

Carbon inoculation of AZ91 magnesium alloy and effects of grain morphology on the microstructure of $\text{Mg}_{17}\text{Al}_{12}$

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This dissertation is submitted for the degree of

Doctor of Philosophy

January 2023

Abstract

This thesis investigates the factors affecting the development of microstructure in Mg-9Al-0.7Zn-0.2Mn (AZ91, wt%) during casting and solution heat treatment, with a focus on the effects of carbon inoculation. Four questions are addressed: (i) how carbides form after carbon inoculation of the melt, (ii) how different types of carbon additives affect carbide formation and grain refinement of α -Mg during casting, (iii) how the α -Mg morphology affects the partially divorced growth of the α -Mg+Mg₁₇Al₁₂ eutectic, and (iv) how the different microstructural features determine the dissolution of Mg₁₇Al₁₂ during solution heat treatment.

Water-free sample preparation methods were developed so that carbides were not hydrolysed before characterisation. Three carbides formed when AZ91 inoculated with graphite, diamond or α -SiC was remelted to 700-900 °C and slow cooled: T1-Al₂MgC₂, T2-Al₂MgC₂ and Al₄C₃. All three carbides grew with the {0001} facet and Al₄C₃ grew with two types of growth twin. Graphite, diamond and α -SiC additions each gave strong grain refinement in gravity castings. Multiple examples were measured of the T2-Al₂MgC₂ carbide with a simple basal-to-basal orientation relationship (OR) with α -Mg. Based on this and the relatively low atomic discrepancy between T2-Al₂MgC₂ and α -Mg, T2-Al₂MgC₂ is considered as the nucleant in the carbon inoculation method.

During partially divorced eutectic growth, Mg₁₇Al₁₂ grew in orientation domains crossing multiple α -Mg grains. The degree of partially divorced growth is shown to depend on a simple geometrical measure for the space available for eutectic growth. Fully coupled eutectic microstructures were generated by manipulating the α -Mg dendrite solidification time and the eutectic cooling rate. During heat treatment, the Mg₁₇Al₁₂ dissolution kinetics were dominated by the α -Mg secondary dendrite arm spacing (SDAS). Dissolution data from samples with a

wide range of α -Mg grain size and SDAS could be approximated as a single curve when all data were normalised by a lengthscale-corrected time.

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I, Cheng-Jung Lin, hereby declare that this thesis and associated research are my own work and that all sources I have used or quoted have been indicated and acknowledged by means of complete referencing.

Parts of this thesis have been published in:

- C.J.Lin, L.Peng, J.W.Xian, Q.Li, C.M.Gourlay, Eutectic solidification in Mg-9Al-0.7Zn: From divorced to coupled growth, J. Alloys Compd. 938 (2023) 168571.
<https://doi.org/10.1016/J.JALLCOM.2022.168571>.

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Acknowledgements

I would like to express my sincere gratitude to my principal supervisor, Professor Christopher M. Gourlay for his advice, professional guidance and trust during the whole research period. His guidance provided me with a deeper understanding of solidification and achieving breakthrough in the research field.

My gratitude also goes to Dr. Qianqian Li for providing me with the cooperation from Department of Aeronautics, and career advice. Without her helps, this project could not go smoothly with the successful outcomes.

I would like to thank Dr. Liuqing Peng, Dr. Jingwei Xian, Dr. Yi Cui, Dr. Thomas Kowk, Dr. Te-Cheng Su, Dr. Zeng Guang, Mr. Di Wang, Mr. Thanasis Zois and Mr. Dan Markcoons for the experimental and theoretical helps. I would like to especially thank Dr. Mahmoud G. Ardakani for the helps and trust on electron microscopes.

Also, Throughout the hard time period of the research, my colleagues, Dr. Jalal R J Al-Lami, Dr. Vasillis Karamitros, Dr. Chris Bilsland, Dr. Dongkuk Kim and Dr. Ruth Birch were encouraging each other to complete the PhD projects.

Finally, I am deeply thankful to my parents, Jih-Huei Lin and Zi-Yu Lai, two sisters, Tsai-Chieh Lin and Yu-Hua Lin, brother-in-law, Kuo-Hui Liu, and family friend, Kit-Moi Wong, for both mental and financial supports. Also, I would like to thank my girlfriend and all friends supporting me throughout the journey. I could not start and finish this journey without their supports.

Deo gratias

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Chapter 1. Introduction

1.1 Background

Magnesium is an abundant element, constituting 2.7% of the Earth's crust and 0.13% in the oceans but it does not exist as a pure metal in nature because of its high reactivity [1]. Instead, it exists commonly in ores such as double chloride carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$), dolomite ($\text{MgCO}_3 \cdot \text{CaCO}_3$) and magnesite (MgCO_3) [1]. Magnesium was firstly isolated by Sir Humphry Davy in 1808 [2]. Today, magnesium is produced commercially from ore by thermal reduction in the Pidgeon process, or by electrolytic reduction [3].

The interest in magnesium as a structural material is because it has a density of 1.7 g/cm^3 , which is substantially lighter than aluminium (2.7 g/cm^3) and steel (7.86 g/cm^3). Also, the strength-to-weight ratio can be better than aluminium alloys and an equal rigidity panel is about 37% of the mass of steel panels [4,5]. Commercial magnesium alloys began their development in the 1920s and the different developed alloys are separated into different groups in Figure 1.1 [4]. Magnesium alloys have considerable potential to reduce mass in moving structural applications such as in automotive and aeronautics. This is particularly important with the need to reduce emissions from petrol/diesel vehicles and increase battery range in electric vehicles to reach zero CO_2 by 2050 [6–8].

magnesium makes up a much smaller proportion of the magnesium industry than is the case for steel and aluminium. Deformation processing of magnesium is possible but it usually requires slower forming rates and higher forming temperatures than aluminium which adds cost. One method to improve formability and reduce cost is to start with a smaller grain size in the cast billet. For example, Luxfer (Magnesium Electron) sell their forging billet at a premium by promising that the “grain size is controlled to below 200 μm for 300 mm diameter billet” [15]. In order to control the grain size of magnesium alloy in a cost-friendly situation, different casting procedures can be applied. One of the methods is adding a grain refiner into the melt to create finer grain size during solidification.

1.2 Grain refinement of magnesium alloys

Grain refinement of magnesium alloys has been an important topic for manufacturing ingots and wrought products (extrusions, forgings and sheet) for many decades [15,16]. Magnesium alloys are categorised into two groups, Al-free and Al-bearing magnesium alloys, because they require different grain refinement methods during casting.

For Al-free magnesium alloys, the effect of Zr was discovered in 1937 and the intense effect can reduce the grain size down to less than 50 μm [17,18] and reduce the grain size by 80% compared with that without Zr addition [19]. Here, Zr additions work by adding numerous HCP-Zr particles which nucleate α -Mg due to their close atomic lattice match to HCP-Mg coupled with growth restricting Zr solute. The reason that Zr additions are ineffective in Al-containing magnesium alloys is because Al reacts with Zr to form Al_xZr_y intermetallics that do not nucleate magnesium [20]. The Zr addition for grain refinement in the Al-free magnesium alloys is widely used, especially in high performance applications, but the cost of Zr as the grain refiner leads to limited use of Al-free magnesium alloys in mass produced motor vehicles [16]. Thus, Mg-Zr refined alloys are mostly used in motor sport, aerospace and military applications [21,22].

Understanding suitable grain refinement methods for Al-bearing magnesium alloys is important for mass-produced magnesium parts that can have the most impact on reducing the mass of road vehicles. Currently, there are four grain refinement methods for Al-bearing magnesium alloys: superheating [23–29], native grain refinement [29–33], the Elfinal process [29,31,34–37] and carbon inoculation [38,39,48–57,40,58–67,41,68–75,42–47]. In these four methods, the responsible nucleants for grain refinement are not clear yet and, unfortunately, the first three methods are unsuitable. For example, cast shops would prefer not to superheat liquid magnesium above 800 °C for safety and cost reasons, native grain refinement requires the removal of alloying additions such as Mn which are important for corrosion resistance, and the Elfinal process adds iron which impairs the corrosion performance. Carbon inoculation has potential but is notoriously unreliable. Thus, further studies on the grain refinement methods for Al-bearing magnesium alloys are required.

1.3 Eutectic $\text{Mg}_{17}\text{Al}_{12}$

Among Al-bearing magnesium alloys, the AM and AZ-series alloys are commonly used both as shape castings such as steering wheels and instrument panels, and as wrought components such as forged automotive wheels [76], helicopter gear boxes and landing gear [15,77]. The chemical compositions of AM and AZ-series alloys normally contain less than the maximum solubility of Al in α -Mg, 10 wt% Al content (at 437 °C). In the as-cast condition, $\text{Mg}_{17}\text{Al}_{12}$ forms in a non-equilibrium eutectic reaction towards the end of solidification [78,79]. Many shape castings are used in the as-cast condition (without heat treatment) where the $\text{Mg}_{17}\text{Al}_{12}$ microstructure plays an important role in the corrosion performance [80,81] and the mechanical performance [82–85].

In the hypoeutectic alloys, $\text{Mg}_{17}\text{Al}_{12}$ grows as partially or fully divorced eutectic morphologies [79,86–88]. In partially divorced eutectic growth, some eutectic α -Mg grows with $\text{Mg}_{17}\text{Al}_{12}$ to show the islands of α -Mg within $\text{Mg}_{17}\text{Al}_{12}$ from 2D cross-sections [88,89].

For the fully divorced growth, all eutectic α -Mg grows on the pre-existing dendrites and the $\text{Mg}_{17}\text{Al}_{12}$ grows alone in the remaining liquid. Some studies [19,78,89,90] reported that the divorced morphology is promoted by higher cooling rate and increase of Zn content. However, another study [79] has indicated a more complex relationship between the dendrite morphology, the cooling rate and the $\text{Mg}_{17}\text{Al}_{12}$ morphology. Therefore, there is a need to develop a deeper understanding of $\text{Mg}_{17}\text{Al}_{12}$ nucleation and growth in Mg-9Al-0.7Zn and how this affects the partially divorced eutectic morphology. For example, it was noted [19,78] that microstructure development would be very different if $\text{Mg}_{17}\text{Al}_{12}$ nucleates in each isolated liquid pocket compared with if the new $\text{Mg}_{17}\text{Al}_{12}$ grows from existing $\text{Mg}_{17}\text{Al}_{12}$ in the contiguous liquid. However, at present, little is known about these factors and a dedicated study is required.

In the industry, heat treatment is often used in magnesium alloys to improve mechanical properties and/or to prepare the material for deformation processing [91,92]. The AM and AZ-series alloys are normally solution heat treated to remove $\text{Mg}_{17}\text{Al}_{12}$ and give the maximum toughness for forging processing first [15,91,93,94]. Deformation processing is often followed by precipitation heat treatment (T6) to produce a fine dispersion of $\text{Mg}_{17}\text{Al}_{12}$ and maximise the strength and hardness [91,95].

In the solution heat treatment stage, it is important to give enough time to dissolve $\text{Mg}_{17}\text{Al}_{12}$ whilst minimising the time to reduce cost. Past work [96–102] shows $\text{Mg}_{17}\text{Al}_{12}$ dissolution is mainly governed by the diffusion in the α -Mg phase [98,100,102] and this relates to the length scale of the microstructure [98]. However, the past work did not explore how the individual factors such as the α -Mg grain size, secondary dendrite arm spacing (SDAS) and $\text{Mg}_{17}\text{Al}_{12}$ morphology affect the dissolution kinetics of $\text{Mg}_{17}\text{Al}_{12}$. This information is needed to select optimum solution treatment times.

1.4 Project aims and objectives

Aims

The overall aim of this thesis is to build the understanding of microstructure formation during each stage of casting and solution heat treatment in AZ91 to enable the industry to optimise their processing routes for optimal microstructures. A key focus is on the mechanism of carbon inoculation and the effects of the α -Mg grain morphology on the microstructure of $\text{Mg}_{17}\text{Al}_{12}$.

Objectives

- Identify the carbides forming during reaction between carbon additives and liquid AZ91, understand their growth morphologies and investigate interactions between different carbides in the solidification sequence. (Chapter 4)
- Examine the relationships between carbides and intermetallics during solidification. (Chapter 4)
- Characterise carbides in gravity castings after carbon inoculation. (Chapter 5)
- Explore the heterogeneous nucleant for α -Mg grains in gravity cast samples after carbon inoculation. (Chapter 5)
- Investigate the nucleation and growth of eutectic $\text{Mg}_{17}\text{Al}_{12}$ by combining crystallographic orientation mapping with imaging of the 3D structure of $\text{Mg}_{17}\text{Al}_{12}$. (Chapter 6)
- Develop quantitative relationships between the α -Mg morphology, the eutectic cooling rate and the $\text{Mg}_{17}\text{Al}_{12}$ morphology and use the understanding to control the level of divorced eutectic $\text{Mg}_{17}\text{Al}_{12}$ in AZ91. (Chapter 6)
- Investigate the dissolution kinetics and microstructure changes of $\text{Mg}_{17}\text{Al}_{12}$ during the solution heat treatment at 410 °C. (Chapter 7)
- Explore models for the dissolution of $\text{Mg}_{17}\text{Al}_{12}$ during the solution heat treatment at 410 °C that account for the relevant microstructural features. (Chapter 7)

Chapter 2. Literature Review

2.1 Nucleation Theory

When liquid metals or alloys cool below their liquidus temperature, there is a thermodynamic driving force for solidification. However, before the solid can grow, it must firstly nucleate. There are two mechanisms by which this can happen: homogenous nucleation and heterogenous nucleation. Both mechanisms depend on the size of solid-like clusters in the melt. If the clusters are too small, the high solid-liquid interfacial energy cannot be overcome by the thermodynamic driving force. Once, a solid-like cluster is large enough such that the volumetric thermodynamic driving force can overcome the interfacial energy, the cluster becomes a nucleus [103].

2.1.1. Homogenous nucleation

Homogeneous nucleation is assumed to be the formation of a large enough solid-like cluster through atomic fluctuations in liquid. Assuming the solid phase starts growing as an isotropic spherical shape as shown in Figure 2.1, the total change in Gibbs free energy is the sum of the Gibbs free energy per unit volume of solid transformed and the interfacial energy of the new solid-liquid interface, and can be expressed as the following [104]:

$$\Delta G = -V_s \Delta G_V + A_{SL} \gamma_{SL} = -\frac{4}{3} \pi r^3 \frac{L_v \Delta T}{T_m} + 4 \pi r^2 \gamma_{SL} \quad (2.1)$$

Where V_s is the volume of the solid, ΔG_V is the difference of Gibbs free energy between the liquid and solid phase per unit volume (which is equal to $\frac{L_v \Delta T}{T_m}$ where L_v is the latent heat of fusion per unit volume, ΔT is the melt undercooling, and T_m is an equilibrium melting temperature), A_{SL} is the interfacial area between the liquid and solid, and γ_{SL} is the interfacial energy per unit area.

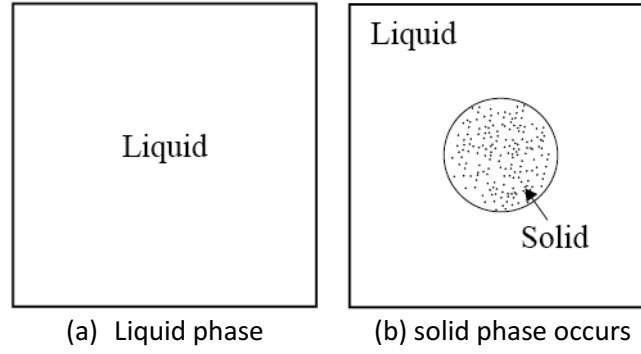


Figure 2.1 Illustration of homogenous nucleation based on Ref.[104].

From Eq.(2.1), the Gibbs free energy difference can be plotted as Figure 2.2 where the maximum energy difference, ΔG^* , is the threshold for the solid to be able to grow. If the radius of solid is smaller the critical radius, r^* , the Gibbs free energy is reduced if the radius reduces, and the solid would dissolve into the liquid. However, if it reaches r^* , solid can decrease G by growth and is thus a stable nucleus. The critical radius can be calculated from differentiating Eq.(2.1) giving the following:

$$r^* = \frac{2\gamma_{SL}}{\Delta G_V} = \frac{2\gamma_{SL}T_m}{L_v\Delta T} \quad (2.2)$$

Eq.(2.2) can be substituted into Eq.(2.1) to give the energy barrier, ΔG^* :

$$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3T_m^2}{3L_v^2}\right) \frac{1}{(\Delta T)^2} \quad (2.3)$$

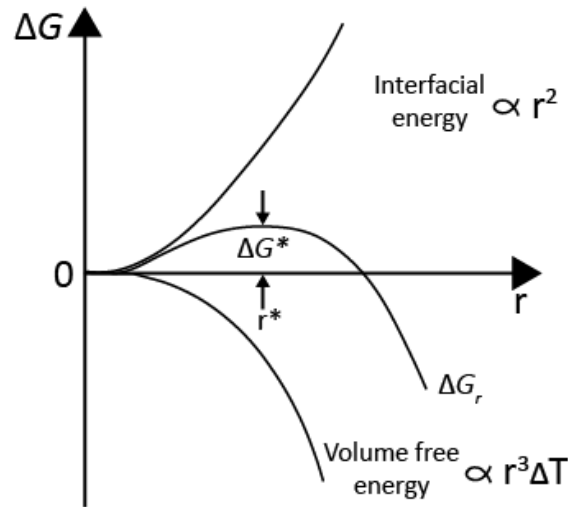


Figure 2.2 The association between interfacial energy and volume free energy based on [104].

The average density of spherical crystal-like clusters with radius (with $r \geq r^*$), n_c , can be written as a Maxwell-Boltzmann distribution [103]:

$$n_c = n_l \exp \left(\frac{-\Delta G^*}{kT} \right) \quad (2.4)$$

Where n_l is the total density of atoms in the liquid, k is Boltzmann's constant, and ΔG^* is the critical change of free energy from liquid to form solid phase which is the same as Eq.(2.3). From the distribution, the dashed line in Figure 2.3 shows a small number of clusters overcome the critical radius.

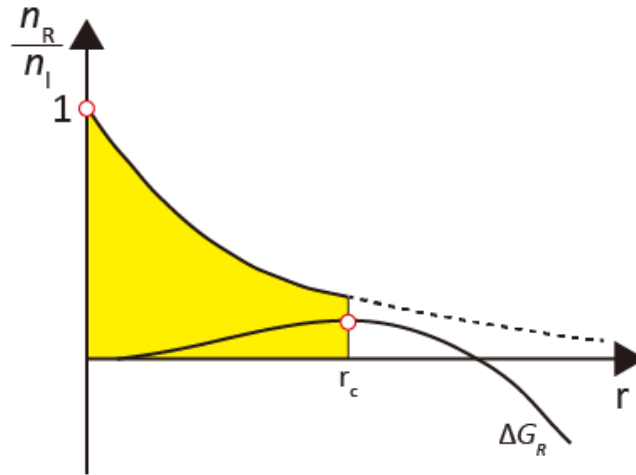


Figure 2.3 The density of embryos versus the radius of the embryos where n_R is density of clusters with size of radius, r , in equilibrium state and n_l is the density of clusters in the liquid based on Ref. [103].

Once one more atom is added onto the clusters at critical radius, R_c , they can transform into the stable nuclei in theory and this can happen with a frequency, f_0 which can be described by [104]:

$$N_{hom} = f_0 n_l \exp \left(-\frac{\Delta G^*}{kT} \right) \text{ nuclei } m^{-3} s^{-1} = f_0 n_l \exp \left(-\frac{A}{(\Delta T)^2} \right) \text{ nuclei } m^{-3} s^{-1} \quad (2.5)$$

Where A is $\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_v^2 kT}$, obtained by substituting Eq.(2.3)

Figure 2.4 shows the importance of the undercooling reaching ΔT_N and shows that the range of ΔT_N is very narrow in nature.

Calculations of the undercooling required for homogenous nucleation at a statistically likely critical nucleus size typically predict undercoolings of hundreds of K in magnitude [103]. While past work on small droplets has measured undercooling on this order of magnitude (e.g. Turnbull [105]), most Mg casting alloys have a nucleation undercooling of less than a few K in contradiction to homogenous nucleation theory [106]. Therefore, homogeneous nucleation rarely (if ever) occurs in alloy solidification and heterogeneous nucleation is the dominant nucleation mechanism.

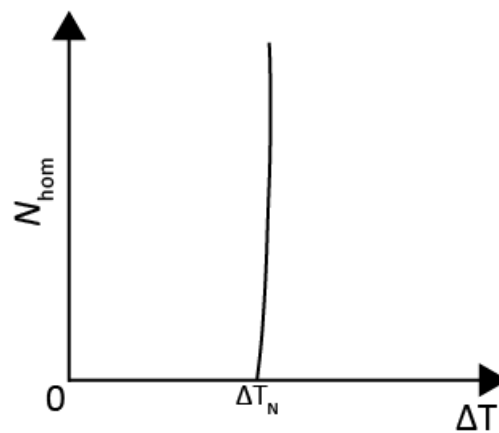


Figure 2.4 The plot of homogeneous nucleation rate N_{hom} versus undercooling ΔT based on Ref. [104].

2.1.2. Heterogeneous nucleation

If solid impurity particles or intentional particle additions are present in liquid alloys, there are pre-existing solid-liquid interfaces that alter the thermodynamics of nucleation. Nucleation on the pre-existing particle can form a contact angle between the pre-existing phase and the spherical cap-shape embryo as shown in Figure 2.5. This contact angle is a wetting angle, and this alters the interfacial energy required for nucleation.

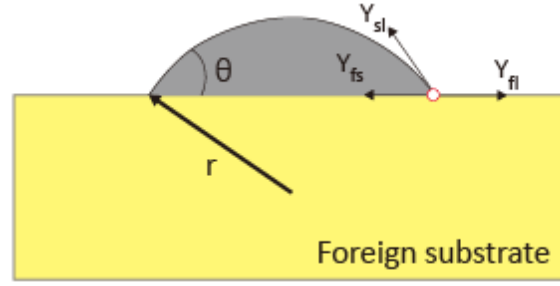


Figure 2.5 A spherical solid cap-shape embryo is attached with a foreign substance with a contact angle (θ) based on Ref. [103].

