. This, together with the fact that it is a high temperature reaction, suggests that equilibrium precipitates are formed in these slow cooling rate conditions. Based on the difference in particle size/morphology and contrast, the corresponding higher magnification images in **Fig 5.6** (b) and (d) reveal that there are at least two different phases present (identified with arrows). The EDX analysis demonstrates that the brighter precipitates are equilibrium MgZn_2 (η -phase) while the grey precipitates are more likely to be Al_2CuMg (S-phase) (as shown in **Fig 5.7**). These results are consistent with previous phase identifications on the same alloy [171]. It is evident that the S-phase is difficult to be distinguished by SEM at cooling rates of more than 0.05 K/s. This corresponds with the fact that the high temperature reaction in the DSC curves can only be found in slow cooling rate conditions. Therefore it is reasonable to assume that the high temperature reaction for alloy 7150 corresponds to the Al_2CuMg (S-phase).

In **Fig 5.6** (e) and (f) at a cooling rate of 1 K/s, the main phase appears to be MgZn_2 (η -phase). It is shown that these particles precipitated out both within grains and on grain boundaries. The corresponding DSC curve in **Fig 5.3** shows that there are at least two peaks at the cooling rate of 1 K/s, but that the low temperature reaction peak is still relatively small at this stage. It is not expected that this low temperature phase should be observable by SEM on this scale due to the small size of such precipitates. Therefore the medium temperature reaction should correspond to the MgZn_2 (η -phase). At cooling rates of 10 K/s and faster, only grain- and sub-grain boundary precipitates can be observed by SEM. This is mainly due to grain- and sub-grain boundaries acting as preferential heterogeneous

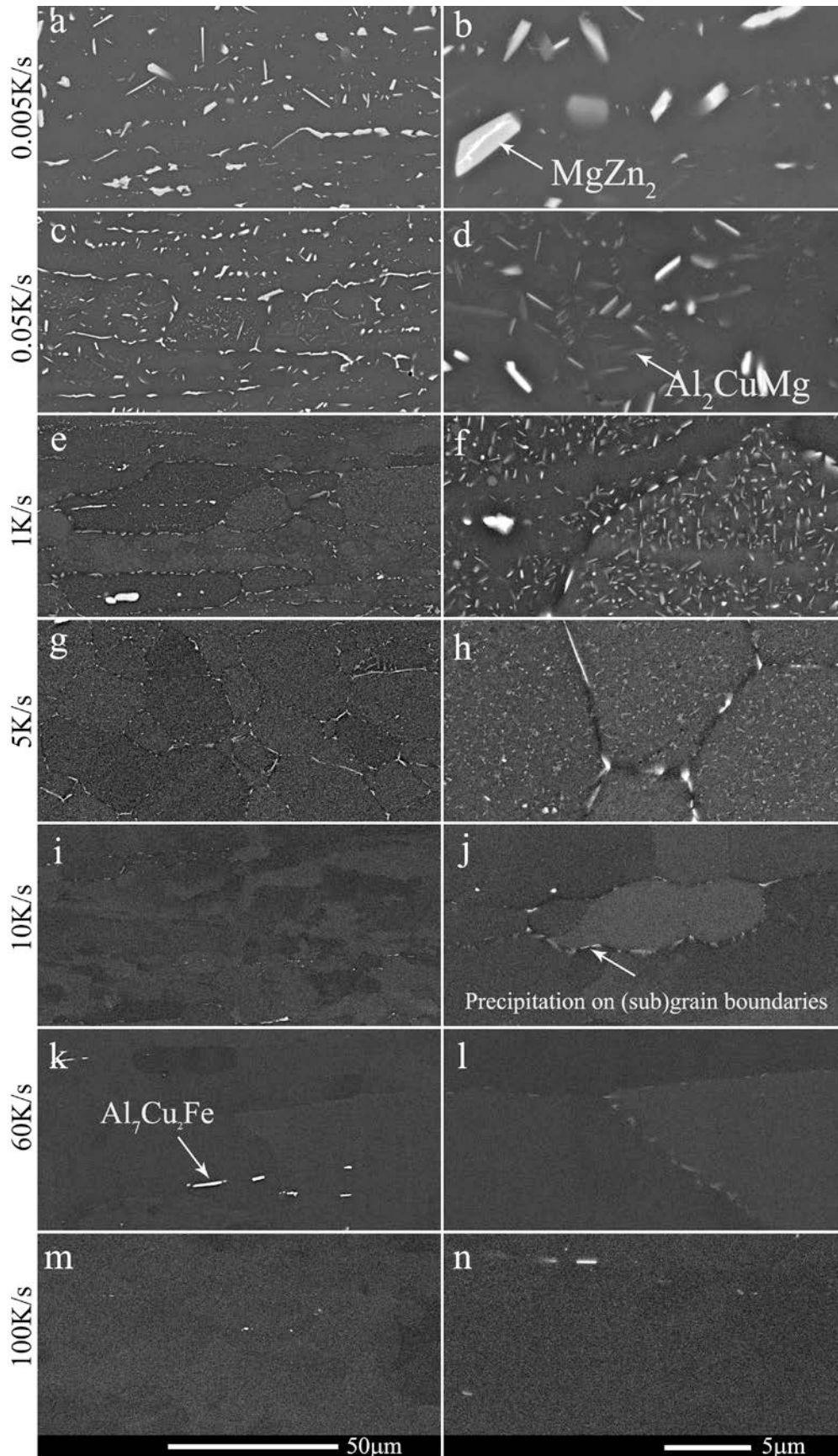


Figure 5.6: Backscattered SEM images of alloy AA7150 samples cooled at different rates. The two columns represent two different magnifications, as indicated by the scale bars at the bottom.

nucleation sites for quench-induced phases. However, at the cooling rate of 100 K/s, almost no precipitation can be found by SEM. This result is in agreement with the extrapolated critical cooling rate range of about 60-300 K/s for alloy 7150 in **Fig 5.4**. It is noted that there are also some coarse intermetallic phases present (highlighted in **Fig 5.6 (k)**). They are identified as $\text{Al}_7\text{Cu}_2\text{Fe}$ particles that do not dissolve during solution treatment, although a small amount of rounded S-phase particles that did not dissolve completely during the solution treatment has also been observed. The precipitation of those particles will not depend on cooling rate.

According to the detected DSC curves, there are at least three different reactions that occur during linear cooling in a certain cooling rate range. The low temperature reaction was detected only at cooling rates of ≥ 0.05 K/s. Besides, the high temperature reaction seems to be suppressed completely at about >3 K/s. However, there is no clear evidence for the presence of low temperature precipitates at this scale of SEM. This is probably due to the small size of the low temperature precipitates at fast cooling rates. The most likely hypothesis is that the low temperature peak corresponds to an unexpected phase, although the possibility of other heterogeneous nucleation phenomena is not ruled out at this stage.

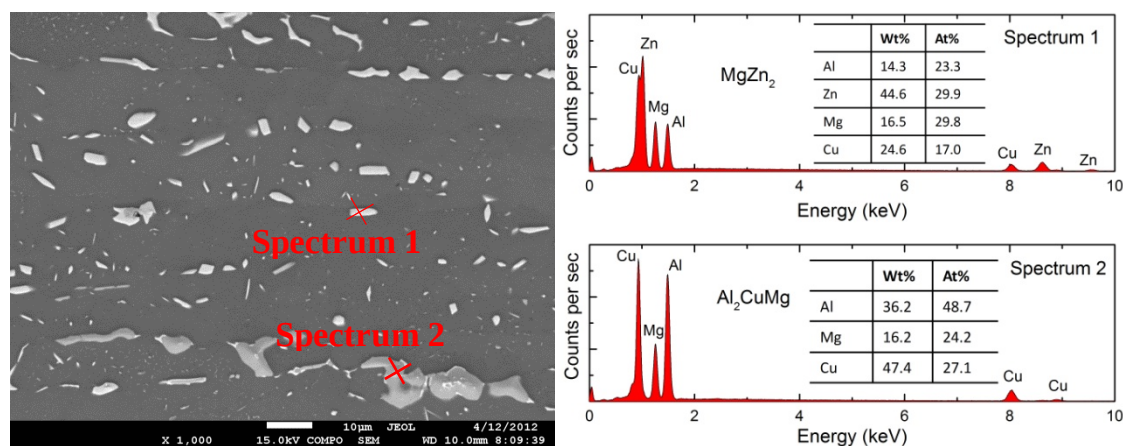


Figure 5.7: EDX analyses of the large particles with two different image contrasts, suggesting that they are equilibrium M-phase and S-phase particles. This sample was cooled at 0.005 K/s.

5.3.3. TEM characterisations

The TEM characterisation was carried out on step quenched specimens with the purpose of understanding the microstructures evolution during non-isothermal cooling conditions. The step quenching was designed to cool the samples to a given temperature at a constant cooling rate, followed by rapid quenching without any isothermal holding. The step quenching experiments were carried out using a quenching dilatometer (Bähr DIL 805A/D). The step quenching conditions for the studied alloys were chosen from the detected DSC curves to correspond to cooling rates where the reaction peaks reach their maximum values so that adequate amounts of quench-induced precipitates would be detectable by TEM. The selected cooling rates and corresponding quench temperatures for alloy 7150 are shown in **Fig 5.8**.

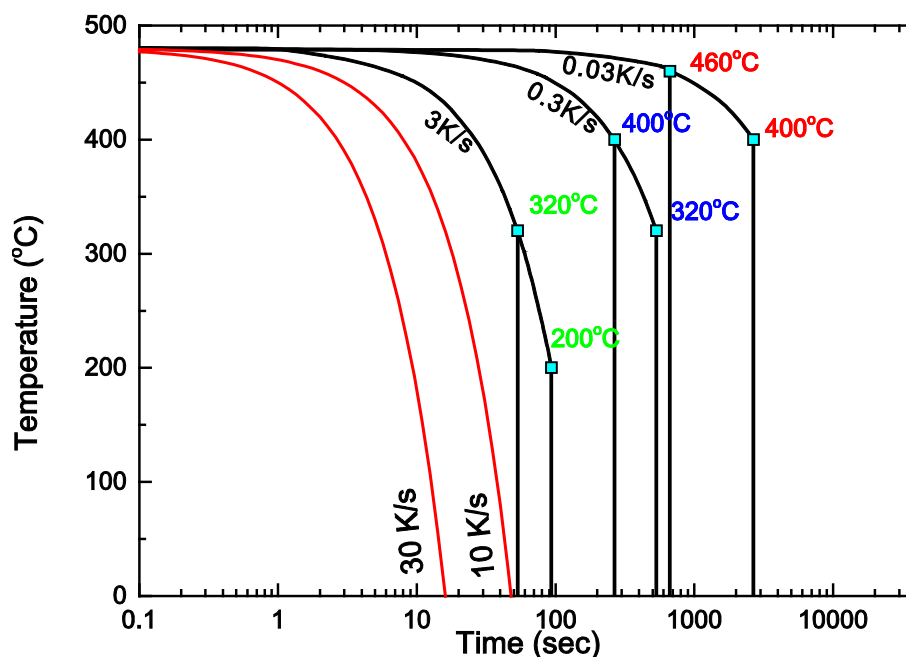


Figure 5.8: Diagram showing step quenching parameters for alloy 7150, as well as two continuous cooling conditions (10 K/s and 30 K/s) to resolve the low temperature reaction.

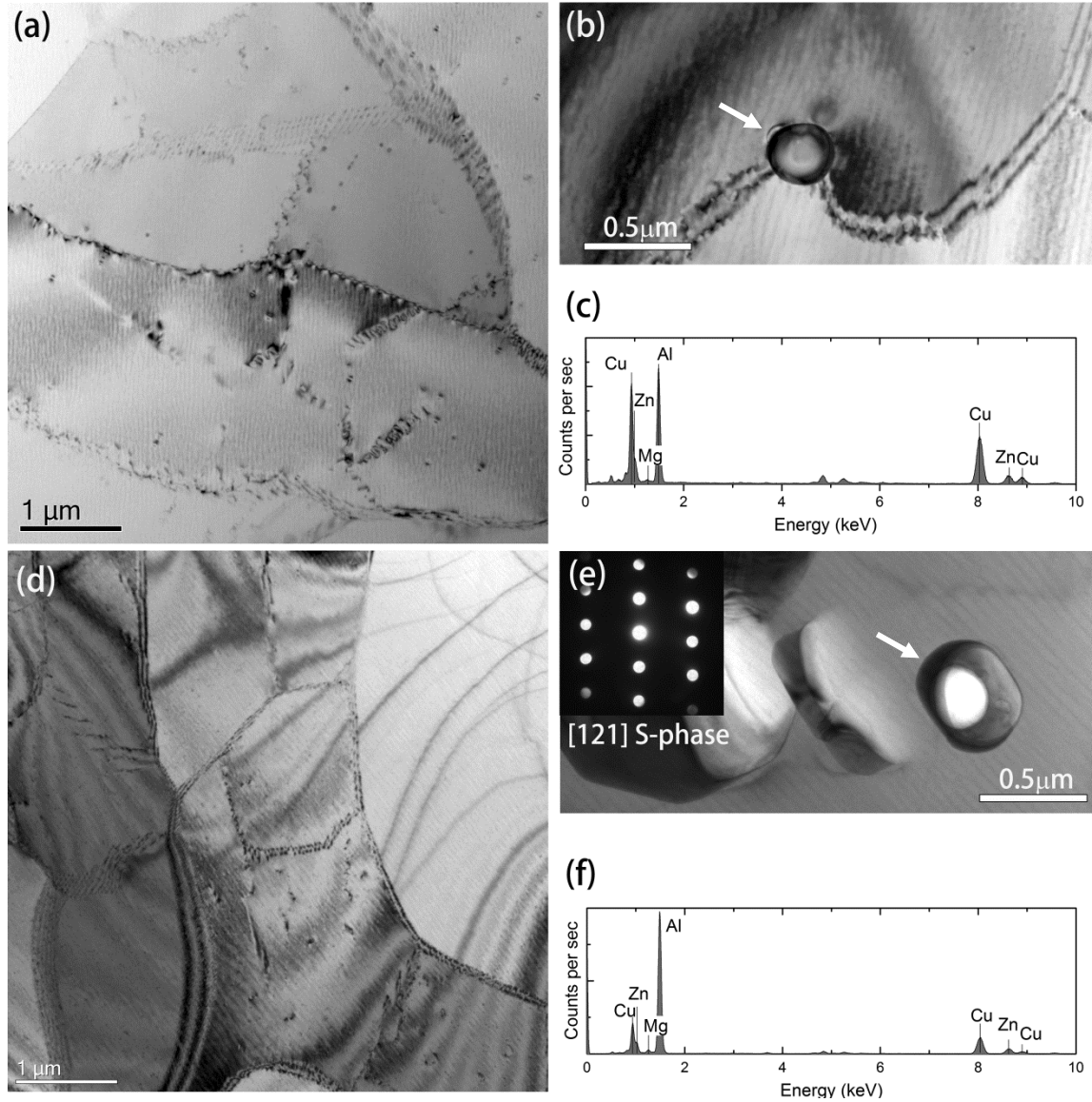


Figure 5.9: TEM images of samples cooled at 0.03 K/s to (a) and (b) 460 °C, (d) and (e) 400 °C followed by rapid quenching.

Two extra continuously cooled samples (10 K/s and 30 K/s) were prepared for the purpose of resolving the low temperature reaction since the precipitation heat still exhibits an incremental trend at the fastest achievable cooling rate of the current DSC technique. It is reasonable to assume that the amount of low temperature reaction reaches its maximum value at cooling rates between 3 K/s and a few hundred K/s. The HT reaction and MT reaction phases can be resolved by SEM

technique due to the relatively large sizes of the precipitates in slow cooling rate conditions. Therefore, more attention will be given to resolving the low temperature reaction in this section.

Fig 5.9 shows the TEM images of samples step quenched at cooling rate of 0.03 K/s to (a) and (b) 400 °C, (d) and (e) 320 °C followed by rapid quenching. It is shown in **Fig 5.9** (a) that almost no quench-induced precipitates can be found within grains/subgrains. There are many Al_3Zr dispersoids can be revealed within the grains/subgrains. There is a small amount of round particles can be observed on grains boundaries. The higher magnification image in **Fig 5.9** (b) demonstrates the morphology of one of the round particles, the EDX analysis shows it is an S-phase particle. The microstructures of step quenched sample of 0.03 K/s to 400 °C have been demonstrated in **Fig 5.9** (d). It is also shown that there are no quench-induced precipitates within grains/sugrains. More S-phase particles with relatively larger sizes have been observed. The diffraction pattern in **Fig 5.9** (e) demonstrates that they are S-phase particles. Therefore the S-phase can correspond to the high temperature reaction. The result here is in agreement with previous SEM analysis and DSC detections.

Fig 5.10 shows the microstructures of samples step quenched at cooling rate of 0.3 K/s to (a) and (b) 400 °C, (c), (d) and (e) 320 °C followed by rapid quenching. It is shown that there are still no big quench-induced precipitates within grains/subgrains. There are some round holes similar in size of S-phase particles can be observed on grain boundaries (as shown in **Fig 5.10** (a)). It appears that the round S-phase particles are being polished out during the electropolishing process for preparing TEM specimens. **Fig 5.10** (b) shows that there are no precipitates co-exist with Al_3Zr dispersoids within grains, suggesting that the S-phase particles are preferentially nucleate on grain/subgrain boundaries at cooling rate of <0.3 K/s.

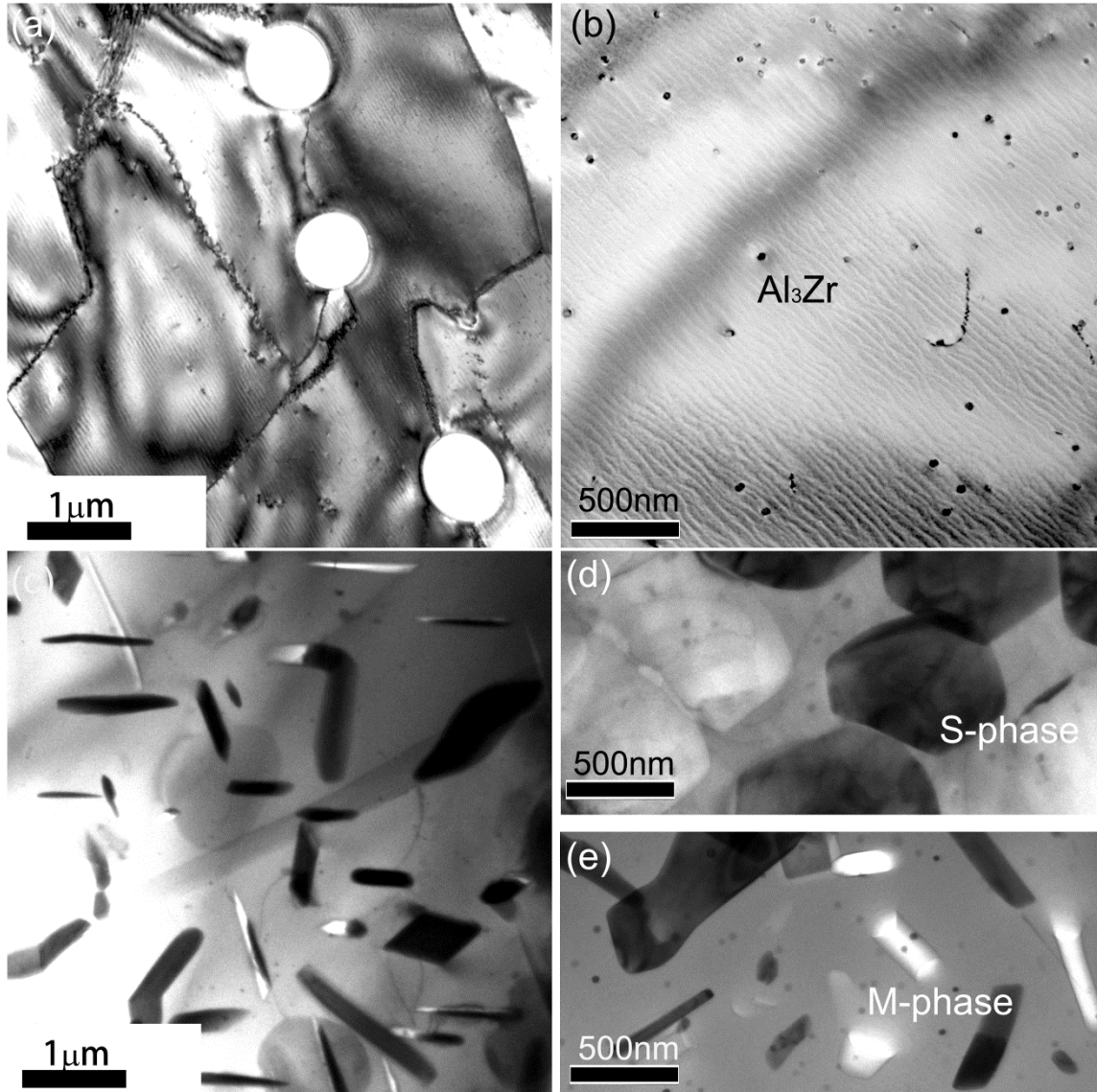


Figure 5.10: TEM images of samples cooled at 0.3 K/s to (a) and (b) 400 °C, (c), (d) and (e) 320 °C followed by rapid quenching

When continuously cooled down to 320 °C at the same cooling rate followed by rapid quenching, there are large amount of rod-shaped particles precipitated (as shown in **Fig 5.10** (c)). There are also some S-phase particles on grain boundaries can be found (as shown in **Fig 5.10** (d)). The higher magnification image in **Fig 5.10** (e) shows the detailed microstructures of these rod shaped particles. They always co-exist with Al₃Zr dispersoids in recrystallised grains.

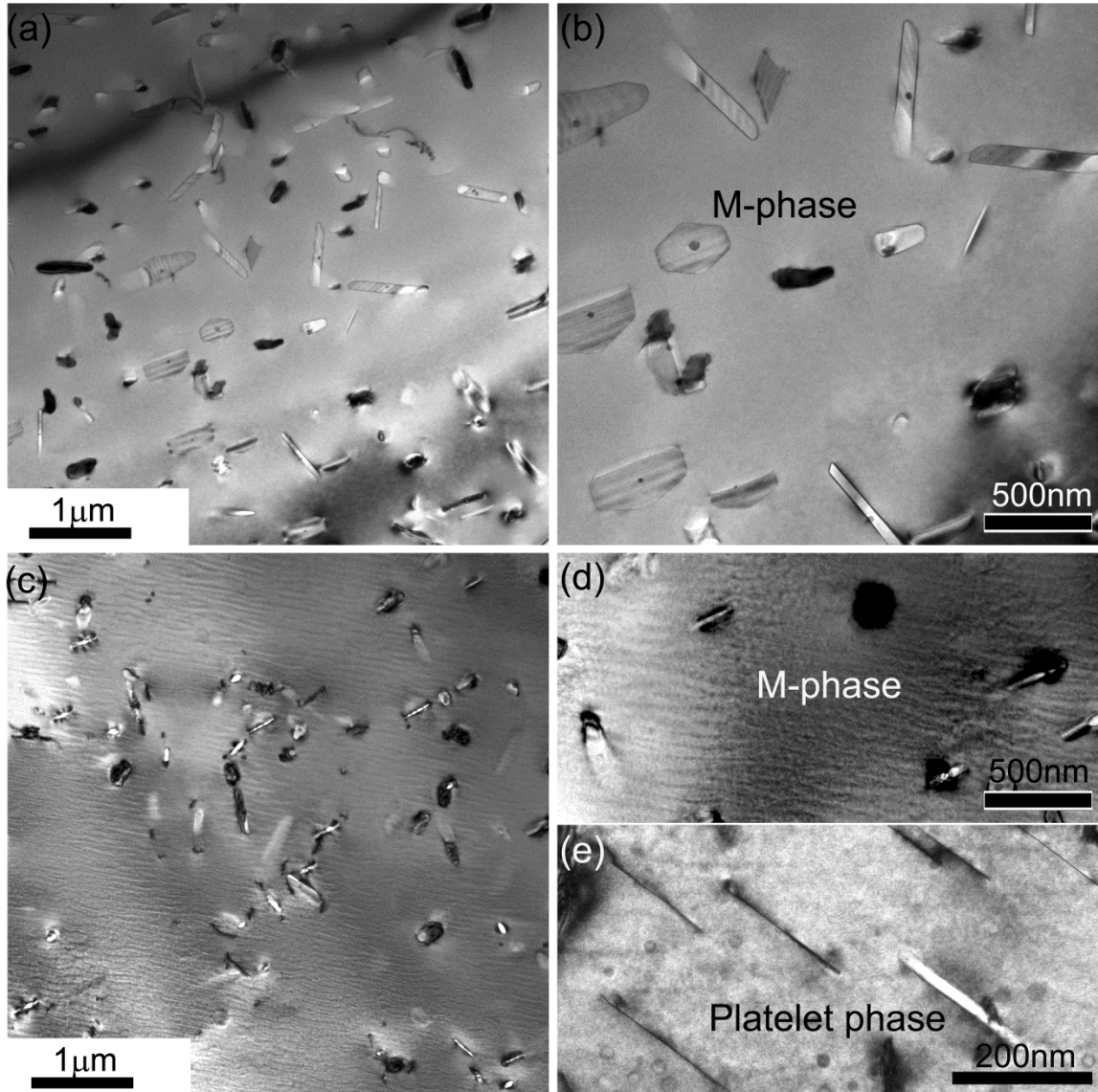


Figure 5.11: TEM images of sample step quenched at cooling rate of 3 K/s to (a), (b) and (c) 320 °C, (d), (e) and (f) 200 °C followed by rapid quenching.

The rod-shaped particles can be confirmed as M-phase precipitates. The results here demonstrate that only S-phase particles can be observed when rapid cooled sample from 400 °C, but the M-phase shows up when sample being cooled rapidly from 320 °C. Therefore the medium temperature reaction corresponds to the M-phase. The M-phase precipitates are preferentially nucleate on Al_3Zr dispersoid in

recrystallised grains. This is also in agreement with previous observations for AC samples (see chapter 4).

Fig 5.11 shows the TEM images of samples step quenched at cooling rate of 0.3 K/s to (a) and (b) 400 °C, (c), (d) and (e) 320 °C followed by rapid quenching. It is shown that there are large amount of M-phase precipitates within recrystallised grain (as shown in **Fig 5.11** (a)). They exhibit a smaller size distribution when compared with those M-phase in **Fig 5.10** (c). The higher magnification image in **Fig 5.11** (b) also demonstrates that the M-phase particles are co-existing with Al_3Zr dispersoids. When the material was cooled down to 200 °C at the same cooling rate (3 K/s), M-phase particles can be found with a relatively smaller size distribution (as shown in **Fig 5.11** (c) and (d)). There are a small amount of platelet precipitates with high aspect ratio in subgrains can be observed in this cooling condition (as shown in **Fig 5.11** (d)).

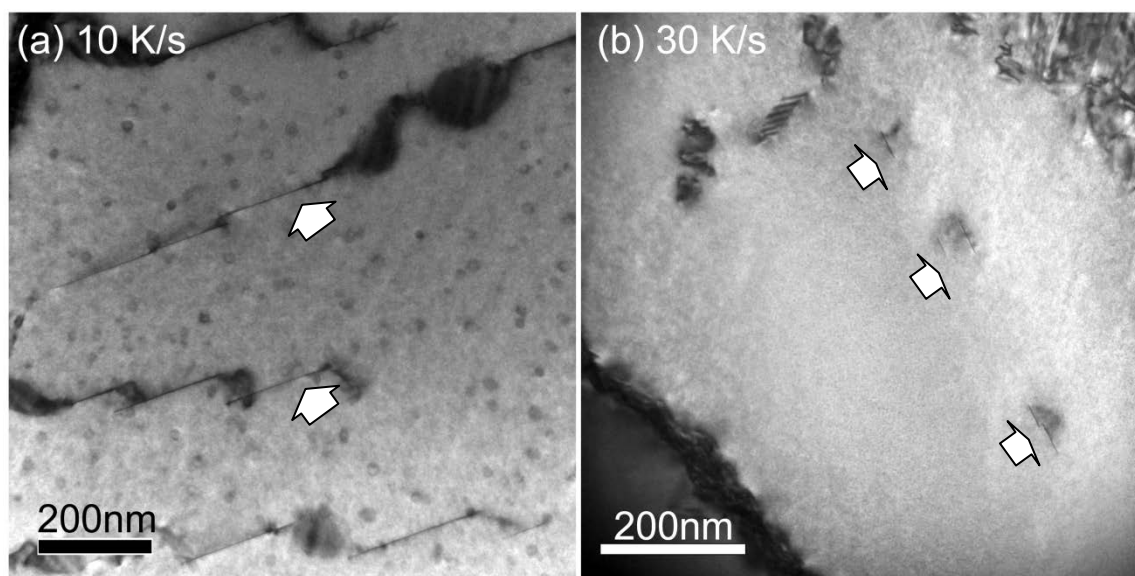


Figure.5.12: The thin plate-shaped low temperature phase can be found in different cooling conditions (30 K/s for (a) and 10 K/s for (b)). It is noted that their length decreases with increasing cooling rate. The images are taken along the $\langle 110 \rangle_\alpha$ zone axis in subgrains.