This phenomenon can be written as the following equation [103]:

$$\gamma_{fl} = \gamma_{fs} + \gamma_{sl} \cos \theta \quad (2.6)$$

Where γ_{fl} is the surface energy between the liquid and foreign substance, γ_{fs} is the surface energy between the foreign substance and embryo, and γ_{sl} is the surface energy between the embryo and liquid

Consider Eq.(2.6) in a condition without the wetting angle, the relationship between three different surface energies can be summarised as the following two points [103]:

1. If $\gamma_{fl} > \gamma_{fs} + \gamma_{sl}$, then the solid is energetically favourable to grow over the foreign substance.
2. If $\gamma_{fs} > \gamma_{fl} + \gamma_{sl}$, then the solid does not wet on the foreign substance and there can be no heterogenous nucleation.

In addition, the excess free energy for heterogeneous nucleation can be derived from Eq.(2.1) and Eq.(2.6), and this can be written as below [104]:

$$\Delta G_{het} = -V_s \Delta G_v + A_{sl} \gamma_{sl} + A_{fs} \gamma_{fs} - A_{fl} \gamma_{fl} \quad (2.7)$$

Where V_s is the volume of the solid cap-shape embryo, A_{sl} and A_{fs} are the area of the solid/the liquid and the foreign substance/solid, and γ_{sl} , γ_{fs} and γ_{fl} are the free energies of the solid/liquid, the foreign substance/solid and the foreign substance/liquid respectively.

In addition, the volume of the solid and the area of interface between the three phases can be written as below [103]:

$$V_s = \frac{\pi r^3}{3} (1 - \cos \theta)^2 (2 + \cos \theta) \quad A_s = 2\pi r^2 (1 - \cos \theta) \quad A_{fs} = \pi (r \sin \theta)^2 \quad (2.8)$$

When Eq.(2.8) is inserted into Eq.(2.7), the following equation shows the relationship between the wetting angle and the Gibbs free energy [104]:

$$\Delta G_{het} = \left\{ \frac{-4}{3} \pi r^3 \Delta G_v + 4\pi r^2 \gamma_{sl} \right\} f(\theta) \quad (2.9)$$

Where
$$f(\theta) = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \quad (2.10)$$

$f(\theta)$ is a shape factor which takes the form of Eq.(2.10) for a cap-shape solid. Eq.(2.9) can be manipulated by the same procedure as Eq.(2.1) to find the critical radius for heterogeneous nucleation. As a result, the equation can be written as the following [103,104]:

$$r^* = \frac{2\gamma_{sl}}{\Delta G_v} = \frac{2\gamma_{sl}T_m}{L_v\Delta T} \quad (2.11)$$

Figure 2.6 The excess free energy comparison between homogenous and heterogenous nucleations based on Ref. [104].

Due to the shape factor, there are two scenarios that can happen with various wetting angles (θ) (Figure 2.7) [103]:

1. When $\theta=\pi$, $f(\theta)=1$, the solid is not wetted on the foreign substance and the excess energy of heterogeneous nucleation is equal to that of homogeneous nucleation.
2. When $\theta=\frac{\pi}{2}$ and $\gamma_{fl}=\gamma_{fs}$, $f(\theta)=0.5$, and a cap-shaped solid is formed as a hemisphere and this reduces half the excess energy compared to the homogenous nucleation to overcome the energy barrier.
3. When $\theta=0$, $f(\theta)=0$ and $\Delta G_{het}=0$. This means the solid is completely wetted on the foreign substance due to the non-energy barrier between the solid and foreign substance.

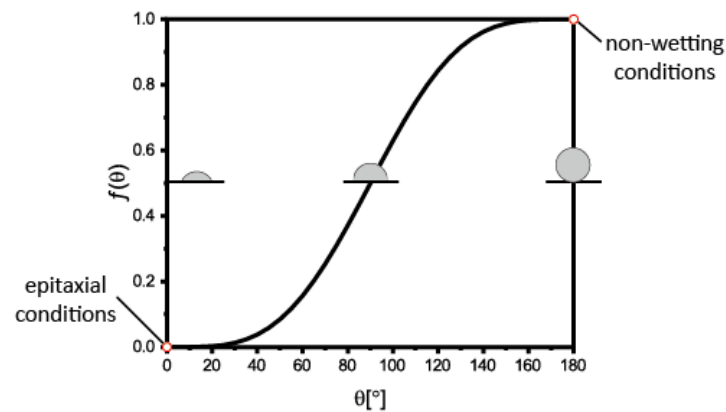


Figure 2.7 The shape factor as a function of the wetting angle based on Ref. [103].

Heterogenous nucleation does not change r^* but it does change the nucleation barrier from the shape factor. In addition, as ΔG^* is lower, the nucleation rate (Eq.(2.5)) will increase.

2.1.3. Nucleant potency

The potency of a heterogenous nucleant is dependent on the crystallographic atomic registry between the embryo and nucleant [107]. As a potent nucleant has low atomic registry, this directly reduces the interfacial energy, γ_{fs} , so the wetting angle becomes smaller from Eq.(2.6) [103]. This promotes heterogenous nucleation at a low undercooling.

2.1.4. Different ways to quantify the lattice match and predict nucleant phases

The first measure of atomic matching was put forward by Turnbull and Vonegut as the linear registry between nucleant and the solid [107]. Later, Bramfitt [108] developed the planar

disregistry at an interface between different phases. In the last decade, Kelly [109] and Zhang [110] have put forward the edge-to-edge matching model (E2EM) that aims to predict the orientation relationship (OR) between new and pre-existing solid phases, and has been used to explain heterogenous nucleation phenomena [111] and as a tool to search for new nucleants [112].

2.1.4.1 Turnbull-Vonegut linear disregistry

In the case of nucleation of ice crystals, it was found that the crystallographic similarity between a nucleant and solid plays an important role in heterogenous nucleation [113]. Therefore, the idea of lattice disregistry, δ , was defined by the following equation [107]:

$$\delta = \left| \frac{\Delta a}{a_0} \right| \quad (2.12)$$

where Δa is the difference of interatomic distance in a low index comparison plane of the nucleant and the solid; a_0 is the interatomic distance in the low index plane of the solid.

In another experiment of nucleation of mercury crystals coated on different films [114], it was observed that the supercooling of mercury sulphide is lower than mercury iodide which is the same as the order of structural similarity [107]. In terms of cast aluminium alloys, it has been found that effective nucleants have δ less or equal to 15% for the closest packed plane [115]. This shows evidence of the crystal structure and lattice parameters affecting the potency of the nucleus. Significant grain-refinement happens when the lattice disregistry in low index planes between the additives and metal melt is less than 10% [107,116]. Additionally, researchers [116–118] showed a definite OR between the nucleant and solid phase when the value of δ is less than 0.1.

The interfacial energy is suggested to be the factor of a coherent lattice that can minimise the energy barrier between a catalyst and crystal structures [107]. The minimum free energy will be when ϵ is less than δ where

$$\epsilon = \left| \frac{x-a_0}{a_0} \right| \quad (2.13)$$

and x and a_0 are the lattice parameters of the nucleus with respect to the strained and normal condition [107]. As a result, $\delta - \epsilon$ is the actual disregistry between the nucleus and liquid, and it is incoherent when $\delta > \epsilon > 0$ [107].

2.1.4.2 Bramfitt planar disregistry

From the experiment of heterogenous nucleation of liquid iron with different carbides [108], it was shown that the degree of undercooling increases with increasing lattice disregistry. This is the same as the observation by Turnbull and Vonegut [107]. In addition, the interfacial energy between the nucleant and nucleus affected by the degree of epitaxy and influences the undercooling directly through the lattice disregistry [119].

However, Bramfitt [108] pointed out that there is a limitation to Turnbull-Vonegut's Eq.(2.12) because it can only be used for planes with similar atomic arrangement between the nucleant and solid. To account for planes of different atomic arrangement, a planar disregistry formula was developed by Bramfitt [108] as the following:

$$\delta_{(hkl)_s}^{(hkl)_n} = \frac{1}{3} \sum_{i=1}^3 \frac{|d[uvw]_n^i \cos \theta - d[uvw]_s^i|}{d[uvw]_s^i} \cdot 100\% \quad (2.14)$$

Where $(hkl)_n$ is a low index plane of the nucleant; $[uvw]_n$ is the low index direction in the nucleant $(hkl)_n$; $(hkl)_s$ is a low index plane in the solid; $[uvw]_s$ is the low index direction in $(hkl)_s$; $d[uvw]_s$ is the interatomic spacing along $[uvw]_s$; $d[uvw]_n$ is the interatomic spacing along $[uvw]_n$; θ is the angle between the $[uvw]_n$ and $[uvw]_s$

From the experimental results, Bramfitt [108] showed that the limit of a potent nucleant is 12% and effective nucleants have less than 12% of planar disregistry which is similar to the result from Turnbull-Vonegut equation (2.12). This method has overcome the limitation of similar atomic arrangement from linear disregistry and matches the plane-to-plane

arrangement between nucleant and nucleus. Also, it has given evidence of the lattice disregistries related to the characteristic undercooling (Figure 2.8).

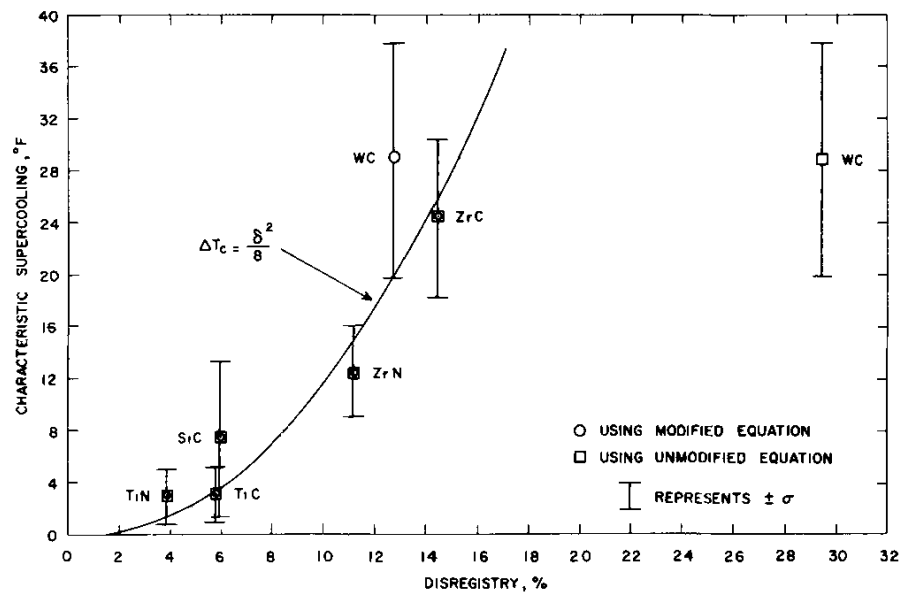


Figure 2.8 Characteristic undercooling versus lattice disregistry percentage calculated by Turnbull-Vonnegut disregistry (unmodified) and planar disregistry (modified) methods with various nucleants additives in ferrite [108].

2.1.4.3 Edge-to-edge matching (E2EM)

The E2EM approach is based on the minimisation of mismatch in rows of atoms within an interphase boundary which was developed from the fcc-bcc interface in Shiflet and Van der Merwe's work [120]. The first work on E2EM was done by interpreting the habit plane between austenite and ferrite in steels [109]. Before developing the E2EM model, there are two fundamental concepts which have been adopted when seeking the habit planes.

Firstly, when two lattices are next to each other, there are certain atomic close matching sites which are called near-coincidence sites (NCS) [121]. The high planar density of NCS indicates no missing atoms near the matching boundary and the orientation relationship can be found between the habit plane and parent lattice. This also corresponds to lower misfit between two lattices. Secondly, the 0-lattice approach calculates the transformation between two crystal lattices from the smallest possible strain [109]. This is done by matching a coincident internal

coordinate point and measuring the distortion from the relative lattice points [122]. Based on the 0-lattice approach, the small shift caused by the strain indicating as good match and the row of atoms will be extended. On the other hand, a large shift indicates that dislocation will form [122].

These two ideas of NCS and O-lattice concludes the area of the low dislocation density is the habit plane between two lattice structures matching. However, both concepts cannot predict the habit plane directly because they are based on the assumption of the lattice boundaries and the orientation relationship between two lattices [109,121,122]. Later, Shiflet and Van der Merwe [120] showed that the minimisation of interfacial energy corresponds to the lower misfit in the interface of the two lattices.

The E2EM model developed by Kelly and Zhang is based on the following features [109,123]:

1. In crystallographic structures of two contacting phases, the habit plane and orientation relationship are established with long range isotropic atomic diffusion. In addition, this condition needs to meet the minimisation of interfacial energy between two lattices.
2. From the research of Shiflet and van der Merwe [120], the minimisation of interfacial energy happens in the close-packed or nearly close-packed atomic arrangement which is located in the NCS. In order to minimise the interfacial energy, the atomic arrangements in the interface need to match closely.
3. One of the most important criteria is that the close-packed or nearly close-packed atomic rows needs to be in the edge of each plane of the two contacted phases.

The practical procedures of the model can be understood by taking the face centred cubic (FCC) and body centred cubic (BCC) crystal structures as the example [109]:

1. The low index planes containing atoms in the two structures are selected and these need to be close-packed or nearly close-packed planes.
2. The d-spacings, the interplanar spacings, as a function of the lattice parameter ratio between two structures, β , are plotted. In the example of FCC and BCC, the ratio is written as

$$\beta = \frac{a_F}{a_B} \quad (2.15)$$

where a_F and a_B are the lattice parameters of FCC and BCC respectively

3. When they meet a point where the d-spacings are the same, it means the two planes are parallel to each other. Hence, this can be treated as an orientation relationship based on the families of the planes.
4. The last step is to identify the lowest misfit of the parallel planes from the previous step and this allows the rows of atoms to happen in different planes within the same family.

Comparing to the concepts of NCS and O-lattice, the E2EM model does not make assumptions about the habit plane and the orientation relationship between two lattices. Instead, it can predict the two main features from minimisation of interfacial energy and less than 10% misfit from the atomic rows and d-spacings.

2.1.5. Athermal nucleation

The concept of heterogeneous nucleation in the previous section considers embryos or nuclei that form spontaneously on a nucleant particle in the liquid. This is determined by the interfacial energy of wetting ability which depends on whether the particles exceed the critical radius, r^* , for growth into grains. However, in a real liquid, there will be a size distribution of particles which vary in potency for nucleation. This leads to the concept of athermal nucleation which was firstly adopted from the research of Fisher et al [124]. Fisher et al. [124] also indicates that

the nucleation process is sensitive to undercooling. The name of “athermal nucleation” came from the phase transformation of martensite. The term refers to processes that depend on temperature changes but not the time [103] so “athermal nucleation” has been used to separate from thermal nucleation.

The initial physical model was found by considering an embryo which grows on a containing different cavities [125]. Turnbull [126] used a conical cavity as the model to calculate that when the temperature increases above the equilibrium melting temperature, T_m , the radius (r) of solid inside the cavity will decrease (Figure 2.9). This is because after decreasing the temperature, the Gibbs free energy favours the solid, and the solid starts forming on approximately flat surface [126]. This indicates that the undercooling, ΔT , activates the embryos to become nucleants when they grow above the surface of the cavity.

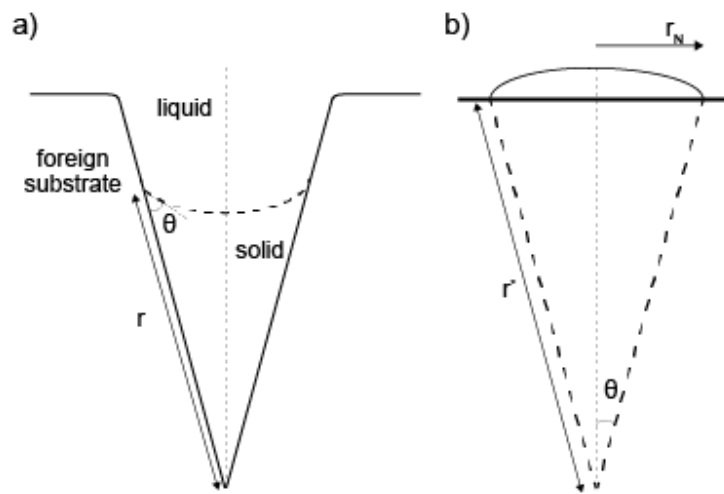


Figure 2.9 (a) A illustration of solid that starts from a cavity when the equilibrium melting temperature, T_m , reaches the solid can only survive on no-flat surface based on Ref. [126]. (b) An example of a solid on a substrate with a wetting angle, θ , and there is potential that $r^* \sin \theta$ can exceed the radius of r_N nucleant based on Ref. [125].

From using the same method for the triple junction in the basic heterogenous nucleation, the method shows that when some certain sizes of embryos go through minimum Gibbs free energy, they can still survive at T_m due to the geometry (Figure 2.10) [103]. As the temperature decreases and approaches T_m , the surface energy between liquid and solid, γ_{sl} , will reduce until

zero. The radius (r) of curvature in Figure 2.9(a) will increase until reaching the mouth of the cavity and then the negative curvature present since the embryo physically cannot extend further on the flat substance [103]. When the temperature drops to T_m , the cavity is filled with the embryo. After the temperature falls below T_m , the embryo starts growing due to the undercooling in the liquid and it will grow in the same manner as the illustration in Figure 2.5.

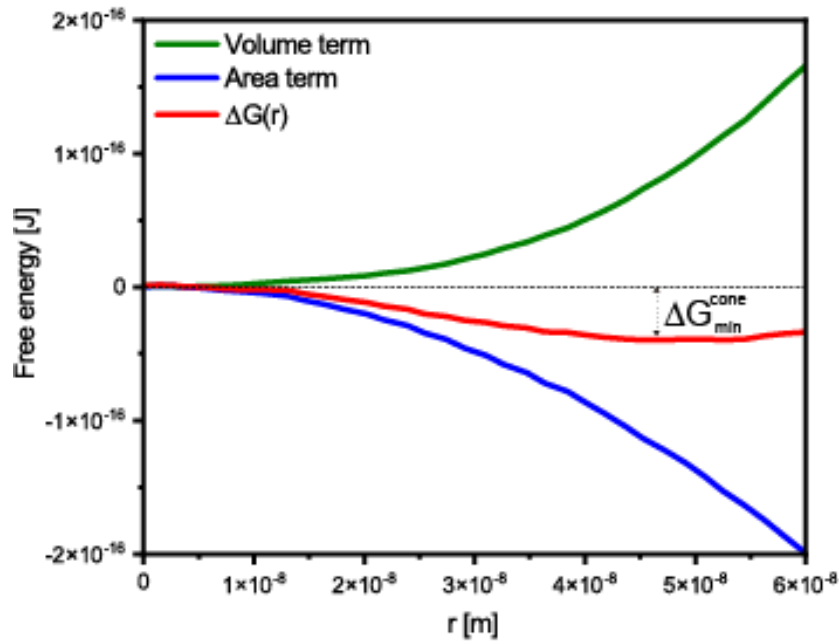


Figure 2.10 The free energies in volume and area terms with respect to an embryos inside a cavity such as the example Figure 2.9(a) when the half angle inside the cone is $\frac{\pi}{3}$, $\theta = \frac{\pi}{10}$ and $T = 983K$ based on Ref [103].

At this stage, the nucleation mechanism is similar to the previous idea of heterogeneous nucleation. The major difference between classical heterogeneous nucleation and athermal nucleation is that in the former one, the nucleants exist at any temperature and once triggered they will grow at certain rate [103]. However, the latter one gives the history of the morphology of embryos that is significantly affected by the undercooling from the temperature above T_m and after the temperature drops below T_m .

From Section 2.1.2, the relationship between three different interfacial energies and the wetting angle is known. From Eq.(2.6), the energy difference between $(\gamma_{fs} + \gamma_{sl})$ and γ_{fl} determines the energy barrier of forming a nucleus. Athermal heterogeneous nucleation also

considers the temperature and undercooling for the free growth of the nucleus on the limited length of foreign substance. The growth of nucleus has the wetting angle of θ and determines the energy barrier of nucleation. When θ is less than 10° , the nucleus will become a monolayer and it no longer presents as a spherical cap as in Figure 2.11 [125,127]. However, when the θ is small, the required r^* becomes too large and this becomes problematic to the foreign substance [125]. In contrast, if the θ is larger than 40° , the undercooling will become too large that the nucleus losses potency [128,129]. From the combination of all the free and surface energies, the total energy balance above T_m can be written as the following [103]:

$$\Delta G = -A_{\text{sub}}\delta(\rho\Delta s_f)\Delta T + A_{\text{sub}}(\gamma_{fs} + \gamma_{sl} + \gamma_{fl}) \quad (2.16)$$

Where A_{sub} means the exposure area of the foreign substance to the melt, δ is the thickness of the solid layer, $\rho\Delta s_f\Delta T$ is the volumetric term of the free energy, which is equal to ΔG_v in Section 2.1.2. The assumption of $\Delta T < 0$ is based on the thickness δ of the solid can be formed above the melting temperature and this is agreed with the top part of Figure 2.11(a).

The above discussion is for the process of the temperature approaching T_m and the limited size of foreign substance is considered in the following which is different from the infinite size in Section 2.1.2. As the nucleus starts forming on the flat surface of the solid, it has the limitation of the growth which covers the foreign substance as a hemispherical shape with the radius, r_N (the bottom of Figure 2.11(a)). This is due to the geometrical undercooling, ΔT_g . This implies the growth of solid is controlled by the geometry of the nucleant and the temperature. The other case is when $\gamma_{fl} - \gamma_{sl} < \gamma_{fs} < \gamma_{fl} + \gamma_{sl}$, it happens in the same way as in the previous section. If $r^* \sin\theta$ is smaller than r_N , then the new solid can grow on the substance. However, if the undercooling is large enough, the surface of substance cannot support the nucleus (Figure 2.11(b)).

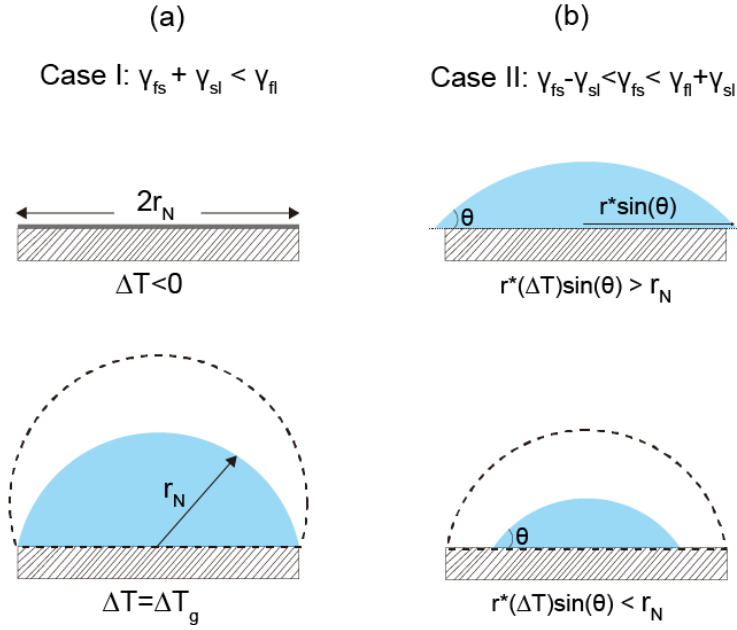


Figure 2.11 An illustration of solid nucleating on a foreign substance and the two cases can happen when: (I) $\gamma_{fs} + \gamma_{sl} < \gamma_{fl}$ and (II) $\gamma_{fl} - \gamma_{sl} < \gamma_{fs} < \gamma_{fl} + \gamma_{sl}$ where ΔT_g is the undercooling for the local geometry, r_N in Figure 2.9(b) and r^* in Figure 2.9(b) based on Ref [103].

To summarise the different situations above, the undercooling and the critical geometrical undercooling can be written as the following [130].

$$\frac{r_N}{r^*} = \frac{\Delta T}{\Delta T_{fg}} = \sin \theta \quad (2.17)$$

Where ΔT_{fg} is the critical undercooling for the set of geometrical shapes.

All kinds of situations can be categorised into three regions: (I) no nucleation, (II) formation of stable embryos, and (III) no barrier to free growth (Figure 2.12). These can be simply differentiated between $\frac{\Delta T}{\Delta T_{fg}} \geq 1$ and less than one. In region (I), the small embryos are not able to form a spherical cap on the foreign substance but in region (II), the embryos can form a spherical cap which is not able to grow because r^* cannot increase over r_N and this causes the embryos to stop growing [125]. In region (III), it shows that the undercooling suppresses the critical undercooling and $r_N > r^*$ so that the initial nucleation forms on the foreign substance [125].

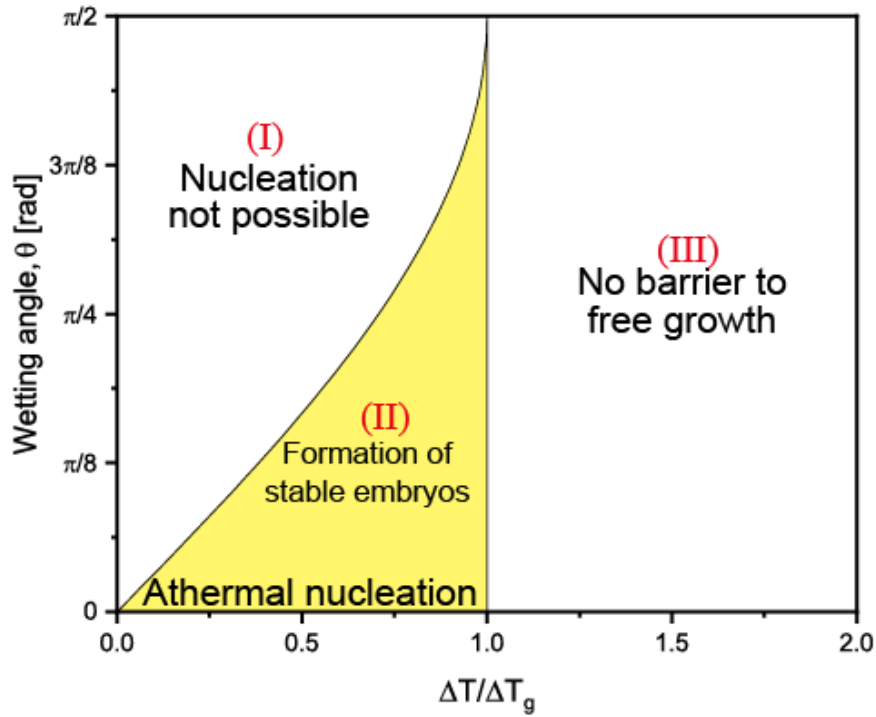


Figure 2.12 The heterogeneous nucleation on a foreign substance as the function of wetting angle and normalized undercooling where ΔT_g is equal to ΔT_{fg} based on Ref [103,125].

In terms of considering the mechanism of grain refinement, in the region (III), the heterogeneous nucleation will have no energy barrier to grow a nucleus but the more considerable area is region (II). This is because in region (II), athermal nucleation happens when the embryos with small wetting angles are formed stably but stop growing due to the limitation of the geometry of the particles. However, when ΔT increases beyond ΔT_{fg} , the embryos will become the nucleus for grains and can grow without the limitation of the substrate sizes [103].

Therefore, in the practical situation, the size distribution of inoculant particles can be similar to Figure 2.13. Only a small number of particles become the active nucleants since the larger particles have lower ΔT_{fg} which can cause nucleation of grains first. After the grains formed by these particles, they will entrap other smaller particles or they can become active if the undercooling reaches the required ΔT_{fg} before being entrapped by the solidified grains [103].

This indicates that the wide particle distribution is detrimental to good grain refinement and a narrow size distribution and smaller particle sizes are required for the effective grain refinement.

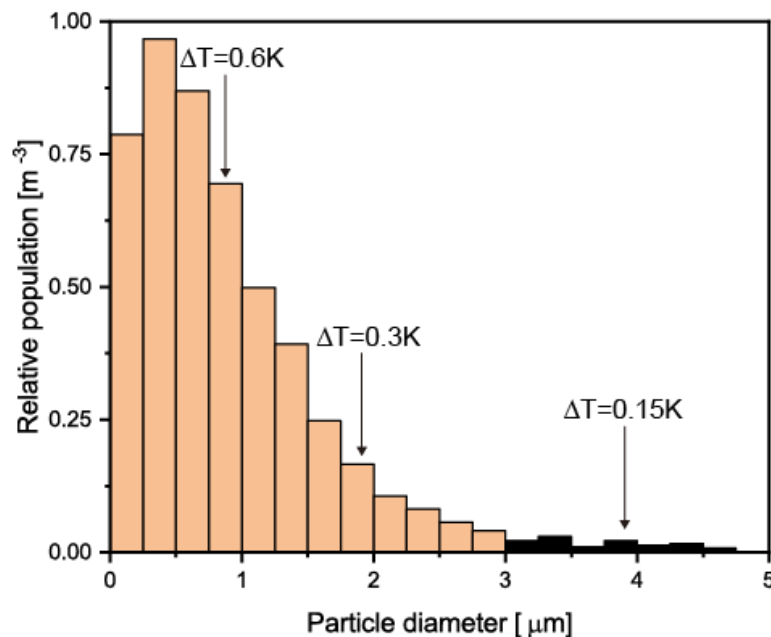


Figure 2.13 The particle distribution of TiB_2 adding into aluminium melt with the required undercooling respect to the particle size where the black regions are the active nucleants based on Ref [103,125,131].

2.1.6. The Interdependence Theory

Apart from inoculant particles, the second considerate factor in grain refinement is the role of solute rejected and diffusing ahead of growing grain (dendrites). Solute results in the development of constitutional supercooling (CS) in the liquid ahead of growing dendrites and restricts growth (CS zone in Figure 2.14). This theory captures how grain refinement can be controlled by the solute inside the melt where only ~1% effective inoculation can become nucleants [130,132]. During the process of solidification, constitutional supercooling will cause nucleation to occur if an inoculant particle is present requiring a nucleation undercooling that is less than the constitutional supercooling at that point in the melt. The distance between every nucleation event then determines the final grain size[106]. This is illustrated in Figure 2.14..

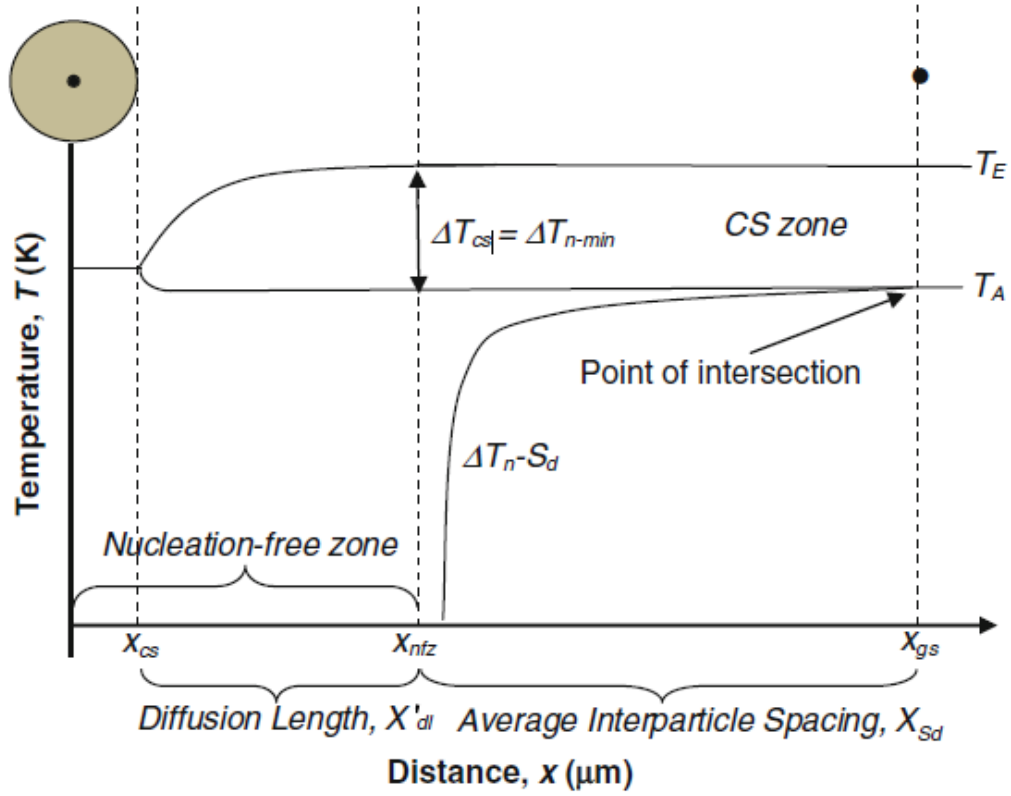


Figure 2.14 The illustration of microstructure of grain growth according to Eq.(2.19). The region of nucleation-free zone is described by $\Delta T_n - S_d$ particle distribution where ΔT_n is the minimum nucleation undercooling and S_d is average particle spacing for particles with diameter d . The point of intersection is when the next most potent particle nucleates when the ΔT_{n-min} is reached. [132].

Tarshis et al [133] proposed an early model of growth restriction factor and showed that a higher parameter value causes finer grains in alloys. However, Greer et al [134] agree that the later work from Maxwell and Hellawell [135] gives a more accurate growth restriction factor to an alloy system which considers as a proportionality to the diffusivity of the solute inside the melt. The redefined growth restriction factor, Q , can be written as [134]:

$$Q = m \cdot C_0 \cdot (k - 1) \quad (2.18)$$

Where m is the liquidus slope from a binary phase diagram, C_0 is the bulk composition in the alloy system, and k is the partition coefficient (concentration of solid over liquid), $k = \frac{C_s}{C_l}$.

However, Eq. (2.18) was used for the binary alloy system and Johnsson [136] proposed that the growth restriction factor for the multi-component alloys can be written as:

$$Q = \sum m_i \cdot C_0 \cdot (k_i - 1) \quad (2.19)$$

Where m_i is the liquidus slope from a binary phase diagram for the solute, and k_i is the distribution of the partition coefficient of the solute.

In general, the growth restriction factor shows the effect of the concentration of solute on the alloy system and this parameter gives some guidance on grain refinement [137]. The growth restriction is inversely proportional to the grain size but this condition is only applied when the effective solutes present in the alloy system since different solutes can interact with each other to form different phases or the solution is saturated [134,137,138]. The more detailed description of how solute influences grain refinement via Q is expressed in the Interdependence Theory [132].

The Interdependence Theory is based on the solidification cycle caused by CS [106]. The illustration of the theory is shown in Figure 2.14. In Figure 2.14, the nucleation undercooling (ΔT_n) with respect to average particle spacing (S_d) is based on the Free Growth Model [106,134,139]. From determining the relationship between ΔT_n and S_d , the next nucleation event can be predicted and the grain size can be summed up from three terms, x_{cs} , x_{dl} , and x_{sd} , as the following equation [132]:

$$d_{gs} = x_{cs} + x'_{dl} + x_{sd} = \frac{D \cdot z \cdot \Delta T_{n-min}}{v \cdot Q} + \frac{4 \cdot 6 \cdot D}{v} \left(\frac{C_l^* - C_0}{C_l^* \cdot (1-k)} \right) + x_{sd} \quad (2.20)$$

Where x_{cs} is the distance of growth required to build up a CS zone (in μm), x'_{dl} is the distance of S-L interface reaching a point when ΔT_{cs} is equal to ΔT_{n-min} (in μm), x_{sd} is the distance of the next potent nucleant (in μm), D is the diffusion coefficient in the liquid (in m^2s^{-1}), $z\Delta T_{n-min}$ is additional undercooling for the next nucleant event ($^{\circ}\text{C}$), v is growth velocity of the S-L interface (in ms^{-1}), Q is the growth restriction factor (in $^{\circ}\text{C}$), C_l^* is the composition of the liquid at the S-L interface (in wt%), C_0 is the bulk composition in the alloy system, and k is the partition coefficient.

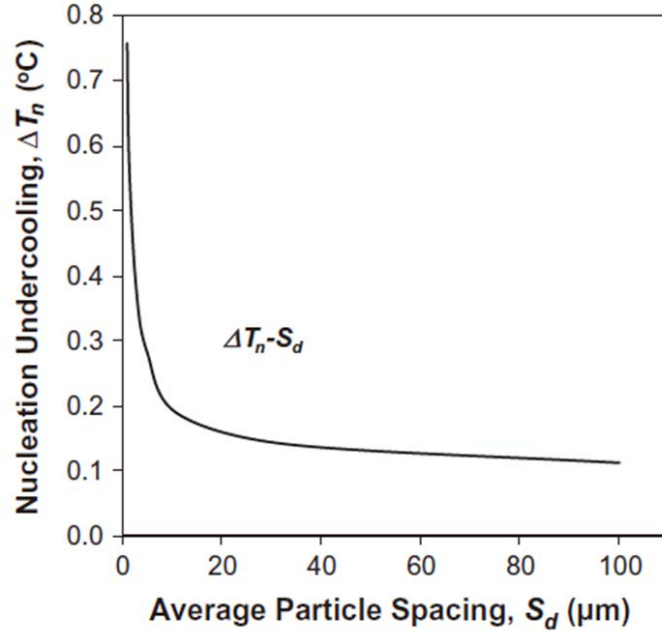


Figure 2.15 The plot of nucleation undercooling, ΔT_n , versus average average particle spacing, S_d , for $\Delta T_n < 0.8$ °C because they are more likely to become active nucleants [132].

Figure 2.16 shows the interpretation of Eq.(2.20) and it shows that x_{cs} and x'_{dl} are defined by the CS condition. These two terms can be combined as the nucleation free zone (x_{nfz}) [132]. However, x_{sd} presents as a contestant factor because it is determined by ΔT - S_d diagram in Figure 2.15.

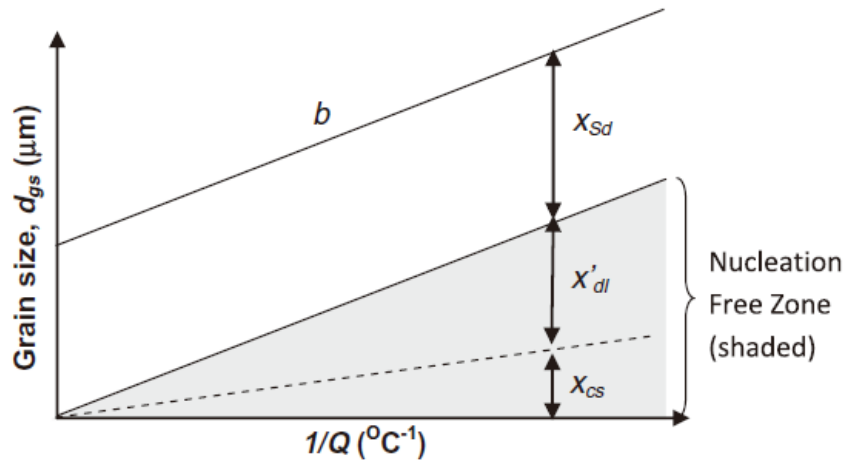


Figure 2.16 A simplified illustration of Eq.(2.20) as $d_{gs} = a + \frac{b}{Q}$ from [140] and this shows the relationship between d_{gs} and $\frac{1}{Q}$. This also indicates when there is no factor of x'_{dl} and x_{cs} , x_{sd} is the constant number for grain sizes where the average spacing between potent nucleants [132].

As $\Delta T_n = m(C_0 - C_l^*)$ and $Q = mC_0(k-1)$ replace the terms in Eq.(2.20), x'_{dl} can be converted into $\frac{4.6.D}{v} \frac{\Delta T_n}{Q}$. This can be applied when ΔT_n is small so C_l^* is close to C_0 [106]. As a result, the equation can be written as the following [106]:

$$d_{gs} = 5.6 \left(\frac{D^* Z \Delta T_n}{v^* Q} \right) + x_{sd} \quad (2.21)$$

Eq.(2.21) corresponds to Figure 2.16 and it shows two terms determining the grain size which are x_{nfz} and x_{sd} [106]. From Eq.(2.21), it shows the higher value of Q from the effective multiple solute elements in the alloy can reduce the grain size. In Figure 2.16, the intersection of the y-axis can be predicted as the maximum number of active particles that can form new grains. The parameter used for the Interdependence Theory in the Mg-Al alloys can be seen Table 2.1 and the best fits of Eq.(2.21) for high purity and commercial purity Mg-Al alloys are considerably different [32,106,141]. One reason may be due to different contents of additional elements such as Fe and Mn inside the commercial alloys. Another factor is that the nucleants inside the melt remain poorly understood in high purity and commercial purity Mg-Al alloys and remain to be determined.

Table 2.1 The parameters for Mg-Al alloys in the use of the Interdependence Theory [106]

Diffusion Coefficient (D)	$5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
Growth Velocity of S-L interface (v)	$2 \times 10^{-6} \text{ m s}^{-1}$
Liquidus Slope (m)	-6.87 K/wt%
Partition Coefficient (k)	0.37
Nucleation undercooling (ΔT_n)	High purity: 2.2 K Commercial purity: 5.5 K
Range of bulk composition (C_0)	Al: <11 wt%

Therefore, in order to produce finer grain sizes, there are two main considerable factors: (i) the type of nucleant with suitable size, particle density and potency, and (ii) the constitutional supercooling and growth restriction controlled by the solute [142].

2.2 Grain refining approaches for Mg-Al alloys

Grain refinement methods for Mg-Al alloys have been researched since the 1930s and include carbon inoculation, superheating, the Elfinal process and native grain refinement [16,29,45,143,144]. Among the four methods, the carbon inoculation method will be the main focus in this project.

2.2.1 Superheating

Typically in metal casting, heating the melt to an elevated temperature far above the liquidus temperature is not recommended because of the promotion of oxidation and grain coarsening [145]. However, usually, superheating of Al-bearing magnesium alloys produces a grain refinement effect. This grain refinement method can be tracked back to 1931 when it was firstly introduced by a British patent [144]. The operating temperature for superheating is between 180 and 250 °C above the liquidus of the alloys and the melt is held for a short time. Then, the rapid cooling system is applied to the melt to reach 720 °C before pouring into the mould. If the holding time before casting is longer than the desirable period, the superheating effect will disappear [23,24,27,29].

The chemical compositions of the alloy play an important role in the success of superheating. Studies [24,27,29,146] have reported that high purity Al-Mg-Zn alloys containing little Mn and Fe content did not respond to the superheating effect. In other words, commercial purity AZ91 can obtain grain refinement from superheating compared with the high purity AZ91 [24]. This leads to the consideration of Mn content in the alloys which may be important to superheating.

The mechanism of superheating remains uncertain. Several hypotheses have been put forward involving different heterogenous nucleant phases: (i) MgO particles [147], (ii) Al_4C_3 phase [148], (iii) Al-Mn intermetallics [25,111,149], and (iv) duplex nucleation of Al_4C_3 and Al-Mn intermetallics [23]. Past works for superheating are summarised in Table 2.2. However,

as mentioned previously, the Mn content seems to be the dominant factor for superheating. The increase of Mn content promotes the formation of Al-Mn intermetallics. Al_8Mn_5 , τ -AlMn and ϵ -AlMn have been considered as candidates phases responsible for superheating [25]. τ -AlMn was calculated as the most potent nucleant for α -Mg from E2EM due to the lowest mismatch value with α -Mg [25]. There was no other research investigating superheating until Jung et al. [24] in 2022.