Fig. 5.12 (a) and (b) shows the TEM image of samples cooled continuously at cooling rate of 10 K/s and 30 K/s respectively. It is hard to find any S-phase or M-phase under these cooling conditions. However, there are still some platelet precipitates can be found in these cooling conditions. It is demonstrated in **Fig 5.12** that these platelet precipitates appear longer at the cooling rate of 10 K/s, while they become shorter at the cooling rate of 30 K/s. Moreover, the detailed observation show that the amount of the platelet precipitates is decreasing with increasing cooling rate. The result here suggests that the growth of the platelet phase is gradually inhibited by cooling process. Different than S-phase and M-phase, the inhabitation of growth of the platelet precipitates happens at relatively fast cooling rate range (i.e >3 K/s). Therefore it is concluded that the observed platelet phase is corresponding to LT reaction.

To the author's best knowledge, this platelet phase has never been reported in 7xxx series alloys before. It shows that the platelet precipitates can only occur under some critical cooling conditions. First, according to DSC detection, they can only precipitate during continuous cooling in a relatively low temperature range of about 150-250 °C. The amount of this phase increases with increasing cooling rate in the cooling rate range of 0.05 K/s-3 K/s. It is possible that this platelet phase can precipitate in very slow cooling conditions, but the amount is very limited as the precipitation heat is very low. The maximum amount of the platelet precipitates can be achieved at a cooling rate of about 3 K/s. It is believed that the platelet precipitates will be totally suppressed by very rapid cooling conditions at 300 K/s.

It is also shown that the platelet precipitates are heterogeneously distributed within subgrains. This situation may due to the fact that they preferentially nucleate in subgrains rather than in recrystallised grains. However, the exact mechanism is unclear so far. **Fig 5.12** demonstrates that the platelet precipitates have a very high aspect ratio (length/thickness ratio) making them clearly visible from edged-on

orientation. Otherwise, they are hardly visible from other orientations, due to very poor image contrast. It is also shown that there are some variants of this platelet phase growing on inclined planes resulting in fringes occurring at specific depths in the crystal and running parallel to the line of intersection of the foil surface and habit plane, as shown in **Figs 5.12 (a) and (b)**.

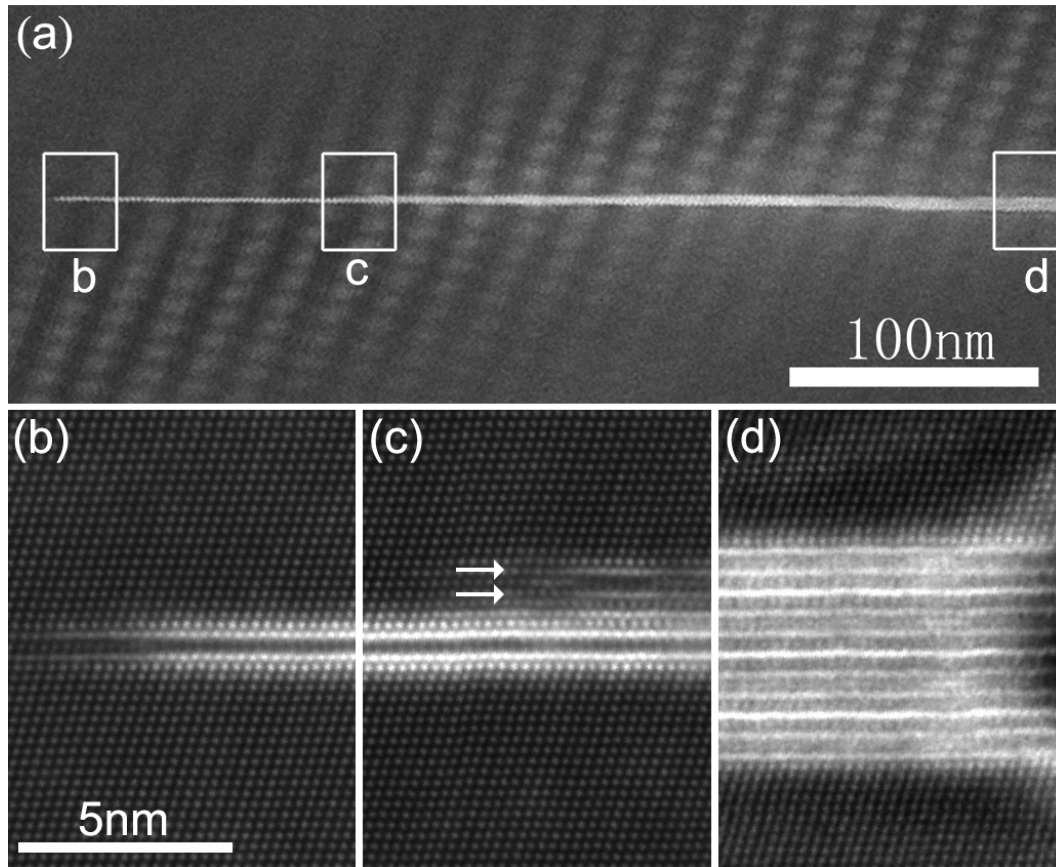


Figure 5.13: HAADF-STEM images of a single platelet precipitate showing that the thickness is varying along the length, with $B=\langle 110 \rangle_{Al}$.

High resolution STEM has been employed to resolve the crystal structure of the platelet phase. The HAADF-STEM was carried out using an FEI Titan³ 80-300 KV FEG-TEM operated at 300 KV, fitted with two CEOS aberration correctors, and a Fischione HAADF detector. By default, images are presented filtered by

removing the high spatial noise. Image analysis was performed using ImageJ software.

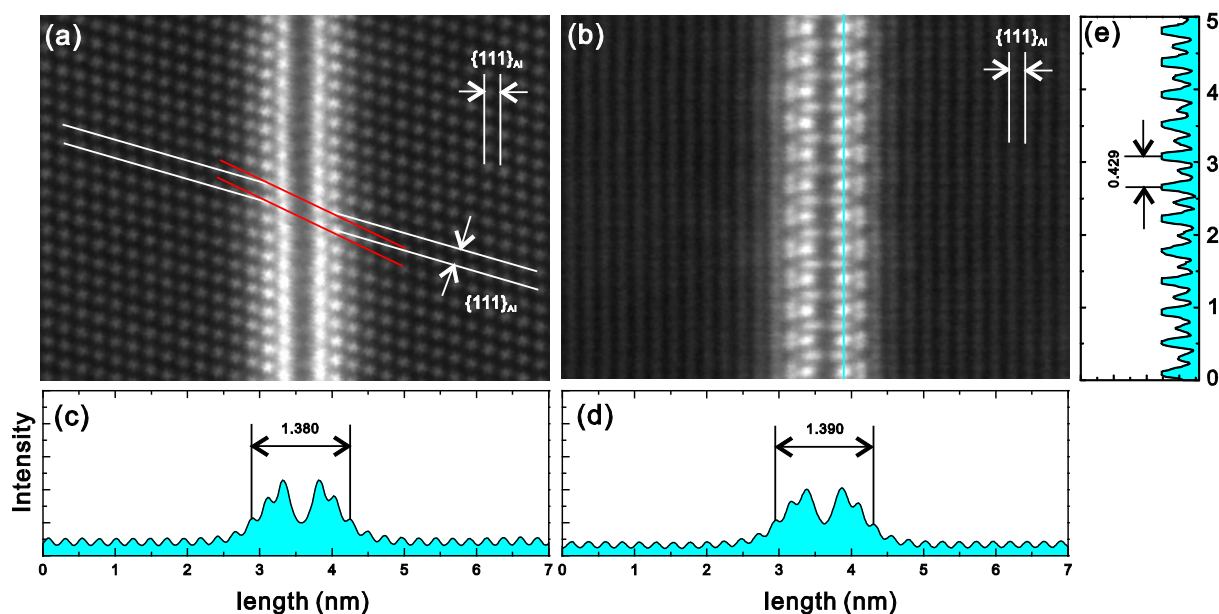


Figure 5.14: Atomic-resolution HAADF-STEM imaging of a single platelet precipitate viewed from (a) $\langle 110 \rangle_{\text{Al}}$ and (b) $\langle 112 \rangle_{\text{Al}}$ directions, with (c) and (d) showing respective plots of image intensity integrated vertically, and (e) showing the distribution of intensity along the length of the precipitate.

Fig 5.13 shows HAADF-STEM images of a single platelet precipitate with electron beam parallel to the $\langle 110 \rangle_{\text{Al}}$ direction. It is evident that the thickness of this platelet precipitate is varying from a double-layer structure (as shown in **Fig 5.13 (b)**) to a multi-layer structure (as shown in **Fig 5.13 (d)**). The growth ledges are indicated by the arrows in **Fig 5.13 (c)**.

It is noted that this platelet phase with high aspect ratio bears some resemblance to T_1 plates that are normally found in Al-Cu-Li alloys [181-188]. The atomic-resolution HAADF-STEM images in **Fig 5.14 (a)** and (b) show that the platelet phase shares the same crystal structure with the T_1 phase. Together with SAD analysis, it can be concluded that the platelet phase has a hexagonal structure

($a=0.429$ nm, $c=1.385$ nm), with the following orientation relationship with the matrix:

$$(0001)_{\text{Platelet-phase}} // (111)_{\alpha} \text{ and } [11\bar{2}0]_{\text{Platelet-phase}} // [112]_{\alpha}$$

The measured cell parameters are based on HAADF-STEM images using the $\{111\}_{\text{Al}}$ plane space ($d_{111}=0.2338$ nm) as a reference. The measured cell parameters for the platelet phase are slightly different to the cell parameters for the T_1 phase ($a=0.496$ nm, $c=1.391$ nm) [188]. It is noted that c is almost exactly 6 $d_{111}=1.4028$ nm, so that the platelet phase is slightly mismatched with the Al matrix, as shown in **Fig 5.14** (a). This can be attributed to the different atomic positions and compositions of the platelet phase. A previous study of the T_1 phase shows that the T_1 phase tends to precipitate by heterogeneous nucleation on dislocations in Al-Cu-Li alloys [189]. This may provide some clues for the nucleation mechanism of the platelet phase in alloy 7150, as the platelet precipitates are mainly found within subgrains.

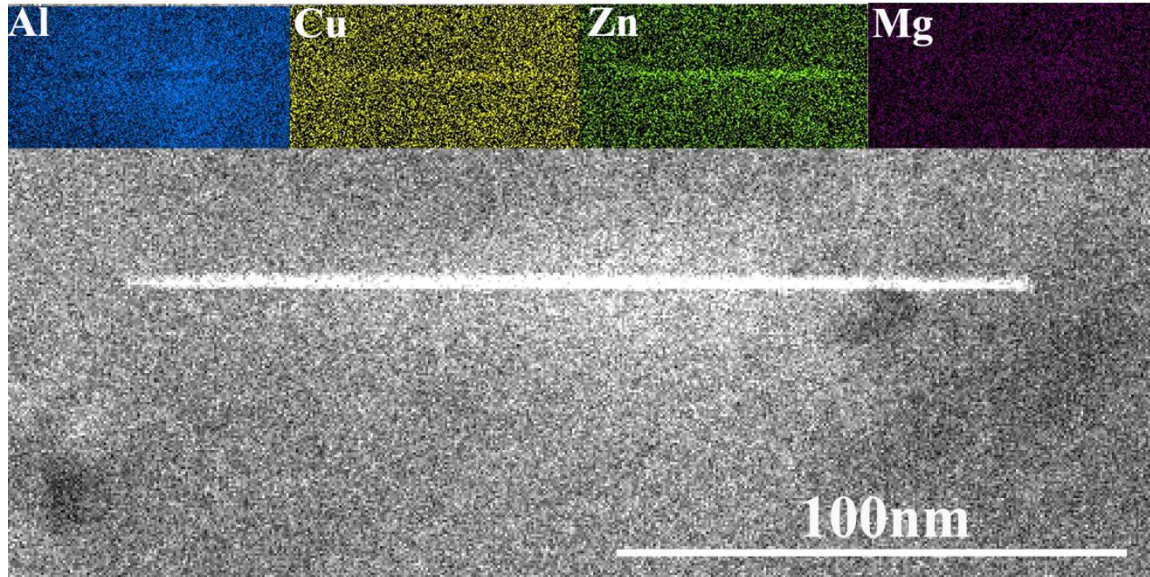


Figure 5.15: EDX mapping of a single platelet phase showing the segregation of Cu and Zn atoms.

Fig 5.15 shows some EDX mappings of a single platelet precipitate. It is shown that there are segregations of Cu and Zn atoms within this particle. Due to the higher atomic numbers of Cu and Zn compared to Al, these elements cause the higher atomic contrast observed in the HAADF image. The analysis of the platelet phase shows that the low temperature reaction corresponds to Cu- and Zn-enriched phase that shared the same crystal structure as the T_1 phase in Al-Cu-Li alloys. The results here suggest that such a crystal structure may occur with different chemical occupancy in different alloy systems.

5.3.4. CCP diagram for alloy 7150

The detected DSC curves and corresponding microstructures have been thoroughly studied with the purpose of understanding the quench-induced precipitation behaviour during continuous cooling. There are three different reactions occurring in different temperature ranges during continuous cooling. The microstructural investigation illustrates that the high temperature reaction corresponds to S-phase (Al_2CuMg) that can only be observed in some slow cooling conditions. The medium temperature reaction corresponds to M-phase ($MgZn_2$). There is another low temperature reaction that corresponds to a Cu- and Zn-enriched platelet phase with high aspect ratio.

As a result, a continuous cooling precipitation (CCP) diagram can be constructed for alloy AA7150 plotting the onset and finishing temperature of each reaction during continuous cooling in a temperature/time diagram. The diagram is scaled with a logarithmic time axis so that the continuous cooling rates from 300 K/s to 0.01 K/s can be evenly plotted. The constructed CCP diagram for alloy 7150 is shown in **Fig 5.16**. The corresponding reaction areas have been labeled. According to these evenly distributed continuous cooling rates, one can determine the critical cooling rates for each reaction. It is shown that the critical cooling rate for the high

temperature reaction (S-phase) is about 3 K/s. The critical cooling rates for the medium temperature reaction (M-phase) and the low temperature reaction are about 10 K/s and 300 K/s, respectively. Due to some of the critical cooling rates being beyond the DSC cooling rate capability, the values are extrapolated based on a combination of detected DSC data, hardness curves and microstructural analysis.

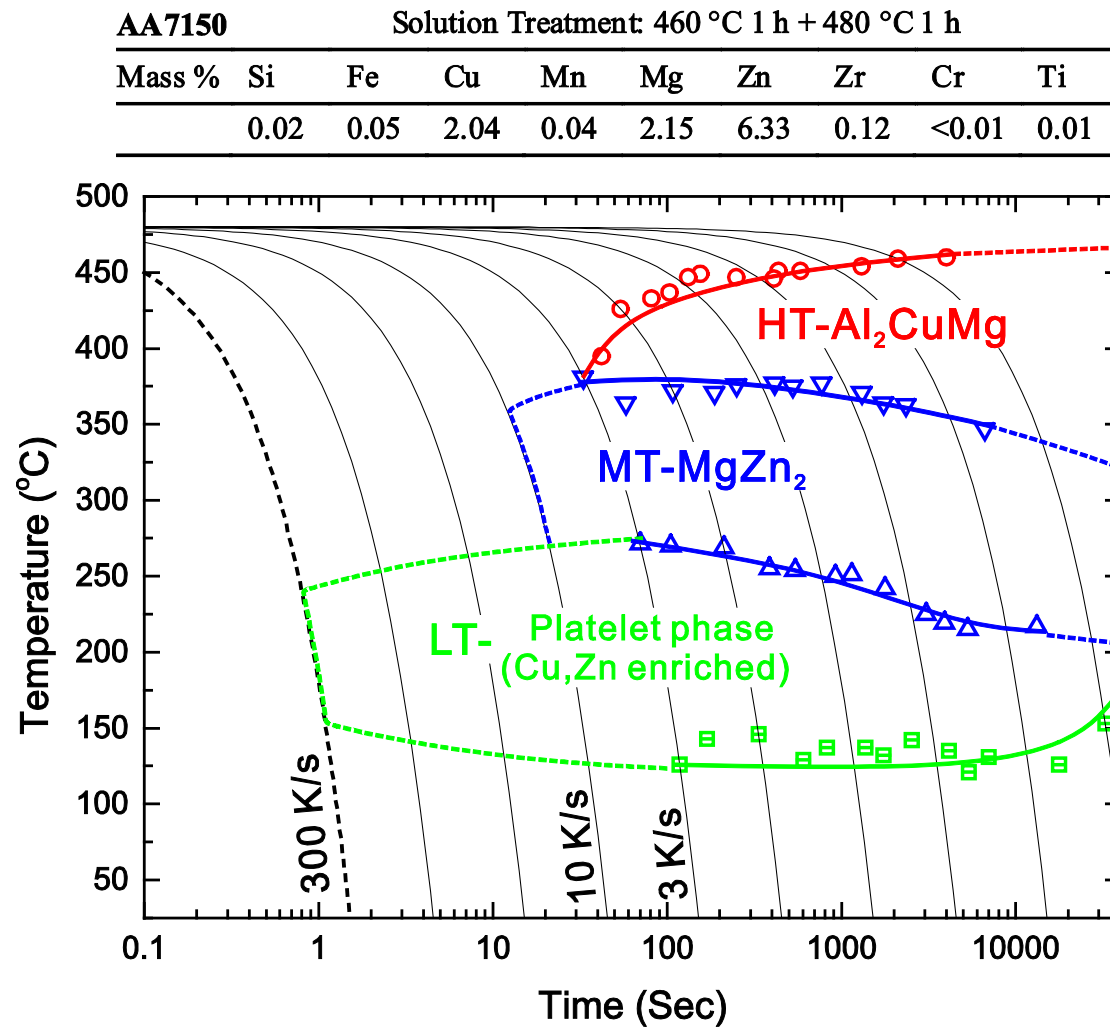


Figure 5.16: Developed continuous cooling precipitation (CCP) diagrams for studied alloy AA7150 after solution treatment, showing linear cooling rates ranging from 300 K/s to 0.01 K/s. The dashed lines indicate regions where the precipitation reactions were extrapolated on the basis of combined evaluations of all the available DSC data, hardness curves and microstructural analysis.

The CCP diagram is very useful for industrial cooling path selections. For example, if the S-phase is undesired due to its negative effect on a specific property, the alloy should be cooled faster than 3 K/s to avoid any quench-induced S-phase. In order to avoid the precipitation of M-phase during continuous cooling, the alloy should be cooled faster than 10 K/s. However, this is very difficult to achieve for thick plates in most industrial applications. Therefore the M-phase is normally considered to be the main quench-induced precipitate for commercially produced thick gauge 7xxx alloy products.

5.4. DSC analysis for plate surface and centre

Chapter 4 has discussed the different quench sensitivity behaviour of the surface layer and the centre layer of a 7150 thick plate. It is therefore of interest to find out whether the DSC method can be used to demonstrate the difference of quench sensitivity of materials cut from different layers of a commercially produced thick plate.

Therefore samples cut from the surface and centre layers of a 7150 thick plate were pre-solution treated in an air furnace followed by water quenching. These samples were then cut into small DSC discs or rods for DSC measurements. The continuous cooling DSC scans were then performed (after a 10-minute solution treatment at 480 °C in the DSC device) using a few selected cooling rates based on previous experience.

Fig 5.17 shows the representative bending-corrected excess specific heat curves for samples cut from the surface layer (presented as blue curves) and centre layer (presented as black curves) of an alloy 7150 thick plate cooled at various linear cooling rates from 0.01 K/s to 3 K/s. It is shown that DSC curves are shifted and arranged in a similar way as shown in **Fig. 5.3**. For the selected cooling rates, it is shown that the intensity of the DSC peaks is still decreasing with increasing

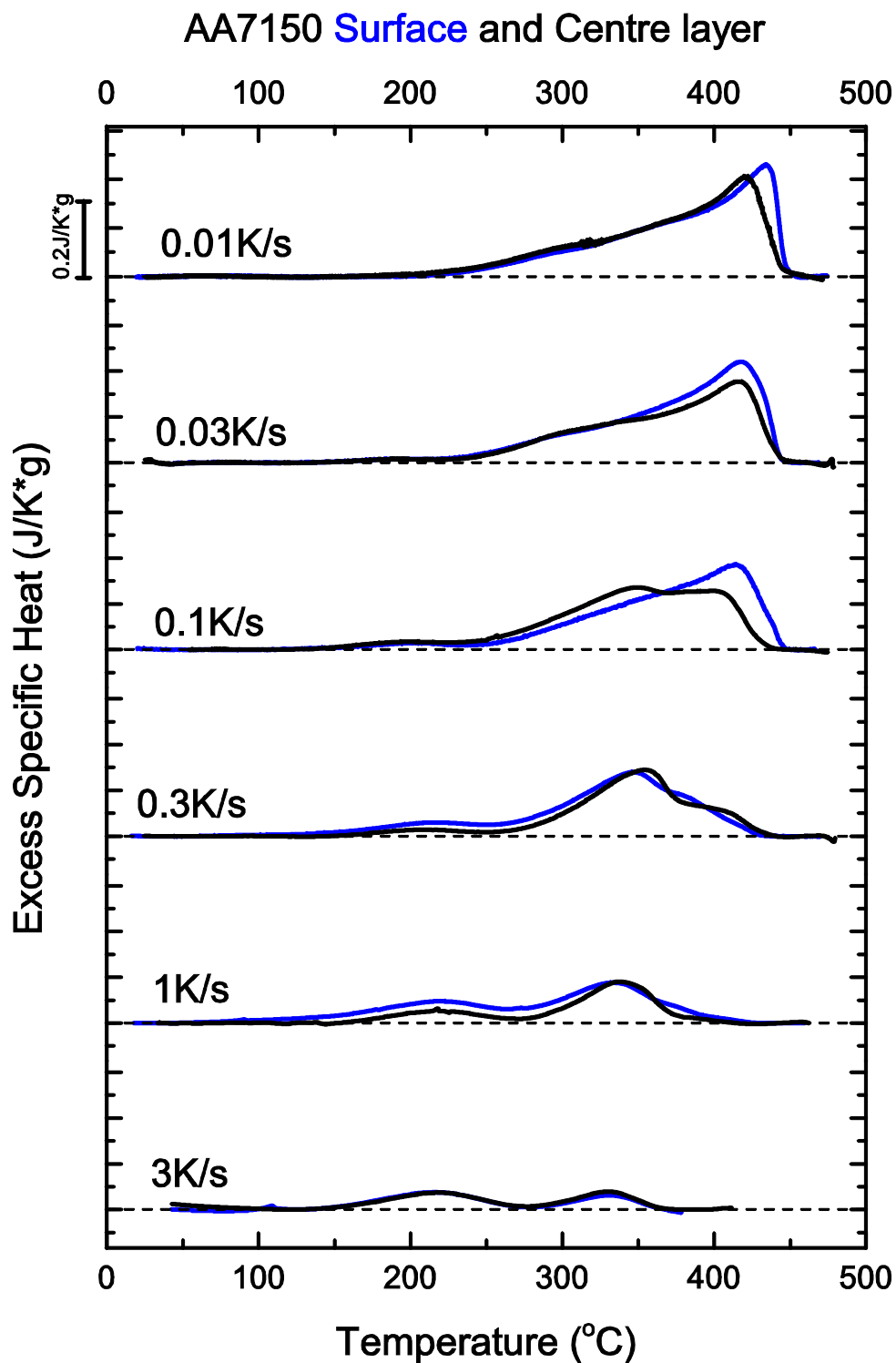


Figure: 5.17. DSC cooling curves after solution annealing for alloys 7150 surface and centre with cooling rates varying from 0.01 to 3 K/s

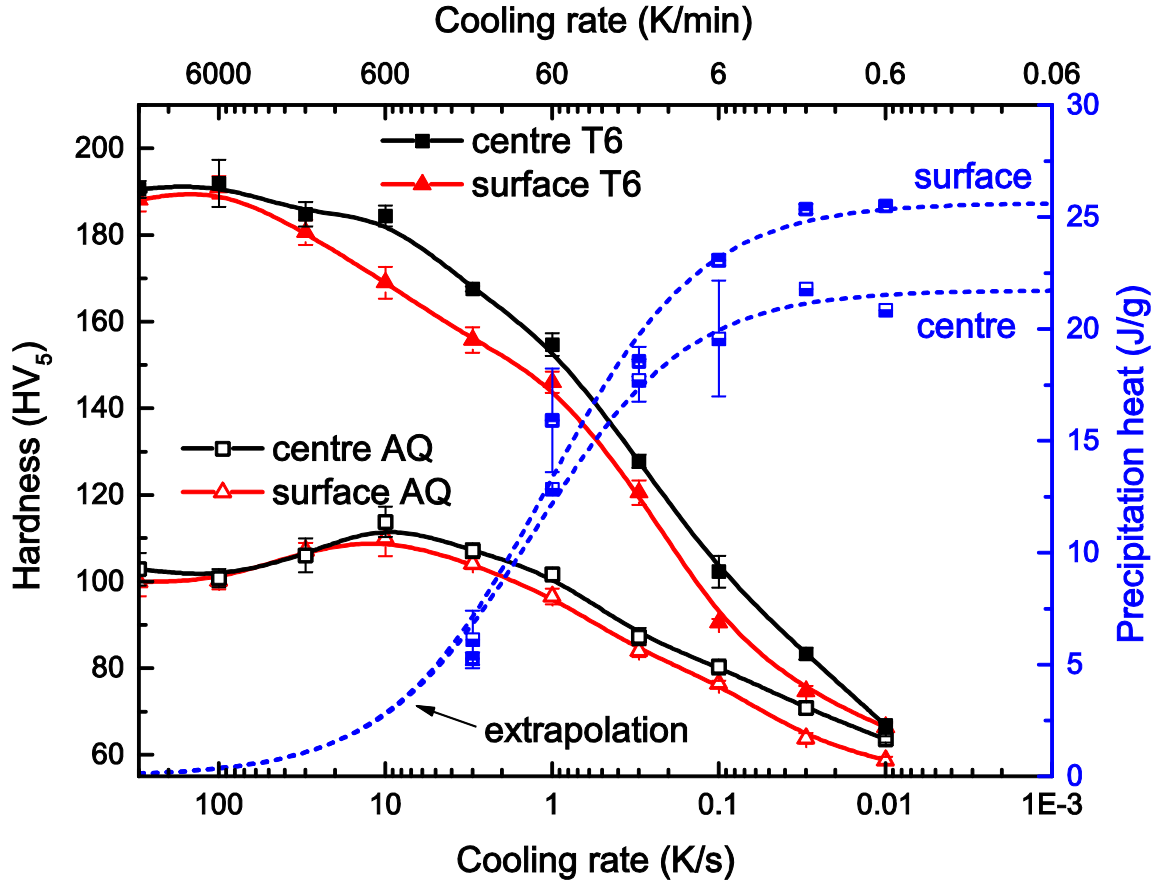


Figure. 5.18. Precipitation heat (ΔH) values from measured DSC curves for both surface and centre layers, and corresponding Vickers hardness values in the as-quenched (AQ) condition and after artificial ageing for 24 h at 120 °C (T6).

cooling rates. The same three reactions can also be identified in different temperature ranges. It is evident that the intensity of the DSC peaks in the slow cooling rate conditions from the surface layer is always greater than that of the centre layer. However, there is no significant difference in the intensity of the DSC peaks in relatively fast cooling conditions. At the cooling rate of 3 K/s, the two DSC curves are totally overlapped, suggesting that the surface layer and the centre layer exhibit the same amount of quench-induced precipitation at this cooling rate.

The overall precipitation heat values and hardness values for the as-quenched and peak-aged (T6) conditions are plotted versus cooling rate on a logarithmic scale in **Fig 5.18**. It is noted that the enthalpy value increases with decreasing cooling rate while the hardness curves decrease with decreasing cooling rate. The enthalpy values for the surface layer in the slow cooling conditions are significantly larger than that those of the centre layer. It appears that the surface layer and centre layer will approach different equilibrium enthalpy values in extremely slow cooling conditions. On the other hand, both layers exhibit similar specific heat value in fast cooling conditions.

It is shown that the change of precipitation heat is an S-shaped curve that changes slowly at the fast cooling end and then increases dramatically with decreasing cooling rates. At very slow cooling rates, the shape of the curve changes slowly as the system approaches its equilibrium state. Such behaviour has also been observed for 6xxx alloys by Milkereit *et al* [119]. Therefore the precipitation heat curve can be described by a sigmoidal function as follows:

$$\Delta H = \frac{1}{a + b(v)^c} \quad \text{Eqn 5.1}$$

where:

a is the reciprocal of the precipitation heat value in the equilibrium state,

b and c are fitting parameters,

v is the cooling rate.

The fitting parameters are listed in **Table 5.1**.

Table 5.1: Fitting parameters for both surface and centre layers.

	Surface	Centre
<i>a</i>	0.039	0.046
<i>b</i>	0.036	0.036
<i>c</i>	0.94	0.94

It is noted that the enthalpy curves versus cooling rate for both layers can be described by **Equation 5.1**. It is shown that the fitted *b* and *c* values are the same for both the surface and centre layers. However, the *a* value (i.e. reciprocal of the precipitation heat in the equilibrium state) is different for the different layers. The results here suggest that the *b* and *c* values may be constant for a given alloy composition, while the *a* value could be changed by thermo mechanical processing. It should be emphasised that this equation is a numerical approach with no clear physical basis so far. It might be worthwhile to explore in the future whether there is any physical meaning to these fitting parameters.