Table 2.2 The research [24,27,146] on superheating grain refinement and their proposed nucleants (T: melting temperature; %: weight percentage; CP: commercial purity; HP: high purity; SH: superheating)

Year	Alloys	Varying temperature s	Casting condition	Proposed mechanism	Most refinement	Ref.
1945	Mg-8.6Al-2Zn-0.3Mn	700, 750, 800, 850, 900, 980 °C	T: the desired temperatures, cooled to 700°C for a short time before pouring to 300°C mould under flux (52.5%KCl, 40%MgCl ₂ , 6% BaCl ₂ and 1.5% CaF ₂).	-	250 μm^2 (700°C) → 286 μm^2 (750°C) → 200 μm^2 (800°C) → 36 μm^2 (850°C) → 42 μm^2 (900°C) → 105 μm^2 (980°C)	[27]
2000	AZ91E	850 °C	T: 800°C for 24 hours→ 850°C for 15 mins and cooled at 750, 700, 650, 600 °C before casting under gas mixed with SF ₆ and CO ₂	Al ₄ C ₃	83 μm (initial) → 59 μm (superheating)	[146]
2022	Mg-9Al-1Zn & Commercial AZ91	670, 770 °C	T: 670→770 → 670°C Al ₂ O ₃ crucible and pour into 250°C mould under 1 %SF ₆ + 99 %N ₂	ϵ -AlMn	HP: 98 μm → 87 μm (SH) CP: 290 μm → 114 μm (SH) → 121 μm (SH 1h) → 290 μm (SH 2h)	[24]

Jung et al. [24] approached the mechanism of superheating by two methods: (i) vacuum-filtering and (ii) 27 wt% Al-73 wt% Mn master alloy addition. The first method was applied to extract the particles from the superheating samples. This method was not successful because there was no grain refinement effect before and after filtering due to the different cooling rates in the samples. In the second method, they deliberately produced ϵ -AlMn from the AlMn master alloy since the Al-Mn intermetallics hypothesis indicates that the Al-Mn phase is the cause of the superheating effect [23,25]. As the result, the grain refinement in AZ91 was found

after adding the AlMn master alloy. The increase of 0.5 wt% AlMn master alloy reduces the grain size from 223 to 139 μm as shown in Table 2.3. The microstructures of ϵ -AlMn was not found in this study [24]. Also, this result is inconsistent with Qiu et al. [25] who suggested that τ -AlMn, with lower planar disregistry, is the nucleant for superheating and that τ -AlMn results from the transformation of ϵ -AlMn at lower temperature [25].

Table 2.3 The AZ91 grain size change by the 27 wt% Al-73 wt% Mn master alloy addition [24]

AlMn addition (wt%)	Grain size (μm)
0	223
0.1	200
0.3	173
0.5	139

Superheating is not considered as a practical method for grain refinement in Al-bearing magnesium alloys for the following reasons [16,42,106]:

1. The cost of casting can be high because furnaces are required to operate at the elevated temperatures with a fairly rapid cooling system. This operating procedure could shorten the lifetime of equipment and increase the energy cost.
2. For melting at elevated temperatures for a long period of time, the melt will start absorbing the elements from the surrounding.
3. The holding time before pouring is important for the grain refinement effect. Once the timing is longer than the limit, the effect will disappear. This becomes difficult to control in the whole process.

2.2.2 Native grain refinement

The earliest work from Nelson [29] showed that keeping manganese and iron contents low in the Mg-Al alloys can reduce the grain size of the alloys. This observation has linked to the recent work [30,32,33,36] regarding controlling the minor elemental contents inside the Mg-Al alloys (Table 2.4).

The experiments from Nelson [29] and Cao et al. [32] demonstrate whether native grain refinement affect Al-free magnesium alloys. The former one used the high purity magnesium with 0.02 wt% Si and normal commercial magnesium, and the latter one used the addition of Zn and Ca contents into magnesium. Both results show that commercial purity magnesium alloys generally have finer grains than high purity magnesium alloys.

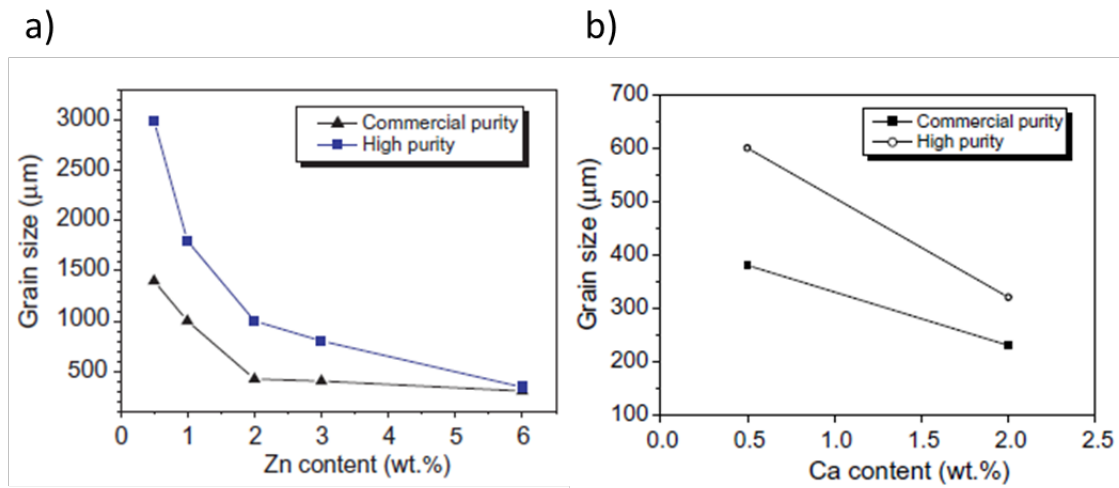


Figure 2.17 The effect of the impurity in Mg-Zn (left) and Mg-Ca (right) alloys as increasing a range of Zn and Ca content [32].

The higher content of Fe and Mn in the commercial Mg-Al alloys shows the negative effect on grain refinement and implied that the potent nucleants have been affected [29,36]. In order to explore the active nucleant for magnesium, the particles in the centre of gains were characterised. Tamura et al. [36] and Cao et al. [32] suggested the Al-C-O particles in the centre of the grains were the oxidation of Al_4C_3 particles, although Cao et al. [32] did not find the nucleants directly.

However, StJohn et al. [132] suggested that the chemical difference inside the melts in commercial and high purity alloys is an important factor of causing grain refinement (Figure 2.18). As the impurity content increases, the nucleation undercooling (ΔT_n) will increase and this affects the amount of potent nucleants. This result is conducive with the interdependence theory [132].

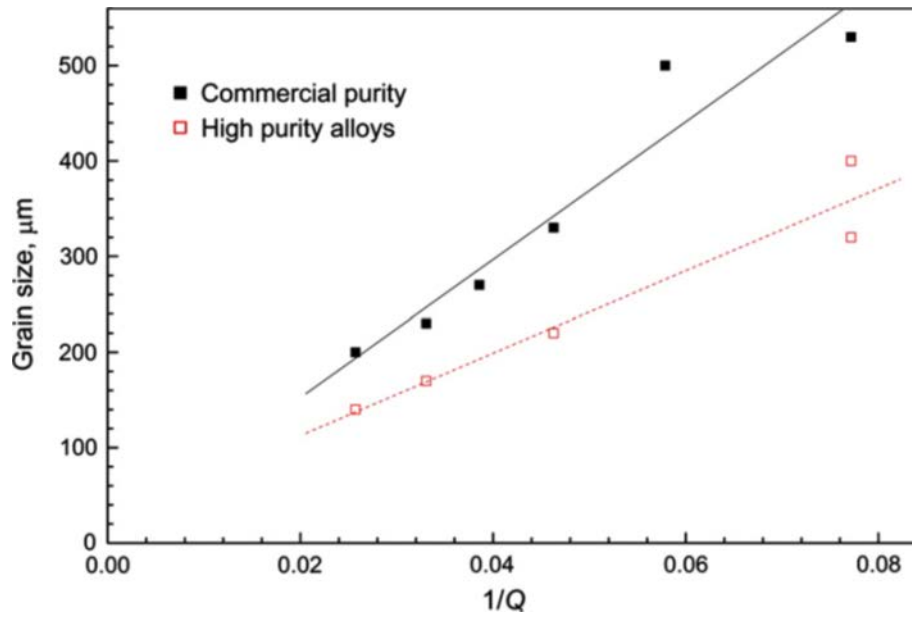


Figure 2.18 Grain size versus $1/Q$ (Q is growth restriction factor) of comparison between commercial purity and high purity Mg-Al alloys varied with Al contents [132] (after Ref. [23]).

Table 2.4 The research[29,32,36] on native grain refinement and their proposed nucleants (T: melting temperature; %: weight percentage)

Year	Alloys	Varying factor	Casting condition	Proposed mechanisms	Most refinement	Ref
1948	AZ92	High-purity and commercial AZ92	T: 760°C	N.S.	191 μm (high-purity AZ92) 660.4 μm (commercial AZ92)	[29]
2000	Mg-9%Al	Given Be,Zr,Fe and Mn from master alloys	T: 800 °C (adding elements) →700°C (cast at room T) SF ₆ gas covered	Al ₄ C ₃	40 μm (<0.001%Fe) →160μm (0.01%Fe) 40 μm (<0.001%Mn) →160μm (0.47%Mn)	[36]
2005	Mg alloys (0.5-9%Al)	High-purity and commercial Mg	T: 730 °C 1 vol%SF ₆ , 49 vol% dry air and 50vol% CO ₂	Al ₄ C ₃	For high-purity Mg, 1500μm (0.5 %Al) →146μm (9%Al) For commercial Mg, 2500μm (0.5%Al) →180μm (9%Al)	[32]

2.2.3 Elfinal process

The earliest studies of the Elfinal process can be tracked back to the 1940s [29,35]. The method was firstly introduced as adding 0.4-1.0 wt% FeCl₃ into Mg-Al-Zn alloys, the grain sizes could be refined [35]. In last 1940s, Partridge [150] observed the grain refinement caused by iron content diffusing from the mild steel crucible into Mg-Al alloys. This is also suggested

the cause of iron diffusing from the steel crucible is because FeCl₃ adding into the melt and the reaction products, HCl, attacks the steel crucible [45]. However, the study of Fe content inside the Al-bearing magnesium alloys becomes more complex with other factors such as carbon in the steel crucible and this leads to different nucleants [151].

FeCl₃ additions into the melt are recognised as increasing Fe content in the alloys because of the release of HCl gas during the process [45]. Fe content becomes the target for understanding the mechanism of Elfinal process. There was no further research until 2000 when Tamura et al. [36] investigated adding iron into high purity Mg-Al alloys. However, their results showed the iron content increasing from 0.001 wt% to 0.01% wt% caused an increase in grain size. They interpreted the phenomenon as being due to the transformation of less potent nucleant, Al-C-O-Fe [36]. This might be because of the factor of native grain refinement from the high purity alloys. Liao et al. [37] reported that Al₂Fe was found in the Mg-3 wt% Al alloy with 0.02 wt% Fe and the mismatch between Al₂Fe and α-Mg was 3.4% which was considered to be a potent nucleant. The orientation relationship between Al₂Fe and α-Mg is determined as the following:

$$\begin{array}{l} (\bar{1}011)_{\text{Mg}} // (01\bar{1})_{\text{Al}_2\text{Fe}} \\ [01\bar{1}1]_{\text{Mg}} // [011]_{\text{Al}_2\text{Fe}} \end{array} \quad (2.22)$$

To summarise with other research, Table 2.5 shows the variation of grain sizes by adding different forms of Fe into Mg-Al alloys. However, it is worth noticing that the alloy systems in Table 2.5 started with pure Mg and Al ingots. The commercial Al-bearing magnesium alloys contain Mn content and it was mentioned by Nelson [29] that Fe content directly did not have grain refinement on commercial AZ series alloys unless FeCl₃ was added. Mn content in the commercial alloys is a well-known element to increase corrosion resistance by the formation of Al-Mn intermetallics dissolving impurity Fe as Al_x(Mn,Fe)_y [152].

Table 2.5 The research [31,36,37] on Elfinal process and their proposed nucleants (T: melting temperature; %: weight percentage)

Year	Alloys	Additions	Casting condition	Proposed mechanisms	Most refinement	Ref.
2000	Mg-9%Al	Given Fe from master alloys	T: 800 °C (adding elements) →700°C (cast at room T) SF ₆ gas covered	Al ₄ C ₃	40 μm (<0.001%Fe) →160μm (0.01%Fe) 40 μm	[36]
2004	Mg-9%Al Mg-3%Al	Anhydrous FeCl ₃	T: 750 °C (adding FeCl ₃) under 1% SF ₆ +49% dry air and 50% CO ₂	Al ₈ (Mn,Fe) ₅	For Mg-3%Al, 305μm (base) →175μm (0.5%FeCl ₃) →115μm (1%FeCl ₃) For Mg-9%Al, 130μm (base) →76μm (1%FeCl ₃) → 62μm (2%)	[31]
2022	Mg-3Al	Fe ₂ O ₃	T: 760 °C (adding Fe ₂ O ₃) under 99.5 vol%N ₂ +0.5 vol% SF ₆	Al ₂ Fe	1135±105 μm (Mg-3Al) →540 μm (Mg-3Al-0.02Fe)	[37]

Since Mn content is important in commercial alloys when adding FeCl₃, τ -Al_{0.89}Mn_{1.11}, ϵ -AlMn and γ_2 -Al₈(Mn,Fe)₅ have been considered to be the nucleant candidates for the Elfinal process. In the work done by Qiu et al.[25], they have calculated the mismatch between α -Mg and τ -Al_{0.89}Mn_{1.11} by the E2EM method and the value is 1.3%. This is considered a good nucleant for α -Mg. However, in the recent work [34], FeCl₃ addition was found to promote τ -Al_{0.89}Mn_{1.11} transferring into γ_2 -Al₈(Mn,Fe)₅ and Fe(Al)/ β -Mn(Al) in AZ31 and AZ63. Thus, γ_2 -Al₈(Mn,Fe)₅ is more likely to form in the higher Al content magnesium alloys such as AZ91. The changes in formation of Al-Mn intermetallics can be seen in Figure 2.19. This makes τ -Al_{0.89}Mn_{1.11} is less likely to become the nucleant for AZ91 treated with the Elfinal process.

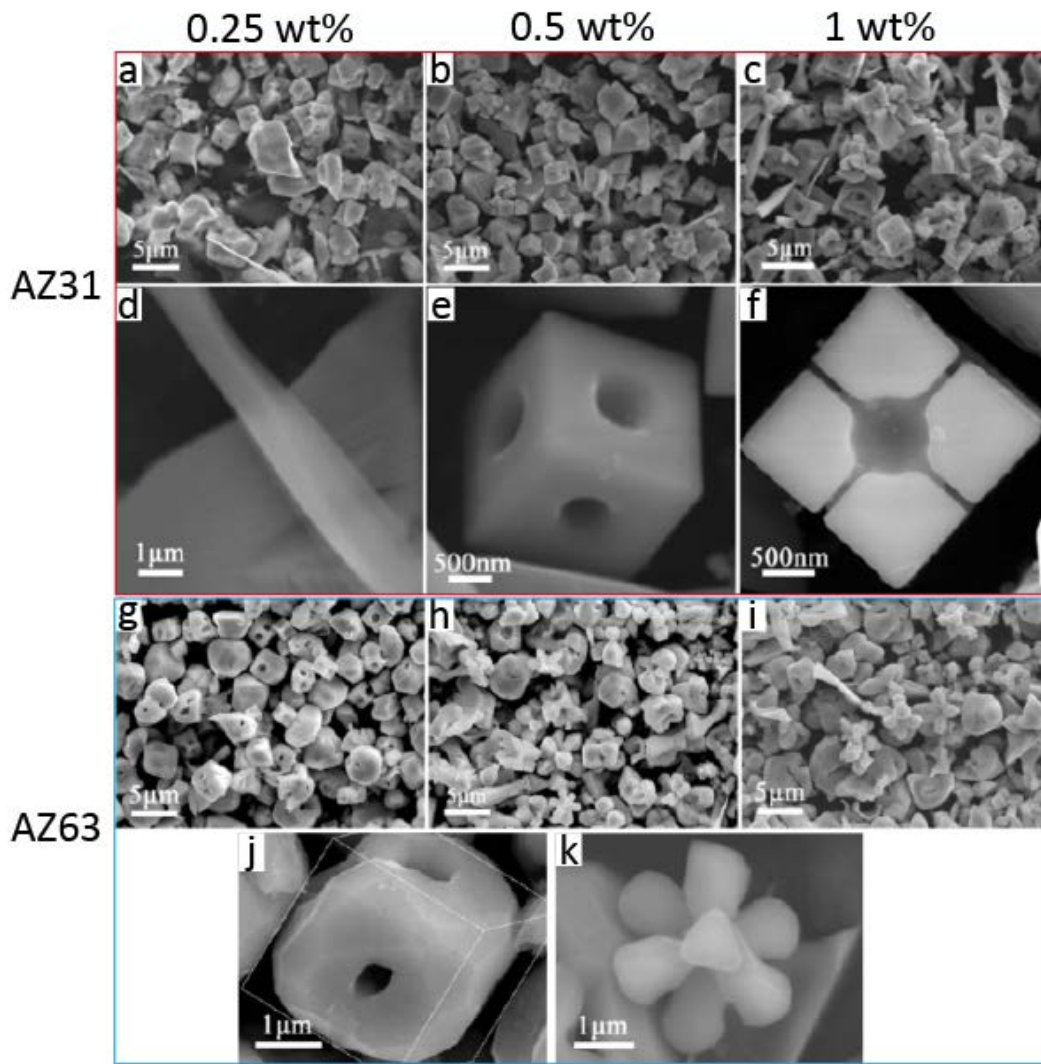


Figure 2.19 Each column presents different FeCl₃ additions in (a)-(f) AZ31 and (g)-(k) AZ63 alloys. FeCl₃ was added in (a), (d), (g) 0.25 wt%, (b), (e), (h) 0.5 wt% and (c), (f), (i) 1 wt%. (a), (d) τ -Al_{0.89}Mn_{1.11} ribbon, (b), (e) dice-like particle and (c), (f) octa-pod particle. Al-Mn-Fe particles formed as (j) the polyhedral and (k) octa-pod particles extracted from 1 wt% FeCl₃ addition in the AZ63 alloy [34].

It seems that the Al and Mn content plays an important role in forming nucleants in the Elfinal process. However, it is still not clear which nucleant is responsible for the Elfinal process. At the same time, the Elfinal process is not attractive to industry due to the reaction product of HCl released from the FeCl₃ addition and the negative effects on galvanic corrosion caused by increasing the Fe content in Al_x(Mn,Fe)_y compounds [16,153].

2.2.4 Carbon inoculation

Carbon inoculation refers to a wide range of additions that contain carbon to achieve efficient grain refinement [154]. Additives of C_2Cl_6 and CCl_4 were used in the early research [29,42]. However, they are toxic for humans so the additives for carbon inoculation have changed to other carbon-based additions [49]. A summary of additives used for carbon inoculation of Mg-Al based alloys is given in Table 2.6.

Table 2.6 Carbon-based additives used for carbon inoculation of Mg-Al based alloys [29,39,49–58,40,59–62,64–66,68–70,41,71–74,146,148,154–157,42,158–166,43–45,47,48]

Carbon inoculation additives	Reference
C_2H_2	[72]
C_2Cl_6	[45,55–57,159]
CCl_4	[29,42]
CO	[29]
CO_2	[29,61]
CH_4	[42]
Paraffin	[167]
Graphite powder/ Carbon powder	[43,44,54,69,73,146,148,154,155,160]
Charcoal powder	[71,161]
SiC powder	[39,40,70,154,156,157,162–165,41,47,52–54,64,65,68]
Al_4C_3 powder	[48,50,57,63,66,70]
Al-C master alloys	[49,51,74]
SiC master alloys	[158]
Al_4C_3 -Mg master alloys	[58,59]
Al_4C_3 -SiC/Al master alloys	[62]
Limestone	[60]

2.2.5 Proposed mechanisms and nucleants

The mechanisms behind carbon inoculation proposed in the literature can be grouped by the type of nucleant phase hypothesised to be responsible for grain refinement. Table 2.7 shows the crystal structures for a range of proposed nucleants compared with α -Mg. The mechanisms associated with each proposed nucleant are reviewed next.

Table 2.7 The crystal structures of hypothetical nucleants for Mg-Al alloys compared with α -Mg [168–174] (SD = Strukturbericht designation, the lattice parameters are measured at room temperature.)

phase	SD	Crystal Structure	Pearson Symbol	Space Group	Lattice Parameters				Ref.
					a(nm)	b(nm)	c(nm)	$\alpha, \beta, \gamma(^{\circ})$	
Mg	A3	Hexagonal	hP2	P6 ₃ /mmc	0.3202	0.3202	0.5200	$\alpha=\beta=90^{\circ}\gamma=120^{\circ}$	[168]
Al ₄ C ₃	D7 ₁	Trigonal	hR7	R $\bar{3}$ mH	0.3335	0.3335	2.4967	$\alpha=\beta=90^{\circ}\gamma=120^{\circ}$	[173]
T1-Al ₂ MgC ₂	N.S.	Hexagonal	N.S.	P6 ₃ /mmc	0.3402	0.3402	1.2292	$\alpha=\beta=90^{\circ}, \gamma=120^{\circ}$	[174]
T2-Al ₂ MgC ₂	D5 ₂	Trigonal	hP5	P $\bar{3}$ m1	0.3377	0.3377	0.5807	$\alpha=\beta=90^{\circ}, \gamma=120^{\circ}$	[169]
Al ₂ CO	B4	Hexagonal	hP4	P6 ₃ mc	0.3170	0.3170	0.5078	$\alpha=\beta=90^{\circ}, \gamma=120^{\circ}$	[172]
α -SiC (6H)	B6	Hexagonal	hP12	P6 ₃ mc	0.3081	0.3081	1.512	$\alpha=\beta=90^{\circ}, \gamma=120^{\circ}$	[170]
β -SiC (3C)	B3	Cubic	cF8	F $\bar{4}$ 3m	0.4358	0.4358	0.4358	$\alpha=\beta=\gamma=90^{\circ}$	[171]

2.2.2.1 Al₄C₃ hypothesis

The first hypothesis concerning Al₄C₃ as the nucleant for α -Mg in the Mg-Al system was introduced by Davis et al. [42]. The concept came from the idea of the essential elements of C and Al required for grain refinement in Mg-Al alloys. It was also reported that grain refinement is caused by carbon segregation due to the low solubility (tens of ppm) of carbon in liquid Mg [55] and that carbon segregation is the cause of grain refinement due to the constitutional undercooling [55,67]. However, Qian and Cao [67] pointed out that if it was the case of carbon segregation causing the grain refinement, the same effect would be observed in pure magnesium added with carbon inoculations. It was concluded that the grain refinement in Mg-Al system must involve the chemical reaction between Al and C [42,67]. The heterogeneous nucleation of α -Mg on Al₄C₃ has been widely considered as the responsible mechanism for grain refinement in Mg-Al system by many authors (Table 2.8) [16], [43], [44], [55], [58]–[60] [68], [78], [80], [83], [85], [88], [99]–[103].