The hardness curves show that the higher precipitation heats at the surface layer correspond with lower hardness values at the surface. The hardness values in the T6 condition at the surface layer are always lower than those at the centre layer, suggesting that less precipitation hardening is obtained at the surface layer. Therefore the surface layer has more quench-induced precipitation during continuous cooling (as shown in **Fig 5.18**). However, it is noted that the surface and centre layers approach the same hardness values at cooling rates of ≥ 100 K/s, indicating that there is no quench-induced precipitation for both layers at cooling rates of ≥ 100 K/s. Even if there is a small amount of precipitation in that cooling rate range, they are believed to be negligible for changing the hardness value.

The hardness curves for AQ samples show similar trends, except that the maximum AQ hardness values that can be achieved for both layers are at a cooling

rate of 10 K/s. The AQ hardness values for both layers decrease by about 10 HV with increasing cooling rate from 10 to 100 K/s and then taper off. At cooling rates below 10 K/s, both hardness curves still exhibit an increasing trend with increasing cooling rate. Moreover, the hardness curve for the surface layer is always lower than that of the centre layer.

According to developed CCP diagram for alloy 7150 and the microstructural analysis at 10 K/s (as shown in **Fig 5.10**), there is a small amount of platelet precipitates that can be found in this cooling rate condition. It is concluded that the platelet precipitates, which correspond to the low temperature reaction, could cause a certain strengthening effect. Therefore the AQ hardness increases with an increasing amount of platelet precipitates. At the cooling rate of 10 K/s, the amount of the platelet phase is close to its maximum value, therefore resulting in a significant strengthening effect. With further increases of cooling rate (>10 K/s), the amount of the platelet phase decreases, causing a corresponding decrease in the hardness values. The AQ hardness curves for both the surface and centre layers demonstrate the existence of this low temperature reaction.

5.5. Discussion

A number of different cooling methods have been explored to understand the quench-induced reactions during quenching process. It should be noted that the Jominy end quench is originally designed for hardenability test for steel [146]. Newkirk and Mackenzie demonstrated that this method can also be applied to light metals [147]. Bryant studied the effect of alloy composition on quench sensitivities for 7xxx series alloys using the Jominy end quench method [64]. The quench sensitivity of an alloy can be described by showing the decreasing hardness profile along the jominy bar. Deng *et al* proposed that the quench sensitivity of an alloy can be described by the depth of 10% drop of the maximum aged hardness values [63, 179]. They showed the higher Mg content 7xxx alloy is

less quench sensitive, because the depth of 10% drop of aged hardness values is greater than other studied alloys [63].

Current work demonstrates that the Jominy bar is cooled nonlinearly within a limited cooling rate range (3 K/s – 100 K/s). When compared to the real industrial cooling process, the Jominy end quench process is not entirely one-dimensional conduction for heat transfer. The Jominy method also does not give quantitative information about precipitation heats and does not cover the slower cooling rates that may be achieved when quenching very thick plates. As a result, the Jominy end quench is not appropriate for quench sensitivity studies.

Instead, the Differential scanning calorimetry (DSC) has been proven to be a useful and reproducible technique for solid state reactions in Al alloys [180, 190, 191]. The DSC technique is sensitive to reactions that happen during non-isothermal or isothermal processes. Therefore the amount of precipitates can be quantitatively analysed by incorporating the detected precipitation heat values [191]. Kessler et al provided a methodology that can be used to construct a continuous-cooling-transformation (CCT) diagram for alloy 7020 (Al-4.5Zn-1Mg, in wt%) [116]. However, they only developed ‘half’ CCT diagram by connecting the precipitation onset temperature data in temperature-time space. Milkereit *et al* developed this method significantly in order to record CCT diagrams over a wide range of cooling rates from 0.0017 K/s (0.1 K/min) to 6.25 K/s (375 K/min) by using three different types of DSC devices for alloy 6005A [118]. By recording the exothermic heat capacity curves of the precipitation reactions during cooling, a full range of CCP diagrams could be obtained.

The current work demonstrates that this DSC technique can be applied to high strength 7xxx series alloys. In addition to detected DSC curves, as-quenched and step quenched microstructures have been characterised to identify the quench-induced precipitates. The results show that there are at least three different

reactions located at different temperature ranges for alloy 7150. The high temperature reaction has been demonstrated to be the S-phase (Al_2CuMg) that occurs mainly existing in slow cooling conditions ($< 3 \text{ K/s}$). The medium temperature reaction has been shown to be the M-phase (MgZn_2) that precipitates in a cooling rate range from about 10 K/s to very slow cooling rates. **Fig 5.4** shows that the precipitation of the M-phase dominates the overall reaction at cooling rates from about 10 to 0.05 K/s . Moreover, the M-phase precipitates consume both Zn and Mg that are necessary for hardening precipitates. This is why the M-phase is believed to be the most critical quench-induced precipitate for alloy 7150.

It is noted that there is another platelet phase has been newly discovered during continuous cooling of alloy 7150 at lower temperature range of about $150\text{-}250 \text{ }^\circ\text{C}$. Detailed analysis shows that this platelet phase is enriched in Cu and Zn. Despite the relatively small amount of these platelet precipitates, they nevertheless increase the hardness by at least 10 HV_5 . According to Nie and Muddle, platelet precipitates on the $\{111\}_\alpha$ planes have the most strengthening potential in aluminium alloys when compared to lath- or rod-shaped precipitates [184]. It is expected that an even higher strength 7150 alloy can be obtained if the precipitation of these platelet precipitates can be manipulated. However, the precipitation mechanism for this phase is unclear so far.

Although, there are a large number of publications discussing about quench sensitivity phenomenon, few of them focusing on the types of quench-induced precipitation reactions. Suzuki *et al* studied the deformation effects on quench sensitivity of 7xxx series alloys containing different transition elements [192]. They proposed that quench sensitivity increases with increasing reduction of cold-working. Conserva *et al* demonstrated that the quench-induced M-phase can be found at the cooling rate of $\leq 15 \text{ K/s}$ of a Zr-containing 7xxx alloy [30]. Qi *et al* demonstrated that the M-phase precipitates can nucleate on grain boundaries or inside the grains [63, 178]. The amount of the M-phase increases with increasing

Mg content. It is noted that the M-phase was believed to be the primary quench-induced precipitation reaction for most research work, however few papers have pointed out the existence of other quench-induced precipitations. Current work demonstrates that there are two other quench-induced precipitation reactions in alloy 7150. They also consumed necessary solute atoms for subsequent ageing process, as they are Cu, Mg and/or Zn enriched phases. The S-phase precipitation reaction is even dominating the quench-induced precipitation reactions at slow cooling rate of ≤ 0.1 K/s. The platelet phase is dominating the quench-induced precipitation reactions at cooling rate of ≥ 3 K/s. The results here suggest that the other two quench-induced precipitation reactions could also significantly affect the quench sensitivity in specific cooling rate ranges.

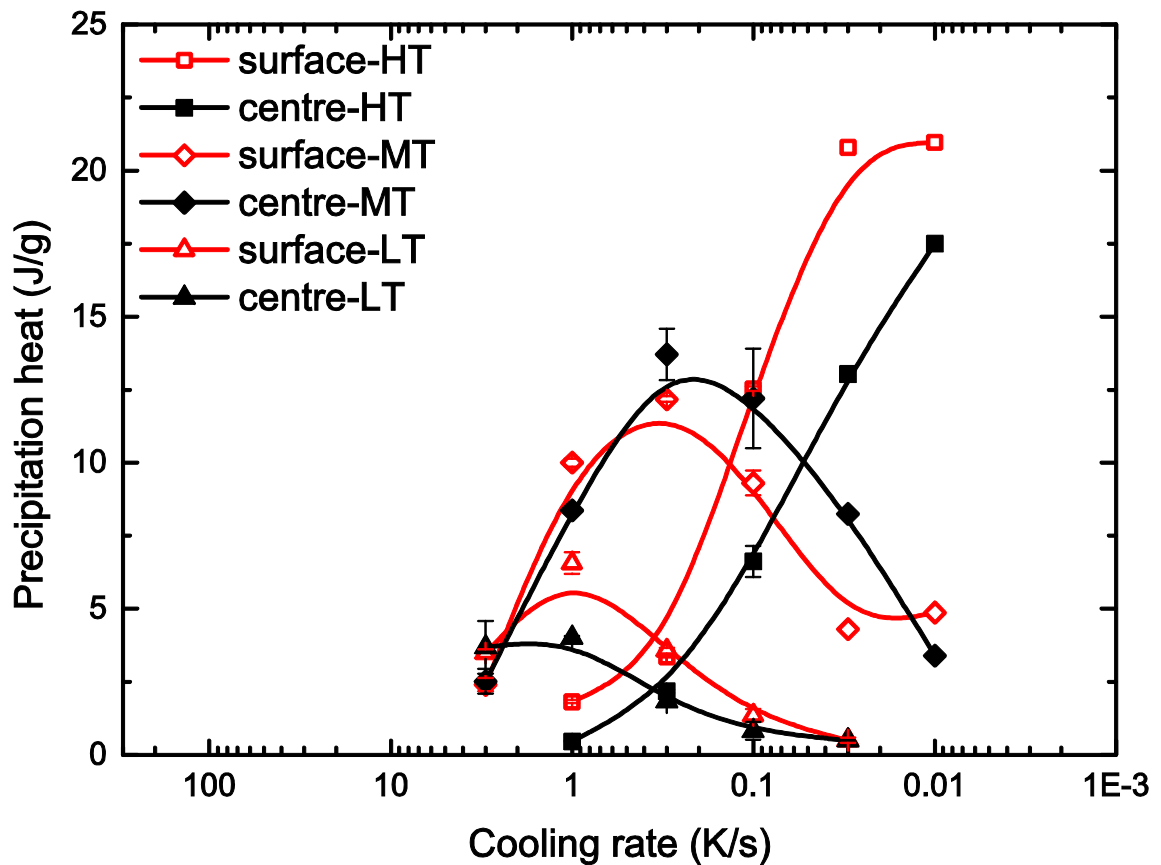


Figure 5.19: Precipitation heat (ΔH) values for HT, MT and LT reactions from measured DSC curves for both surface and centre layers.

Fig 5.19 shows the precipitation heat values of HT, MT and LT reactions for both surface and centre layers. It demonstrates that the precipitation heat values for HT and LT reactions in the surface layer are greater than those in the centre layer. However, the precipitation value of MT reaction is greater for centre layer in the cooling rate range of 0.3-0.01 K/s. The previous discussion showed that the overall precipitation heat values for the surface layer are greater than those for the centre layer, suggesting that the surface layer is more quench sensitive than the centre layer (as shown in **Fig 5.18**). The results here show that the quench sensitivity is not only affected by the amount of the M-phase precipitates, but also affected by the amount of the S-phase and the platelet phase precipitates. There are more S-phase precipitates in the surface layer because the surface layer contains more grain/subgrain boundary areas that are preferentially for the S-phase particles. There is no difference in the onset temperatures for each quench-induced reaction, suggesting that the onset temperatures of quench-induced reactions are related more to the alloy composition rather than to thermo mechanical processing.

5.6. Conclusions

The key findings from this chapter are summarised as follows:

1. The Jominy end quench method was used to obtain a series of samples with different cooling rates. However, the average cooling rate along the Jominy bar covers a limited range from 3 - 100 K/s. The hardness curve shows that its value drops from about 200 HV at the quenched end to about 175 HV at about 100 mm away from the quenched end.
2. The DSC technique can be used to cool specimens over a wide range of cooling rates. Based on a combination of precipitation heats detected by DSC, hardness data and microstructural analysis, a continuous cooling precipitation (CCP) diagram was constructed for alloy 7150. The CCP

diagram can enable engineers to choose appropriate cooling paths to achieve desired property combinations.

5. It was be found from the evaluated DSC curves and constructed CCP diagram of alloy 7150 that there are at least three quench-induced reactions. The high temperature reaction from about 350 to 470 °C corresponds to S-phase (Al_2CuMg), the medium temperature reaction from about 200 to 400 °C corresponds to M-phase (MgZn_2) and the low temperature reaction from about 250 to 150 °C corresponds to a unique platelet phase containing both Cu and Zn. The critical cooling rates were determined to be 3 K/s for the S-phase, 10 K/s for the M-phase, and 300 K/s for the unique platelet phase in alloy 7150.
3. The overall ΔH_C curves for alloy 7150 show a decreasing trend with increasing cooling rate, indicating that the amount of quench-induced precipitation is decreasing with increasing cooling rate. However, the precipitation heat curves for individual reactions are different. The precipitation heat curve for the S-phase is decreasing with increasing cooling rate. The precipitation heat curve for the M-phase increases with increasing cooling rate and then decreases with increasing cooling rate after it reached its maximum value at a cooling rate of about 0.2 K/s. The precipitation heat for the platelet phase, however, keeps increasing with increasing cooling rate. It is believed that the maximum value can be obtained at cooling rate somewhere between 3 and 10 K/s. It will be totally inhibited by extremely fast cooling conditions.
4. The low temperature reaction is corresponding to the platelet phase. These platelet precipitates with high aspect ratio have a hexagonal structure ($a=0.429$ nm, $c=1.385$ nm), and share the following orientation relationship with the Al matrix:

$$(0001)_{\text{Platelet-phase}} // (111)_{\alpha} \text{ and } [11\bar{2}0]_{\text{Platelet-phase}} // [112]_{\alpha}$$

The as-quenched hardness curves show that the platelet phase can make contributions to strengthening in a certain cooling rate range. Despite the relatively small amount of these platelet precipitates, they nevertheless increase the hardness by an estimated 10 HV at a cooling rate of 10 K/s. This platelet phase and its ability to harden 7xxx alloys have not been reported previously.

5. The results show that the amount of the S-phase precipitates and the platelet phase precipitates are greater in the surface layer than in the centre layer. Despite more M-phase precipitate can be found in the centre layer, the overall precipitation heat values shows that the surface layer is more quench sensitive than the centre layer. There is no difference in the onset temperatures for each quench-induced reaction, suggesting that the onset temperatures of quench-induced reactions are related more to the alloy composition rather than to thermo mechanical processing.

Chapter 6. CCP diagrams for other studied 7xxx alloys

6.1. Introduction

The previous chapter introduced a feasible method that can develop reliable CCP diagrams for aluminium alloys relying on a specialised DSC technique. The constructed CCP diagrams for aluminium alloys can be used to describe how sensitive an alloy is to different cooling rates over a wide cooling rate range. It is noted that a CCP diagram demonstrates the onset/finish temperatures for quench-induced reactions that happen during continuous cooling. The amount of precipitation (i.e. precipitation heat) may not be presented in the developed CCP diagram, but the precipitation heat values can be presented versus cooling rate in separate figures.

Different precipitation behaviours are expected for different 7xxx series alloys, and so different CCP diagrams are expected for the studied alloys. The studied alloy compositions have been presented in **Table 3.1**. These alloys are designed to illustrate the effect of alloying elements on quench sensitivity behaviour. For example, alloy 7150 and 7085 have the same Cu content but different Zn/Mg ratios. Therefore a comparison of these two alloys can illustrate the Zn/Mg ratio effects on quench sensitivity. Alloys 7085 and 7037 have similar Zn and Mg

contents but different Cu contents. The comparison of these two alloys can demonstrate the Cu effects on quench sensitivity. As a result, CCP diagrams for all the additional 7xxx alloys (7020, 7085, 7037 and 7055) have been developed by the previously introduced DSC method. Moreover, quench factor analysis (QFA) is used to interpret different quench sensitivity behaviours by incorporating continuous cooling rates and hardness values (HV) or precipitation heat values (J/g).

6.2. CCP diagram for alloy 7020

The 7020 alloy belongs to the heat treatable Al-alloys with medium static strength compared with the other studied alloys. It is reported that alloy 7020 has been widely used in welded structural components in railway shells, structural truck components, containers and building construction, due to its desirable corrosion resistance and weldability [193-195]. Alloy 7020 is known for its low quench sensitivity due to its low alloying content. This alloy contains 4.0-5.0 wt% Zn, 1.0-1.4 wt% Mg and ≤ 0.20 wt% Cu. The chemical composition of the studied alloy 7020 is given in **Table 3.1**. It is of interest in the current study to make a comparison between the other high strength 7xxx series alloys and the medium strength alloy 7020 for with the purpose of understanding the different quench sensitivity behaviours.

Alloy 7020 samples were cut from a commercially produced 30 mm diameter extruded rod. The solution treatment for alloy 7020 was performed by heating up samples directly to 480 °C and holding isothermally for 30min. The samples were then cooled linearly after solution treatment within different DSC devices.

For alloy 7020, two distinct peaks can be found clearly at slow cooling rates (as shown in **Fig 6.1**). The high temperature reaction starts immediately with the onset of cooling at a temperature of about 475 °C. The peak area value decreases significantly with increasing cooling rate. It can hardly be distinguished from the

zero level at a cooling rate of 1 K/s. The medium temperature reaction peak is so significant at the slower cooling rates, such as 0.0083 K/s, that it dominates the quench-induced reactions. It occurs at a relatively low temperature regime of about 310 - 150 °C at 0.083 K/s, compared to the high temperature reaction. In comparison with previous DSC results that have been published by Kessler *et al.* in 2006 [116] and Deschamps *et al.* in 2009 [117], it is evident from all these three independent investigations on alloy 7020 that the DSC peak detection limit is of the same order (i.e. DSC peaks are observed only at cooling rates of < 3 K/s) despite slight differences in alloy composition and device configuration. In the previous publications, only one main peak spanning a temperature range from about 320 °C to 200 °C was found. In the current work, this peak appears to consist of the medium temperature reaction. Nevertheless, the enthalpies for this peak are comparable for all three studies. Moreover, the current work also clearly shows the existence of an additional high temperature peak that has not been reported before. This is ascribed to the significantly higher alloy Si content and the relatively larger cooling rate range in the current study. Thus it is important to analyse a broad range of cooling rates from very slow rates close to equilibrium conditions to very fast cooling rates beyond the critical cooling rate to get a full understanding of the whole precipitation process.

Fig 6.2 shows typical backscattered SEM images of alloy 7020 at different cooling rates ranging from 0.005 K/s to 5 K/s. It shows the same basic trend as for 7150 in **Fig 5.6** that the quench-induced precipitates decrease in size and volume fraction with increasing cooling rate. However, the precipitates at a given slow cooling rate are much smaller than those in alloy 7150, and the total volume fraction is also much smaller. This observation is in agreement of the results that the excess specific heat of alloy 7020 at a given cooling rate is much smaller than that of alloy 7150.

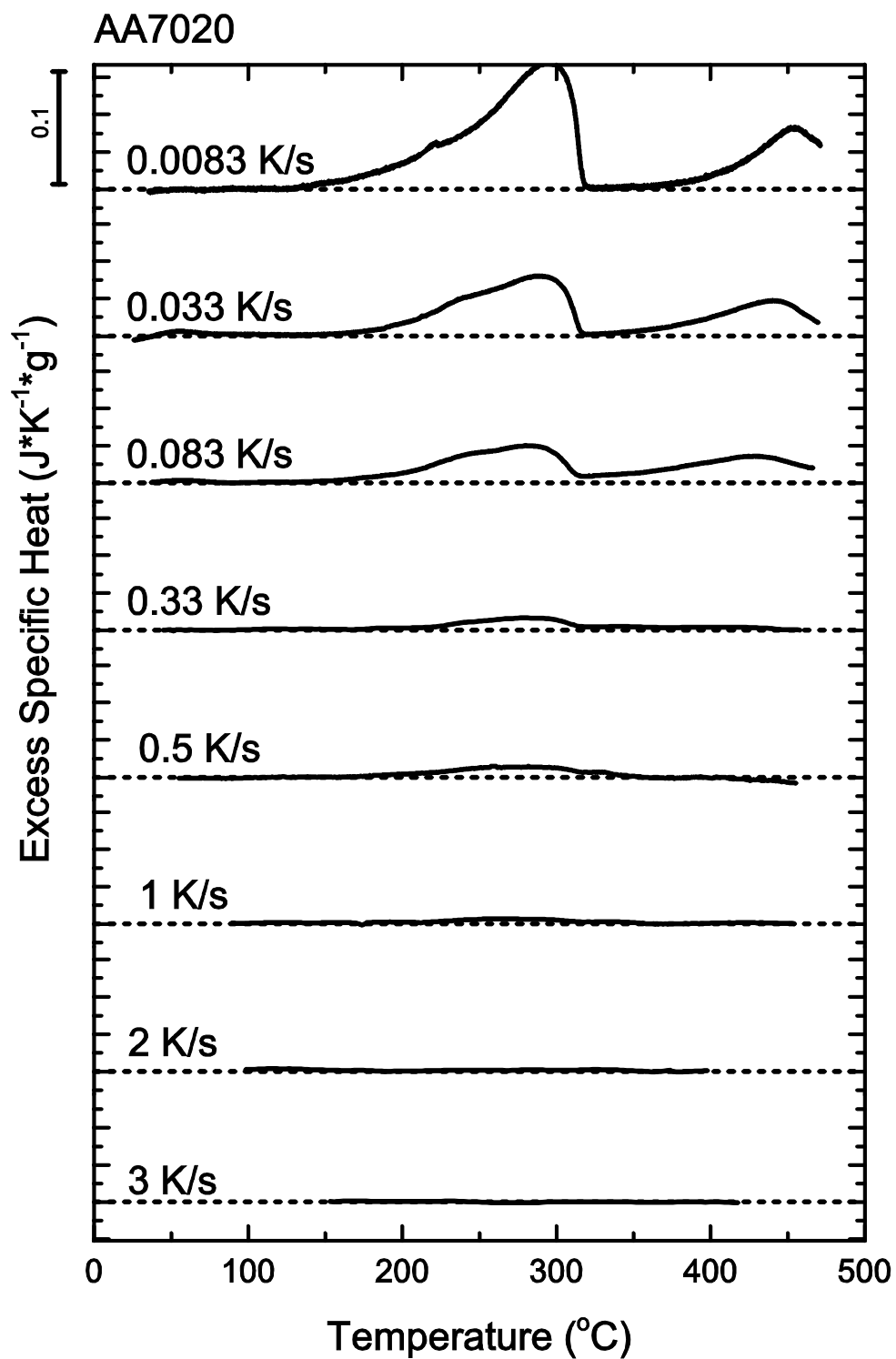


Figure 6.1: DSC cooling curves after solution treatment for alloy 7020 with cooling rates varying from about 0.01 to 3 K/s.

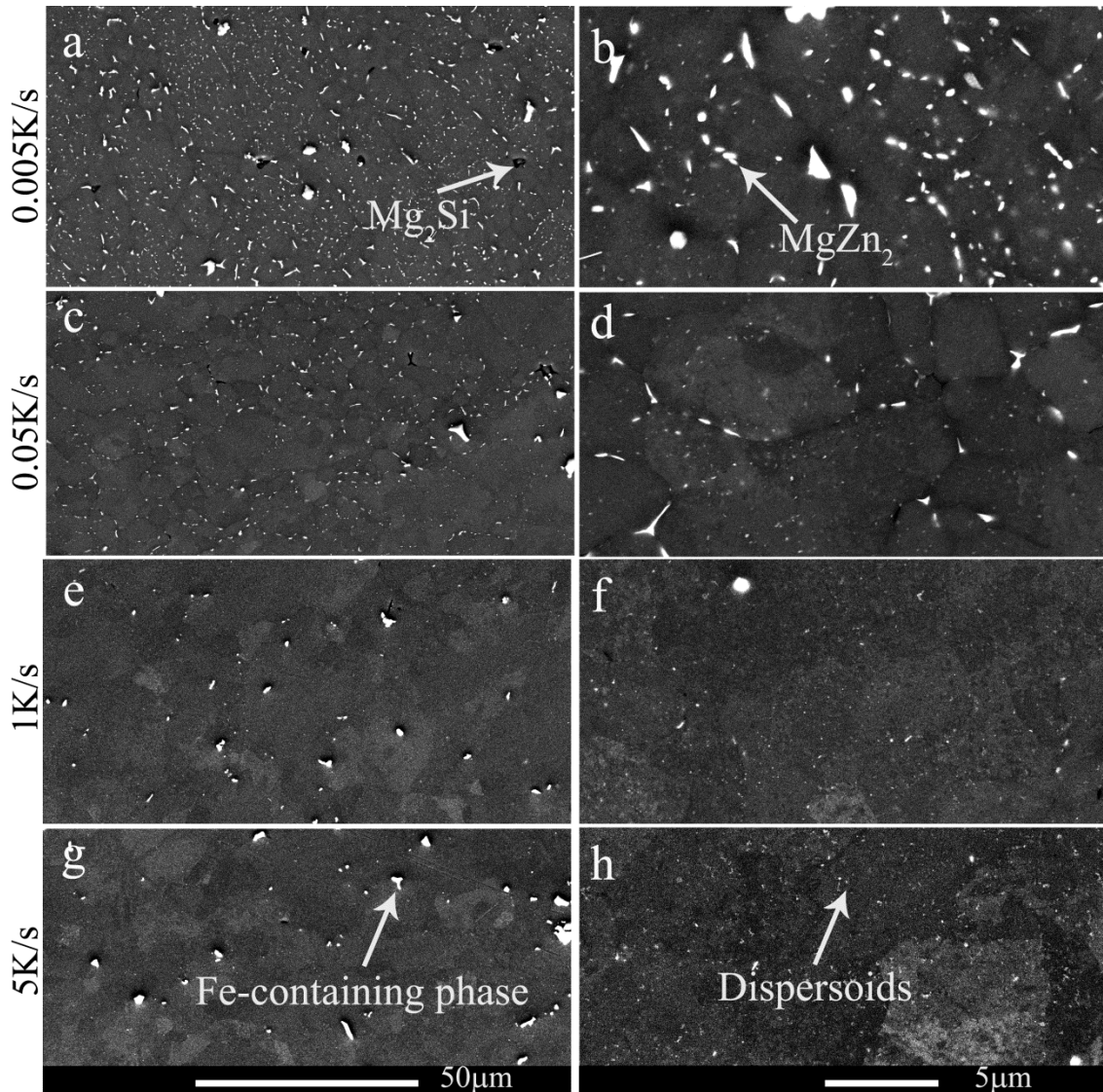


Figure 6.2: Backscattered SEM images of alloy AA7020 DSC and dilatometer samples cooled at different rates. The two columns represent two different magnifications, as indicated by the scale bars at the bottom. The main phases are labelled.

In **Fig 6.2** (a) at a cooling rate of 0.005 K/s, there are a large amount of bright precipitates together with some coarse dark precipitates (identified with an arrow). The dark precipitates are identified as Mg_2Si by EDX analysis (as shown in **Fig 6.3**). They appear as dark particles due to the fact that they are easily etched and Mg, O and H all have lower atomic numbers than the Al matrix. The EDX results also indicate that most of the bright precipitates are equilibrium MgZn_2 (M-phase)

(as shown in **Fig 6.3**). It is also interesting to note that the volume fraction of Mg_2Si is much smaller than that of the M-phase. It is shown that the high temperature reaction peak values are much smaller than the medium temperature reaction peak values in very slow cooling conditions, and all the peak areas decrease dramatically with increasing cooling rate in the slower cooling rate range. It is therefore reasonable to assume that the high temperature reaction corresponds to the Mg_2Si phase. These Mg_2Si particles were clearly visible by SEM after slow cooling but were hardly visible after faster cooling. This is in agreement with the DSC curves in **Fig 6.1**, where the high temperature DSC peaks become smaller with increasing cooling rate. At cooling rates of $> 0.33 \text{ K/s}$, the high temperature peak disappears and the SEM images show that almost no precipitated Mg_2Si can be found. However, it is possible that a small amount of Mg_2Si may have been present that did not dissolve completely during solution annealing. If so, then the amount of such undissolved Mg_2Si would be very small (in relation to the amount that precipitated during cooling) and hence their size/spacing would be such that they are difficult to resolve by SEM.

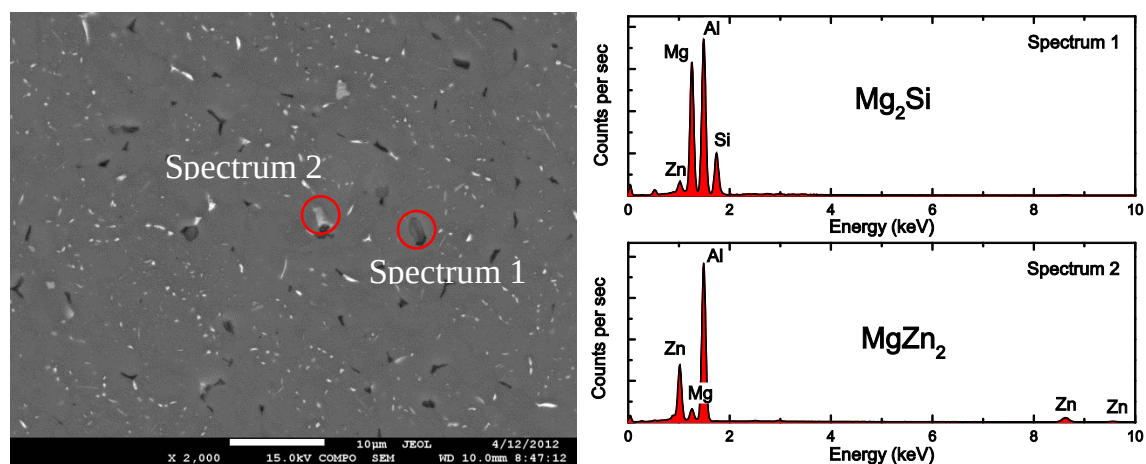


Figure 6.3: EDX analysis results for the large particles with different image contrast in a sample cooled at 0.0054 K/s , showing that they correspond to M-phase (MgZn_2) and β -phase (Mg_2Si) separately.

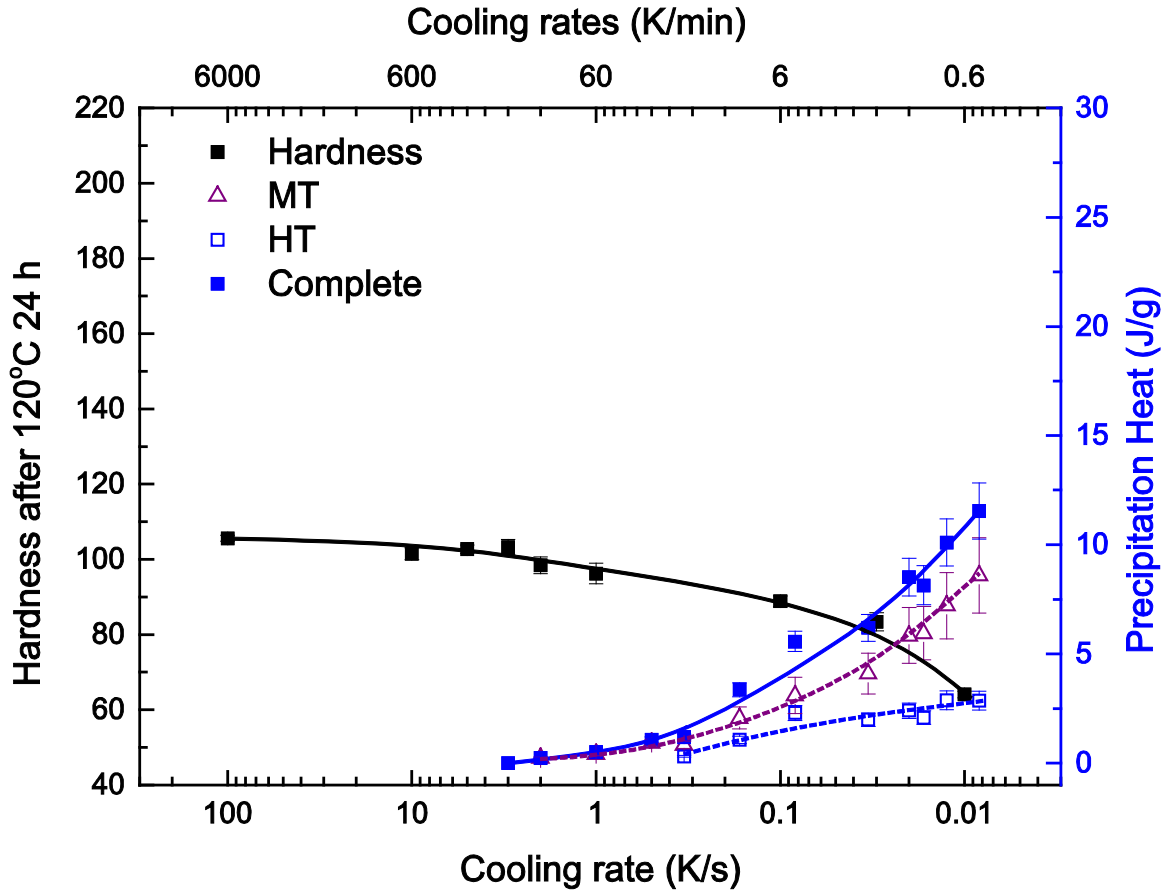


Figure 6.4: Precipitation heats for HT and MT reactions for alloy 7020 after cooling to room temperature from solution treatment at 480 °C. Vickers hardness values were measured after artificial ageing for 24 hours at 120 °C.

In **Fig 6.2** (c) and (d), it is evident that many M-phase particles are distributed along the grain boundaries. It is shown that the amount of M-phase is significantly decreased with increasing cooling rate. When approaching and exceeding the critical cooling rate of 3 K/s for this alloy, **Fig 6.2** (e)-(h) show that there is no further change in the microstructure and that both fine and coarse particles remain. These uniformly distributed small particles at cooling rates of 1 K/s and 5 K/s are believed to be Mn- and Cr- containing dispersoids that do not dissolve during solution treatment and therefore exist in all cooling conditions. There are also some coarse Fe-containing intermetallics, as indicated in **Fig 6.2** (g). This is due to

the relatively high Fe content of 0.17 wt% in this batch of alloy 7020. These particles are insoluble at the solution treatment temperature and their volume fraction did not change with increasing cooling rate.

There are some significant differences in the results between alloy 7150 and alloy 7020. In the first place, the released enthalpy at a given cooling rate in alloy 7150 is much higher than that in alloy 7020. It is believed that the difference in excess specific heat is attributed to the higher alloying content in alloy 7150. Furthermore, the onset temperatures of the high temperature reactions in the two alloys are different. The high temperature reaction in alloy 7150 occurs about 30 °C below the solution annealing temperature (i.e. at about 450 °C). On the other hand, the first reaction for alloy 7020 starts immediately upon cooling. This suggests that dissolution of the soluble phases might not be fully completed within a solution treatment of 30 minutes at 480 °C for alloy 7020. It seems that the onset temperature for M-phase in alloy 7020 is lower than that in alloy 7150. A third significant difference is in relation to the overlapping of the peaks. For alloy 7150, the high and medium temperature reactions strongly overlap at slower cooling rates in a temperature range of about 450 °C to 330 °C, so that at best only an approximate separation can be achieved. The low temperature reaction is well separated in alloy 7150. For alloy 7020, however, the high temperature reaction is well separated while the low temperature reaction can barely be found.

As a result, the CCP diagram for alloy 7020 can be constructed, as illustrated in **Fig 6.5**. It is shown that only two reaction regions have been labeled compared to three reactions in alloy 7150. The M-phase reaction is still the main reaction for alloy 7020. However, it happens in a slightly lower temperature range (150 °C - 330 °C) compared to that in alloy 7150 (250 °C -380 °C). It is also noted that the two reactions in alloy 7020 mainly occur in slow cooling conditions, so that the critical cooling rate for alloy 7020 is about 3 K/s. This is much slower than for alloy 7150 and indicates that alloy 7020 is less quench sensitive than alloy 7150.

However, the critical cooling rate values do not tell which quench-induced reactions are more sensitive to cooling rate. Moreover, the critical cooling rate values are hard to be determined, especially for these high alloying content materials.

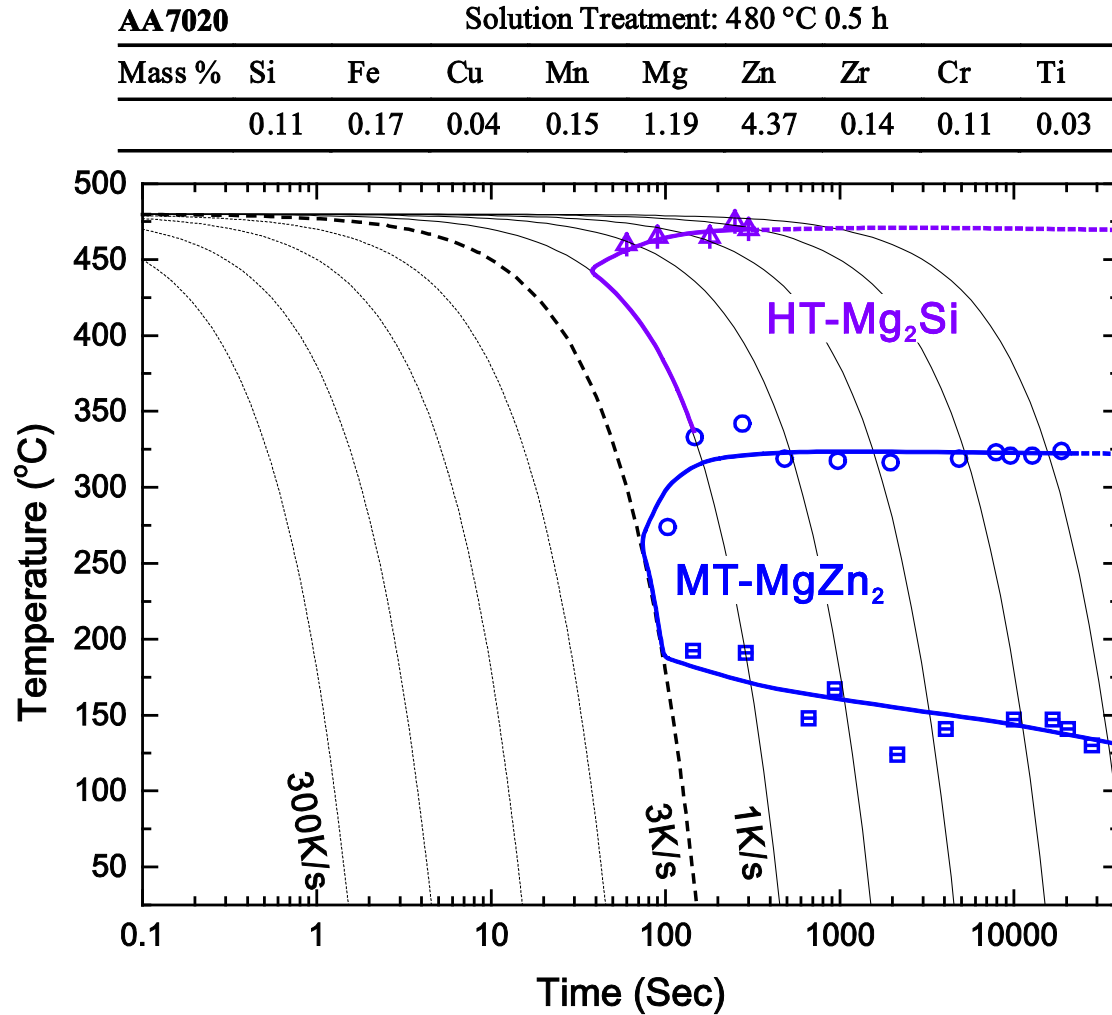


Figure 6.5: Developed continuous cooling precipitation (CCP) diagram for alloy 7020 after solution treatment. Different linear cooling paths ranging from 300 K/s to 0.005 K/s are shown. The dashed line indicates that the critical cooling rate for alloy 7020 is about 3 K/s.

6.3. CCP diagram for alloy 7085

Alloy 7085 was developed by Alcoa in 2002 in response to aerospace markets needs for an aluminium alloy with improved thick section properties [196]. This alloy has been widely used for airplane wing box structures due to its unprecedented thick section mechanical properties and its improved fracture toughness and fatigue properties. It has been shown that alloy 7085 can be produced as thick as 305 mm due to its higher purity composition and low quench sensitivity behaviour [61, 109]. This alloy has a higher Zn content (7.0-8.0 wt%), a slightly lower Cu content (1.3-2.0 wt%) and a reduced Mg content (1.2-1.8 wt%) compared with alloy 7150 [197]. The total alloy content is about 11 wt% , which is within the same range as other high strength 7xxx alloys such as alloys 7150 and 7055. It is therefore of interest to understand why alloy 7085 exhibits a significantly reduced quench sensitivity.

The DSC cooling method was then employed to detect the DSC curves of a lab-produced alloy 7085. The materials had been hot-rolled from 25 mm slabs to 3 mm plate with a total reduction rate of about 88%. It is believed that this deformation amount is comparable to the surface layer of a commercially produced aluminium thick plate. Therefore the DSC curves of the surface layer of commercially produced 7150 thick plate have been included for comparison.

Fig 6.6 demonstrates two sets of the DSC curves of alloy 7150S (S for surface, presented as **black** curves) and alloy 7085 (presented as **red** curves). The two alloys have a similar Cu content, but a different Zn/Mg ratio (2.94 for alloy 7150 versus 5.59 for alloy 7085, in wt%). It is noted that the total precipitation heat of alloy 7085 is smaller than that of alloy 7150S at a given cooling rate. But the precipitation heat values for the medium temperature reaction in alloy 7085 are greater than those in alloy 7150S. It is shown that the onset temperatures for the high temperature reaction are shifted to lower temperatures in alloy 7085.

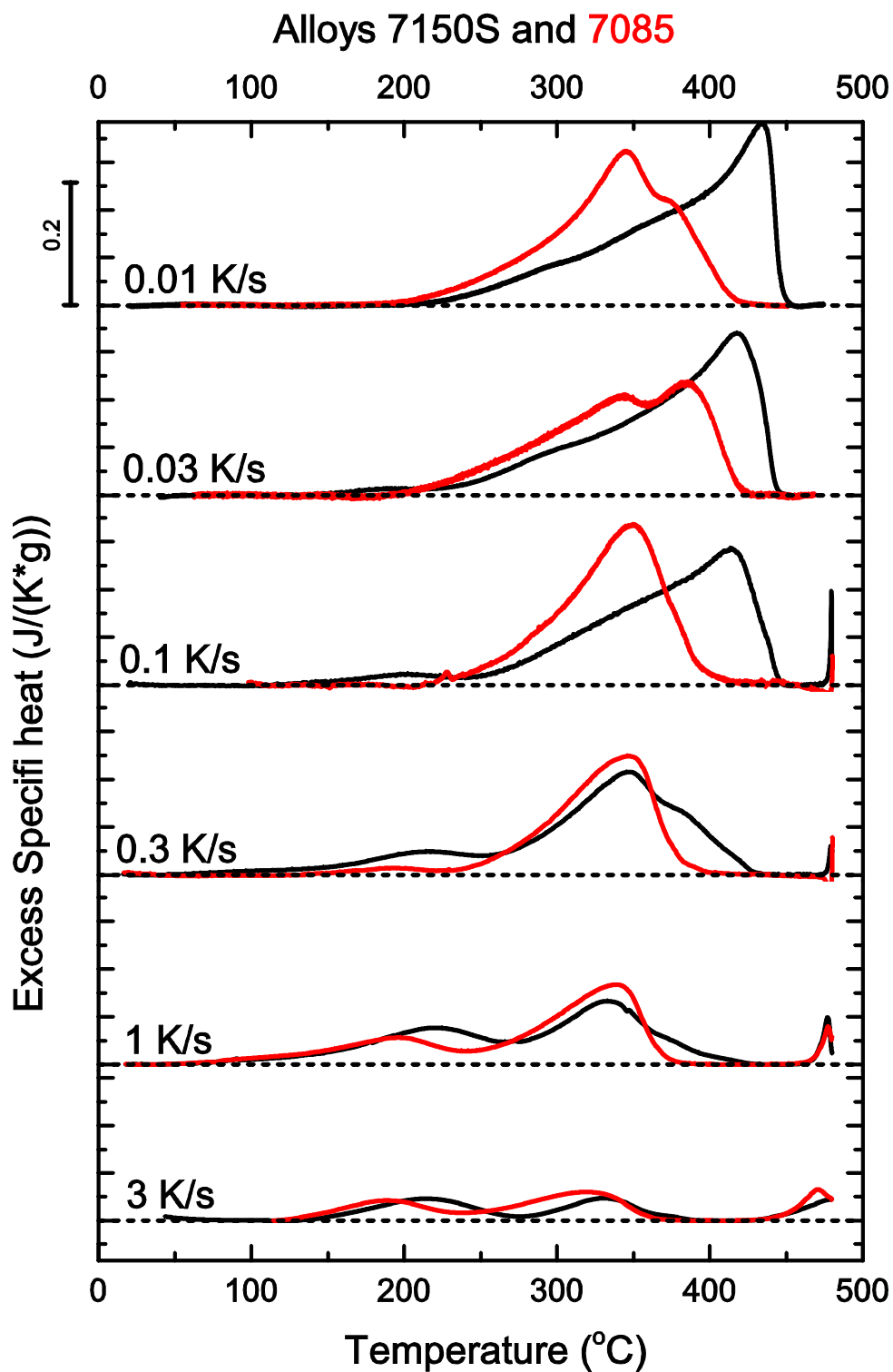


Figure 6.6: A comparison between detected DSC curves for alloys 7150S and 7085 cooled at different cooling rates.

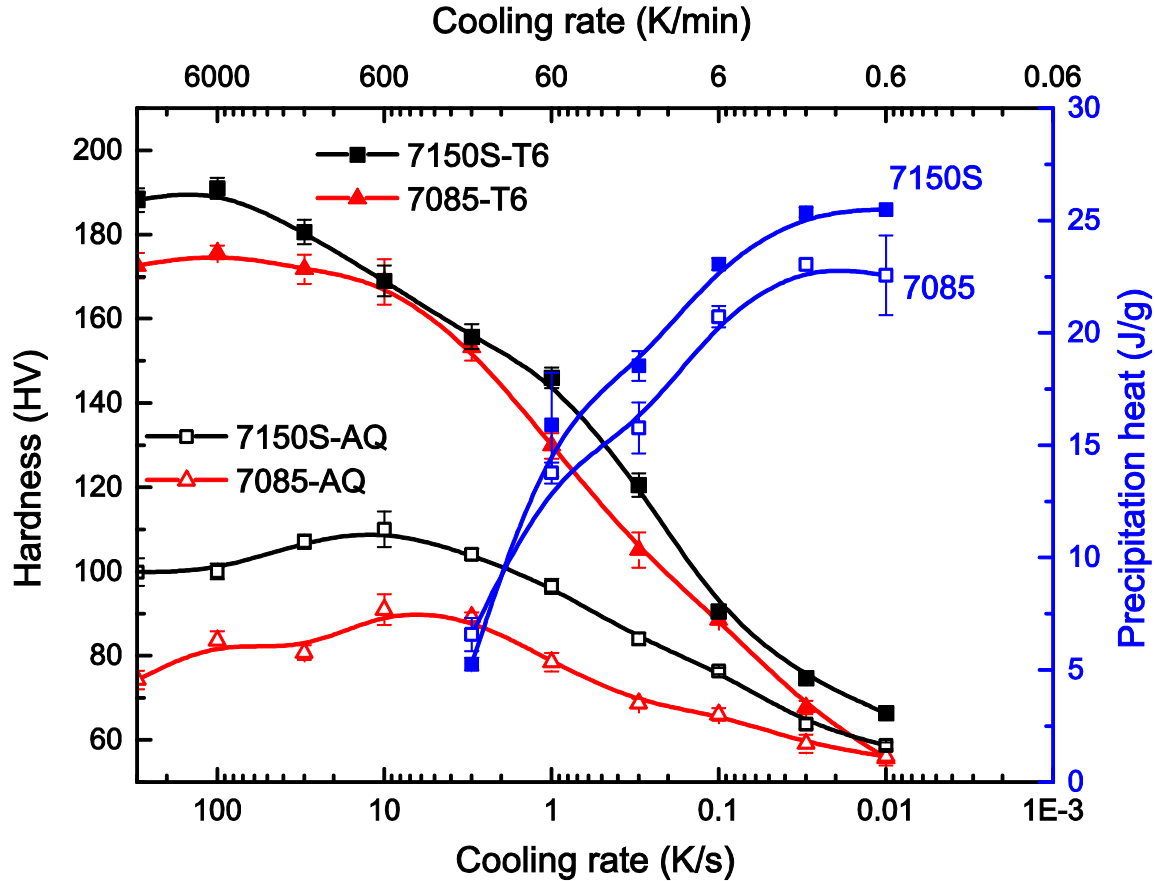


Figure 6.7: Precipitation heat values of the measured DSC curves for both alloys 7150S and 7085. Hardness values for the AQ state and the T6 state (after artificial ageing for 24 hours at 120 °C) have been illustrated.

For example, at the cooling rate of 0.01 K/s, the onset temperature for the high temperature reaction in alloy 7085 is about 410 °C, which is significantly lower than that for alloy 7150S (about 450 °C). There is no significant difference in the onset temperatures for the medium and low temperature reaction for both alloys. The high temperature reaction in alloy 7085 decreases dramatically with increasing cooling rate. It can hardly be detected at cooling rates of ≥ 0.1 K/s. However, there is a slight ‘shoulder’ in alloy 7150S at the cooling rates of 0.3 K/s and 1 K/s, suggesting that there is still an appreciable amount of high temperature reaction occurring in these cooling conditions.

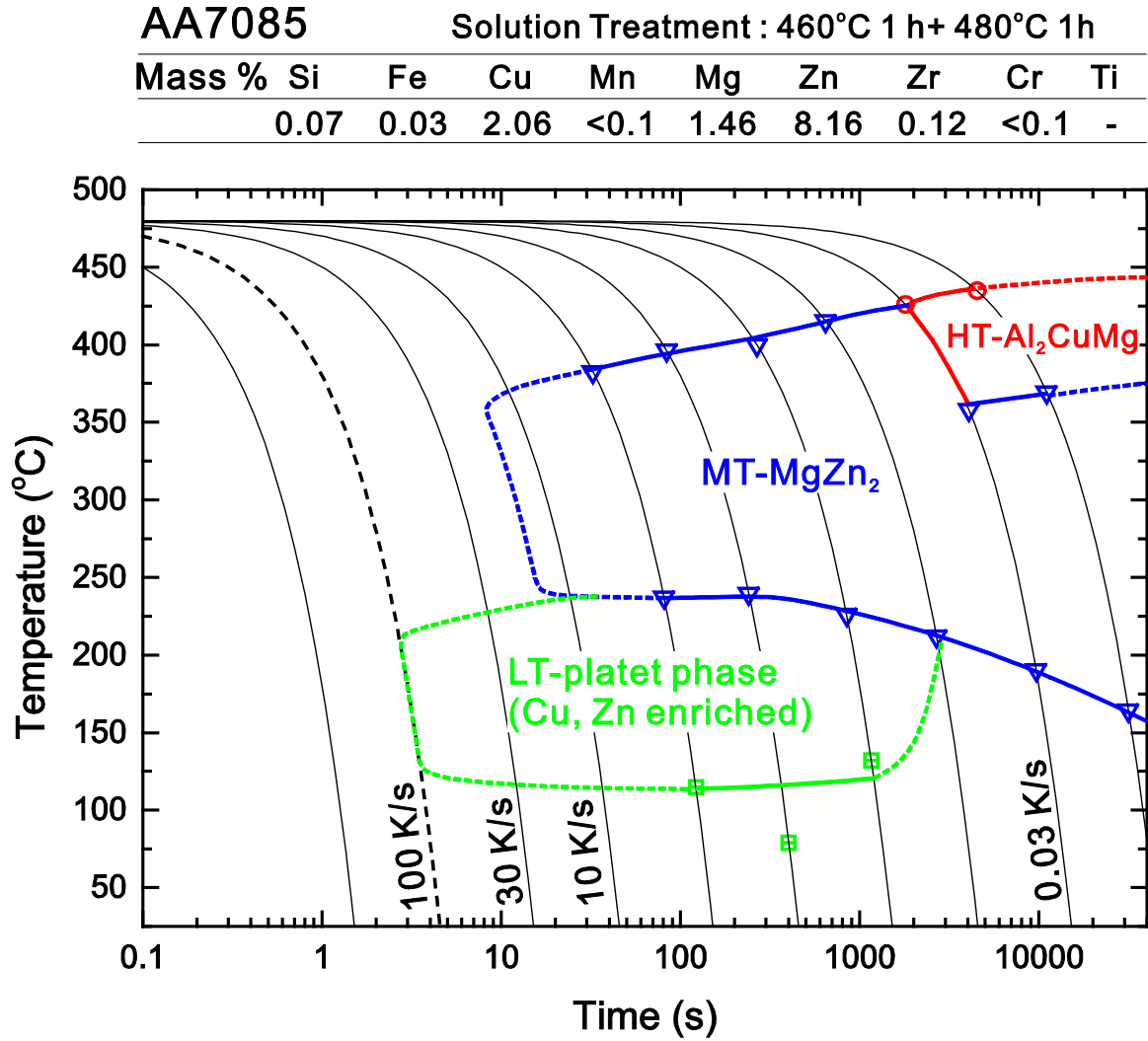


Figure 6.8: Developed CCP diagram for alloy AA7085 after solution treatment, with the dashed lines indicating regions where the precipitation reactions were extrapolated.

The precipitation heat values of the detected DSC curves versus cooling rate have been shown in **Fig 6.7**. It is demonstrated that the precipitation heat for alloy 7085 is lower than that of alloy 7150S. The AQ hardness of alloy AA7085 is significantly lower than that of alloy 7150S. It is evident that the aged hardness values (T6) for both alloys are close to each other in some cooling conditions, suggesting that alloy 7085 has greater age hardening potential than alloy 7150S (i.e. $\Delta HV = HV_{T6} - HV_{T4}$). The AQ hardness curves show that alloy 7085 is less

quench sensitive, as the hardness changes little comparing with the changes in alloy 7150S.

The developed CCP diagram for alloy AA7085 is shown in **Fig 6.8**. It is demonstrated that the Cu-containing precipitate (S-phase and platelet phase) regions are smaller compared to the CCP diagram for alloy 7150 (as shown in **Fig 5.14**). The S-phase reaction happens in very slow cooling conditions (<0.03 K/s). The M-phase is dominating the quench-induced reactions in all cooling conditions over a temperature range of 220-420 °C. The platelet phase can also be detected, but the reaction region is shifted to a lower temperature range (< 220 °C).

6.4. CCP diagram for alloy 7037

Alloy 7037 exhibits attractive property combinations for thick gauge components [198, 199]. For 180 mm thick components, the yield strength of alloy 7037-T7652 is 533 MPa (L), 521 MPa (LT) and 490 MPa (ST) compared with 490 MPa (L), 460 MPa (LT) and 440 MPa (ST) for alloy 7085-T7651 [149, 198]. Alloy 7037-T7652 exhibits higher fracture toughness of $K_{IC}=27 \text{ MPa}\sqrt{m}$ (ST) compared with $K_{IC}=24 \text{ MPa}\sqrt{m}$ (ST) for alloy 7085-T7651. Consequently, the new alloy 7037 is qualified for heavy forgings for airplane applications.

Alloy 7037 contains 7.8-9.0 wt.% Zn compared with 7.0-8.0 wt% Zn for alloy 7085 [197]. Both alloys 7037 and 7085 contain similar amounts of Mg, with 1.3-2.1 wt% for alloy 7037 and 1.2-1.8 wt% for alloy 7085. Alloy 7037 contains much less Cu (0.6-1.1 wt%) compared to alloy 7085 (1.3-2.0 wt% Cu). It is therefore very interesting to find out whether alloys 7037 and 7085 can exhibit different quench sensitivities.

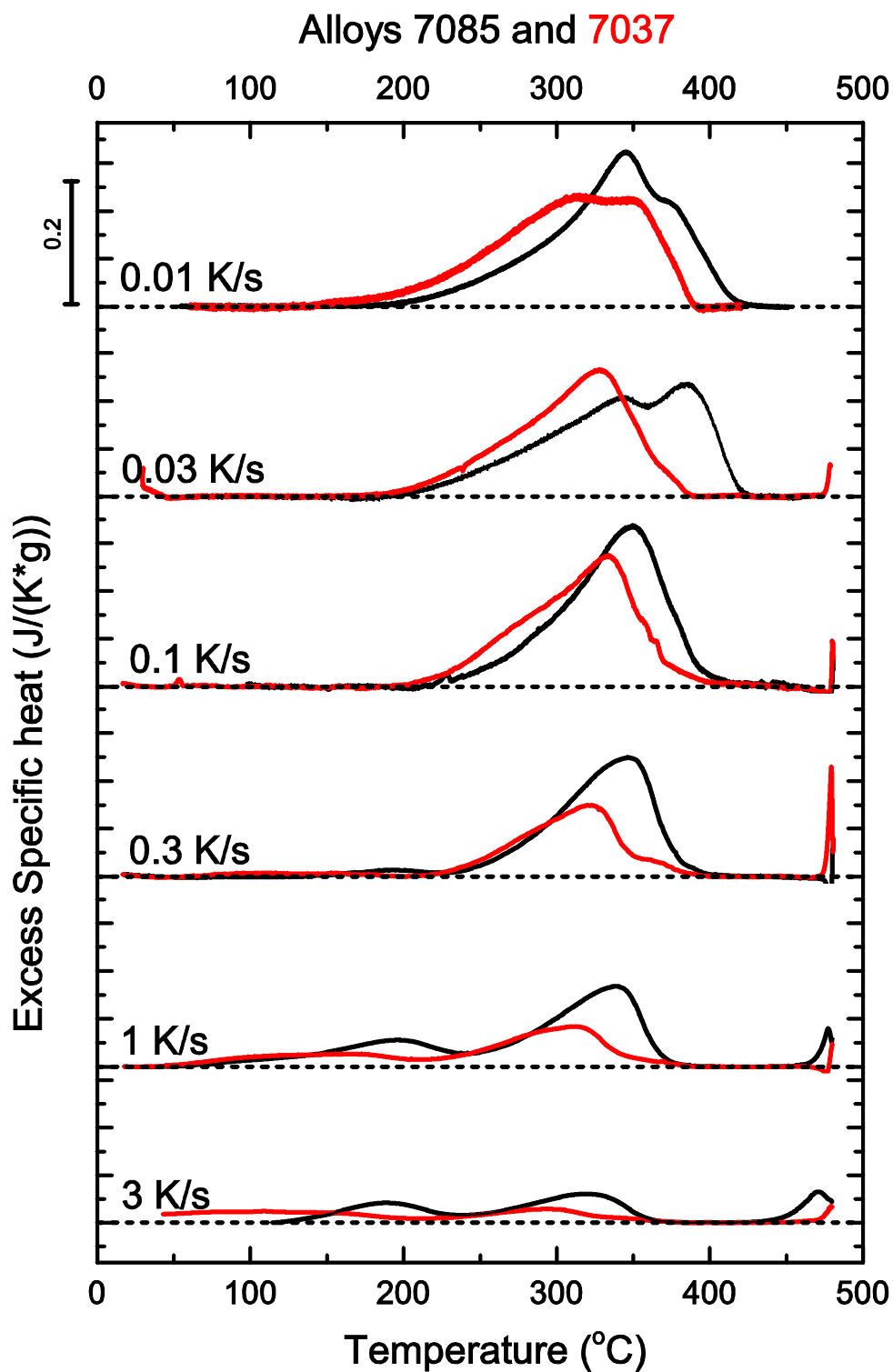


Figure 6.9: A comparison of detected DSC curves for alloys 7085 and 7037 cooled at different cooling rates.