Al₄C₃ has been suggested as a good nucleant for α -Mg due to the similarity of crystal structures between the two phases of trigonal and hexagonal crystal structures [49]. The OR has been predicted from E2EM and it can be written as the following [111]:

$$[1\bar{2}10]_{\text{Al}_4\text{C}_3} // [11\bar{2}0]_{\text{Mg}} \text{ \& } (10\bar{1}2)_{\text{Al}_4\text{C}_3} \text{ has } 0.35^\circ \text{ misfit with } (0002)_{\text{Mg}} \quad (2.23)$$

The lattice disregistry between Al_4C_3 and $\alpha\text{-Mg}$ is 3.4% which is worse than Al_2CO but better than Al_8Mn_5 . However, it has been pointed out that Al_4C_3 is much more energetically favourable to form than Al_2CO in a Mg-Al melt [63,176].

The Al_4C_3 hypothesis is complicated by the difficulty of characterising this phase in Mg microstructures. Al_4C_3 is easily hydrolysed by water or humid air and the compounds containing Al, C and O that have been reported have sometimes been attributed to Al_4C_3 reacting with water during sample preparation [44,46,161,48,50,58,63,73,146,148,155]. The reaction between Al_4C_3 and water is shown in Eq. (2.24) [146]:

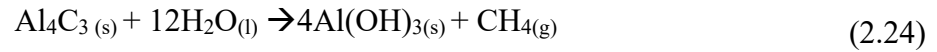


Table 2.8 Researchers [48,49,51,55,66,146,148,154,157,175] proposing Al_4C_3 as the nucleation site for α -Mg (T: melting temperature; %: weight percentage)

Year	Alloys	additives	Casting condition	Proposed mechanisms	Most refinement	Ref.
2000	AZ91E	High-purity carbon powders	T:973-1073K (adding for 300-1500s) Ar gas covered	$\text{Al}_4\text{C}_3 \rightarrow \alpha\text{-Mg}$	87.5 $\mu\text{m} \rightarrow 65\mu\text{m}$ (for 1800s, 1023K) $\rightarrow 75\mu\text{m}$ (for 600s at 1053K) $\rightarrow 60\mu\text{m}$ (for 600s 1073K)	[146]
2002	Mg-9%Al (0.002wt%C)	No additions, Al-50%Fe, FeCl_3 and Al-10%Mn	T: 1023K/1123K (for superheating) $\text{SF}_6 + \text{CO}_2$	$\text{Al}_4\text{C}_3/\text{Al}_2\text{OC} \rightarrow \alpha\text{-Mg}$	158 $\mu\text{m} \rightarrow 74\mu\text{m}$ (0.01%Fe) 158 $\mu\text{m} \rightarrow 73\mu\text{m}$ (0.47%Mn)	[175]
2005	AZ91E	High-purity carbon powders (0.02-0.1wt%)	T: 973K-1073K $\text{SF}_6 + \text{CO}_2$	$\text{Al}_4\text{C}_3 \rightarrow \alpha\text{-Mg}$ (with superheat treated)	300 $\mu\text{m} \rightarrow 80\mu\text{m}$ (0.08 wt%)	[148]
2006	Mg-Al alloys (1-9Al)	0.15, 0.3wt% SiC and MnCl_2 flake	T: 700°C (cast at 200°C) Stirring: 5min	$3\text{SiC} + 4\text{Al} \rightarrow \text{Al}_4\text{C}_3 + 3\text{Si}$	In Mg-1Al, 706 $\mu\text{m} \rightarrow 284\mu\text{m}$ (0.3wt%) In Mg-9Al, 129 $\mu\text{m} \rightarrow 78\mu\text{m}$ (0.3wt%)	[157]
2006	Mg-3%Al	Synthetic graphite and SiC	T: 735 °C & 785 °C Stirring: 10-30 min AM-covered	$4\text{Al}_{(l)} + 3\text{C}_{(s)} \rightarrow \text{Al}_4\text{C}_{3(s)}$ $3\text{SiC}_{(s)} + 4\text{Al}_{(l)} \rightarrow \text{Al}_4\text{C}_3$ (s) $\text{Al}_4\text{C}_3 \rightarrow \alpha\text{-Mg}$	380 $\mu\text{m} \rightarrow 175\mu\text{m}$ (graphite) 380 $\mu\text{m} \rightarrow 180\mu\text{m}$ (SiC)	[154]
2009	AZ31, AZ63	0.4 wt% Al_4C_3	T: 750°C (cast at 80°C) Stirring: 30s	For AZ31, Al_4C_3 coated $\text{Al}_{0.89}\text{Mn}_{1.11} \rightarrow \alpha\text{-Mg}$ For AZ63, Al_4C_3 coated $\text{Al}_8\text{Mn}_5 \rightarrow \alpha\text{-Mg}$	For AZ31, 850 $\mu\text{m} \rightarrow 180\mu\text{m}$ (0.4 wt%) For AZ63, 650 $\mu\text{m} \rightarrow 170\mu\text{m}$ (0.4wt%)	[48]
2009	AZ31	1, 2 wt% Al-1C master alloy	T: 760°C (cast at 420°C) Stirring: 30s	$\text{Al}_{(l)} + \text{C}_{(s)} \rightarrow \text{Al}_4\text{C}_{3(s)}$	580 $\mu\text{m} \rightarrow 230\mu\text{m}$ (1wt%) 580 $\mu\text{m} \rightarrow 140\mu\text{m}$ (2wt%)	[49]
2010	AM60B	Al_4C_3 microparticles	T: 725°C Ultrasonic probe: 13 mins $\text{SF}_6 + \text{CO}_2$	Al_4C_3 coated $\text{Al}_8\text{Mn}_5 \rightarrow \alpha\text{-Mg}$	254 $\pm$ 142 $\mu\text{m} \rightarrow 60\pm 14\mu\text{m}$	[66]
2017	AZ91	0.5 wt% Al-3C master alloy	T: 720°C (cast at 200°C) Stirring: a few sec 1 vol% RJ-2 ¹	$\text{Al}_4\text{C}_3/\text{Al}_8\text{Mn}_5$ act as clusters in $\alpha\text{-Mg}$	350 $\mu\text{m} \rightarrow 78\mu\text{m}$	[51]

¹ RJ-2 is the combination of 40-50% MgCl_2 , 35-45% KCl, 5-8% CaF_2 , 5-8% Na+ CaCl_2 .

2.2.2.2 Al_2MgC_2 hypothesis

Other researches [52,54,70,71,161] support a different hypothesis, that a ternary carbide Al_2MgC_2 is the nucleant causing Mg-Al grain refinement in carbon inoculation (Table 2.9).

The first observation of chemical reaction between Al, C and Mg was from Mg-Al-based composites with carbon fibre reinforcement [177]. Viala et al. [177] found that Al_4C_3 and Al_2MgC_2 can be formed in Mg-Al based alloys and that Al_4C_3 is thermodynamically favourable in Al-rich alloys (Al > 33 wt%) and Al_2MgC_2 is stable in Al-poor alloys (Al < 17 wt%). Further research [178] found that Al_4C_3 would start forming once the Al content is higher than 19 wt% ± 2 wt% due to kinetic factors and Al_2MgC_2 is formed in the Mg-Al system containing between 0.6 and 19 ± 2 wt% Al content. Al_4C_3 and Al_2MgC_2 were also found to coexist when the Mg content inside the sample evaporates to cause the alloy in an Al-rich situation [169,179]. Investigations of Al_2MgC_2 have either used synthesis by powder metallurgy [169,177–179] and/or carbon fibre additives [174,178,180,181].

In addition, Al_2MgC_2 is believed to exist as two polymorphs, namely T1- Al_2MgC_2 and T2- Al_2MgC_2 , [169,177,178]. T1- and T2- Al_2MgC_2 are stable at lower and higher temperatures respectively where 990 $\pm$ 10K ($\sim 717 \pm 10^\circ\text{C}$) is the temperature boundary and the volume fraction change between the two phases can be seen from Figure 2.20 [178,179]. However, Viala et al. [178] pointed out that T1- and T2- Al_2MgC_2 exhibit a certain degree of thermodynamic metastability. For example, the mixture of T1- and T2- Al_2MgC_2 can be found below 1000K but only pure T2 exists above 1000K [178]. In addition, at the temperature of 1237 K for 240 hours, the weight loss of the sample is around 60% of the initial sample from the work of Deffrennes et al.[169] and this correlates with Figure 2.20(b). While the crystallography of the T2- Al_2MgC_2 phase has been characterised in detail [169,177–179], so far the T1- Al_2MgC_2 phase was unsuccessfully synthesised for detailed X-ray diffraction analysis due to the low yield at 700 $\pm$ 4 $^\circ\text{C}$ for 240 hours [169]. However, the crystal structure

of T1-Al₂MgC₂ has been proposed based on the close relationship between Al₄C₃ and (0003) plane distance with the atomic arrangement of Al₄C₃ [174]. The crystal structures are summarised in Table 2.7.

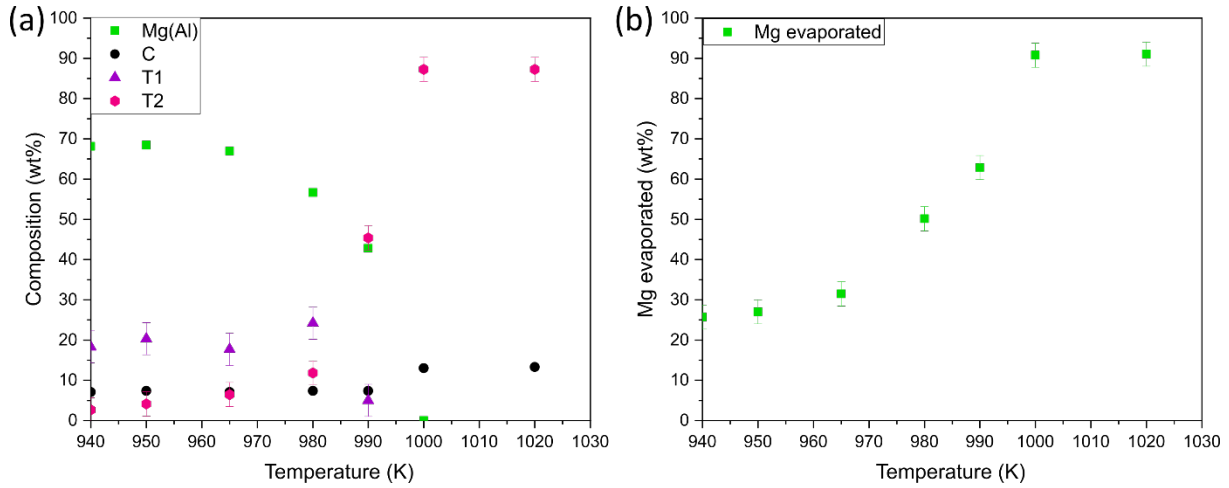


Figure 2.20 (a) The compositions of four phases after the Mg-Al-C mixtures (in 76, 14 and 10 wt% respectively) after heating at 950-1020K for 300 hours (b) The percentage of Mg vapour between 940 and 1020 K for 300 hours [179].

An isothermal section through the Mg-Al-C ternary phase diagram at 1000K has been proposed by Viala et al. [178] and is replotted from their work in Figure 2.21.

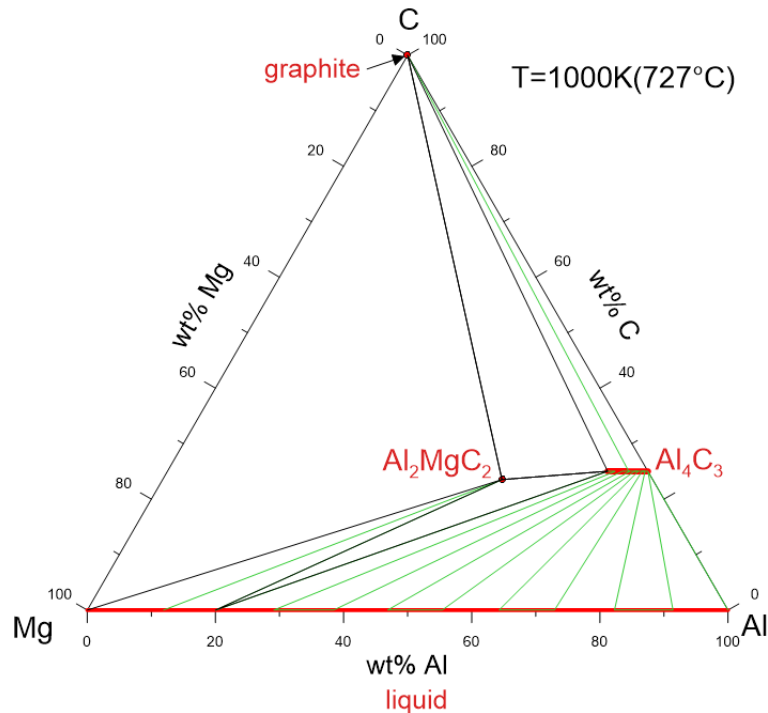


Figure 2.21 1000K isothermal section of the Mg-Al-C ternary phase diagram. Replotted based on Ref. [178]. Single phase regions are red. Tie lines are green.

The plate-shaped morphology of Al_2MgC_2 (Figure 2.22) is proposed to grow in the perpendicular direction to the c-axis of the hexagonal unit cell [180].

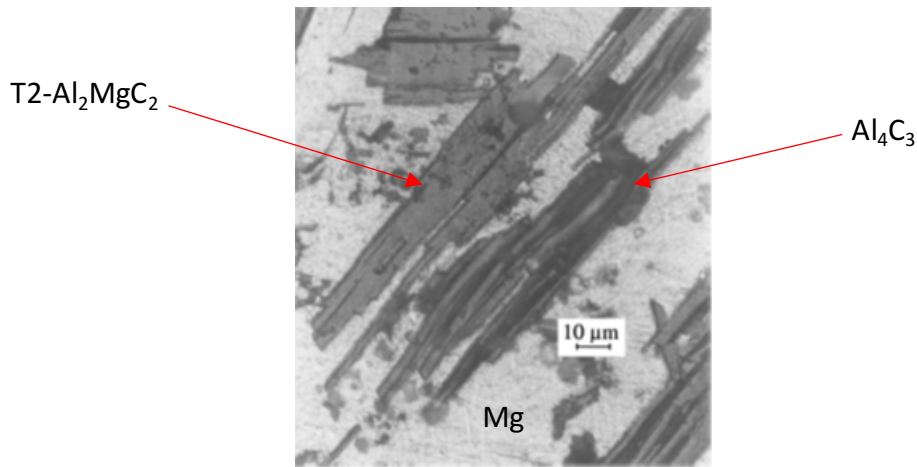


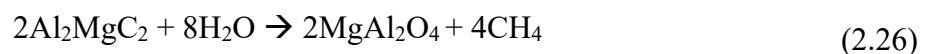
Figure 2.22 Optical microscope image of a sample containing 21 wt% Mg, 57 wt% Al and 22 wt% C that was heat-treated at 1237 K for 10 hours. The dark region is Al_4C_3 and the grey platelet region is $\text{T2-Al}_2\text{MgC}_2$ [178].

Furthermore, the interfacial energy was calculated from first-principle density functional theory calculations that the Mg terminated Al_2MgC_2 contacting with α -Mg has lower interfacial energy than the Al terminated Al_2MgC_2 and this implies the OR between Al_2MgC_2 and α -Mg should be based on basal plane matching [182]. Also, from the growth morphology, the OR between Al_2MgC_2 and α -Mg is suggested as the following [52,181]:

$$\begin{aligned} (110)_{\text{Al}_2\text{MgC}_2} // (110)_{\text{Mg}} \ \& \ [001]_{\text{Al}_2\text{MgC}_2} // [001]_{\text{Mg}} \ \text{with } 5.7\% \text{ misfit} \\ (001)_{\text{Al}_2\text{MgC}_2} // (001)_{\text{Mg}} \ \& \ [\bar{1}10]_{\text{Al}_2\text{MgC}_2} // [\bar{1}10]_{\text{Mg}} \ \text{with } 5.32\% \text{ misfit} \end{aligned} \quad (2.25)$$

It can be imagined as two hexagonal unit cells parallel to each other [181]. Although Al_4C_3 has the lower lattice disregistry, it has been proposed that Al_2MgC_2 has a similar crystal structure to α -Mg and they have closer c-axis parameter (cf. Table 2.7) [52,54].

It was also indicated that Al_2MgC_2 is as sensitive to moisture as Al_4C_3 which causes problems for sample preparation including cutting, grinding and polishing [52,177]. The ternary carbide reacts with water and water vapour via the following proposed equation [54]:



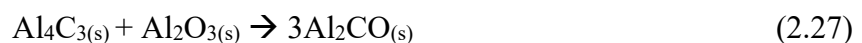
The production of CH₄ gas causes the voids and cracks on the sample surface [52]. However, from the past literature [183,184], the formation of the spinal MgAl₂O₄ starts with solid MgO reacting with Al content substances such as solid Al₂O₃, liquid Al, CoAl₂O₄, Al₄C₃ and AlCl under different experimental conditions. Thus, the spinal phase is less likely to form based on the hydrolysis of Al₂MgC₂ (Eq. (2.26)) due to the Gibbs free energy. The oxidised chemical composition of Al₂MgC₂ should be other forms rather than the spinal phase.

Table 2.9 Past work [52,54,70,71] proposing Al₂MgC₂ as the nucleant (T: melting temperature N.S.: not stated)

Year	Alloys	additives	Casting condition	Proposed mechanisms	Most refinement	Ref.
2009	AZ31	0-2wt% SiC & 0-2wt% Al ₄ C ₃	T:700±5°C Stirring:2min 1 vol%SF ₆ +Ar covered	2SiC+2Al+5Mg→ 2Mg ₂ Si+Al ₂ MgC ₂ Al ₂ MgC ₂ → α-Mg	For 1.5µm SiC, 1150µm→300µm(2wt%) For Al ₄ C ₃ , 1005µm→ 350 µm(2wt%)	[70]
2010	Mg-3wt%Al	0-0.3wt% Graphite or SiC	T:700°C (cast at 200°C) Stirring: 30&60min Ar+0.2 vol%SF ₆	Al ₂ MgC ₂ → α-Mg (Al-rich)→ α-Mg	420µm→ 130µm(0.3wt%)	[54]
2011	Mg-3wt%Al	0.3&3wt% SiC	T: 700°C (cast at 200°C) Stirring: N.S. Ar+0.2 vol%SF ₆	(001) Al ₂ MgC ₂ //(001)Mg [110] Al ₂ MgC ₂ //[110]Mg	417±213µm → 120±32µm(3wt%)	[52]
2013	AZ91	0-0.5wt% Charcoal particles	T:740°C (cast at 300°C) Stirring: 10min Flux covered	Al ₄ C ₃ , Al ₂ MgC ₂ → α-Mg	100µm→14µm(0.4wt%)	[71]

2.2.2.3 Al₂CO hypothesis

Another hypothesis is that the nucleation site is Al₂CO based on the repeated measurement of Al, C, and O in particles after carbon inoculation [56,73]. Al₂CO has been proposed to form by the following chemical reaction [176]:



In addition, the OR between Al₂CO and α-Mg has been predicted by E2E matching as the following [111]:

$$[1\bar{2}10]_{\text{Al}_2\text{CO}}//[11\bar{2}0]_{\text{Mg}} \text{ and } (10\bar{1}0)_{\text{Al}_2\text{CO}} \text{ has } 2.8^\circ \text{ misfit with } (0002)_{\text{Mg}} \quad (2.28)$$

This habit plane and orientation relationship has 1.23% lattice discrepancy between Al_2CO and $\alpha\text{-Mg}$ and from the result, it has been predicted as the more potent nucleant compared with Al_4C_3 which has a misfit of 3.4% [111]. However, it has been argued that Al_2CO is unlikely to form in the melt after adding carbon additives based on the activity coefficient [63,176].

2.2.2.4 SiC additions

Magnesium grain refinement by SiC has worked reasonably well [39–41,47,64,65] as summarised in Table 2.10. The mechanism of grain refinement has been suggested as (1) heterogeneous nucleation on newly added particles and (2) constitutional undercooling from additives [64]. On the other hand, the undercooling of AZ91 with $\beta\text{-SiC}$ was measured as 0.9°C which has been suggested to be more potent as a nucleant than other phases in AZ91 [65]. In addition, the work of Lelito et al [164] showed that the grain density depends on the mass fraction of SiC in the melt and the actual undercooling. It was pointed out that the higher volume fraction of SiC particles in the melt were pushed by Mg-rich dendrites towards the grain boundary during the end of solidification and they appear around eutectic $\text{Mg}_{17}\text{Al}_{12}$ [39–41,65,156,185]. The effect of nucleating and ‘pushing particles’ can reduce the grain size due to the restriction of diffusion [65]. In addition, experiments show the higher content of SiC in the melt reduces the grain size significantly [47,65]. Thus, it appears that a small amount of SiC becomes the nucleants site. Although most researchers [41,64,65,156,185] have shown SiC particles are in the centre of grains, with the common method of T4 heat treatment, it is difficult to identify whether the particles grow from the centre of dendritic structure of $\alpha\text{-Mg}$.

There are two different types of SiC particles used for the experiments: $\alpha\text{-SiC}$ and $\beta\text{-SiC}$ (Table 2.7) with hexagonal and cubic crystal structures respectively. $\alpha\text{-SiC}$ is the more

frequently used additive [170]. However many studies [47,52,54,154,156,157] did not state the type of SiC used for the experiments.

Luo [65] reported the OR between β -SiC and the α -Mg as the following equation:

$$(111)_{\beta\text{-SiC}}// (0001)_{\text{Mg}} \text{ with 4\% lattice disregistry} \quad (2.29)$$

The lattice disregistry was calculated by the Turnbull-Vonegut linear disregistry and this is within the limitation of a good nucleant of 10% lattice disregistry.