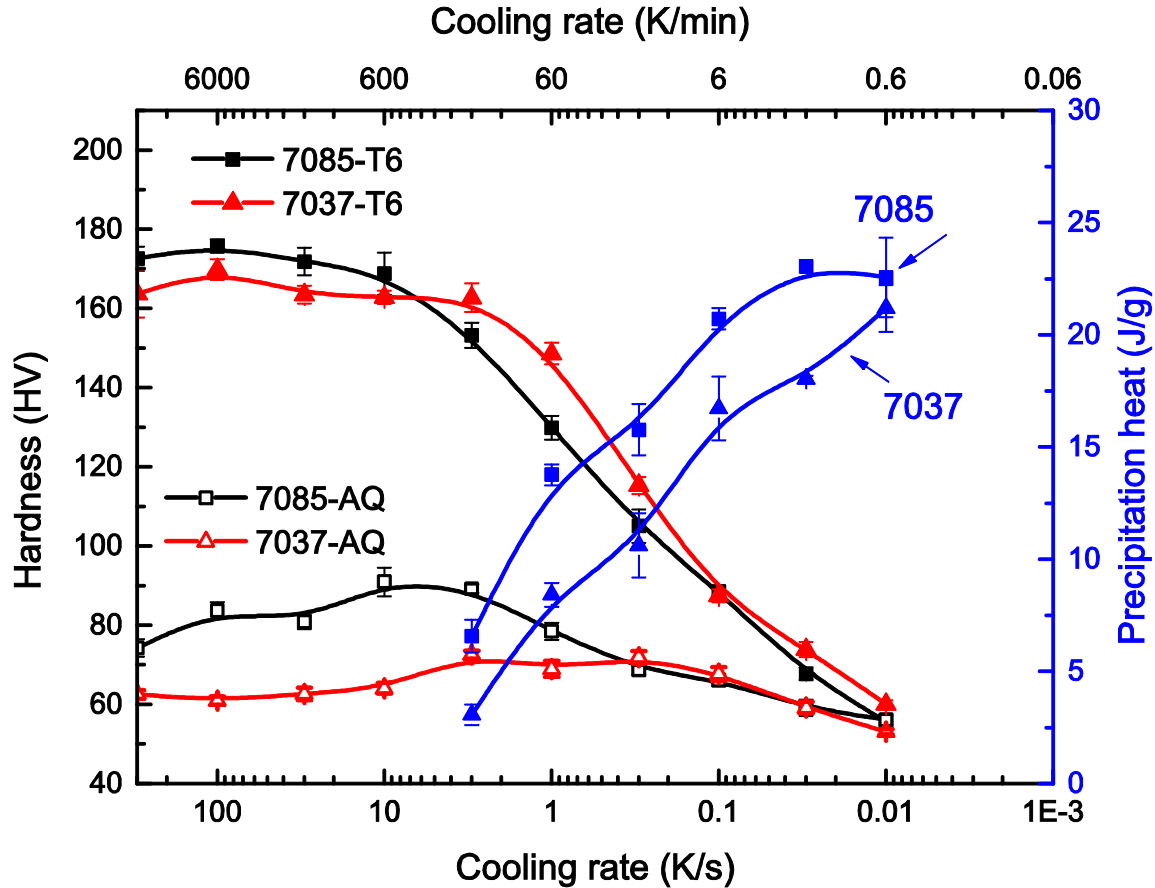


Figure 6.10: Precipitation heat values of measured DSC curves for alloys 7085 and 7037. Hardness curves for the AQ state and the T6 state (after artificial ageing for 24 hours at 120 °C) have been illustrated.

Fig 6.9 shows a comparison of the DSC curves between alloy AA7085 and alloy 7037. It is shown that alloy 7037 always presents a relatively lower specific heat compared to alloy 7085. The high temperature reaction in alloy 7037 can only be found at the cooling rate of 0.01 K/s. The medium temperature reaction can also be found in the temperature range of 200-350 °C in all cooling conditions. It is shown that the onset temperature of high temperature in alloy 7037 is significantly lower than that in alloy 7085. However, there is no significant difference between the onset temperatures for the medium low temperature reactions in both alloys. Nevertheless, the precipitation heat values for the medium and low temperature

reactions in alloy 7037 are lower than those in alloy 7085. It is therefore concluded that alloy 7037 is less sensitive to cooling rate than alloy 7085 in terms of precipitation heat values during continuous cooling. This result is in agreement with previous work by Bryant showing that an increase of Cu content can cause an increased quench sensitivity [64].

The precipitation heat values from the detected DSC curves for alloys 7085 and 7037 have been shown in **Fig 6.10**. It is evident that the precipitation heats for alloy 7037 are lower than those of alloy 7085. At the cooling rate of 3 K/s, the precipitation heat value for alloy 7037 is approaching 0, suggesting that the critical cooling rate for alloy 7037 is close to 10 K/s. There is no significant AQ hardness difference for both alloys at cooling rate of ≤ 0.3 K/s. The AQ hardness values for alloy 7085 become significantly larger than those for alloy 7037 at cooling rates of ≥ 1 K/s. The previous discussion demonstrated that the increment of AQ-hardness at relatively fast cooling rates is ascribed to the precipitation of the platelet phase. The results here are in agreement with the DSC results that amount of low temperature reaction in alloy 7085 is higher than that of alloy 7037. The AQ hardness curve also indicates that alloy 7037 is less quench sensitive, as the hardness value is hardly changed with variations of cooling rate. Therefore the aged hardness for alloy 7037 is significantly increased. On the other hand, the increment of the hardness value for alloy 7085 after ageing is not as much as that in alloy 7037. Based on the precipitation heat and AQ-hardness curves from **Fig 6.10**, it is concluded that alloy 7037 is less quench sensitive.

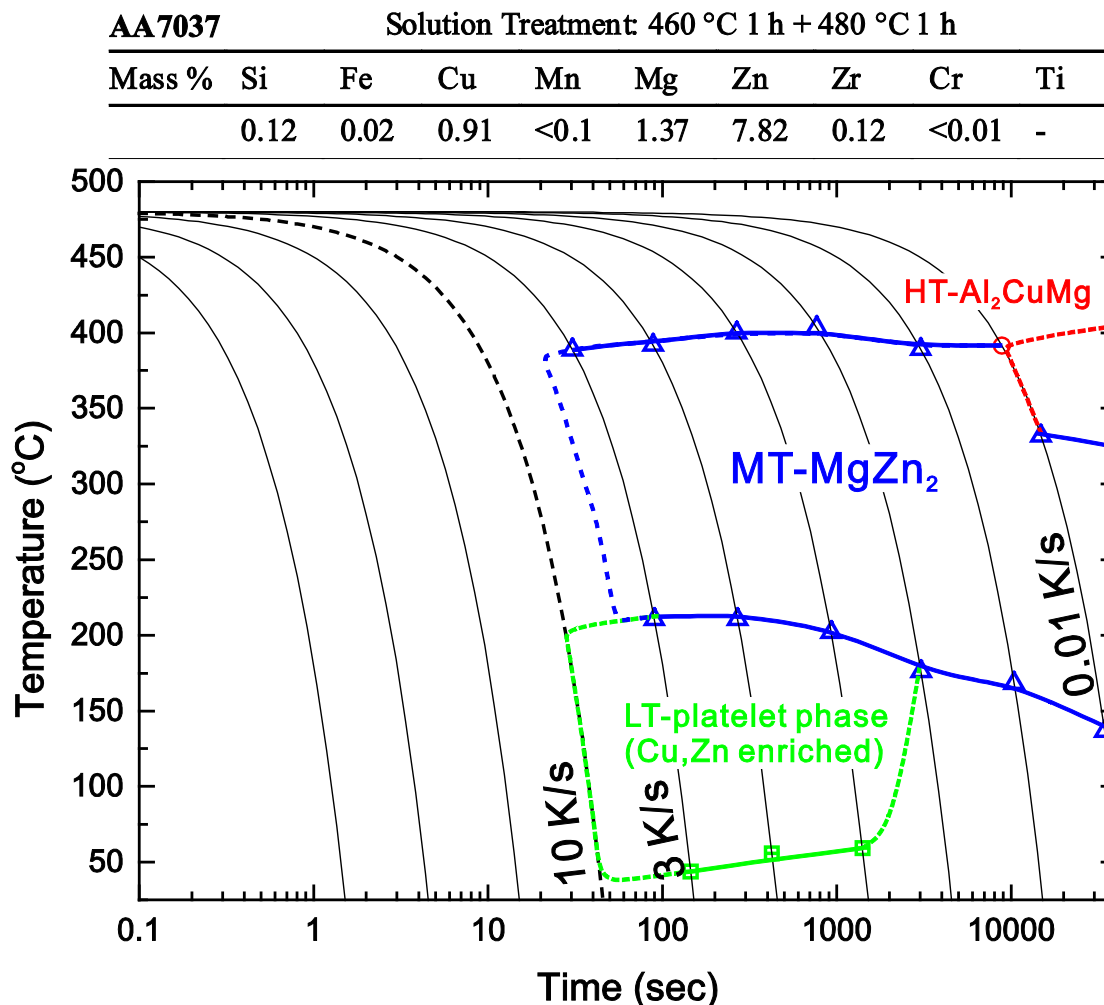


Figure 6.11: Developed CCP diagram for alloy 7037 after solution treatment, with dashed lines indicating regions where the precipitation reactions were extrapolated.

The developed CCP diagram for alloy 7037 is shown in **Fig 6.11**. It is shown that the Cu-containing phase regions (S-phase and platelet phase) are further squeezed. The S-phase is clearly detected at the cooling rate of 0.01 K/s only. The platelet phase can be detected at cooling rates of ≥ 0.3 K/s. It is noted that the platelet phase region is shifted to a lower temperature range (50-200 °C). The M-phase is the main quench-induced precipitate in the temperature range of 200-400 °C.

6.5. CCP diagram for alloy 7055

Fig 6.12 illustrates the comparison of DSC curves of alloys 7150S (presented as **dark** curves) and 7055 (presented as **red** curves). These two alloys have similar Cu and Mg contents, but alloy 7055 contains more Zn (8.12 wt% in alloy 7055 compared to 6.33 wt% in alloy 7150S). As a result, the continuous cooling precipitation heat values for the medium temperature reaction in alloy 7055 are significantly higher. Due to the similar Cu and Mg contents, the precipitation heat values for the high temperature reaction in alloy 7055 are almost the same as those in alloy 7150S. The precipitation heat values for the low temperature reaction in alloy 7055 are slightly lower than those in alloy 7150S in fast cooling conditions (>0.1 K/s) but increase with increasing cooling rate. Overall, the total amount of precipitation for alloy 7055 is larger than that of alloy 7150S. The DSC curves also demonstrate that the onset temperatures for the high temperature reaction are only slightly shifted to a lower temperature range for alloy 7150S than for alloy 7055 (despite similar peak areas). It is therefore concluded that the higher Zn content has little effect on the high temperature reaction.

Fig 6.13 shows the precipitation heat curves and hardness curves for both alloys. It is shown that the precipitation heat values of alloy 7055 are larger than those of alloy 7150S, suggesting that alloy 7055 is more quench sensitive in terms of precipitation heat. The aged hardness values for alloy AA7055 are almost as same as those for alloy 7150S, despite slightly lower AQ hardness values for alloy 7055. The result here shows that although a large amount of medium temperature reaction precipitation has occurred during continuous cooling in alloy 7055, it still contains adequate solute for the subsequent ageing process. It is therefore reasonable to assume that the precipitation of Cu-containing precipitates during continuous cooling may be a critical factor with respect to quench sensitivity.

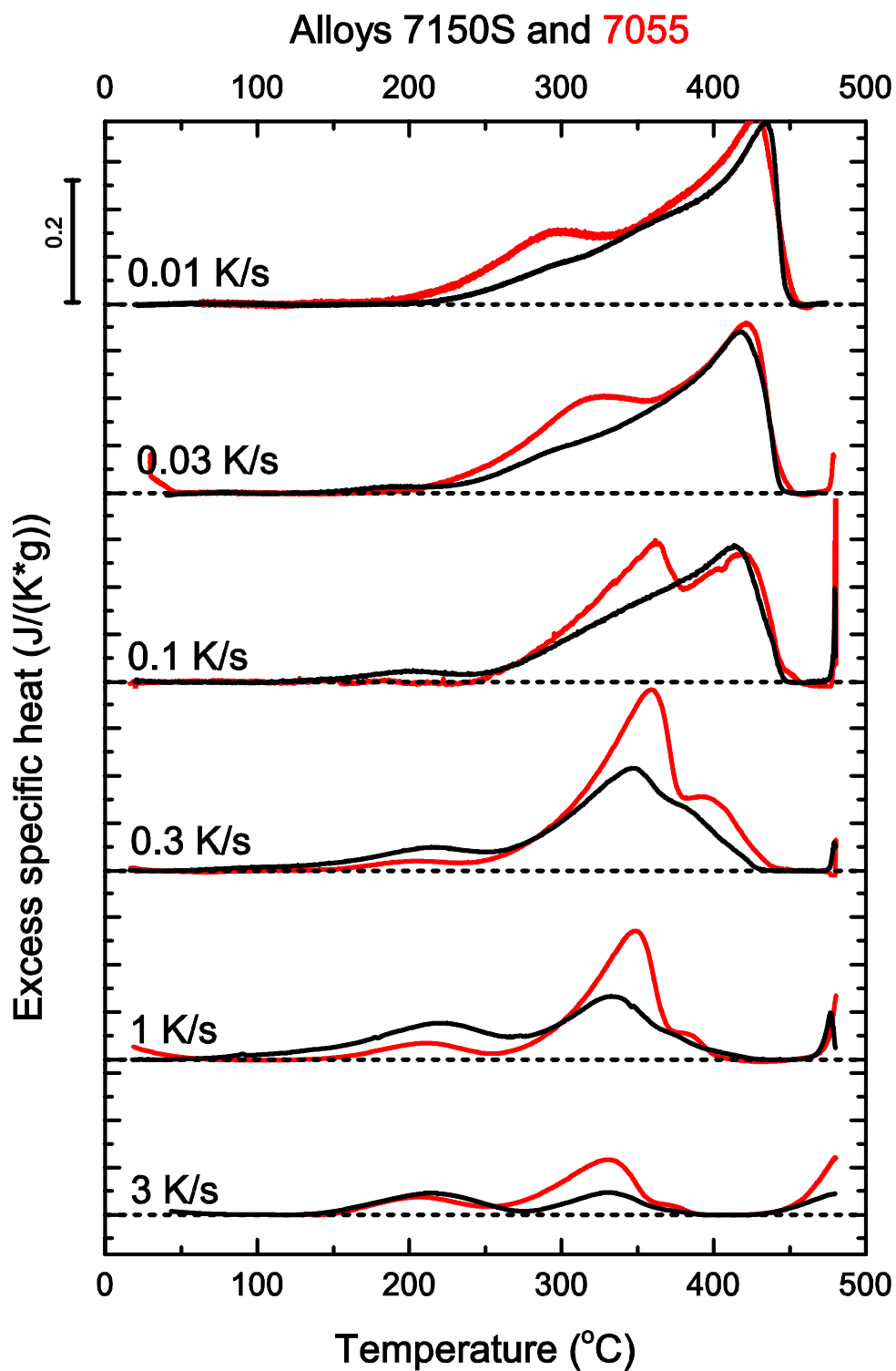


Figure 6.12: A comparison of detected DSC curves for alloys 7150S and 7055 (marked as red) cooled at different cooling rates.

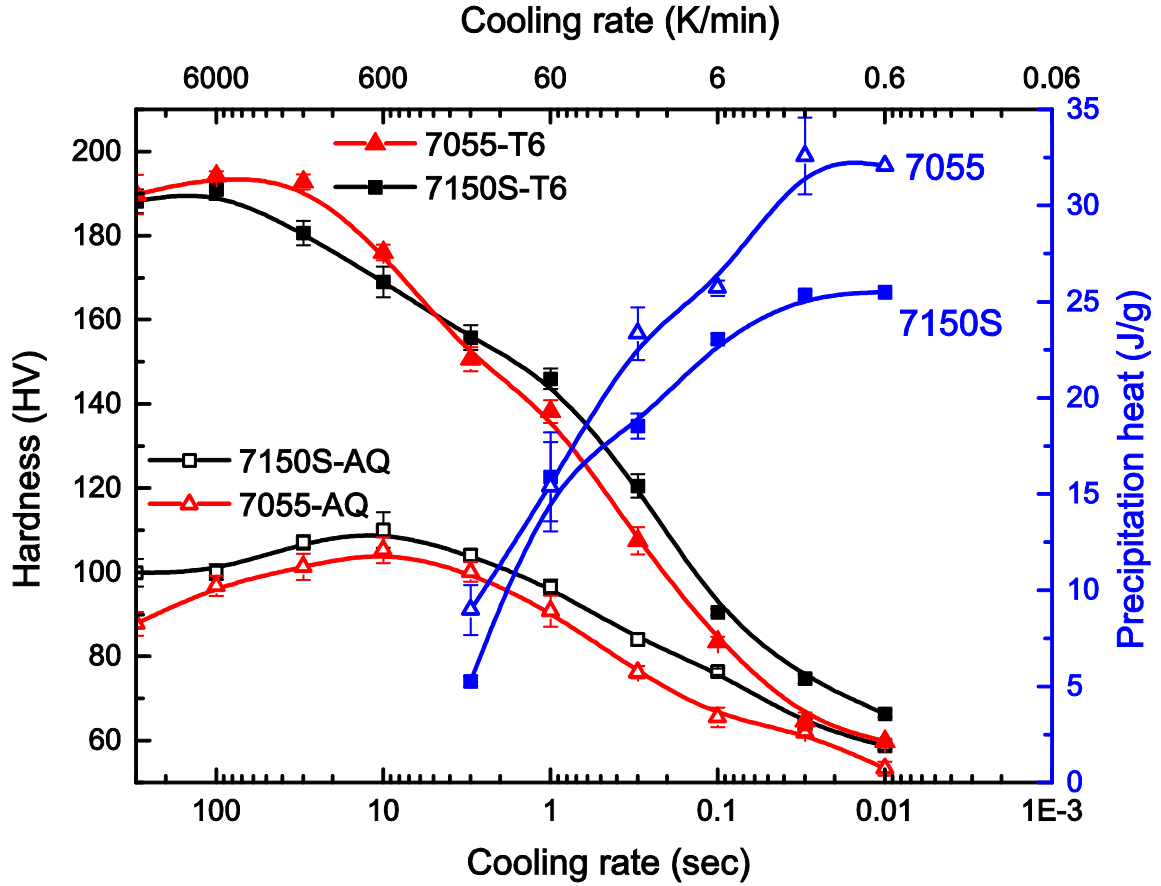


Figure 6.13: Precipitation heat values of measured DSC curves for alloys 7055 and 7150S. Hardness values for the AQ state and the T6 state (after artificial ageing for 24 hours at 120 °C) have been illustrated.

Fig 6.14 shows the constructed CCP diagram for alloy 7055. It looks very similar to the developed CCP diagram for alloy 7150 (as shown in **Fig 5.14**), despite different precipitation heats for different quench-induced reactions in given cooling rate condition. As mentioned earlier, these two alloys have similar Cu and Mg contents, but alloy 7055 has almost 2 wt% more Zn than alloy 7150. This suggests that the Zn content has little effect on changing the onset temperatures of the quench-induced reactions.

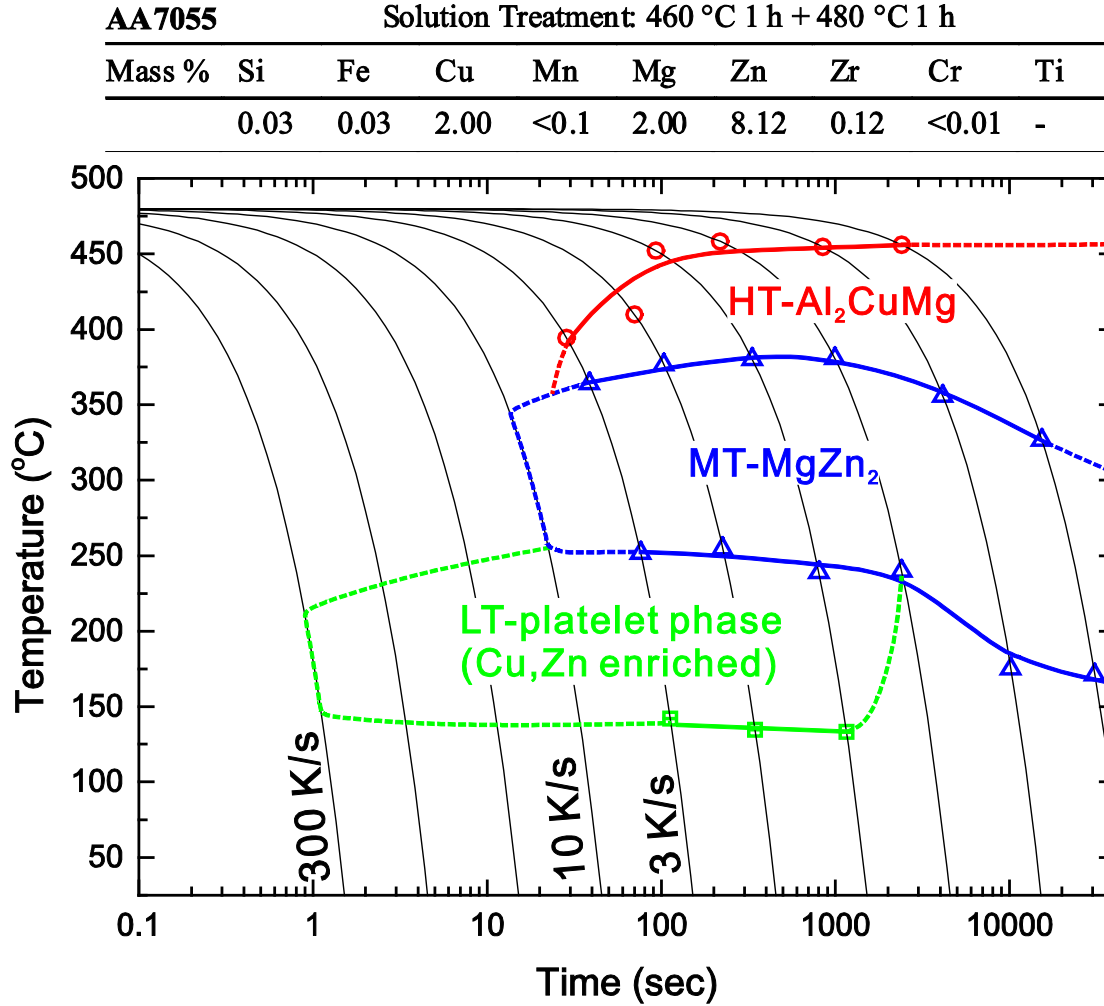


Figure 6.14: Developed CCP diagram for alloy 7055 after solution treatment, with dashed lines indicating regions where the precipitation reactions were extrapolated.

6.6. Quench factor analysis for studied alloys

The previous discussion of CCP-diagrams for the studied 7xxx alloys demonstrates the different quench-induced precipitation reactions during continuous cooling processes. However, for most classical phase transformation theories, isothermal kinetics is preferred as it is easier to be modelled and interpreted. The understanding of non-isothermal transactions, on the other hand, is very useful for industrial applications, which include multiple non-isothermal

heating and cooling processes. A few attempts have been made to extract isothermal information from non-isothermal processes.

Fink and Willey designed a step quenching experiment that cooled the samples to an intermediate temperatures from the solution temperature [108]. The property changes have been tested as an indication of the isothermal phase transformation. By assuming the reaction is isokinetic, the isothermal curve of property changes can be described by C_t :

$$C_t = -k_1 k_2 \exp\left(\frac{k_3 k_4^2}{RT(k_4 - T)^2}\right) \exp\left(\frac{k_5}{RT}\right) \quad \text{Eqn. 6.1}$$

where

k_1 = constant equivalent to $\ln(\text{fraction untransformed during the quench})$,

k_2 = constant related to the reciprocal of the number of nucleation sites,

k_3 = constant related to the energy required to form a nucleus,

k_4 = constant related to the solvus temperature,

k_5 = constant related to the activation energy for diffusion,

R = gas constant = $8.3143 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$,

T = temperature in Kelvin.

Then the changes in a property during continuous cooling can be given by the integral:

$$Q = \int_{t_0}^{t_f} \frac{1}{C_t} dt = \sum \frac{\Delta t}{C_t} = \frac{\Delta t_1}{C_1} + \frac{\Delta t_2}{C_2} + \dots + \frac{\Delta t_{f-1}}{C_{f-1}} \quad \text{Eqn. 6.2}$$

where

Q = quench factor,

C_t = critical time required to change a constant amount of a given property at a given temperature,

t_0 = the time at start of cooling,

t_f = the time at finish of cooling.

A C-curve for a given property, such as yield strength, corrosion resistance or fracture toughness can be obtained from interrupted quenching experiments in which samples are cooled from the solution temperature to different intermediate temperatures (normally higher than the ageing temperature), and held at these intermediate temperatures for different durations. A real C-curve can be plotted by connecting the same fraction of a property transformed with respect to the maximum value of that property in a time-temperature matrix. **Equation 6.1** describes this C-curve and can be obtained by fitting the interrupted quenching data using non-linear regression analysis.

A C-curve for a given property can also be determined by using an iterative approach with hypothetical constants in Equation 6-1 until the predicted results give the best fit of the measured data using an equation such as [138]:

$$\frac{\sigma - \sigma_{\min}}{\sigma_{\max} - \sigma_{\min}} = \exp(k_1 Q^n) \quad \text{Eqn.6.3}$$

where

σ = predicted property

$\sigma_{\min}$ = minimum property attained with very slow cooling rate,

$\sigma_{\max}$ = maximum property attained with very fast cooling rate,

$k_1 = \ln((\sigma_x - \sigma_{\min}) / (\sigma_{\max} - \sigma_{\min}))$, σ_x is the nominal property for a given C-curve,

Q = quench factor,

n = Avrami exponent value that gives the best fit to the experimental data.

According to Evancho and Staley, this equation can help to predict the property changes for different cooling conditions if the cooling paths are incorporated [111, 138]. In order to improve the reliability of the QFA model, different cooling experiments need to be carried out in this case and a wider range of cooling paths is always preferred. The current DSC work shows that a large amount of

continuous cooling experiments have been carried out. Corresponding hardness values and precipitation heat values have also been measured. Therefore QFA can be carried out.

The Avrami exponent value n , according to Christian, varies from 0.5 to 2.5 for different type of diffusion controlled growth [123]. Some other publications suggest that $n = 1$ is a reasonable approximation for wrought aluminium alloys [46, 135]. In the current work on 7xxx alloys, it was found that an n -exponent other than 1 gave the best fitting to the experimental data. However, the n -value was iterated within the range of 0.5 to 1 to minimise the uncertainties that may be caused by changing the n -values too much.

It is evident that **Equation 6.1** contains five different variables, which requires a large number of iterations and may result in covariant random errors. It is therefore common to keep k_4 and k_5 constant at values determined from thermodynamic and published data [100, 126, 136, 200]. In this case, k_4 is fixed for all the studied alloys at the value of the solution temperature, as all the alloys were solutionised at 480 °C (753K). The constant k_5 is fixed at the activation energy for Cu diffusion ($Q_{Cu}=132$ kJ/mol [201, 202]) to form the S-phase (Al_2CuMg). This is because the S-phase is typically the first precipitation reaction during slow cooling, and the kinetics are assumed to be limited by the slowest diffusing species (i.e. Cu diffuses more slowly than Zn and Mg). It should be noted that although the constants k_2 - k_5 are related to different metallurgical entities, their values are not necessarily equivalent to these entities [111]. A number of published TTP diagrams show that k_4 is normally higher than the real solution temperature, and k_5 is normally larger than the value of activation energy for diffusion [108, 111, 128, 132, 136, 137, 200].

The other two variables, k_2 and k_3 , are changed by incorporating continuous cooling curves and detected properties, in this case the hardness value (HV) and

the detected precipitation heat (J/g). Chapter 4 has discussed the nucleation sites for heterogeneous nucleation during the cooling process. It was shown that the grain boundaries, dispersoids-matrix interfaces and dislocations can act as nucleation sites for quench-induced precipitates. These lab-made alloys (7085, 7037 and 7055) were all processed in the same way: they were hot-rolled with the same amount of deformation at the same temperature, the Zr contents are the same, and the solution treatments were performed at the same temperature. For simplicity, it is thus assume that alloys 7085, 7037 and 7055 all have the same k_2 values.

It should be noted that since the maximum hardness value in the T6 temper corresponds to the minimum precipitation heat during continuous cooling, the predicted T6 hardness (HV) and the precipitation heat (ΔH) after continuous cooling are given by:

$$HV = HV_{\min} + (HV_{\max} - HV_{\min}) \cdot \exp(k_1 \cdot Q^n) \quad \text{Eqn 6.4}$$

$$\Delta H = \Delta H_{\max} + (0 - \Delta H_{\max}) \cdot \exp(k_1 \cdot Q^n) \quad \text{Eqn 6.5}$$

It is obvious that the minimum precipitation heat that can be obtained after the cooling process is 0 (i.e. over-critical cooling rate). The root-mean-squared error (RMSE) is calculated to evaluate the differences between values predicted by the QFA model and the detected values. The RMSE is defined as the square root of the mean squared error:

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (X_{\text{obs},i} - X_{\text{model},i})^2}{n}}$$

where

X_{obs} = observed values

X_{model} = modeled values.

The RMSE value can range from 0 to infinity, with 0 indicating a perfect match between modeled and experimental values. The calculated constants and corresponding RMSE values for each alloy are presented in Table 6.1.

Table 6.1: Fitted variables for different 7xxx alloys

99% of Maximum Hardness						
	n	k_2	k_3	k_4	k_5	RMSE
7150S	0.55	5.32e-15	1861	753	132000	7.9
7020	0.68	9.57e-13	1513	753	132000	3.5
7055	0.60	9.05e-15	1962	753	132000	5.5
7085	0.69	9.05e-15	2430	753	132000	6.4
7037	0.60	9.05e-15	2327	753	132000	7.0
1% of Maximum Precipitation Heat						
	n	k_2	k_3	k_4	k_5	RMSE
7150S	0.55	5.32e-15	1765	753	132000	0.55
7020	0.68	9.57e-13	1476	753	132000	0.70
7055	0.60	9.05e-15	1892	753	132000	1.50
7085	0.69	9.05e-15	1615	753	132000	1.12
7037	0.60	9.05e-15	2148	753	132000	1.22

Although the constants for each alloy in **Table 6.1** are not necessarily very meaningful in themselves, a comparison of relative changes from alloy to alloy may provide some clues about the underlying mechanism causing different quench sensitivities for different alloys. Since k_4 and k_5 have been fixed in this work, it is anticipated that the QFA model will provide information about how nucleation sites and the activation energy to form a nucleus could influence the quench sensitivity behaviour of an alloy. It should also be emphasised that the nucleation

sites saturate early on in the continuous cooling reaction. As a result, k_2 should be constant regardless of which property is being considered.

A comparison of k_2 and k_3 for the different alloys listed in **Table 6.1** reveals that alloy 7150S has a similar k_2 value when compared with alloy 7055, 7085 and 7037, suggesting that alloy 7150S has a similar number of nucleation sites. It is shown that alloy 7020 has fewer nucleation sites. This is mainly due to 7020 having different dispersoids and a different grain structure since it was extruded while the other alloys were hot-rolled. Higher k_3 values were obtained for alloys 7055, 7085 and 7037, suggesting that the energy required to form a nucleus is higher in these alloys. It is known from **Table 3.1** that these three alloys have relatively higher Zn/Mg ratios. Especially for alloys 7085 and 7037, the Zn/Mg ratio exceed 5 (in wt.%). The other two alloys, 7150 and 7020 have lower Zn/Mg ratios and may therefore exhibit lower k_3 values.

Fig 6.15 (a) shows the time-temperature property (TTP) curves related to hardness values for the different alloys as predicted by QFA. It is shown that the noses of the TTP diagrams (99% of maximum hardness) for alloys 7150 and 7055 occur at shorter times than those for the other alloys. The TTP diagram (99% of maximum hardness) for alloy 7020, on the other hand, exhibits a longer nose time. Therefore it is concluded that alloy 7020 is less quench sensitive than any of the other studied alloys. According to QFA, this is because there are less nucleation sites for quench-induced precipitates in alloy 7020 (large k_2 value for alloy 7020).

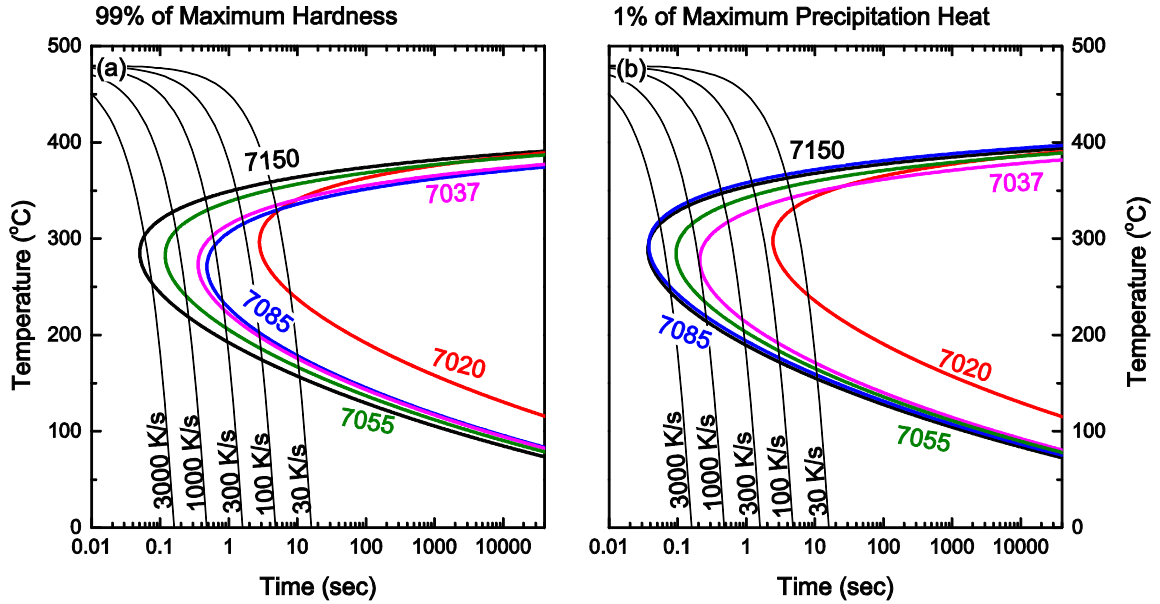


Figure 6.15: Predicted TTP curves based on (a) T6 hardness and (b) precipitation heat after continuous cooling for different 7xxx alloys.

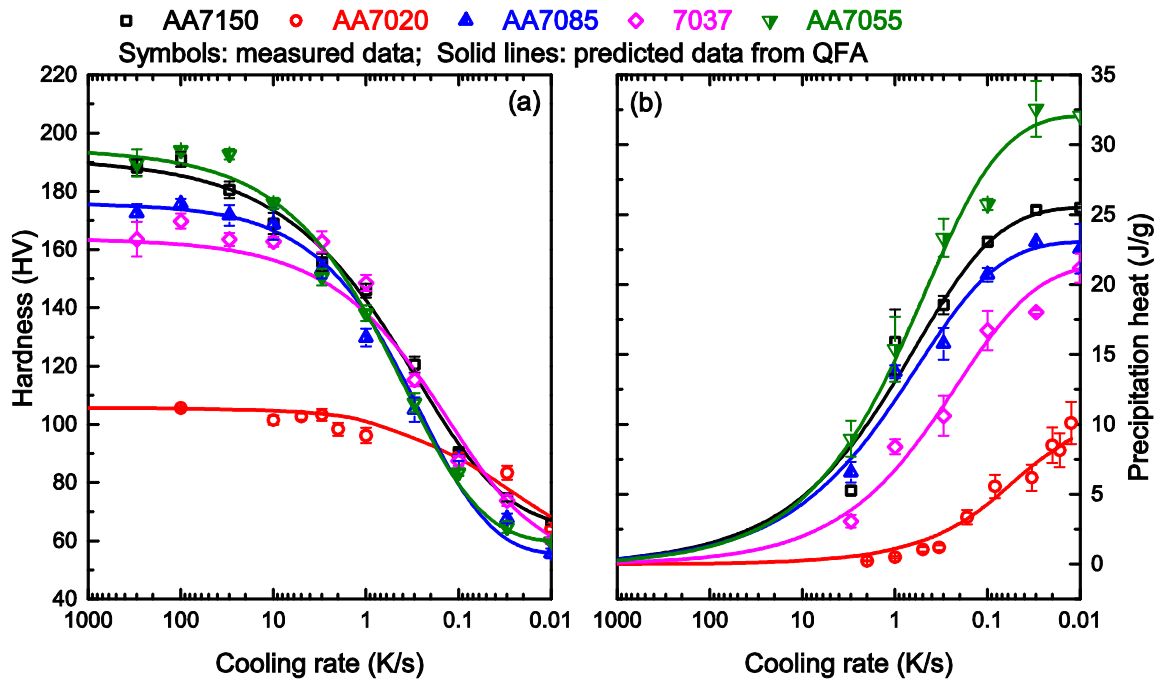


Figure 6.16: Comparison of QFA model predictions (curves) and experimental data (symbols) for the different alloys presented as (a) T6 hardness vs. cooling rate and (b) precipitation heat vs. cooling rate.

The TTP diagrams (99% of maximum hardness) for alloys 7085 and 7037 are located in between alloys 7055 and 7020 in **Fig 6.15** (a). Therefore alloys 7085 and 7037 are less quench sensitive when compared with alloys 7150 and 7055. However, there is no significant difference in quench sensitivity between alloys 7085 and 7037.

Fig 6.15 (b) shows the TTP curves (predicted by QFA) related to precipitation heat after continuous cooling for the studied alloys. These diagrams were calculated by iterating only the k_3 value and using the constant k_2 values that had been fitted for the hardness values. It is shown that all the TTP diagrams (1% of maximum precipitation heat) are shifted to shorter nose times with decreasing k_3 values. This is in agreement with the fact that the changes in precipitation heat are more sensitive to cooling rate than changes in hardness. **Fig 6.16** exhibits a comparison of QFA model predictions and experimental data (T6 hardness values and overall precipitation heat values) for different alloys. It is shown that either way, the predicted data by the models are relatively close to the experimentally determined data, suggesting that the model predictions are applicable to alloys in T6 hardness and precipitation heat during continuous cooling.

It is also evident that alloys 7085 and 7150 are the most quench sensitive alloys with respect to precipitation heat. This due to the fact that more medium temperature reaction (M-phase) has been precipitated out during continuous cooling in this alloy (as shown in **Fig 6.6**). The predicted TTP curves mainly cover the temperature range of M-phase precipitation (200 - 400 °C). The high temperature precipitation and platelet phase precipitation are less considered in this case since this form of QFA only predicts one overall C-curve. Therefore it would be more reasonable for QFA to be applied for precipitation heat values for each separated reaction. It is noted that the precipitation heat values are measured based on the peak separation method that defines the intersection points between two overlapping peaks as the onset temperatures for the lower temperature

reaction and the finishing temperatures for the higher temperature reaction (see chapter 3). It has been shown that many of the quench-induced reactions are heavily overlapped. For example, the start temperature of the M-phase is overlapping with the S-phase reaction at higher temperatures, so that the defined onset temperature of the M-phase is lower than the real onset temperature. On the other hand, the finishing temperature of the M-phase overlaps the low temperature reaction, causing a higher finishing temperature to be judged in this case. As a result, the overall reaction range of the M-phase is narrower due to the peak separation method that was used in this work. In order to better understand the phase transformations occurring during continuous cooling, a more sophisticated peak separation method is needed to determine the real onset/finish temperatures for each reaction. This is left for future work, along with the potential prediction of separate TTP curves for each reaction (by QFA) that should become feasible after a more sophisticated peak separation method has been implemented.

6.7. Discussion of quench sensitivity of studied 7xxx series alloys

The CCP diagrams for different 7xxx alloys have been presented in this chapter. It was demonstrated that for the studied high strength 7xxx series alloys, 7150, 7085, 7037 and 7055 all contain three different quench-induced reactions. Alloy 7020 only contains two main quench-induced reactions. Due to the different alloy compositions, the quench-induced precipitation reaction regimes vary as demonstrated through the developed CCP diagrams.

Fig 6.17 shows the designed alloys in the form of a Zn/Mg ratio vs. Cu content graph, and a Mg vs. Zn content graph. It is shown in **Fig 6.17** (a) that the 7085, 7055 and 7150 compositions designed for this work all have the same Cu content, but their Zn/Mg ratios are different. Alloys 7037 and 7085 have a similar Zn/Mg ratio but alloy 7037 has less Cu. **Fig 6.17** (b) shows that alloys 7055, 7085 and 7037 have similar Zn contents while alloy 7055 has more Mg than the other two

alloys. Alloys 7150 and 7055 have similar Mg contents but 7150 has less Zn. Alloy 7020 contains much less Cu, Mg and Zn when compared with the other studied 7xxx series alloys. Therefore alloy 7020 has the lowest total alloying content among all the studied alloys. There are two other conventional 7xxx alloys (namely alloys 7075 and 7050) that are marked in **Fig 6.17** for reference. Overall, the main purpose of this alloy design work was to explore the effects of Zn/Mg ratio and Cu content on the quench sensitivity of 7xxx series alloys.

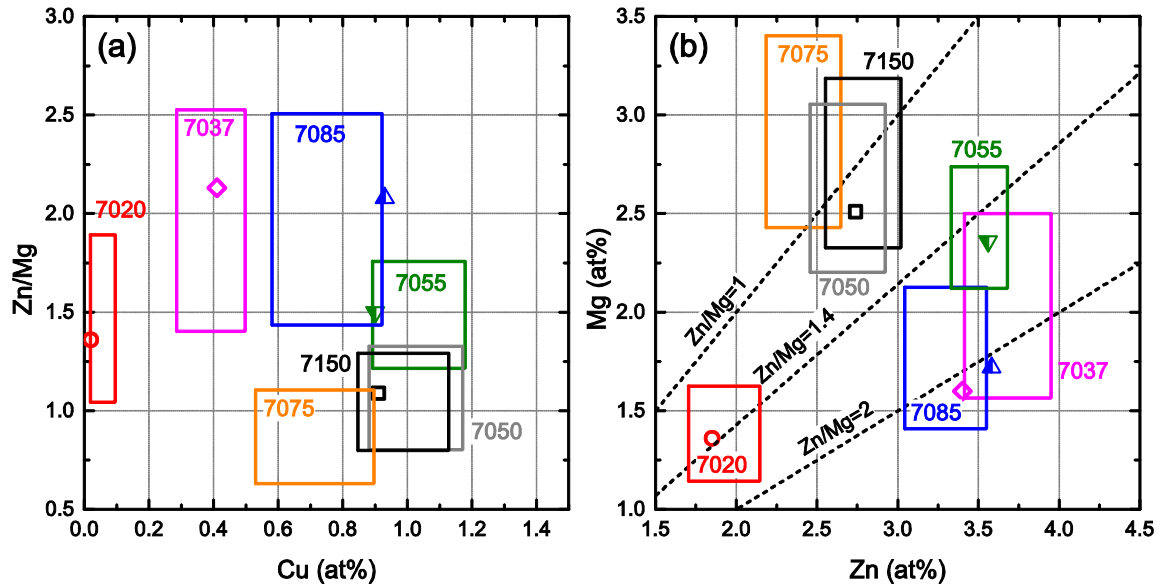


Figure 6.17: Alloy design overview of the studied alloys in the form of (a) Zn/Mg ratio vs. Cu content graph and (b) Mg vs. Zn content graph. Another two common 7xxx alloys (namely AA7075 and AA7050) have been included for comparison. The rectangular boxes show the nominal composition limits for the different alloys.

It was demonstrated that the quench sensitivity in terms of precipitation heat values generally increases with increasing total alloy content. Therefore alloy 7020 exhibits the lowest quench sensitivity in terms of both hardness values (as shown in **Fig 6.16** (a)) and precipitation heat values (as shown in **Fig 6.16** (b)) compared to the other studied alloys. This is consistent with classical theory, as an increase of total alloying content will increase the total amount of solute

supersaturation during quenching and hence the driving force for precipitation [167].

For the other studied high strength 7xxx alloys with similar total alloying content (about 6 at% or about 11 wt%), the quench sensitivity may depend on the Zn/Mg ratio, the Mg content and/or the Cu content. Moreover, the quench sensitivity behaviour will also be affected by the number of nucleation sites and the thermo-mechanical processing history (see Chapters 4 and 5).

The Zn/Mg ratio has been shown to be a critical factor affecting the quench sensitivity of alloys having similar amounts of total alloying contents. Lim *et al* studied the effects of Zn/Mg ratios on the quench sensitivity of alloy 7175 (a purified version of alloy 7075 with lower Fe and Si content). They found more heterogeneous M-phase precipitates in the lower Zn/Mg ratio alloys [60]. However, their studied alloys are within a limited range of Zn/Mg ratios of about 2-3% (in wt%). **Fig 6.17** (b) shows that the more traditional 7xxx series alloys 7075, 7050 and 7150 have relatively low Zn/Mg ratios (about 3 in wt% or about 1 in at%). The more newly developed 7xxx alloys 7085 (registered in 2002) and 7037 (registered in 2006) have relatively higher Zn/Mg ratios (about 5 in wt% or about 2 in at%). Although alloys 7085 and 7037 are specifically designed for thick products, it still shows a trend in modern 7xxx series alloy design. The higher Zn/Mg ratios in these alloys are achieved by increasing the Zn content to about 8% in wt% (about 3.5% in at%), accompanied by decreasing the Mg content to about 1.5% in wt% (about 1.7% in at%). Therefore there are more Zn atoms available to form MgZn_2 , which results in a more significant M-phase precipitation during cooling. It is shown in **Fig 6.18** that the maximum precipitation heat (J/g) for M-phase is increasing with increasing Zn content. It is demonstrated that alloy 7085 (8.16 wt% Zn) exhibits a higher precipitation heat for the M-phase than any other studied alloy. Alloy 7020 exhibits the lowest precipitation heat for the M-phase as it has the lowest Zn content (4.37 wt% Zn).

It is also shown in **Fig 6.18** that, for all the high strength alloys, the precipitation heats for the M-phase first increase with increasing cooling rate then drop dramatically with increasing cooling rate after reaching their maximum values. The precipitation heat values for the medium strength alloy 7020, however, show a monotonically decreasing trend with increasing cooling rate. This is due to the precipitation of S-phase in the high strength alloys (as shown in **Fig 5.6**) but not in 7020. It is shown that the precipitation of the M-phase is suppressed by the prior precipitation of the S-phase in slow cooling conditions (< 0.1 K/s). The detected DSC curves show that the S-phase reaction peak values are always greater than those of any other reactions in the slow cooling conditions, and that M-phase precipitation becomes more significant when the S-phase precipitation is suppressed at more rapid cooling rates. This effect is more dramatic in the higher Zn alloys since their atomic Zn/Mg ratios are close to the stoichiometry of the M-phase (i.e. MgZn_2). Any prior precipitation of S-phase (Al_2CuMg) would therefore consume Mg and reduce the amount of M-phase that can be formed.

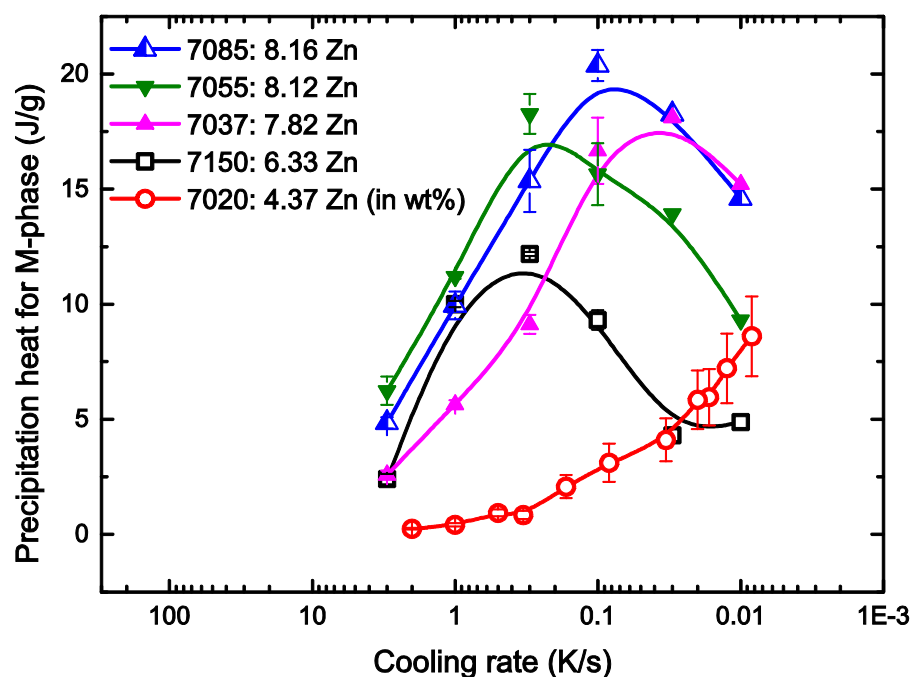


Figure 6.18: Detected precipitation heat values for M-phase in the different studied alloys.

Fig 6.19 shows the precipitation heat values for the S-phase reaction in the high strength alloys. It is shown that the precipitation of S-phase mainly happens in slow cooling conditions for all the studied high strength 7xxx alloys. There is no S-phase reaction in the medium strength alloy 7020, as the Cu content in this alloy is very limited (only about 0.04 wt%). It is shown that the amount of S-phase at a given cooling rate decreases significantly with increasing Zn/Mg ratio. As a result, alloys 7085 and 7037 with higher Zn/Mg ratios exhibit relatively smaller S-phase precipitation heats than the lower Zn/Mg ratio alloys 7150 and 7055. The result is in agreement with some publications that only fine M-phase precipitates can be found in high Zn/Mg ratio alloy 7085, while both M-phase and S-phase can be found in low Zn/Mg ratio alloy 7050 [109, 196]. **Fig 6.19** shows that the precipitation of S-phase in high Zn/Mg ratio alloys happens in very slow cooling conditions and in very limited amounts. However, it is shown that there is a much larger amount of S-phase precipitates in the low Zn/Mg ratio alloys for the same cooling conditions.

The results here demonstrate that the precipitation of S-phase can be suppressed by increasing the Zn/Mg ratio. The QFA model also demonstrates a higher k_3 value can be found in the high Zn/Mg ratio alloys 7085 and 7037, suggesting that the energy required to form a nucleus is higher in these two alloys (as shown in **Fig 6.20**). In other words, the precipitation of different phases becomes harder with higher Zn/Mg ratio. The detected DSC curves demonstrate that the onset temperature for S-phase precipitation is shifted to an even lower temperature range in alloys 7085 and 7037 (as shown in **Fig 6.20**). However, the onset temperatures for the M-phase and platelet phase have not been changed significantly.

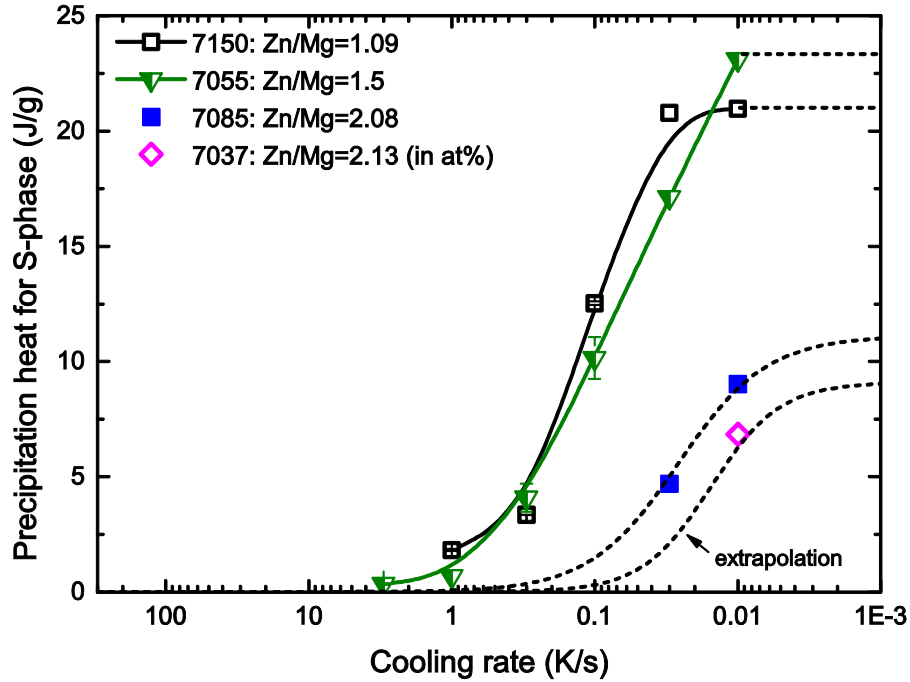


Figure 6.19: Detected precipitation heats for the S-phase in the high strength alloys. Alloy 7020 is not included as there is no S-phase reaction in this alloy.

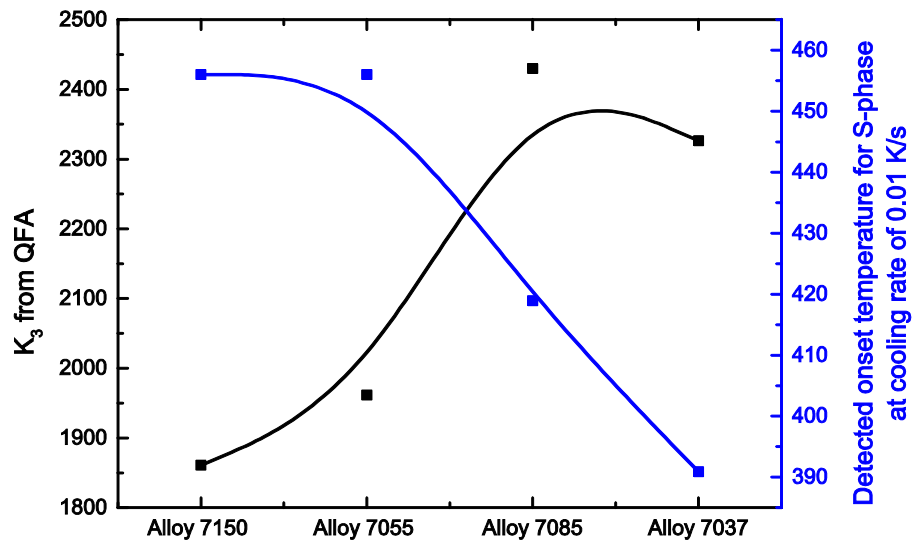


Figure 6.20: Variations in k_3 value and detected onset temperature for S-phase precipitation in the different alloys.

Fig 6.21 shows calculated equilibrium phase diagrams for Al alloys based on 6 wt%Zn, 2 wt%Mg and 2 wt%Cu. The solution temperature for the current study was 480 °C. It is demonstrated that the solvus temperature for the S-phase is decreasing with increasing Zn content (as shown in **Fig 6.21** (a)). Within the Zn content range of 6-8 wt%, the solvus temperature has been slightly decreased. This is in agreement with the result in **Fig 6.12**, that the higher Zn content alloy 7055 exhibits a slightly higher onset temperature for S-phase precipitation than the lower Zn content alloy 7150.

Decreasing the Mg content within the range of 1-2.5 wt% causes a significant decrease in the solvus temperature for S-phase. Therefore the S-phase solvus temperatures in high Zn/Mg ratio alloys 7085 and 7037 are expected to be lower than those in alloys 7150 and 7055. Moreover, the onset temperature of S-phase precipitation occurs at lower temperature in alloys 7085 and 7037 and less S-phase precipitation occurs in these alloys (compared to alloys 7150 and 7055) since the rate of Cu diffusion becomes increasingly sluggish at lower temperatures. **Fig 6.21** (c) demonstrates that reducing the Cu content can also decrease the solvus temperature for the S-phase. This is in agreement with the DSC detection results that the onset temperature for the S-phase is lower in the low Cu content alloy 7037 than in the high Cu content alloy 7085. It is noted that no S-phase should precipitate out during continuous cooling at Cu content below 1.2 wt%, as shown in **Fig 6.21** (c). There are only M-phase and/or T-phase regions below the solvus temperature for such alloys. Therefore, the high temperature reaction in alloy 7037 may actually correspond to T-phase ($\text{Al}_2\text{Mg}_3\text{Zn}_3$), but it is still referred to as S-phase precipitation until further proof is obtained.