Cai et al. [39–41] showed the OR between α -SiC and α -Mg and it can be written as the following equation:

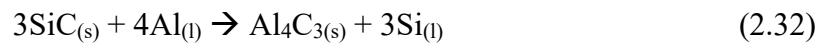
$$(0001)_{\alpha\text{-SiC}}// (10\bar{1}0)_{\text{Mg}} \& [\bar{1}5\bar{4}0]_{\alpha\text{-SiC}}// [0001]_{\text{Mg}} \text{ with 2.3\% lattice disregistry} \quad (2.30)$$

The lattice disregistry was calculated by Bramfitt planar disregistry and gives 2.3% misfit which is within the range of reasonable nucleation potency. Eq.(2.29) and (2.30) show β - and α -SiC are potentially good nucleants based on lattice matching with the small lattice disregistries from the α -Mg.

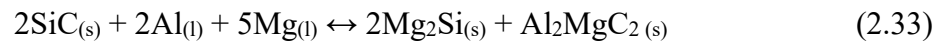
Some researchers [39–41,64,65,156] claimed there is no phase formed between SiC and Mg-Al system. However, Rauber et al.[156] showed the presence of Mg_2Si phase which indirectly indicates that SiC particles are not stable in Mg-Al melts. Hence, the reaction between the liquid melt and SiC during casting is an important factor for the interfacial contact between α -Mg and SiC phase [186]. This can indirectly improve the wetting angle to promote heterogeneous nucleation. Additionally, there is evidence of chemical reactions between SiC and Mg-Al system [52–54,70,154,157]. The Si element decomposed from SiC bonds with Mg to form Mg_2Si inside the melt at 700 °C and the chemical reaction is shown as the following [54,70]:



Mg₂Si forms during the chemical reaction between the melt and SiC. Mg₂Si has been observed more frequently with the increase of the stirring time and the amount of SiC added into the melt [53,54,70]. Thus, it shows SiC particles are not stable in the Mg-Al melt [157]. Even though Easton et al. [157] did not have a direct evidence of Al₄C₃ in the samples but it was considered as a missing phase after sample preparation due to contamination with water (Eq.(2.24)). Hence, based on the concept of chemical reaction between Al and C in the melt, Easton et al. [157] and Lu et al. [154] suggested that the addition of SiC causes chemical reaction between SiC and Al in the Mg-Al melt by the following equation:



Alternatively, chemical reaction between the Mg-Al melt and SiC has been proposed to create Al₂MgC₂ by Eq.(2.33) [70] :



This mechanism is shown in Figure 2.23 from Huang et al. [53]:

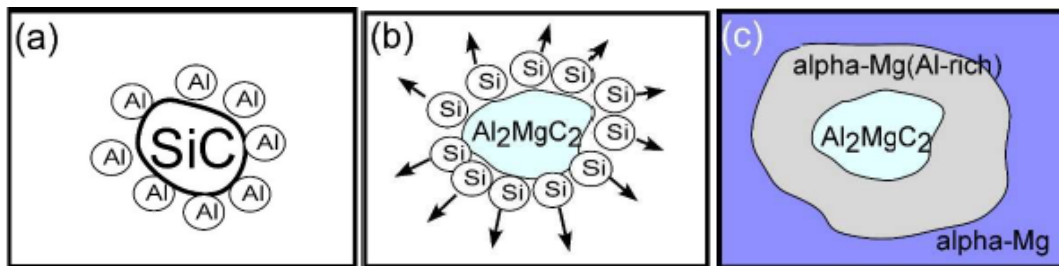


Figure 2.23 A simplified schematic diagram of Al₂MgC₂ formation process (a) the segregation of Al content surrounds SiC (b) the chemical reaction of Al₂MgC₂ formation and Si content releases and (c) during the solidification, Al₂MgC₂ is surrounded by Al-rich α-Mg [53].

For the morphologies of T2-Al₂MgC₂, the SEM image in Ref. [70] shows needle-like and plate-like phases which are characterised as Al₂MgC₂.

In summary, the mechanism of grain refinement by SiC additives has been proposed to be either (i) nucleation on SiC itself, or on (ii) Al₄C₃, or (iii) Al₂MgC₂ which form at the interfacial contact between SiC particles and α-Mg.

Table 2.10 The Research [39–41,47,64,65] proposing SiC is responsible for grain refinement. (P: purity; T: melting temperature; S: particle size; N.S.: not stated)

Year	Alloys	additives	Casting condition	Proposed mechanisms	Most refinement	Ref.
1994	AZ91	16 wt% β -SiC (P:98.5%)	Hold and casting T:700°C Stirring:2 min SF ₆ /CO ₂ covered	SiC→ α -Mg	126.9 μ m→41.8 μ m	[64]
1996	AZ91	16 & 1 wt% β -SiC (P: 98.5%)	Hold and casting T:700°C Stirring:2 min SF ₆ /CO ₂ covered	(111)SiC//(0001)Mg with 4% lattice disregistry	126.09 μ m→41.8 μ m (16 wt%)	[65]
1997	AZ80	24 wt% SiC	T: 700°C Stirring: 15-30 min 400rpm Ar gas covered	[1 $\bar{1}$ 01]SiC//[1 $\bar{1}$ 1]Mg ₁₇ Al ₁₂ (01 $\bar{1}$ 1)SiC//(110)Mg ₁₇ Al ₁₂	N.S.	[40]
1999	Mg-9Al-Zn	24 wt% SiC	Heated to semi-solid state and above liquidus Ar gas covered	[0001]Mg//[$\bar{1}$ 5 $\bar{4}$ 0]SiC (10 $\bar{1}$ 0)Mg//(0001)SiC With 2.3% lattice disregistry	N.S.	[39]
2000	Mg-9Al-Zn	24 wt% SiC	Melt: 610 °C→587 °C (adding powder)→620 °C Stirring: 5 min 600 rpm Ar gas covered	[0001]Mg//[$\bar{1}$ 5 $\bar{4}$ 0]SiC (10 $\bar{1}$ 0)Mg//(0001)SiC	N.S.	[41]
2010	AZ91	0.06-3.5 wt% SiC	T: liquid melt Stirring:180-240s	SiC→ α -Mg	566.2 μ m (S:40 μ m, 0.06 wt%) →113 μ m(3.5wt%)	[47]

2.2.2.5 Al₈Mn₅ hypothesis

Byun et al. [187] proposed that Al₈Mn₅ particles are the heterogenous nucleants for α -Mg in AZ91 and research discussing the mechanisms of Al₈Mn₅ are shown in Table 2.11.

Calculation by E2EM identified the best matching OR between Al₈Mn₅ and α -Mg as the following [111]:

$$\{30\bar{3}3\}_{\text{Al}_8\text{Mn}_5} \text{ with } 4.5^\circ \text{ from } \{0002\}_{\text{Mg}} \ \& \ \langle 10\bar{1}1 \rangle_{\text{Al}_8\text{Mn}_5} // \langle 10\bar{1}0 \rangle_{\text{Mg}} \quad (2.34)$$

From this, Al₈Mn₅ is predicted as a poor nucleant because the interatomic spacing along the directions corresponding to the interplanar spacing (d-value) is 17.8% which is much greater

than the 6% of the threshold of potent nucleants [111,188]. Moreover, Wang et al. [189] showed there is no clear defined OR and this reinforces the idea of an incoherent lattice match between Al_8Mn_5 and $\alpha\text{-Mg}$. Laser et al. [190] point out that formation temperature of Al_8Mn_5 is higher than the $\alpha\text{-Mg}$ liquidus and, thus, Al_8Mn_5 is available as a nucleating substrate. However, they also point out that there is no distinguishable grain refinement when increasing the volume percentage of Al_8Mn_5 . This can be clearly shown in the effect of Mn content by Cao et al. [191]. It includes the Mn additive range operated by Ref. [187,190] where the grain sizes of AZ31 and AZ91 did not reduce significantly with the increase Mn content. As a result, the researchers [111,188–190] agree that Al_8Mn_5 is a poor nucleant in AZ91. If there is a more potent phase present in the melt, Al_8Mn_5 will not act as the nucleant in AZ91.

Table 2.11 Research [57,69,189] that discusses whether Al_8Mn_5 is a heterogeneous nucleation sites for $\alpha\text{-Mg}$ (T: melting temperature)

Year	Alloys	additives	Casting condition	Proposed mechanisms	Most refinement	Ref.
2007	AZ91	0.6wt% C_2Cl_6	T: 740°C (cast at 200 °C mould) SF_6/CO_2 covered	Al-C $\rightarrow \text{Al}_8(\text{Mn,Fe})_5 \rightarrow \alpha\text{-Mg}$	$460 \pm 30 \mu\text{m} \rightarrow 97 \pm 11 \mu\text{m}$	[57]
2010	AZ91D	0-0.22wt% Mn inside AZ91D	T: 675°C (3.5K/s cooling rate) Stirring: 45s 500 rpm 0.4 vol% SF_6/N_2	Other phases are responsible	$188 \pm 20 \mu\text{m} \rightarrow 180 \pm 18 \mu\text{m}$	[189]
2018	AZ91, Mg-9 wt% Al	0.3, 0.6 and 1wt% carbon powder	T: 750-780°C Gently stirring	$(0002)\text{Mg} // (30\bar{3}0)\text{Al}_8\text{Mn}_5$ $\langle 10\bar{1}0 \rangle \text{Mg} // \langle 10\bar{1}1 \rangle \text{Al}_8\text{Mn}_5$ With 4.5° misfit $\text{Al}_4\text{C}_3 \rightarrow \text{Al}_8(\text{Mn,Fe})_5 \rightarrow \alpha\text{-Mg}$	At 750°C, $440 \mu\text{m}$ (0 wt%) $\rightarrow 118 \mu\text{m}$ (1 wt%) At 780°C, $440 \mu\text{m}$ (0 wt%) $\rightarrow 112 \mu\text{m}$ (1 wt%)	[69]

In the cases of carbon additives, some researchers [57,69] reported that Al_8Mn_5 grows as a duplex nucleant with Al-C compounds. Duplex clusters of Al_8Mn_5 and Al_4C_3 have been reported by [44,48,51,57,66]. The first observation of duplex nucleation of Al_8Mn_5 and Al_4C_3 was in the work of Kim et al. [57] which held the opposite opinion to the nucleation mechanism of Al_4C_3 . However, Du et al. [44] suggested that Al_4C_3 grows on Al-Mn compounds in the melt

and acts as a nucleant to the α -Mg. This is also indicated that Al_4C_3 forms before the formation of Al_8Mn_5 during solidification and Al_8Mn_5 is coated by Al_4C_3 due to the preference of crystal structures with α -Mg [49]. In order to prove the reaction product and the effect of Mn content, the AZ91 alloy was held at 720°C for 24 hours and Al_4C_3 was still the main product in the sample which showed the stability in the melt and it was not influenced by Mn content [51]. In addition, researchers [51,66] found Al_8Mn_5 particles were attached with Al_4C_3 after holding the samples over 720°C and they explained why the work of Kim et al. [57] observed the clusters containing Al_8Mn_5 with Al_4C_3 (Figure 2.24). Although the clusters containing Al_8Mn_5 reduce the refinement efficiency, there were still many Al_4C_3 particles containing high-effectivity of grain refinement in AZ91 [51].

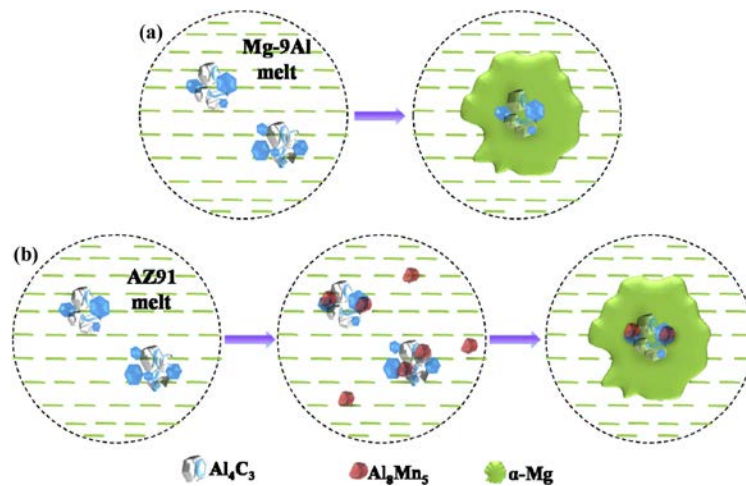


Figure 2.24 schematic diagrams of nucleation sites formation in (a)Mg-Al melt and (b) AZ91 melt [51].

2.2.2.6 Other Al-rich compounds

In addition to the specific compounds suggested in the work reviewed above, many papers attribute heterogeneous nucleation to undefined Al-rich compounds as summarised in Table 2.12 [56,59,73,155,160]. The Al-C-O compounds were not identified as any phases but they have sometimes been considered as a part of Al_4C_3 hypothesis due to the reaction of Al_4C_3 with H_2O during sample preparation [59]. In terms of Al-O-C-Fe, the O content may be contamination products from Al-C-Fe, and Al-Fe during the sample preparations [155,160].

However, all the complex oxidised compounds were not stated as specific phases [56,59,73,155,160].

Table 2.12 Research[59,73,155] proposing Al-C, Al-Fe and Al-C-O phases as the nucleation site for α -Mg (T: melting temperature; %: weight percentage)

Year	Alloys	additives	Casting condition	Proposed mechanisms	Most refinement	Ref.
2003	AZ91E	0.6ks feeding of graphite	T: 973-1073 K (cast at 973K) Ar gas covered	Al-C-O $\rightarrow$ α -Mg	158 μ m (973°C) $\rightarrow$ 69 μ m(1073°C)	[73]
2010	Mg-3%Al	Al-15%Fe (for 0.1% Fe) Carbon powder (for 0.2% C)	T: 760°C (cast at 500°C) Stirring: 1min 45%MgCl ₂ , 35%KCl, 10%CaF ₂ , 10%NaCl covered	Al-C $\rightarrow$ α -Mg Al-C-Fe $\rightarrow$ α -Mg	610 $\pm$ 135 μ m $\rightarrow$ 183 $\pm$ 25 μ m (only C addition)	[155]
2010	AZ91D	Mg-50%Al ₄ C ₃ and ZS-Mn75(for 0-0.7% Mn additives)	T: 750°C (cast at 200°C) 1 vol%RJ-2 flux covered	Al-C-O-Mn-Fe compounds (coated with Al-C-O film) $\rightarrow$ α -Mg	360 μ m $\rightarrow$ 138 μ m (0.6% Al ₄ C ₃ +0.67%Mn)	[59]

2.3 α -Mg dendrite morphology

Once α -Mg nucleates in AZ91, it grows into hexagonal dendrites due to the anisotropic interfacial energy between the liquid and hexagonal close-packed (hcp) structure. The hexagonal shape can be viewed from a normal direction to the growth direction [192]. The growth directions depend on the growth conditions. Unidirectional growth of α -Mg in AZ91 alloys was found to be in $\langle 11\bar{2}0 \rangle$ directions with dendrite arms in the basal plane and four in $\{1\bar{1}01\}$ planes under a low temperature gradient (G) and high growth velocity (V) [192]. Pettersen et al [193] reported that the dendrites grow in $\langle 22\bar{4}5 \rangle$ direction when the G/V ratio is high and the growth direction had a relationship between G/V ratios [193].

AZ91 usually solidifies into equiaxed dendrites (and not columnar dendrites) because the high solute content leads to a relatively high degree of constitutional supercooling in which new nucleation events can be continuously triggered as heat is extracted. In equiaxed dendrites, there are two important lengthscale; the grain size and the secondary dendrite arm spacing (SDAS). The grain size depends on heterogenous nucleation as reviewed in section 2.1. The SDAS is primarily determined by coarsening and therefore, depends on the local solidification time [194]. A body of past works [194–200] all agree that the relationship between SDAS and the local solidification time can be written as Eq.(2.35).

$$\lambda_2 = A\Delta t^n \quad (2.35)$$

Where λ_2 is SDAS, A is a constant for a given alloy which depends on chemical compositions, the diffusion coefficient of solute in the liquid and the partition coefficient, Δt is the solidification time, and n is an exponent.

Eq.(2.35) is able to be rewritten as Eq.(2.36) in terms of the cooling rates and n was calculated between 0.31 and 0.34 [195–201].

$$\lambda_2 = B\left(\frac{\Delta T}{\Delta t}\right)^{-n} \quad (2.36)$$

Where B is a constant, ΔT is the freezing range.

The experimental data from the past work on AZ91 [193,195–199] are shown in Figure 2.25 and the numerical best-fit equation is calculated as Eq.(2.37). The n value is in the region between 0.31 and 0.34. Note that the error bars for the data points in Figure 2.25 were not provided in the literature [193,195–199] but since the data scatters around the best-fit line, Eq.(2.37) presents a good relationship between the SDAS and the average cooling rate.

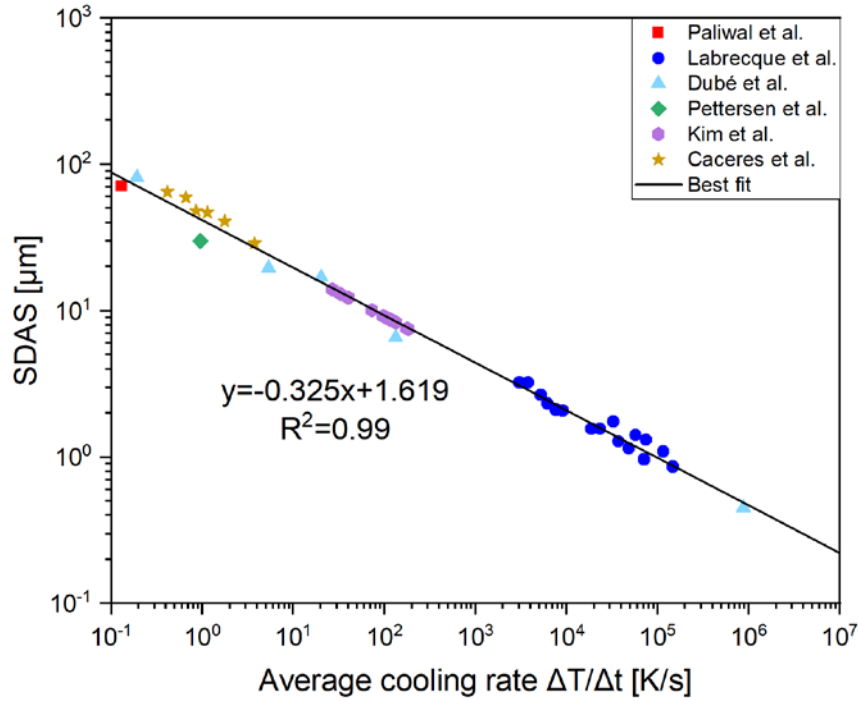


Figure 2.25 The relative between the secondary dendrite arm spacing (SDAS) and the average cooling rate from the past work on AZ91 [193,195–199].

$$\lambda_2 = 41.59 * \left(\frac{\Delta T}{\Delta t}\right)^{-0.325} \quad (2.37)$$

2.4 α -Mg+Mg₁₇Al₁₂ eutectic growth

2.4.1. The α -Mg + Mg₁₇Al₁₂ eutectic in Mg-33wt%Al

In the Mg-Al binary system, the eutectic point is at 33 wt% Al and 453.3 °C (Figure 2.26). The volume fraction of α -Mg and Mg₁₇Al₁₂ phases in the eutectic mixture can be calculated from the mass fraction measured by the lever rule at the eutectic point and the densities of the phases. From Eq.(2.38), the mass fractions are 69.4 wt% so for Mg, it is 30.6 wt% and, using Eq.(2.39), the volume fractions of Mg and Mg₁₇Al₁₂ are 34.4 vol% and 65.6 vol% respectively. From the result of the calculations, it shows that Mg is the minor phase in the eutectic mixture.

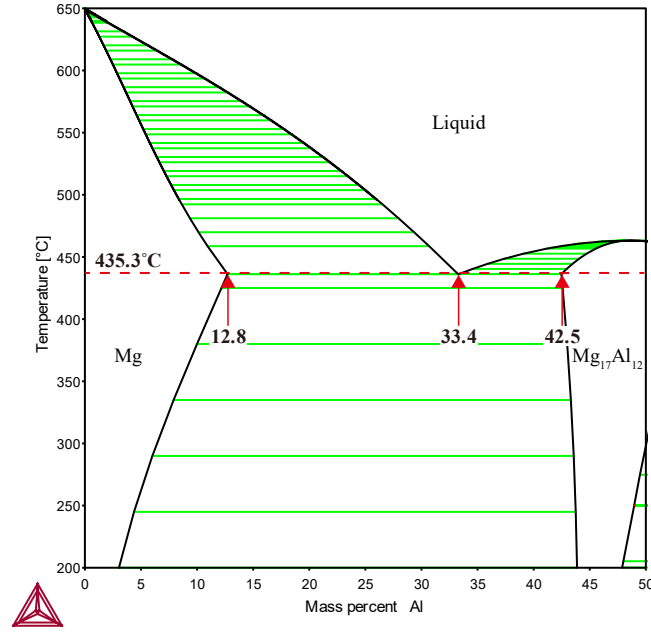


Figure 2.26 The binary phase diagram of Mg-Al within the range of 0 and 50 wt% Al content. Calculated by Thermo-Calc TCMG magnesium database version 4 [202].

$$f_{Mg_{17}Al_{12}} = \frac{C_{eutectic} - C_{Mg}}{C_{Mg_{17}Al_{12}} - C_{Mg}} \quad (2.38)$$

Where $f_{Mg_{17}Al_{12}}$ is the mass fraction of Mg₁₇Al₁₂, $C_{eutectic}$ is the Al content at the eutectic point, C_{Mg} is the Al content in α -Mg and $C_{Mg_{17}Al_{12}}$ is the Al content in Mg₁₇Al₁₂ at 435 °C.

$$g_{Mg} = \frac{\left(\frac{f_{Mg}}{\rho_{Mg}}\right)}{\left(\frac{f_{Mg}}{\rho_{Mg}}\right) + \left(\frac{f_{Mg_{17}Al_{12}}}{\rho_{Mg_{17}Al_{12}}}\right)} \quad (2.39)$$

Where g_{Mg} is the volume fraction of Mg, ρ_{Mg} is the density of Mg (1.748 g/cm³) and $\rho_{Mg_{17}Al_{12}}$ is the density of Mg₁₇Al₁₂ (2.088 g/cm³).

A common method of predicting the eutectic morphology is to calculate: (i) whether the phases will have a faceted or non-faceted solid-liquid interface, and (ii) the volume fraction of phases in the eutectic mixture [203–205]. Regarding whether a solid-liquid interface will become faceted or non-faceted, it can be approximated from the dimensionless entropy of

fusion [203]. This can be calculated from Eq.(2.39) and when $\Delta S_f^m/R < 2$, it indicates a non-faceted interface and vice versa.

$$\frac{\Delta S_f^m}{R} = \frac{\Delta H_f}{RT_m} \quad (2.40)$$

Where ΔS_f^m is the molar entropy, ΔH_f is the enthalpy of fusion, T_m is the melting point and R is the gas constant.

Figure 2.27 shows how the eutectic growth morphology depends on the volume fraction in multiple eutectic systems [206]. The morphology of the eutectic growth is rod-like for volume fractions up to around 0.3 of minor phase (β -phase), and the growth then becomes lamellar above 0.3 [204–206].

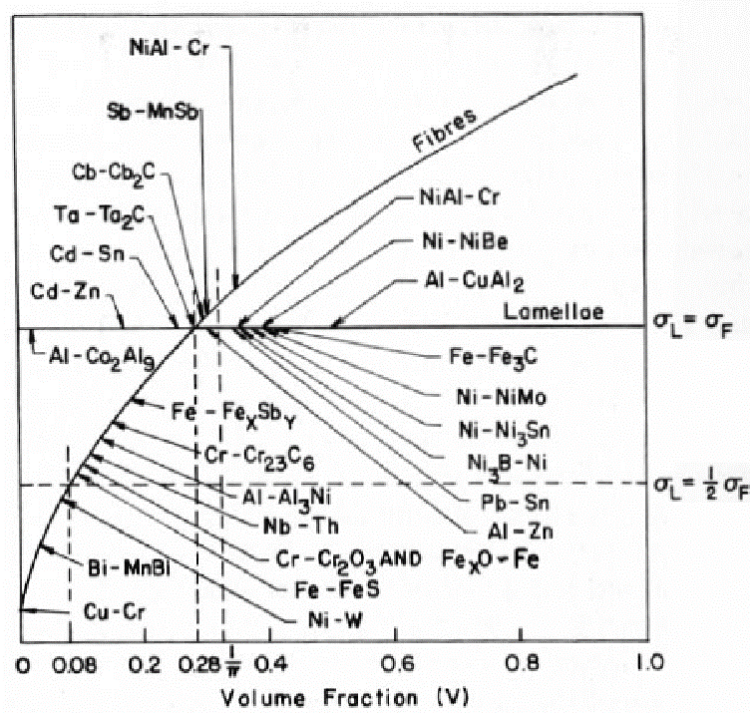


Figure 2.27 The experimental data on the interfacial energy with volume fraction of the β -phase for rod and lamellar morphologies. The line of $\sigma_L = \sigma_F$ is the assumption of isotropic interfacial energy between two phases. The line of $\sigma_L = \frac{1}{2}\sigma_F$ is the assumption of preferred interfacial orientation from the half interfacial energy of lamellar morphology for the rod morphology. From Ref. [206].

The combination of both faceting behaviour and volume fraction can be simply illustrated as Figure 2.28 which categorises eutectic growth into four different types. For Mg-33 wt% Al, Table 2.13 has summarised the calculations for Mg and Mg₁₇Al₁₂. The $\Delta S_f^m/R$ values predict that α -Mg and Mg₁₇Al₁₂ should both grow with non-faceted solid-liquid interfaces and since α -Mg is the minor volume fraction, the volume fraction of Mg will govern the types of eutectic growth. From Eq.(2.39), the volume fraction of Mg is 0.34. Thus, the overall calculation predicts that α -Mg+Mg₁₇Al₁₂ eutectic growth should occur with regular lamellar morphology.

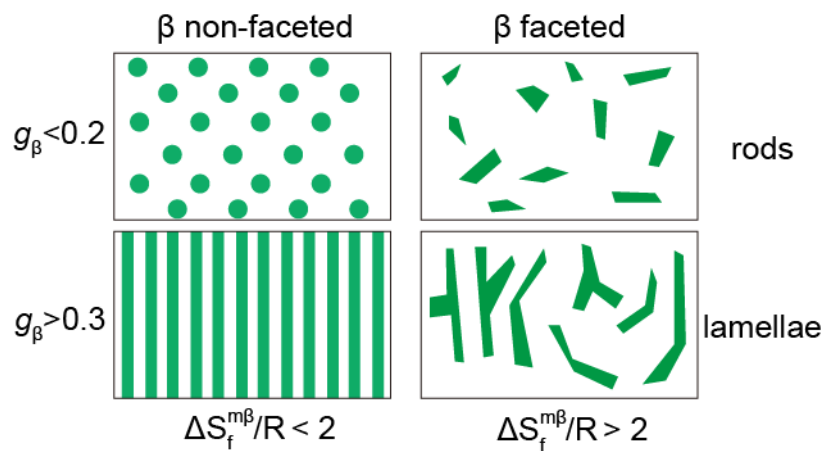


Figure 2.28 The illustration of eutectic morphologies under the condition of non-faceted α -phase (primary) with either non-faceted or faceted β -phase (minor phase). The left-hand side is the determination of the volume fraction of minor phase (g_β) and the bottom is the molar entropy of β -phase ($\Delta S_f^{m\beta}$). R is the ideal gas constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$). This is based on Ref. [206,207].

Table 2.13 The formation enthalpy, the melting point and molar entropy of Mg and Mg₁₇Al₁₂ with the ratio of ideal gas, R, based on [208,209].

Phase	ΔH_f (J mol^{-1})	T_m (K)	ΔS_f^m ($\text{J mol}^{-1} \text{ K}^{-1}$)	$\frac{\Delta S_f^m}{R}$	Ref.
Mg	8522	924	9.2	1.1	[208]
Mg ₁₇ Al ₁₂	7352	735	10	1.2	[209]

From the past experimental work [210], Figure 2.29 clearly shows that the lamellar morphology is indeed formed in alloys of eutectic composition, Mg-33 wt% Al.

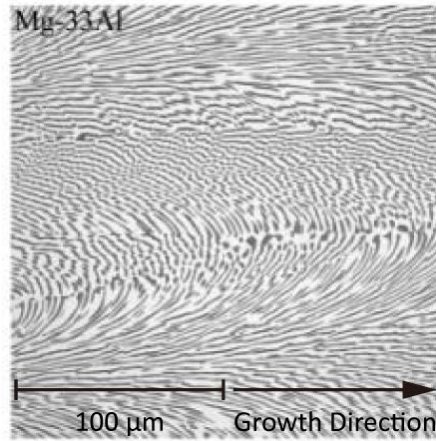


Figure 2.29 The lamellar eutectic morphology was formed in Mg-33wt%Al alloy. From Ref. [210]

In Mg-33 wt% Al, eutectic growth occurs as an invariant reaction to form a lamellar structure between α -Mg and $\text{Mg}_{17}\text{Al}_{12}$. The lamellar eutectic growth from the general diffusion equation was theoretically derived by Jackson and Hunt [211] based on Zener's finding [212]. The relationship between lamellar spacing and the growth rate is expected as shown in Eq.(2.41) [204,213–215]. The higher the growth rate, the less time there is for lateral diffusion in the liquid so the eutectic grows with a narrower lamellar spacing [213].

$$\lambda_e V^2 = C \quad (2.41)$$

where V is the growth rate, λ_e is the lamellar spacing, C is the constant

Figure 2.30(a) based on the past experimental data on Mg-33 wt% Al [213–215] shows that the best fit equation is shown as Eq.(2.42) is close to the theoretical Eq.(2.41). If the growth rates of $\text{Mg}_{17}\text{Al}_{12}$ are all converted into $1/\sqrt{V}$, then the plot becomes Figure 2.30(b) where the x-axis is linear instead of log scale. Here, Eq.(2.41) has been forced into the plot and Figure 2.30(b) shows that the theoretical equation, Eq.(2.43), still matches well with most of the experimental data [213–215].

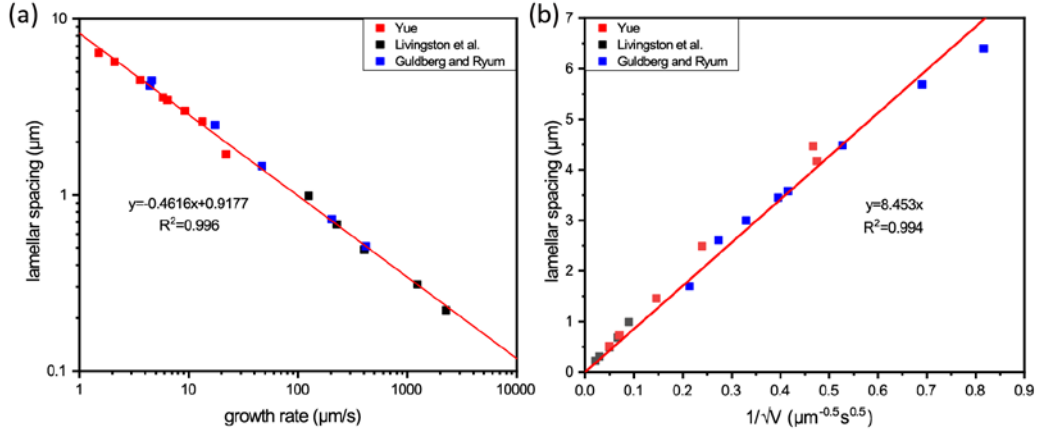


Figure 2.30 (a) the relationship between lamellar spacing and growth rate with a best fit numerical model based on past literature [213–215] and (b) a plot of lamellar spacing related to $1/\sqrt{V}$ with a best fit equation based on Eq.(2.42).

$$\lambda_e = 8.27V^{-0.46} \quad (\text{Figure 2.30(a)}) \quad (2.42)$$

$$\lambda_e = 8.45V^{-0.5} \quad (\text{Figure 2.30(b)}) \quad (2.43)$$

Jackson and Hunt [204] showed that when the lamellar spacing is momentarily either too wide or too narrow, the undercooling of the lamellar structure will be larger than the minimum undercooling for rod structure. This causes the lamellar faults formation to change the lamellar spacing. As a result, the rod structure is stabler than the lamellar structure. The interplay between two structures can be manipulated by the growth rate conditions. The change of the lamellar to rod structure was also reported as the dependence on the significantly altered growth rate due to the minimisation of surface energy [204,213].

Gulberg and Ryum [215] reported that when the eutectic grew in the following condition: growth rate $< 18 \mu\text{m/s}$, lamellar spacing $\geq 2.5 \mu\text{m}$; the orientation relationship between $\alpha\text{-Mg}$ and $\text{Mg}_{17}\text{Al}_{12}$ can be listed as the following in Eq.(2.44):

$$\begin{aligned} [11\bar{2}0]_{\text{Mg}} // [111]_{\text{Mg}_{17}\text{Al}_{12}} \\ (\bar{1}\bar{1}01)_{\text{Mg}} // (10\bar{1})_{\text{Mg}_{17}\text{Al}_{12}} \end{aligned} \quad (2.44)$$

The low index direction in the OR between $\alpha\text{-Mg}$ and $\text{Mg}_{17}\text{Al}_{12}$ are tiled away from the growth direction and the angles depend on the growth rate [215]. The higher the growth rate,

the smaller the angle between the lower index direction of the interfacial plane and the growth direction [215]. This OR is the same as the Potter OR [216] and in past research [217,218], the formation of $\text{Mg}_{17}\text{Al}_{12}$ through solid state precipitation was also found to have the Potter OR with $\alpha\text{-Mg}$ in some cases.

Although the past works [204,210,213] showed the change of the morphology structure by extreme conditions, the boundary of local undercooling needs to be investigated.

2.4.2. $\alpha\text{-Mg}+\text{Mg}_{17}\text{Al}_{12}$ eutectic growth in hypoeutectic alloys

In the previous section, we have discussed about the eutectic lamellar growth of $\text{Mg}_{17}\text{Al}_{12}$ in an alloy of eutectic composition, Mg-33 wt% Al. The morphology of $\text{Mg}_{17}\text{Al}_{12}$ starts to change as the Al content decreases in the Mg-Al system. In this section, eutectic solidification in hypoeutectic Mg-Al based alloys are discussed.

For alloys containing 9 wt% Al and less, $\text{Mg}_{17}\text{Al}_{12}$ generally presents as partially or fully divorced microstructures and the morphology depends on cooling rate and chemical compositions such as zinc and aluminium content [78,83,86–88,219]. The $\text{Mg}_{17}\text{Al}_{12}$ morphology changed by the Al content can be clearly seen in Figure 2.31. As the Al content decreases from 33 wt% to 9 wt%, the $\text{Mg}_{17}\text{Al}_{12}$ morphology in the system changes from coupled lamellar structure (33 wt% Al) to lamellar eutectic between the $\alpha\text{-Mg}$ dendrites (21 wt% Al) and then to partially divorced growth between $\alpha\text{-Mg}$ dendrite arms (9 wt% Al). The change of the $\text{Mg}_{17}\text{Al}_{12}$ morphology is governed by the volume fraction of $\alpha\text{-Mg}$ [19].

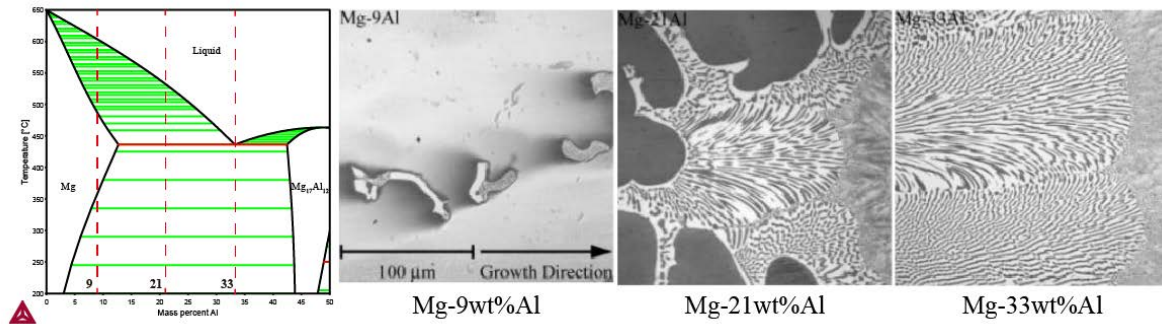


Figure 2.31 Dependence of α -Mg+ $\text{Mg}_{17}\text{Al}_{12}$ eutectic growth morphology on alloy composition in unidirectional solidification at $30 \mu\text{m s}^{-1}$. Mg-9Al: divorced eutectic growing through/between α -Mg dendrites. Mg-21Al: lamellar eutectic growing through/between α -Mg dendrites. Mg-33Al: lamellar eutectic growth. Adapted from Ref. [210].

The Zn content in the alloy also changes the $\text{Mg}_{17}\text{Al}_{12}$ morphology [90]. In the work of Nave et al. [90], two types of Mg-Al alloy (9 and 15 wt% Al) were added with 0.8 and 1.6 wt% Zn content individually. The results showed the $\text{Mg}_{17}\text{Al}_{12}$ morphology changes from partially divorced to fully divorced in the same position of the samples after increasing the Zn content in both Mg-Al alloys. They [90] suggested the likely mechanism for this effect is that the Zn is rejected to the front of and enriches the liquid ahead of the α -Mg dendrites before the nucleation of $\text{Mg}_{17}\text{Al}_{12}$ happens. The higher Zn content in the liquid increases the constitutional undercooling for α -Mg and this makes $\text{Mg}_{17}\text{Al}_{12}$ difficult to form a lamellar-like morphology.

The cooling rate is another factor of changing the morphology of $\text{Mg}_{17}\text{Al}_{12}$ [89,90,220]. Nave et al. [89] reported that the wide range of Al content in magnesium alloys had the same phenomenon that $\text{Mg}_{17}\text{Al}_{12}$ in the centre of the samples with lower cooling rate was less divorced than the edge of the samples. The effect was suggested that the $\text{Mg}_{17}\text{Al}_{12}$ morphology is significantly affected by the α -Mg morphologies determining the width of liquid channels [19,89]. Figure 2.32 summarises all three factors (Al content, Zn content and cooling rate) affecting the $\text{Mg}_{17}\text{Al}_{12}$ morphology. However, for the cooling rate factor, Dargusch et al. [79] found the $\text{Mg}_{17}\text{Al}_{12}$ morphology has the opposite results from the results from Nave et al. [89] and this implies that cooling rate is not the only factor effecting the $\text{Mg}_{17}\text{Al}_{12}$ morphology.

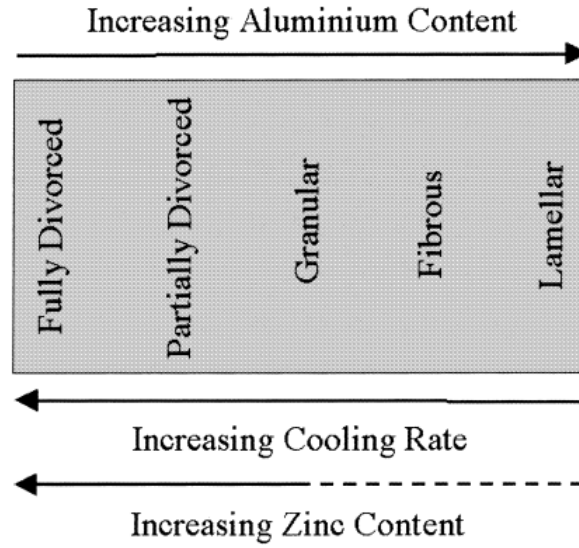


Figure 2.32. The illustration of how Al content, Zn content and cooling rate affect $Mg_{17}Al_{12}$ morphology in hypoeutectic Mg-Al systems [78].

The past works [19,78,83,87–90,219,220] show there is a need to understand the morphology of α -Mg affecting to the morphology of $Mg_{17}Al_{12}$ from the changing factors of Al, Zn contents and cooling rate. Also, there is no developed measurements to quantify the level of divorced $Mg_{17}Al_{12}$ which allow the prediction and control of the microstructure of $Mg_{17}Al_{12}$.

In the previous section, all the $Mg_{17}Al_{12}$ morphologies are understood based on the hypoeutectic Mg-Al phase diagram which shows the phase equilibrium state. Also, the mass and volume fractions are based on the lever rule which can be written as Eq. (2.45) and illustrated in Figure 2.33(a) [221]:

$$f_s = \frac{C_0 - C_L}{C_s - C_L} = \frac{C_0 - C_L}{(k - 1)C_L} \quad (2.45)$$

Where the notations are the same as in Figure 2.33(a) and k is the partition coefficient ($k = \frac{C_s}{C_L}$)

The main assumption of the equilibrium solidification is that the solid composition will be uniformly changed according to the phase diagram. However, it is not true for the real-life

situation because the local solidification time needs to be more than 1000s to achieve equilibrium state [222].

The long local solidification time implies the diffusion in the solid hardly happens so the Scheil model in Figure 2.33(b) [223] was developed to simulate the actual solidification. This model was after a first proposed model done by Gulliver [224]. The assumptions of the Scheil model are different from the equilibrium solidification because here, the diffusion does not happen in the solid and at the interface between the solid and liquid, the compositions of both phases depend on the phase diagram. The calculation of the Scheil equation can be written as Eq. (2.46) [223].

$$f_s(T) = 1 - \left(\frac{C_L}{C_0}\right)^{\frac{1}{k-1}} = 1 - \left(\frac{T_m - T}{T_m - T_L}\right)^{\frac{1}{k-1}} \quad (2.46)$$

Where the notations are the same as in Figure 2.33(b).

A comparison of the two solidification models is summarised in Table 2.14. In the real-life situation, the actual solidification is closer to Scheil model but it is in between the two models due to the back-diffusion. In the following sections, both models are used to compare the phase formation in Mg-Al alloy system.

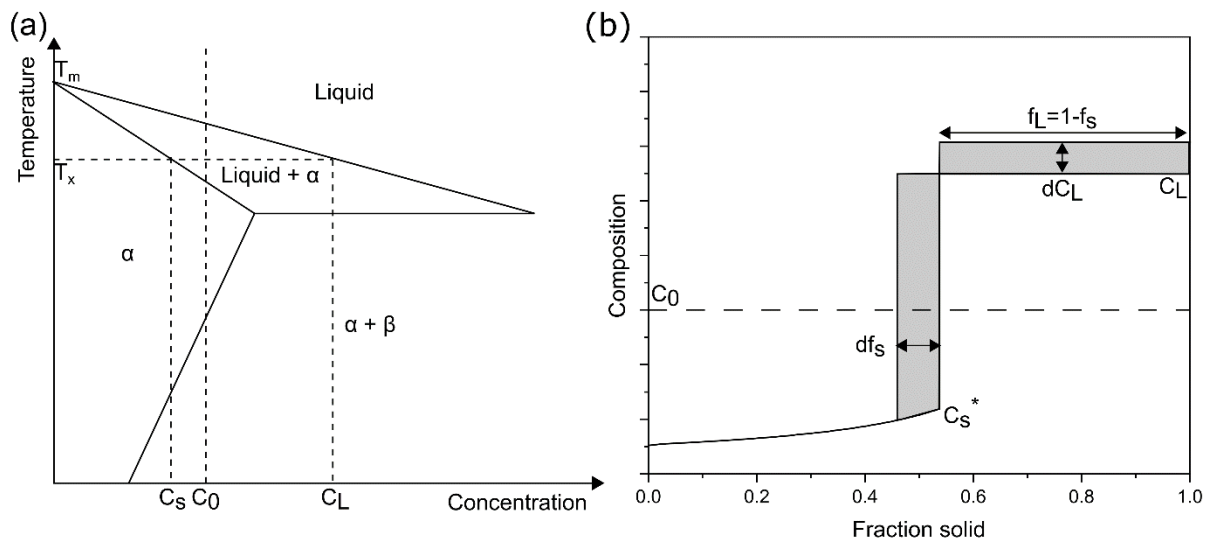


Figure 2.33 (a) A typical binary linear phase diagram (T_m : melt temperature, T_x : temperature for the composition, C_s : solid composition, C_0 : hypoeutectic composition, C_L : liquid composition). (b) An illustration of the partitioning of liquid and solid interface in Scheil model (C_s^* : solid of composition at interface, df_s : the change of solid fraction; f_s : solid fraction, dC_L : the change of liquid composition, f_L : liquid fraction). Adapted from Ref. [225].