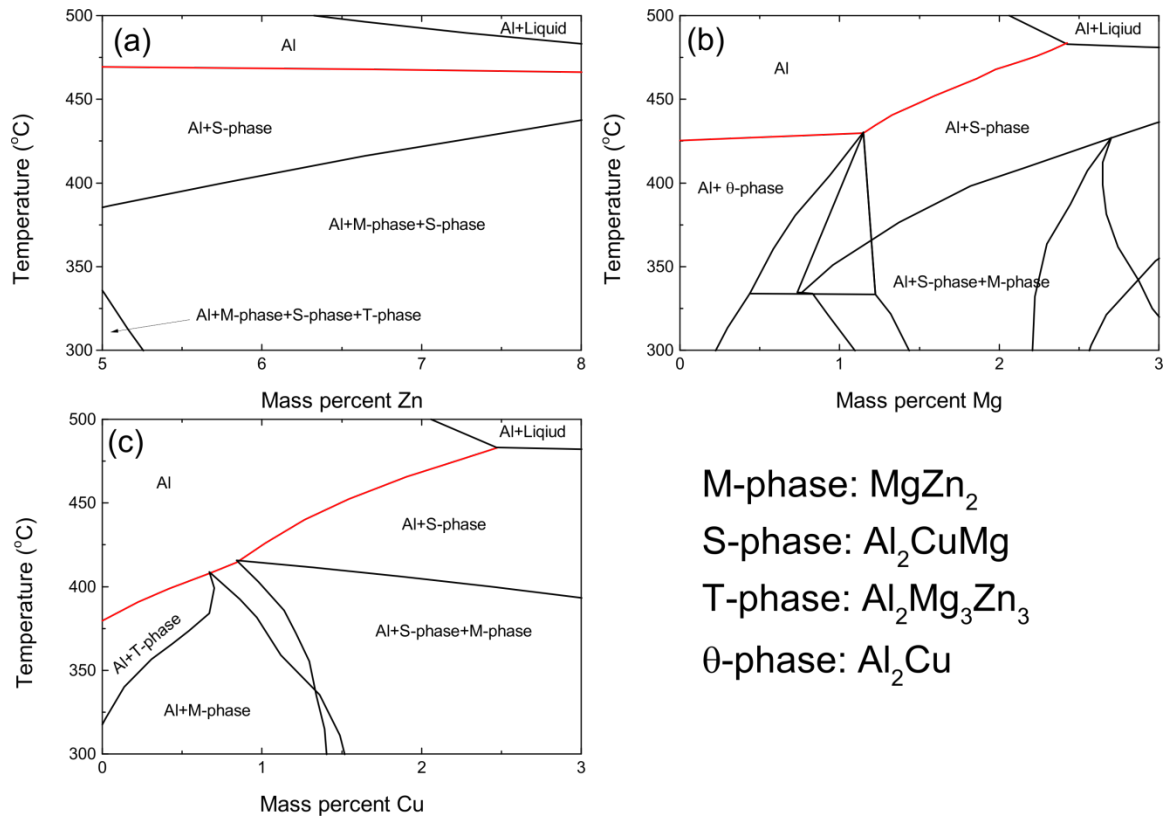


Figure 6.21: Calculated phase diagrams for Al alloys based on 6 wt%Zn, 2 wt%Mg, 2 wt%Cu, showing how the various solvus temperatures change with different major alloying additions. The diagrams have been predicted using Thermocalc (TCAL2 database).

The results here confirm that the quench sensitivity can be decreased by increasing the Zn/Mg ratio. However, with increasing Zn content, the amount of M-phase precipitation is significantly increased, as shown in **Fig 6.18**. Therefore the high Zn content alloy 7085 is the most sensitive to cooling rate in terms of M-phase precipitation (as shown in **Fig 6.18**). Due to the suppression of S-phase precipitation in the high Zn/Mg ratio alloys, more Cu may be preserved in solution (as shown in **Fig 6.19**). According to Deschamps *et al*, the addition of Cu may affect the precipitation kinetics of 7xxx series alloys. They proposed that the addition of Cu could increase the strengthening ability of the precipitates [68]. This is in agreement with the result that the low Cu content alloy 7037 exhibits

lower hardness values in the T6 state when compared with the high Cu content alloy 7085 in the fast cooling conditions (as shown in **Fig 6.10**). Fang *et al* proposed that the Cu in solution can be used as substitute atoms for age hardening precipitates [59, 69]. Moreover, such Cu-containing precipitates are more thermally stable compared with Cu-free precipitates, due to a relatively lower diffusivity of Cu atoms compared with Mg and Zn atoms in an Al matrix [59, 69]. Mondolfo demonstrated that there is a tendency for Cu atoms to form S-phase rather than participate in age hardening precipitation when the Cu content is above 2.5 wt% [58]. Therefore, although a large amount of solute has been lost due to the formation of M-phase in high Zn/Mg ratio alloys, the remaining Cu in solution may have an important role to play during subsequent ageing.

The current work demonstrates that Cu in solution can also contribute to the formation of the platelet phase at temperatures of about 200 °C (as shown in **Fig 5.16**). However, there are still some uncertainties related to this newly discovered phase. For example, the exact composition and the nucleation sites for this platelet phase are not yet known. Moreover, the detected DSC curves show that the precipitation heat of this platelet phase increases with increasing cooling rate in a relatively fast cooling rate range (as shown in **Fig 6.22**). Although the precipitation heat values will decrease afterwards with increasing cooling rate (as demonstrated for alloys 7150 and 7085 in **Fig 6.22**), the exact shapes of these curves are not known for cooling rates that are faster than the limits of the current DSC technique (e.g. alloys 7037 and 7055 in **Fig 6.22**). Therefore, a detailed analysis is needed to understand the precipitation mechanisms of this platelet phase. This is left for future work.

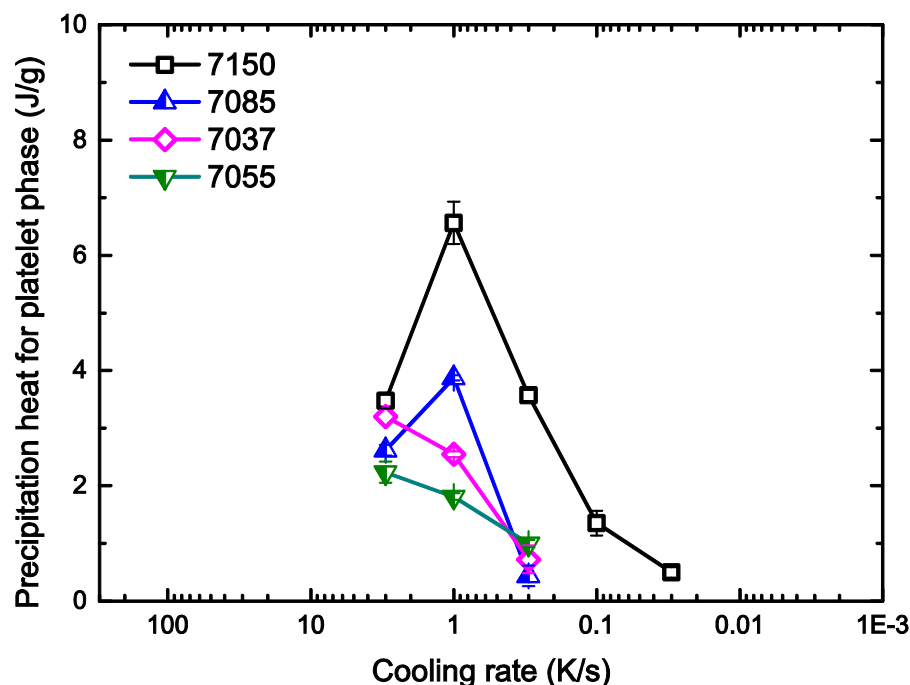


Figure 6.22: Precipitation heats for the platelet phase reaction in the different alloys.

6.8. Conclusions

The key findings from this chapter are summarised as follows:

1. Four more CCP diagrams have been developed to include alloys 7020, 7085, 7037 and 7055 with different alloy compositions. It was demonstrated that the quench sensitivity generally increases with increasing total alloy content. Therefore alloy 7020 exhibits the lowest quench sensitivity when compared with the other studied alloys. There are three main quench-induced precipitation reactions in the high strength alloys 7150, 7085, 7037 and 7055, but only two main quench-induced reactions in the medium strength alloy 7020.
2. It was shown that M-phase precipitation occurs in all the studied alloys in a temperature range of about 200-400 °C. The M-phase is the main quench-induced precipitate for all the studied 7xxx series alloys in the cooling rate

range of 0.1 K/s-3 K/s. The results show that the amount of M-phase increases with increasing Zn content. Therefore the higher Zn content alloys 7085, 7037 and 7055 precipitate more M-phase during continuous the cooling than lower Zn content alloys 7150 and 7020. Nevertheless, the higher Zn content alloys still achieve higher T6 hardness values and low quench sensitivities with respect to T6 hardness because the S-phase precipitation has been significantly suppressed causing more Cu being preserved in solution. The remaining Cu in solution may play an important role during subsequent ageing.

3. It was shown that the onset temperatures for S-phase precipitation in the studied high strength alloys 7150, 7085, 7037 and 7055 shift to lower temperatures and to slower cooling rates with increasing Zn/Mg ratio and decreasing Cu content. Therefore the onset temperature for S-phase precipitation in the high Zn/Mg ratio alloys 7085 and 7037 is much lower than that in the other alloys. Quench factor analysis (QFA) also indicates that higher k_3 values can be found for the higher Zn/Mg ratio alloys 7085 and 7037, suggesting that the energy required to form a nucleus is higher in these two alloys. This is in agreement with experimental observations that these two alloys contained less S-phase and exhibited relatively low quench sensitivities.
4. The platelet phase reaction occurs in the high strength alloys 7150, 7085, 7037 and 7055. It is shown that the amount of the platelet phase increases with increasing cooling rate in a relatively fast cooling rate range (0.3 -1 K/s). In alloys 7150 and 7085, the precipitation heat values decrease with increasing cooling rate after reaching their peak values. In alloys 7037 and 7055, this expected decrease in precipitation heat could not be verified since the cooling rates are beyond the limit of the current DSC technique.

Chapter 7. Conclusions and future work

7.1. Conclusions

The quench sensitivities for different 7xxx series alloys with systematic changes of alloy composition have been thoroughly discussed in the current work. The results are summarised as follows:

1. The quench sensitivity increases with increasing amount of recrystallisation within the materials. This is mainly due to the fact that the Al_3Zr dispersoids tend to maintain their metastable structure and orientation when recrystallisation occurs. Therefore the Al_3Zr dispersoids lose their coherency with the Al matrix after recrystallisation, which causes them to become more potent heterogeneous nucleation sites for quench-induced precipitation. This result is consistent with the observation that the surface layer of a 7150 thick plate is more sensitive to cooling rate than the centre layer due to a relatively higher degree of recrystallisation in the surface layer. Therefore there are more nucleation sites for quench-induced precipitates in the surface layer for a given cooling condition. It was confirmed with DSC analysis that the precipitation heat values for the

surface layer are higher than for the centre layer, demonstrating that there is more quench-induced precipitation occurring in the surface layer.

2. The quench sensitivity can be described using a continuous cooling precipitation (CCP) diagram. A CCP diagram for commercially produced alloy 7150 has been developed based on a combination of DSC measurements, microstructure analysis and hardness testing over a wide range of cooling rate conditions. The results show that there are three main quench-induced precipitation reactions located in different temperature ranges. It is demonstrated that the high temperature reaction from about 350 to 470 °C corresponds to S-phase (Al_2CuMg), the medium temperature reaction from about 200 to 400 °C corresponds to M-phase (MgZn_2) and the low temperature reaction from about 150 to 250 °C corresponds to a unique platelet phase containing both Cu and Zn. The critical cooling rates were determined to be 3 K/s for the S-phase, 10 K/s for the M-phase, and 300 K/s for the unique platelet phase in alloy 7150. The platelet phase has not been previously reported for alloy 7150. The platelets precipitate with a high aspect ratio and have a hexagonal structure ($a=0.429$ nm, $c=1.385$ nm) according to HAADF-STEM images. Not only has this platelet phase not been previously reported for alloy 7150, but it was also demonstrated that this platelet phase contributes to strengthening while the other quench-induced precipitates have the opposite effect.
3. The same DSC method was used to develop additional CCP diagrams for alloys 7085, 7037, 7055 and 7020. It was found that the quench sensitivity generally increases with increasing total alloy content. The results show that alloy 7020 exhibits the lowest quench sensitivity in terms of both hardness values and precipitation heat values when compared with the other more concentrated studied alloys. This is consistent with classical theory, as an increase of total alloying content will increase the total amount of solute

supersaturation during quenching and hence the driving force for precipitation.

4. The quench sensitivity was found to decrease with increasing alloy Zn/Mg ratio. The higher Zn/Mg ratios were achieved by increasing the Zn content accompanied by decreasing the Mg content. Therefore there are more Zn atoms available to form M-phase, which results in a more significant M-phase precipitation during cooling. The results also show that the precipitation heat values for M-phase are greater for high Zn content alloys 7085, 7037 and 7055 when compared with lower Zn content alloys 7150 and 7020. However, the precipitation of S-phase (Al_2CuMg) during continuous cooling was found to be significantly suppressed with increasing Zn/Mg ratio. Therefore more Cu and Mg may be preserved in solution, causing the high Zn/Mg ratio alloy to exhibit less quench sensitivity. Quench factor analysis (QFA) also indicates that higher k_3 values can be found for the higher Zn/Mg ratio alloys 7085 and 7037, suggesting that the energy required to form a nucleus is higher in these two alloys. This is in agreement with experimental observations that these two alloys contained less S-phase and exhibited relatively low quench sensitivities.
5. The quench sensitivity was found to decrease with decreasing alloy Cu content. The low Cu content alloy 7037 exhibits less quench sensitivity when compared with the high Cu content alloy 7085. The DSC curves show that the onset temperature for the S-phase is lower in the low Cu content alloy 7037 than in the high Cu content alloy 7085. This is in agreement with the calculated phase diagram, which shows reducing the Cu content can decrease the solvus temperature for S-phase precipitation. Furthermore, Cu in solution can also participate in the age hardening precipitation process during subsequent ageing.

7.2. Recommendations for future work

It was shown that there are a number of aspects that could benefit from further detailed work and lead to fresh insights into quench sensitivity.

1. Understanding, characterising and quantifying the preferential nucleation sites for the different quench-induced precipitation reactions. In current study, the M-phase precipitates were found to preferentially nucleate on both Al_3Zr dispersoids in recrystallised grains and on grain boundaries. The preferential nucleation sites for the S-phase precipitates and the platelet phase precipitates are not fully understood so well.
2. It was noted that the precipitation heat values for different quench-induced precipitation reactions can be measured based on the peak separation method that defines the intersection points of two overlapped peaks as the onset temperature for the lower temperature reaction and the finishing temperature for the higher temperature reaction. It has been shown that these quench-induced reactions are often heavily overlapped. For example, the start temperature of the M-phase is overlapping with the S-phase reaction at higher temperatures, so that the defined onset temperature of the M-phase is lower than the real onset temperature. On the other hand, the finishing temperature of the M-phase overlaps with the low temperature reaction, causing a higher finishing temperature to be judged in this case. As a result, the overall reaction range of the M-phase is narrower due to the current peak separation method. In order to better understand the phase transformations occurring during continuous cooling, a more sophisticated peak separation method is needed to determine the real onset/finish temperatures for each reaction.
3. The precipitation heat values have been used in the current study to represent the amount of precipitates from the different quench-induced reactions. It could be very useful to determine robust quantitative

relationships between the volume fractions and sizes of different types of quench induced precipitates as a function of continuous cooling rate (with or without subsequent ageing). It is noted a small angle X-ray scattering (SAXS) technique can be used to detect information on the volume fractions, sizes and morphologies of nano-precipitates [55, 113, 203, 204]. Moreover, with optimum beamline settings, the SAXS data can be used to understand the chemical compositions of the precipitates [205]. It is therefore possible to measure the SAXS patterns from quench-induced precipitates in samples that have been quenched at different cooling rates. If the quench-induced precipitates are too large for SAXS, then useful information can still be inferred from studying precipitates that formed during subsequent ageing. Raw SAXS data to this effect has already been obtained for all the studied alloys at Australian Synchrotron. After completion of the data analysis, the results will be compared to the existing DSC and microstructure analysis results.

4. The DSC method and devices could be improved to extend the technique to faster cooling rates. There is a possibility to measure the precipitation heat values in extremely fast cooling conditions (>10 K/s) using an in direct differential fast scanning calorimeter (DFSC) [120]. However the DFSC samples ($20\text{ }\mu\text{m} \times 100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$) may be too small to capture adequate information about the quench-induced precipitation.
5. Further modelling could be performed, such (a) predicting separate C-curves for each quench-induced reaction by quench factor analysis once a more sophisticated peak separation method has been developed, or (b) developing a physically-based heterogeneous nucleation model and applying it to continuous cooling process.

Publications and Presentations

Publications:

1. Y. Zhang, P.A. Rometsch, and B.C. Muddle, *Characterisation and Control of Al_3Zr dispersoids in Al-Zn-Mg-Cu-Zr alloys*, in European Conference on Aluminium Alloys, 2011, DGM: Bremen, Germany. **(Conference Paper)**
2. Y. Zhang, C. Bettles, and P.A. Rometsch, *Effect of recrystallisation on Al_3Zr dispersoid behaviour in thick plates of aluminium alloy AA7150*. Journal of Materials Science, 2014. **49**: p. 1709-1715. **(Impact Factor: 2.163)**
3. Y. Zhang, B. Milkereit, O. Kessler, C. Schick, P.A. Rometsch, *Development of continuous cooling precipitation diagrams for aluminium alloys AA7150 and AA7020*. Journal of Alloys and Compounds, 2014. **584**: p. 581-589. **(Impact Factor: 2.390)**
4. P.A. Rometsch, Y. Zhang, and S. Knight, *Heat Treatment of 7xxx Series Aluminium Alloys – Some Recent Developments*. Transactions of Nonferrous Metals Society of China, 2014. Accepted. **(Impact Factor: 0.917)**

Manuscripts in preparation:

1. Y. Zhang, P.A. Rometsch, B. Milkereit, M. Weyland, *A unique quench-induced platelet phase in commercial alloy AA7150*, to be submitted for publication in Scripta Materialia.
2. Y. Zhang, P.A. Rometsch, D. Pelliccia, B. Milkereit, O. Kessler, C. Schick, *A quantitative analysis of quench-induced precipitation of several 7xxx series alloys using small angle X-ray scattering*, to be submitted for publication in Acta Materialia.
3. Y. Zhang, P.A. Rometsch, N. Birbilis, S. Knight, *Quench sensitivity of alloy 7150 corresponding to corrosion resistance*, to be submitted for publication in Corrosion Science.

Conference attendance:

Tri-University Research Workshop on Advanced Engineering

Melbourne, Australia, 8 November 2010

The 1st European Conference on Aluminium Alloys (ECAA 2011)

Bremen, Germany, 05-07 October 2011 – poster presentation

ARC Centre of Excellence for Design in Light Metals Annual Workshop

Melbourne, Australia, 12-14 November 2012

The 1st Asian Conference on Aluminium Alloys (ACAA 2013)

Beijing, China, 13-17 October 2013 – oral presentation

References

1. *Aerospace materials*, ed. H.A. Brian Cantor, Patrick Grant. 2001: Institute of Physics.
2. I.N. Fridlyander, et al., *Advanced High-strength Aluminum-base Materials*. Metal Science and Heat Treatment, 2005. **47**(7-8): p. 269-275.
3. W. Soboyejo, *Mechanical Properties of Engineered Materials*. 2002, New Jersey: Marcel Dekker, Inc.
4. I.J. Polmear, *Light Alloys: Metallurgy of the Light Metals*. 4th ed. 2006, Melbourne.
5. E.A. Starke and J.T. Staley, *Application of Modern Aluminum Alloys to Aircraft*. Progress in Aerospace Sciences, 1996. **32**: p. 131-172.
6. A. Heinz, et al., *Recent Development in Aluminium Alloys for Aerospace Applications*. Materials Science and Engineering A, 2000. **280**: p. 102-107.
7. A. Wilm, *Physikalisch-metallurgische Untersuchungen über magnesiumhaltige Aluminiumlegierungen*. Zeitschrift für de gesamte Hüttenkunde, 1911. **8**(8): p. 225-227.
8. A. Wilm, *Verfahren zum Veredeln von magnesiumhaltigen Aluminiumlegierungen*, 1909: Germany.
9. R.B. Nicholson, G. Thomas, and J. Nutting, Journal of Institute of Metals, 1958. **87**: p. 429.
10. I.J. Polmear, *Aluminium Alloys - A Century of Age Hardening*. Materials Forum, 2004. **28**: p. 1-13.
11. J.K. Park and A.J. Ardell, *Microstructures of the Commercial 7075 Al Alloy in the T651 and T7 Tempers*. Metallurgical Transactions A, 1983. **14A**: p. 1957-1965.
12. H.Y. Hunsicker, *Development of Al-Zn-Mg-Cu Alloys for Aircraft*. Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences, 1976. **282**: p. 359-376.
13. I.N. Fridlyander, *Aluminum Alloys in Aircraft in the periods of 1970-2000 and 2001-2015*. Metal Science and Heat Treatment, 2001. **43**(1-2): p. 6-10.

14. R.J. Bucci, C.J. Warren, and E.A.S. Jr., *Need for new materials in aging aircraft structures*. Journal of Aircraft, 2000. **37**(1): p. 122-129.
15. R.J.H. Wanhill, *Milestone case histories in aircraft structural integrity*, 2002, National Aerospace Laboratory NLR.
16. E.A. Starke and J.T. Staley, *Application of Modern Aluminum Alloys to Aircraft* Progress in Aerospace Sciences, 1995. **32**(1-2): p. 131-172.
17. U.S.A. Force, *Airplane Strength And Rigidity Reliability Requirements, Repeated Loads And Fatigue*.
18. J. Liu and M. Kulak, *A New Paradigm in the Design of Aluminum Alloys for Aerospace Applications*. Materials Science Forum, 2000. **331-337**: p. 127-142.
19. J. Liu, *Advanced Aluminum and Hybrid Aerostructures for Future Aircraft*. Materials Science Forum, 2006: p. 519-521.
20. T. Dursun and C. Soutis, *Recent developments in advanced aircraft aluminium alloys*. Materials and Design, 2014. **56**: p. 862-871.
21. J.C. Williams and E.A.S. Jr., *Progress in structural materials for aerospace systems*. Acta Materialia, 2003. **51**: p. 5775-5799.
22. Alcoa, *7055 Alloy-T7751 Plate and -T77511 Extrusions*.
23. Alcoa, *Alloy 7150-T7751 Plate and 7150-T77511 Extrusions*.
24. S. Aerospace, *AMS 4252B*, in *Aluminum Alloy, Plate 6.4Zn - 2.4Mg - 2.2Cu - 0.12Zr (7150-T7751) Solution Heat Treated, Stress Relieved, and Overaged*2005, SAE to advance the state of technical and engineering sciences.
25. S. Aerospace, *AMS 4325*, in *Aluminum Alloy, Extruded Wide Panel Profiles (7150-T77511) 6.4Zn - 2.4Mg - 2.2Cu - 0.12Zr Solution Heat Treated, Stress-Relieved, Straightened and Overaged*2007, SAE to advance the state of technical and engineering sciences.
26. B.M. Cina and R. Gan, *Reducing the susceptibility of alloys, particularly aluminium alloys, to stress corrosion cracking*, 1973: United States.
27. Y. Liu, et al., *Effect of cooling aging on microstructure and mechanical properties of an Al-Zn-Mg-Cu alloy*. Materials and Design, 2014. **57**: p. 79-86.
28. S. Aerospace, *AMS 4050H*, in *Aluminium alloy, Plate 6.2Zn-2.3Cu-2.2Mg-0.12Zr (7050-T7451) Solution Heat Treated, Stress Relieved, and Overaged*2003, SAE to advance the state of technical and engineering sciences.
29. S. Aerospace, *AMS-2772*, in *Heat Treatment of Aluminum Alloy Raw Materials*2011, SAE to advance the state of technical and engineering sciences.
30. M. Conserva and P. Fiorini, *Interpretation of Quench-Sensitivity in Al-Zn-Mg-Cu Alloys*. Metallurgical Transactions, 1972. **4**: p. 857-862.
31. J.E. Hatch, *Aluminum: Properties and Physical Metallurgy* ed. J.E. Hatch. 1984: Aluminum Association Inc. and ASM International.
32. S.T. Lim, I.S. Eun, and S.W. Nam, *Control of Equilibrium Phases (M,T,S) in the Modified Aluminum Alloy 7175 for Thick Forging Applications*. Materials Transactions, 2003. **44**(1): p. 181-187.
33. A. Deschamps and Y. Brechet, *Influence of quench and heating rates on the ageing response of an Al-Zn-Mg-(Zr) alloy*. Materials Science and Engineering A, 1998. **251**: p. 200-207.

34. A. Deschamps and Y. Bréchet, *Nature and Distribution of Quench-Induced Precipitation in an Al-Zn-Mg-Cu Alloy*. Scripta Materialia, 1998. **39**: p. 1517-1522.
35. P.A. Rometsch, *Process Modelling of Heat Treatment of Aluminium Casting Alloys*, in *Department of Mining, Minerals and Materials Engineering* 1999, University of Queensland.
36. H. Suzuki, et al., *Effects of Zirconium Addition on Quench-Sensitivity of Al-Zn-Mg-Cu Alloys*. Journal of Japan Institute of Light Metals, 1983. **33**(1): p. 29-37.
37. X. Zhang, et al., *Effect of Processing Parameters on Quench Sensitivity of an AA7050 sheet*. Materials Science and Engineering A, 2011. **528**: p. 795-802.
38. V.S. Zolotarevsky, N. Belov, and M.V. Glazoff, *Casting Aluminum Alloys*. 2007.
39. C. Mondal and A.K. Mukhopadhyay, *On the nature of T(Al₂Mg₃Zn₃) and S(Al₂CuMg) phases Present in As-cast and Annealed 7055 Aluminum Alloy*. Materials Science and Engineering A, 2005. **391**: p. 367-376.
40. J. Dong, et al., *A New Way to Cast High-alloyed Al-Zn-Mg-Cu-Zr for Super-high Strength and Toughness* Journal of Materials Processing Technology, 2006. **171**(3): p. 399-404.
41. N.A. Belov, D.G. Eskin, and A.A. Aksenov, *Multicomponent Phase Diagrams Applications for Commercial Aluminum Alloys*. 2005.
42. N.M. Doroshenko, et al., *Effect of admixtures of iron and silicon on the structure and cracking of near-edge volumes in rolling of large flat ingots from alloy 7075*. Metal Science and Heat Treatment, 2005. **47**(1-2): p. 30-35.
43. H.A. Holl, *Investigations into the Possibility of Reducing Quench-sensitivity in High Strength Al-Zn-Mg-Cu alloys*. Journal of the Institute of Metals, 1969. **97**: p. 200-205.
44. J.T. Staley, *Aging Kinetics of Aluminum Alloy 7050*. Metallurgical Transactions, 1973. **5**: p. 929-932.
45. F. Viana, et al., *Retrogression and Re-ageing of 7075 Aluminium Alloy: Microstructural Characterization*. Journal of Materials Processing Technology, 1999. **92-93**: p. 54-59.
46. S. Liu, et al., *Investigation of Quench Sensitivity of High Strength Al-Zn-Mg-Cu alloys by time-temperature-properties Diagrams*. Materials & Design, 2010. **31**: p. 3116-3120.
47. J.C. Werenskiold, A. Deschamps, and Y. Bréchet, *Characterization and Modeling of Precipitation Kinetics in an Al-Zn-Mg Alloy*. Materials Science and Engineering A, 2000. **293**: p. 267-247.
48. J.A. Wagner and R.N. Shenoy, *The Effect of Copper, Chromium, and Zirconium on the Microstructure and Mechanical Properties of Al-Zn-Mg-Cu Alloys*. Metallurgical Transactions A, 1991. **22A**: p. 2809-2818.
49. G. Sha and A. Cerezo, *Early-stage Precipitation in Al-Zn-Mg-Cu alloy (7050)*. Acta Materialia, 2004. **52**: p. 4503-4516.
50. G. Sha and A. Cerezo, *Field Ion Microscopy and 3-D atom Probe Analysis of Al₃Zr Particles in 7050 Al alloy*. Ultramicroscopy, 2005. **102**: p. 151-159.
51. W. Sha, *Application of Simple Practical Models for Early Stage Ageing Precipitation Kinetics and Hardening in Aluminium Alloys*. Materials and Design, 2007. **28**: p. 528-533.

52. R. Ferragut, A. Somoza, and A. Tolley, *Microstructural Evolution of 7012 Alloy during the Early Stages of Artificial Ageing*. Acta Materialia, 1999. **47**: p. 4355-4364.
53. A.K. Mukhopadhyay, Q.B. Yang, and S.R. Singh, *The influence of zirconium on the early stages of aging of a ternary Al-Zn-Mg alloy*. Acta Materialia, 1994. **42**(9): p. 3083-3091.
54. A. Deschamps and Y. Bréchet, *Influence of Predeformation on Ageing in an Al-Zn-Mg Alloy-I. Microstructure Evolution and Mechanical Properties*. Acta Materialia, 1999. **47**: p. 281-292.
55. M. Dumont, et al., *Characterisation of the composition and volume fraction of η' and η precipitates in an Al-Zn-Mg alloy by a combination of atom probe, small-angle X-ray scattering and transmission electron microscopy*. Acta Materialia, 2005. **53**: p. 2881-2892.
56. J. Yan, L. ChunZhi, and Y. MingGao, *On the η' precipitate phase in 7050 Aluminium Alloy*. Materials Science and Engineering A, 1991. **141**.
57. J. GjØnnes and C.J. Simensen, *An electron microscope investigation of the microstructure in an Al-Zn-Mg alloy*. Acta Metallurgica, 1970. **18**: p. 881-890.
58. L.F. Mondolfo, *Metallography of Aluminum Alloys*. 1943, New York.
59. X. Fang, et al., *Effect of Cu and Al on the crystal structure and composition of h ($MgZn_2$) phase in over-aged Al-Zn-Mg-Cu alloys*. Journal of Materials Science, 2012. **47**: p. 5419-5427.
60. S.T. Lim, S.J. Yun, and S.W. Nam, *Improved Quench Sensitivity in Modified Aluminum Alloy 7175 for Thick Forging Applications*. Materials Science and Engineering A, 2004. **371**: p. 82-90.
61. J. Boselli, D.J. Chakrabarti, and R.T. Shuey, *Metallurgical Insights into the Improved Performance of Aluminum Alloy 7085 Thick Products*, in *11th International Conference on Aluminium Alloys* 2008: Aachen, Germany. p. 202-208.
62. D.J. Chakrabarti, et al., *New Generation High Strength High Damage Tolerance 7085 Thick Alloy Product with Low Quench Sensitivity*. Materials Forum, 2004. **28**: p. 969-974.
63. Y. Deng, et al., *Influence of Mg content on quench sensitivity of Al-Zn-Mg-Cu aluminium alloys*. Journal of Alloys and Compounds, 2011. **509**: p. 4636-4642.
64. A.J. Bryant, *The Effect of Composition upon the Quench-Sensitivity of Some Al-Zn-Mg Alloys*. Journal of the Institute of Metals, 1966. **94**: p. 94-99.
65. D. Chakrabarti, J., et al., *Aluminum alloy products*, E. Patent, Editor 2001: United States. p. 43.
66. I.N. Fridlyander, *High-Strength Aluminum Alloys with Zinc, Magnesium, and Copper*. Metal Science and Heat Treatment, 2003. **45**: p. 9-10.
67. B. Sarkar, M. Marek, and E.A.S. Jr., *The effect of copper content and heat treatment on the stress corrosion characteristics of Al-6Zn-2Mg-X Cu alloys*. Metallurgical Transactions, 1980. **12A**: p. 1981-1939.
68. A. Deschamps, Y. Bréchet, and F. Livet, *Influence of copper addition on precipitation kinetics and hardening in Al-Zn-Mg alloy*. Materials Science and Technology, 1999. **15**: p. 993-1000.

69. X. Fang, et al., *Effects of Cu content on the precipitation process of Al-Zn-Mg alloys*. Journal of Materials Science, 2012. **47**: p. 8174-8187.
70. R.J. Livak and J.M. Papazian, *Effects of copper on precipitation and quench sensitivity of Al-Zn-Mg alloys*. Scripta Materialia, 1984. **18**: p. 483-488.
71. M.O. Speidel, *Coherent particles and stress corrosion cracking of high strength aluminium alloys*, in *Air Force Materials Laboratory 50th Anniversary Corrosion of Military and Aerospace Equipment Symposium* 1967: Denver.
72. D.D. Hall and I. Mudawar, *Predicting the Impact of Quenching on Mechanical Properties of Complex-Shaped Aluminium Alloy Parts*. Journal of Heat Transfer, 1995. **117**: p. 479-488.
73. H. SUZUKI, M. KANNO, and H. SAITOH, *The Effect of Zr or Cr Addition on the Recrystallization Behavior of Al-Zn-Mg-Cu Alloys*. The Journal of Japan Institute of Light Metals, 1984. **34**(11): p. 630-636.
74. H. SUZUKI, M. KANNO, and H. SAITOH, *Different Effects between Zr and Cr Additions on Recrystallization of Hot-rolled Al-Zn-Mg-Cu Alloys*. The Journal of Japan Institute of Light Metals, 1986. **36**(1): p. 22-28.
75. N. KONO, et al., *Influence of Sn and Mn Addition on Quench Sensitivity of Al-4%Cu alloy*. Journal of Japan Institute of Light Metals, 1988. **38**(3): p. 172-176.
76. N. Seiichi, N. Nobuo, and S. Tetsuo, *General Evaluation of Zr Addition in Improving Recrystallization Characteristics of Aluminium*. The Journal of Japan Institute of Light Metals, 1965. **15**(1): p. 23-36.
77. Y. Baba, *Influence of Additional Elements on the Quench-Sensitivity and Nucleation of Precipitates in Al-Zn-Mg Alloys*. The Journal of the Japan Institute of Metals 1967. **31**: p. 910-915.
78. R.C. Dorward and D.J. Beerntsen, *Grain Structure and Quench-Rate Effects on Strength and Toughness of AA7050 Al-Zn-Mg-Cu-Zr Alloy Plate*. Metallurgical and Materials Transactions A, 1995. **26A**: p. 2481-2484.
79. S.T. Lim, Y.-Y. Lee, and I.-S. Eun, *Dilute Alloy Designs of 7xxx Aluminum Alloys for Thick Forging Applications*. Materials Science Forum, 2005. **475-479**.
80. P. Li, et al., *Quench sensitivity and microstructure character of high strength AA7050*. Transactions of Nonferrous Metals Society of China, 2012. **22**: p. 268-274.
81. S. Liu, et al., *Effect of microstructure on the quench sensitivity of AlZnMgCu alloys*. Journal of Alloys and Compounds, 2010. **507**: p. 53-61.
82. C. Sigli, *Zirconium Solubility in Aluminum Alloys*. Materials Forum, 2004. **28**: p. 1353-1358.
83. I.J. Polmear, *The Ageing Characteristics of Complex Al-Zn-Mg Alloys Distinctive Effects of Copper and Silver on the Ageing Mechanism*. The Institute of Metals, 1960. **89**: p. 51-59.
84. I.J. Polmear, *The Properties of Commercial Al-Zn-Mg Alloys Practical Implications of Trace Additions of Silver*. Journal of the Institute of Metals, 1960. **89**: p. 193-202.
85. J.T. Vietz, K.R. Sargant, and I.J. Polmear, *The Influence of Small Additions of Silver on the Ageing of Aluminium Alloys: Further Observations on Al-Zn-Mg Alloys*. Journal of the Institute of Metals, 1964. **92**: p. 327-333.

86. J.T. Vietz and I.J. Polmear, *The Influence of Small Additions of Silver on the Ageing of Aluminium Alloys: Observations on Al-Cu-Mg Alloys*. Journal of the Institute of Metals, 1966. **94**: p. 410-419.
87. I.J. Polmear, *Tensile Properties of Modified Aluminium-Zinc-Magnesium Alloys Containing Silver*. Journal of the Institute of Metals, 1966. **94**: p. 36-37.
88. S.P. Ringer, T. Sakurai, and I.J. Polmear, *Origins of Hardening in Aged Al-Cu-Mg-(Ag) Alloys*. Acta Materialia, 1997. **45**(9): p. 3731-3744.
89. C.E. Macchi, et al., *Secondary Precipitation in Al-Zn-Mg-(Ag) Alloys*. Acta Materialia, 2003. **51**: p. 5151-5158.
90. R.N. Lumley, I.J. Polmear, and A.J. Morton, *Interrupted Aging and Secondary Precipitation in Aluminium Alloys* Materials Science and Technology, 2003. **19**: p. 1483-1490.
91. R.N. Lumley, I.J. Polmear, and A.J. Morton, *Development of Mechanical Properties during Secondary Aging in Aluminium Alloys*. Materials Science and Technology, 2005. **21**(9): p. 1025-1032.
92. S.K. Maloney, et al., *The Effects of a Trace Addition of Silver upon Elevated Temperature Ageing of an Al-Zn-Mg Alloy*. Micron, 2006. **32**: p. 741-747.
93. T. Ogura, S. Hirose, and T. Sato, *Quantitative Characterization of Precipitate Free Zones in Al-Zn-Mg-(Ag) Alloys by Microchemical Analysis and Nanoindentation Measurement*. Science and Technology of Advanced Materials, 2004. **5**: p. 491-496.
94. B.C. Peters, *The Effect of Quench Rate and Silver Addition on the Precipitate Free Zone Width in an Al-4.3pct Zn-1.3pct Mg Alloy*. Metallurgical Transactions, 1970. **2**: p. 1255-1257.
95. R.W. Elkington and A.N. Turner, *The Effect of Silver on the Stress-Corrosion-Resistance of High-Strength Al-Zn-Mg-Cu Alloys*. Journal of the Institute of Metals, 1967. **95**: p. 294-298.
96. B. Grushko, et al., *The Constitution of Aluminum-Cobalt Alloys between Al_5Co_2 and Al_9Co_2* . Journal of Alloys and Compounds, 1996. **233**: p. 279-287.
97. Г.Л. Шнейдер, *Alloy composition effects on quench sensitivity*. Light Alloy Fabrication Technology, 1994. **11**: p. 36-39.
98. C.S. Jyothi Menon, *Metallography of a Melt-Quenched Aluminum-Cobalt Alloy*. Metallography, 1988. **21**: p. 179-197.
99. D.A. Porter and K.E. Easterling, *Phase Transformations in Metals and Alloys*. Second ed. 1992.
100. M. Tiryakioğlu and R.T. Shuey, *Quench sensitivity of 2219-T87 aluminium alloy plate*. Materials Science and Engineering A, 2010. **527**: p. 5033-5037.
101. P. Archambault and D. Godard, *High Temperature Precipitation Kinetics and TTT Curve of a 7xxx alloy by in-situ Electrical Resistivity Measurements and Differential Calorimetry*. Scripta Materialia, 2000. **42**: p. 675-680.
102. N. Saunders. *The Modelling of Stable and Metastable Phase Formation in Multi-Component Al-Alloys*. in *9th International Conference on Aluminium Alloys*. 2004. Brisbane, Australia.
103. L.B. Ber, *Accelerated Artificial Ageing Regimes of Commercial Aluminium Alloys. II: Al-Cu, Al-Zn-Mg-(Cu), Al-Mg-Si-(Cu) Alloys*. Materials Science and Engineering A, 2000. **280**: p. 91-96.

104. L.B. Ber, *Accelerated Artificial Ageing Regimes of Commercial Aluminum Alloys. I. Al-Cu-Mg Alloys*. Materials Science and Engineering A, 2000. **280**: p. 83-90.
105. J.D. Embury and R.B. Nicholson, *The Nucleation of Precipitates: The System Al-Zn-Mg*. Acta Materialia, 1965. **13**(4): p. 403-417.
106. J. Buha, R.N. Lumley, and A.G. Crosky, *Secondary ageing in an aluminium alloy 7050*. Materials Science and Engineering A, 2008. **492**: p. 1-10.
107. T. Williams, *A Study of the Ageing Characteristics and Tensile Properties of Step-Quenched Al-Zn-Mg-Cu Alloys*. Journal of the Institute of Metals, 1963. **91**: p. 324-327.
108. W.L. Fink and L.A. Willey, *Quenching of 75S Aluminum Alloy*. Transactions AIME, 1947. **175**: p. 414-427.
109. R.T. Shuey, et al., *Experimental and analytical investigations on plane strain toughness for 7085 aluminium alloy*. Metallurgical and Materials Transactions A, 2009. **40A**: p. 365-376.
110. R.T. Shuey, et al., *Toughness after Interrupted Quench*. Materials Science Forum, 2006. **519-521**: p. 1017-1022.
111. J.T. Staley, *Quench factor analysis of aluminium alloys*. Materials Science and Technology, 1987. **3**: p. 923-935.
112. A. B871-01, *Standard Test Method for Tear Testing of Aluminum Alloy Products*, 2007.
113. D. Dumont, A. Deschamps, and Y. Bréchet, *A Model for Predicting Fracture Mode and Toughness in 7000 Series Aluminum alloys*. Acta Materialia, 2004. **52**: p. 2529-2540.
114. D. Dumont, A. Deschamps, and Y. Bréchet, *On the Relationship between Microstructure, Strength and Toughness in AA7050 Aluminum alloy*. Materials Science and Engineering A, 2003. **356**: p. 326-336.
115. T. Herding, et al., *An Approach for Continuous cooling Transformation (CCT) Diagrams of Aluminium Alloys*. Materials Science Forum, 2002. **396-402**: p. 869-874.
116. O. Kessler, et al., *Continuous Cooling Transformation (CCT) Diagram of Aluminum Alloy Al-4.5Zn-1Mg*. Materials Science Forum, 2006. **519-521**: p. 1467-1472.
117. A. Deschamps, et al., *Influence of cooling rate on the precipitation microstructure in a medium strength Al-Zn-Mg alloy* Materials Science and Engineering A, 2009. **501**: p. 133-139.
118. B. Milkereit, O. Kessler, and C. Schick, *Recording of continuous cooling precipitation diagrams of aluminium alloys*. Thermochemica Acta, 2009. **492**: p. 73-78.
119. B. Milkereit, et al., *Continuous cooling precipitation diagrams of Al-Mg-Si alloys*. Materials Science and Engineering A, 2012. **550**: p. 87-96.
120. D. Zohrabyan, et al., *Precipitation enthalpy during cooling of aluminum alloys obtained from calorimetric reheating experiments*. Thermochemica Acta, 2012. **529**: p. 51-58.
121. H.-y. Li, et al., *Testing of continuous cooling transformation curve of Al-Zn-Mg-Cu alloy*. The Chinese Journal of Nonferrous Metals, 2008. **18**(9): p. 1613-1612.

122. H. Li, et al., *Establishment of continuous cooling transformation diagrams of aluminum alloys using in situ voltage measurement*. Transactions of Nonferrous Metals Society of China, 2011. **21**: p. 1944-1949.
123. J.W. Christian, *The Theory of Transformations in Metals and Alloys*. Third Edition ed. 2002. 1191.
124. J.W. Cahn, *Transformation kinetics during continuous cooling*. Acta Materialia, 1956. **4**: p. 572-575.
125. F. Liu, et al., *Additivity rule, isothermal and non-isothermal transformations on the basis of an analytical transformation model*. Acta Materialia, 2007. **55**: p. 5255-5267.
126. J.T. Staley and M. Tiryakioglu. *The use of TTP curves and quench factor analysis for property prediction in aluminium alloys*. in *Advances in the Metallurgy of Aluminium alloys*. 2001.
127. D.S. Mackenzie and J.W. Newkirk, *The Use of the Jominy End Quench for Determining Optimal Quenching Parameters in Aluminum*, in the *International Federation of Heat treatment and Surface Engineering Conference 2001*: Dubrovnik, Croatia.
128. G.P. Dolan and J.S. Robinson, *Residual stress reduction in 7175-T73, 6061-T6 and 2017A-T4 aluminium alloys using quench factor analysis*. Journal of Materials Processing Technology, 2004. **153-154**: p. 346-351.
129. I. Mitchell, *Residual Stress Reduction During Quenching of Wrought 7075 Aluminum Alloy*, in *Materials Science & Engineering 2004*, Worcester Polytechnic Institute.
130. S. Moldenhauer, et al., *Recent Improvement in High Strength Thick AA7050-Plate*. Materials Science Forum, 2000. **331-337**: p. 1101-1106.
131. M. Tiryakioglu and R.T. Shuey, *Quench sensitivity of an Al-7Pct Si-0.6Pct Mg alloy: Characterisation and Modelling*. Metallurgical and Materials Transactions B, 2007. **38B**: p. 575-582.
132. M. Fontecchio, *Quench Probe and Quench Factor Analysis of Aluminum Alloys in Distilled Water*, in *Materials Science and Engineering 2002*.
133. G.E. Totten, G.M. Webster, and C.E. Bates, *Quench Factor Analysis: Step-by-Step Procedures for Experimental Determination*.
134. G.P. Dolan, et al., *Quench Factor Analysis of Aluminium Alloys Using the Jominy end Quench Technique*. Materials Science and Technology, 2005. **21**(6): p. 687-692.
135. A.Z. Yazdi, et al., *Prediction of hardness at different points of Jominy specimen using quench factor analysis method*. Journal of Materials Processing Technology, 2008. **199**: p. 124-129.
136. P.A. Rometsch, M.J. Starink, and P.J. Gregson. *An Integrated Hardening Model for the Heat Treatment of Extruded 6082*. in *Materials Solutions Conference*. 2001. Indianapolis.
137. P.A. Rometsch, M.J. Starink, and P.J. Gregson, *Improvements in quench factor modelling*. Materials Science Engineering A, 2003. **A339**: p. 255-264.
138. J.W. Evancho and J.T. Staley, *Kinetics of Precipitation in Aluminum During Continuous Cooling*. Metallurgical Transactions, 1974. **5**: p. 43-47.

139. P.A. Rometsch, M.J. Starink, and P.J. Gregson, *Improvements in quench factor modelling*. Materials Science & Engineering A, 2003. **339**: p. 255-264.
140. L.K. Ives, et al., *The NBS: Processing/Microstructure/Property Relationships in 2024 Aluminum Alloy Plates*, 1983, National Bureau of Standards.
141. P.R. Rios, *Relationship between non-isothermal transformation curves and isothermal and non-isothermal kinetics*. Acta Materialia, 2005. **53**: p. 4893-4901.
142. G.W.H. Höhne, W.F. Hemminger, and H.-J. Flammersheim, *Differential Scanning Calorimetry*. 2nd ed, ed. Second. 2003, Braunshweig.
143. B. Milkereit, *Kontinuierliche Zeit-Temperatur-Ausscheidungs-Diagramme Von Al-Mg-Si-Legierungen*, 2011, University of Rostock: Rostock, Germany.
144. C.S.T. Chang and J. Banhart, *Low-Temperature Differential Scanning Calorimetry of an Al-Mg-Si alloy*. Metallurgical and Materials Transactions A, 2010. **42A**: p. 1960-1964.
145. B. Milkereit, et al., *Precipitation kinetics of an aluminium alloy during Newtonian cooling simulated in a differential scanning calorimeter*. Thermochimica Acta, 2011. **522**: p. 86-95.
146. W.E. Jominy, *Hardnability Test*, U.S.P. Office, Editor 1941: USA.
147. J.W. Newkirk and D.S. MacKenzie, *The Jominy End Quench for Light-Weight Alloy Development*. Journal of Materials Engineering and Performance, 2000. **9**(4): p. 408-415.
148. D.S. Mackenzie and J.W. Newkirk, *Heat Treatment Optimization of 7xxx Aluminum Alloys*, in the *International Federation of Heat treatment and Surface Engineering Conference 2001*: Dubrovnik, Croatia.
149. S. Aerospace, AMS 4329A, in *Aluminium alloy, Plate (7085-T7551) 7.5Zn-1.6Cu-1.5Mg-0.12Zr Solution Heat Treated, Stress-Relieved, and Overaged* 2006, SAE to advance the state of technical and engineering sciences.
150. S. Aerospace, AMS 4306B, in *Aluminum Alloy, Plate 6.4Zn - 2.4Mg - 2.2Cu - 0.12Zr (7150-T6151) Solution Heat Treated, Stress Relieved, and Aged* 2007, SAE to advance the state of technical and engineering sciences.
151. J.D. Robson, *Microstructural Evolution in Aluminium alloy 7050 during Processing*. Materials Science and Engineering A, 2004. **382**: p. 112-121.
152. J.D. Robson and P.B. Prangnell, *Modelling the Variation in Recrystallized Fraction Through the Thickness of AA7050 Plate*. Materials Science Forum, 2002. **396-402**: p. 545-550.
153. J.D. Robson and P.B. Prangnell, *Modelling Al₃Zr Dispersoid Precipitation in Multicomponent Aluminium Alloys*. Materials Science and Engineering A, 2003. **352**: p. 240-250.
154. J.D. Robson, *A new model for prediction of dispersoid precipitation in aluminium alloys containing zirconium and scandium*. Acta Materialia, 2004. **52**: p. 1409-1421.
155. J.D. Robson, *Modelling the Evolution of Particle Size Distribution During Nucleation, Growth and Coarsening*. Materials Science and Technology, 2004. **20**: p. 441-448.
156. J.D. Robson, *Modelling the Overlap of Nucleation, Growth and Coarsening During Precipitation*. Acta Materialia, 2004. **52**: p. 4669-4676.

157. S. Liu, et al., *Effect of Zr Content on Quench Sensitivity of AlZnMgCu alloys*. Transactions of Nonferrous Metals Society of China, 2007. **17**: p. 787-792.
158. H. Chen, et al. *Dissolution and Melting of Constituent Particles in a DC-cast Al-Zn-Mg-Cu Alloy 7150 During Homogenisation*. in *12th International Conference on Aluminium Alloys*. 2010. Yokohama, Japan.
159. H.P. Degischer, *Diffraction Contrast from Coherent Precipitates in Elastically-anisotropic Materials*. Philosophical Magazine, 1972. **26**(5): p. 1137-1151.
160. N.L. Peterson and S.J. Rothman, *Impurity diffusion in aluminium*. Physical Review B, 1970. **1**(8): p. 3264-3273.
161. K. Hirano and S. Fujikawa, *Impurity diffusion in aluminium*. Journal of Nuclear Materials, 1978. **69&70**: p. 564-566.
162. E. Nes, *Precipitation of the Metastable Cubic Al₃Zr-phase in Subperitectic Al-Zr Alloys*. Acta Materialia, 1972. **20**(4): p. 499-506.
163. P.M. Toor, *A review of some damage tolerance design approaches for aircraft structures*. Engineering Fracture Mechanics, 1973. **5**: p. 837-880.
164. B. Vermeulen and M.J.L.v. Tooren, *Design Case Study for a Comparative Performance Analysis of Aerospace Materials*. Materials and Design, 2006. **27**: p. 10-20.
165. Y.E. Ma, W. He, and S. Yun, *The Effects of Bonded Retarder on Fatigue Crack Growth in 7085 Aluminium Alloy*. Advanced Materials Research, 2011. **217-218**: p. 1135-1140.
166. R.S. Moirans, et al., *Thick Al-Zn-Mg-Cu Alloy Products with Improved Properties*, P. Rhenalu, Editor 1999: France.
167. L. Bozidar, et al., *Quenching theory and technology*. 2009.
168. R.J. Elger, *Design of a 4000/6000-Ton Plate Stretcher*. Journal of the Institute of Metals, 1962. **92**: p. 1-5.
169. A.R. Martin, *Practical Aspects of Stretching Aluminium Alloy Plate for Aircraft*. Journal of the Institute of Metals, 1962. **92**: p. 6-11.
170. J. Adrien, et al., *Influence of the Thermomechanical Treatment on the Microplastic Behaviour of a Wrought Al-Zn-Mg-Cu Alloy*. Acta Materialia, 2004. **52**: p. 1653-1661.
171. D.K. Xu, P.A. Rometsch, and N. Birbilis, *Improved solution treatment for an as-rolled Al-Zn-Mg-Cu alloy. Part I. Characterisation of constituent particles and overheating*. Materials Science and Engineering A, 2012. **534**: p. 234-243.
172. M.J. Starink and X.M. Li, *A Model for the Electrical Conductivity of Peak-aged and Overaged Al-Zn-Mg-Cu Alloys*. Metallurgical and Materials Transactions A, 2007. **34**(4): p. 899-911.
173. M. Schöbel, P. Pongratz, and H.P. Degischer, *Coherency loss of Al₃(Sc,Zr) precipitates by deformation of an Al-Zn-Mg alloy*. Acta Materialia, 2012. **60**(10): p. 4247-4254.
174. N. Ryum, *The Effect of Fine Disperse Al₃Zr on the Recrystallization of Aluminum*. Journal of the Institute of Metals, 1966. **94**: p. 191-192.
175. N. Ryum, *Precipitation and Recrystallization in an Al-0.5 wt.% Zr-Alloy*. Acta Materialia, 1968. **17**: p. 269-278.

176. J.D. Robson and P.B. Prangnell, *Dispersoid Precipitation and Process Modelling in Zirconium Containing Commercial Aluminium Alloys*. Acta Materialia, 2001. **49**: p. 599-613.
177. J.D. Robson, *Optimizing the Homogenization of Zirconium Containing Commercial Aluminum alloys using a Novel Process Model*. Materials Science and Engineering A, 2002. **338**: p. 219-229.
178. X. Qi, et al., *Effect of minor Sc on quench sensitivity of 7085 aluminium alloy*. The Chinese Journal of Nonferrous Metals, 2013. **23**(3): p. 666-672.
179. J. Zhang, et al., *Design of multi-stage quenching process for 7050 aluminium alloy*. Materials and Design, 2014. **56**: p. 334-344.
180. X.M. Li and M.J. Starink, *DSC study on Phase transitions and their Correlation with Properties of Overaged Al-Zn-Mg-Cu alloys*. Journal of Materials Engineering and Performance, 2011. **21**(6): p. 977-984.
181. J.M. Galbraith, M.H. Toshten, and P.R. Howell, *On the nucleation of θ and T_1 on Al_3Zr precipitates in Al-Li-Cu-Zr alloys*. Journal of Materials Science, 1987. **22**: p. 27-36.
182. M. Kanno and B.-L. Ou, *Heterogeneous Precipitation of Intermediate Phases on Al_3Zr Particles in Al-Cu-Zr and Al-Li-Cu-Zr Alloys*. Materials Transactions, JIM, 1991. **32**(5): p. 445-450.
183. J.-G. Yang and B.-L. Ou, *Hot Ductility Behavior and HAZ Hot Cracking Susceptibility of 7475-T7351 Aluminum alloy*. Scandinavian Journal of Metallurgy, 2001. **30**: p. 146-157.
184. J.F. Nie and B.C. Muddle, *On the form of the age-hardening response in high strength aluminium alloys*. Materials Science & Engineering A, 2001. **A319-321**: p. 448-451.
185. R. Yoshimura, et al., *Transmission electron microscopy study of the evolution of precipitates in aged Al-Li-Cu alloys: the θ and T_1 phases*. Acta Materialia, 2003. **51**: p. 4251-4266.
186. S.C. Wang and M.J. Starink, *Precipitates and intermetallic phases in precipitation hardening Al-Cu-Mg-(Li) based alloys*. Institute of Materials, 2005. **50**(4): p. 193-214.
187. P. Donnadieu, et al., *Atomic structure of T_1 precipitates in Al-Li-Cu alloys revisited with HAADF-STEM imaging and small-angle X-ray scattering*. Acta Materialia, 2011. **59**: p. 462-472.
188. C. Dwyer, et al., *Combined electron beam imaging and ab initio modeling of T_1 precipitates in Al-Li-Cu alloys*. Applied Physics Letters, 2011. **98**.
189. W.A. Cassada, G.J. Shiflet, and E.A. Starker, *Mechanism of $Al_2CuLi(T_1)$ nucleation and growth*. Metallurgical Transactions A, 1991. **22A**: p. 287-297.
190. X. Li and M.J. Starink, *Analysis of Precipitation and Dissolution in Overaged 7xxx Aluminium Alloys using DSC*. Materials Science Forum, 2000. **331-337**: p. 1071-1076.
191. M.J. Starink, *Analysis of aluminium based alloys by calorimetry: quantitative analysis of reactions and reaction kinetics*. International Materials Reviews, 2004. **49**(3-4): p. 191-226.

192. H. Suzuki, M. Kanno, and H. Saitoh, *The Influence of Working on Quench Sensitivity of Al-Zn-Mg-Cu Alloy Containing Transition Elements*. Journal of Japan Institute of Light Metals, 1983. **33**(7): p. 399-406.
193. C. Bloem, et al., *Aluminium 7020 Alloy and Its Welding Fatigue Behaviour*.
194. C.H. Gür and I. Yıldız, *Non-destructive investigation on the effect of precipitation hardening on impact toughness of 7020 Al-Zn-Mg alloy*. Materials Science and Engineering: A, 2004. **382**(1-2): p. 395-400.
195. A.K. Jha, et al., *Cracking of AFNOR 7020 aluminium alloy component: A metallurgical investigation*. Engineering Failure Analysis, 2006. **13**(8): p. 1233-1239.
196. L. Mueller, et al., *Alcoa 7085 die forgings 7th generation structural solutions*, 2006, Alcoa.
197. T.A. Association, *International Alloy Designations and Chemical Composition Limits for Wrought Aluminum and Wrought Aluminum Alloys*, 2009-2012.
198. M. Hilpert, et al., *Aerospace Applications: AA 7037-A New High Strength Aluminum Alloy for Aerospace Applications*, in *11th International Conference on Aluminium Alloys*, B.S. Jurgen Hirsch, Gunter Gottstein, Editor 2008: Aachen, Germany. p. 209-214.
199. M. Hilpert, T. Witulski, and G. Terlinde. *Introduction of the New Aluminum Alloy OTTO FUCHS AZ93 (AA7037) for High Strength Heavy Aerospace Forgings*. in *European Conference on Aluminium Alloys*. 2011. Bremen, Germany.
200. M. Tiryakioglu and R.T. Shuey, *Modeling Quench Sensitivity of Aluminium Alloys for Multiple Tempers and Properties: Application to AA2024*. Metallurgical and Materials Transactions A, 2010. **41A**: p. 2984-2990.
201. T. Takahashi, et al., *Quaternary diffusion in the α solid solutions of Al-Zn-Mg-Cu alloys*. Materials Transactions, JIM, 1999. **40**(9): p. 997-1004.
202. T. Takahashi, Y. Minamino, and T. Yamane, *Quaternary diffusion in 7000 aluminum alloys*. Materials Transactions, 2002. **43**(2): p. 232-238.
203. A. Deschamps, et al., *A comparative study of precipitate composition and volume fraction in an Al-Zn-Mg alloy using tomographic atom probe and small-angle X-ray scattering*. Philosophical Magazine A, 2001. **81**: p. 2391-2414.
204. A. Deschamps, L. Lae, and P. Guyot, *In situ Small-angle Scattering Study of the Precipitation Kinetics in an Al-Zr-Sc alloy*. Acta Materialia, 2007. **55**: p. 2775-2783.
205. A. Deschamps, et al., *A comparative study of precipitate composition and volume fraction in an Al-Zn-Mg alloy using tomographic atom probe and small-angle X-ray scattering*. Philosophical Magazine A, 2001. **81**(10): p. 2391-2414.