Table 2.14 A summary of common and different assumptions between equilibrium and Scheil solidifications [221,223,224].

	Equilibrium solidification	Scheil solidification
Common	- The liquid composition is completely mixed and uniform. It depends on the phase diagram corresponding to the temperature. - There is no nucleation barrier when the temperature reaches the liquidus temperature and the solidification begins.	
Difference	The solid composition is uniform and depends on the phase diagram corresponding to the temperature.	- The solid is non-diffusible. - The liquid and solid compositions at the interface depend on the phase diagram corresponding to the temperature.

Note from Figure 2.31(a) that Mg-9Al is less than the α -Mg composition on the eutectic tie line and so, for full-equilibrium, we could expect no eutectic reaction in this alloy. That is to say, assuming the lever rule, the liquid would have completely transformed into α -Mg at 485°C. However, as the solidification process is relatively fast, there is insufficient time for diffusion in the solid phases which leads to a form of non-equilibrium solidification. The Scheil equation assumes no diffusion occurs in the solid phases and predicts that the liquid composition will

always reach the eutectic composition as illustrated in Figure 2.34 where the end of Scheil solidification involves the $L \rightarrow \alpha\text{-Mg} + \text{Mg}_{17}\text{Al}_{12}$ reaction. In reality, the solidification process is closer to the prediction from the Scheil equation than the Lever rule (full equilibrium).

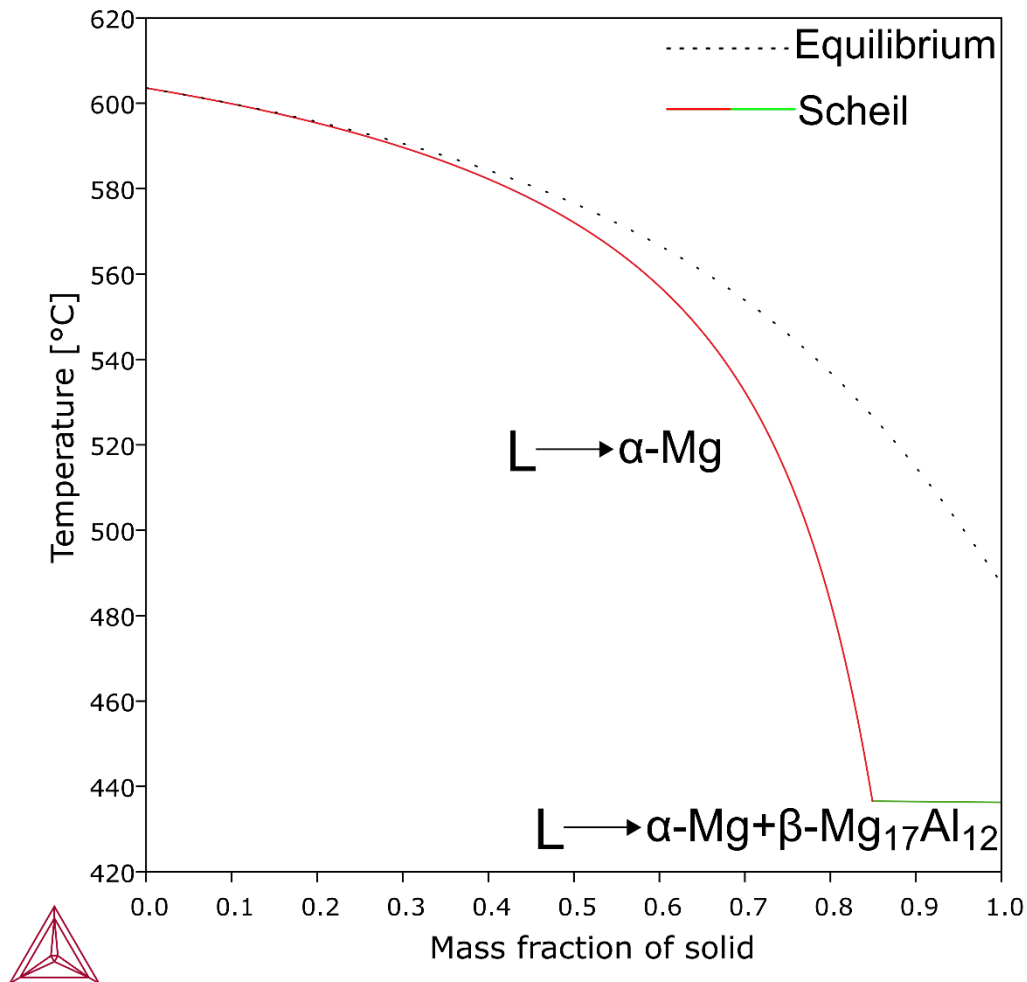


Figure 2.34 The phase transformation during the solidification in Mg- 9 wt% Al system illustrated by equilibrium and Scheil solidification. The calculation is done by Thermo-Calc TCMG magnesium database version 4 [202].

2.4.3. Dissolution of $\text{Mg}_{17}\text{Al}_{12}$ during heat-treatment

$\text{Mg}_{17}\text{Al}_{12}$ plays an important role in material properties of AM and AZ series magnesium alloys. Some parts are used in the as-cast condition where $\text{Mg}_{17}\text{Al}_{12}$ is a eutectic phase. It is also common to change the material properties through solid state heat treatment which manipulates the $\text{Mg}_{17}\text{Al}_{12}$ phase [91]. The common heat treatment methods used in the industry are: (i) solution heat treatment to dissolve all the $\text{Mg}_{17}\text{Al}_{12}$ into the $\alpha\text{-Mg}$ matrix which (for

example) improves the forgeability and subsequent machinability [91,93,94], and (ii) precipitation hardening of solutionised material which produces a fine dispersion of $Mg_{17}Al_{12}$ precipitates to maximise yield strength [15,91,226]. The recommended heat treatment temperatures for the commercially used AM and AZ series magnesium alloys are shown in Table 2.15. In this project, only the solution heat treatment is considered.

Table 2.15 The standard solution heat treatment and precipitate hardening temperatures for the commercial AZ and AM series based on Ref [91].

Alloy	Temperature ± 6 ($^{\circ}C$)	
	Solution treatment	Precipitate hardening
AM100	424	232
AZ81	413	218
AZ91	413	168

AZ series [95,96,98–102], AM series [97], Mg-Al binary [227] alloys have been used to study the dissolution kinetics of $Mg_{17}Al_{12}$ into α -Mg and most solutionising studies [95,98–102,227] set the heat treatment temperature in the range of 400 to 440 $^{\circ}C$. The reason for choosing the temperature in the range of 400 to 440 $^{\circ}C$ can be seen in Figure 2.35 where the Mg-9Al lies in the single-phase α -Mg region. From holding for a long-term period, $Mg_{17}Al_{12}$ will dissolve into α -Mg leading to the increase of Al content in α -Mg. Most studies [95,98,101,227] agree that $Mg_{17}Al_{12}$ is mainly dissolved within 24 hours as listed in Table 2.16. Their results agree with industrial practice which suggest the solution heat treatment for AZ series is between 16 and 24 hours [91].

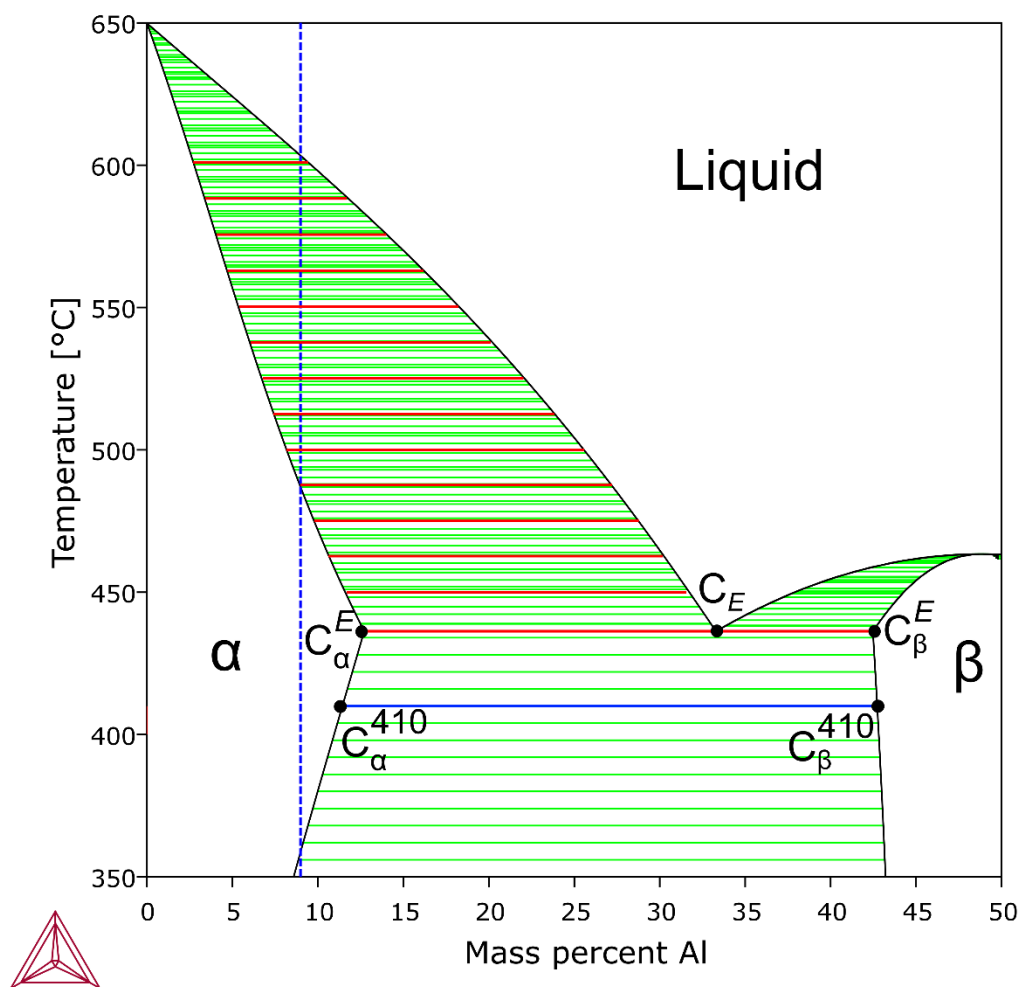


Figure 2.35 Tie lines in the binary Mg-Al phase diagram with the label of the tie line in eutectic reaction and the tie line at 410°C. The contact line of 9 wt% Al is drawn as the blue vertical line. α and β present as α -Mg and $\text{Mg}_{17}\text{Al}_{12}$ respectively. The phase diagram is from Thermo-Calc TCMG magnesium database version 4 [202].

Table 2.16 Solution heat treatment for dissolving $\text{Mg}_{17}\text{Al}_{12}$ in as-cast AZ series [95,98–101,227]

Alloy	Type	Temperature (°C)	Required Time (hour)	Ref.
AZ91	Gravity casting	400	>16	[98]
		420	>4	
	High-pressure die casting (HPDC)	400	0.5	
		420	0.17	
AZ80	Gravity casting	439	< 74.5	[100]
		400	74.5	
Mg-9wt%Al	Gravity casting	400	8	[227]
AZ80	Gravity casting	410	24	[99]
			(75 vol% dissolved)	
AZ80	Gravity casting	420	20	[101]
AZ80	Gravity casting	420	8	[95]

In Table 2.16, we can notice that the same type of alloy and casting methods have different solution heat treatment times. This raises the question on what factor governs the dissolution kinetics of $\text{Mg}_{17}\text{Al}_{12}$. Grain size [95,99] and SDAS [98] were discussed in past works. Yeoh et al.[95] and Palai et al. [99] observed the dissolution of $\text{Mg}_{17}\text{Al}_{12}$ from the grain boundaries but the eutectic $\text{Mg}_{17}\text{Al}_{12}$ does not only form in the grain boundaries but also between the dendrite arms. Also, it was unclear how the grain size affects the dissolution kinetics since the grain size seems to increase during the solution heat treatment [99]. In the work of Zhu et al. [98], the thickness of $\text{Mg}_{17}\text{Al}_{12}$ is considered to be dependent by the SDAS and the distinguished examples are the comparison between gravity cast and HPDC samples. They used energy dispersive spectroscopy (EDS) to determine Al content distribution across the α -Mg dendrite for as-cast and heat treated 30-min samples. The experimental data was similar to the approach from the solute profile calculation model for 4.5 wt% Cu aluminium alloy in reference [228]. This approach to the dissolution kinetics was also calculated from three types of distances, grain boundary [227], the gap between $\text{Mg}_{17}\text{Al}_{12}$ plates [102] and dendrite arms [96]. However, the Al content diffuses away from $\text{Mg}_{17}\text{Al}_{12}$ which is solidified between the α -Mg dendrite arms so it is clearer to show the $\text{Mg}_{17}\text{Al}_{12}$ dissolution happens in the dendrite arms. Figure 2.36 shows the Al content in α -Mg through the solidification path in Mg-9 wt% Al calculated by the Scheil calculation [202]. The mass fraction of solid 0.8-1 in Figure 2.36 is also the region where $\text{Mg}_{17}\text{Al}_{12}$ forms but the Al content in $\text{Mg}_{17}\text{Al}_{12}$ is much higher than in α -Mg. This shows there is a driving force of Al content diffusing into the lower Al content α -Mg by giving enough temperature which is the single-phase region in Figure 2.35.

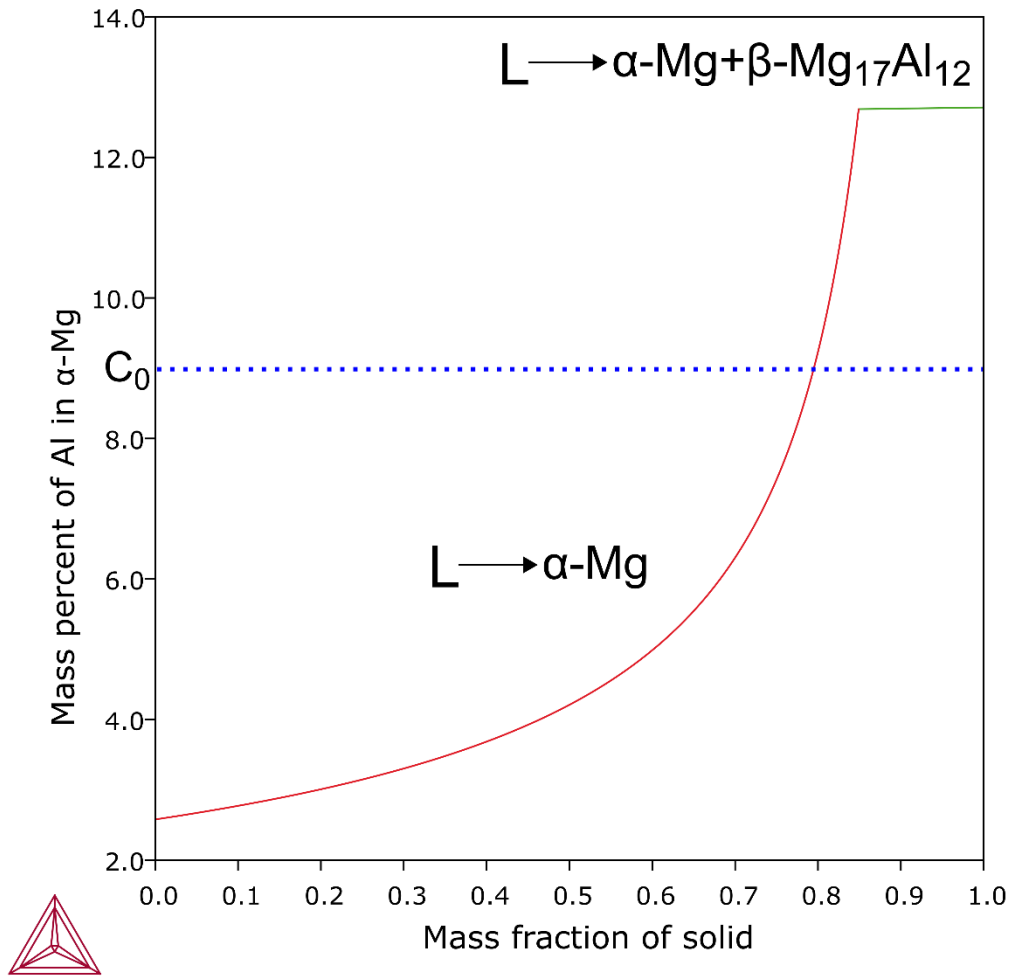


Figure 2.36 The Scheil calculation of Mg- 9 wt% Al system for the composition of Al content in α -Mg with the mole fraction of solid through solidification processing. The calculation is from Thermo-Calc TCMG magnesium database version 4 [202].

However, the effect of partially divorced $\text{Mg}_{17}\text{Al}_{12}$ morphology on dissolution kinetics was not discussed in the past works [95,98–102,227]. In addition, SDAS seems to be not the only factor affecting on the dissolution kinetics. Note that Al-Mn intermetallics also form throughout solidification in AZ91 alloy. This has been extensively studied recently [229–234] and, since the Al-Mn compounds occupy less than 0.25% of the microstructure, they are not be reviewed here.

Based on this literature review, four main questions were identified for detailed study: (i) Which carbides form after carbon inoculation of liquid AZ91 and how do these affect the solidification sequence?; (ii) how do these carbides affect heterogenous nucleation and grain

refinement of α -Mg during casting?; (iii) how does the α -Mg dendrite morphology affect the growth of the α -Mg+Mg₁₇Al₁₂ eutectic including the “divorcedness” of eutectic growth?; And (iv) how does each microstructural feature affect the dissolution of Mg₁₇Al₁₂ during solution heat treatment? These questions will be answered by different cooling-rate samples with various SDAS to make a wide range of solidification conditions.

Chapter 3. Experimental Methods

This Chapter overviews the experimental methods and techniques that are common to all subsequent Chapters. Additionally, each later Chapter also contains a small Methods section covering the experimental methods that are specific to that Chapter.

3.1 Gravity casting experiment

The batch of AZ91 used in all Chapters had the chemical compositions shown in Table 3.1. The standard gravity casting procedure was as follows. The ingots were cut and prepared to fit in a tapered stainless-steel crucible with inner diameter of 60 mm at the bottom and 70 mm at the top and height of 89 mm. All carbon additives were enveloped within aluminium foils (W: 8cm, L: 16cm, T: 13 μ m) and put into the 120 g melt when the alloy reached 685°C and were covered by argon gas. After adding the carbon-based additives, the melt was stirred at 780 rpm for one hour before pouring into a pre-heated 200°C mould coated with BN (Diameter: 12 mm, H: 150 mm) as shown in Figure 3.1.

Table 3.1 Chemical compositions of AZ91 used in each Chapter was analysed by inductively coupled plasma-optical emission spectroscopy (ICP-OES).

Alloy	Composition (wt%)									
	Mg	Al	Zn	Mn	Cu	Si	Ni	Fe	Be	Sr
AZ91	Bal.	8.95	0.72	0.19	0.001	0.039	<0.001	<0.001	0.007	-



Figure 3.1 The casting sample with four cylinders in a pre-heated BN coated steel mould.

3.2 Growth reaction product experiments

For understanding carbide formation after carbon inoculation, No.3 bar of all gravity casting samples in Chapter 4 and Chapter 5 were sliced into 2 cm cylinders to fit into alumina crucibles (internal diameter: 10mm, internal height: 25 mm) with lids on the top. The whole alumina crucibles containing a sample was then sealed in a quartz tube under argon gas as illustrated in Figure 3.2. The quartz tube was placed into a resistance furnace preheated to a chosen peak temperature and held in the liquid state for a required period (4 to 40 hours; detail is described in each chapter). One of two cooling systems was then applied to the liquid samples: (i) fast cooling was when the samples were taken out directly to a cylindrical hole in a room-temperature steel mould; and (ii) slow cooling was when the furnace was turned off with the lid on until reaching 400°C, when the tubes were taken into the room-temperature steel mould. The second part of method (ii) was to minimise any solid-state transformation that may occur during slow cooling. The specific peak temperatures and time scales are listed in Chapter 4 and Chapter 5.

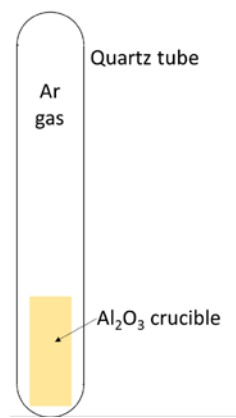


Figure 3.2 The illustration of enclosed system for high temperature holding.

3.3 Characterisation

3.3.1. Metallurgical sample preparation

All samples were sliced with water-free oil before the cross-sections were mounted. The samples were, then, ground with ethanol and polished with 20 vol% OP-S with ethanol to minimise hydrolysis reaction of the carbides. The sample preparation process is shown in Table 3.2. For the diamond and α -SiC samples in Chapter 4 and Chapter 5, broad ion polishing was applied under a PECS-II instrument (Table 3.3) for two hours to reduce the height difference between the carbon additives and α -Mg phases.

Table 3.2 Metallurgical sample preparation for characterisation

Hot mounting				
Material	Mounting temperature	Mounting time		
Black bakelite	175°C	10-15 mins heating setting and 3 mins cooling time		
Grinding				
Grinding papers	Rotation speed	Applied force	Grinding time	
Grit 2000 SiC	100-200 rpm	10 N	1 min	
Grit 4000 SiC	100-200 rpm	10 N	3-5 mins	
Polishing				
Polishing cloth	Polishing solution	Rotation speed	Applied force	Polishing time
MD-Chem, 200mm dia	20% OP-S NonDry dissolved in absolute ethanol	60-150 rpm	10 N	12 mm
In the final step, the samples were immersed in ethanol and cleaned by ultrasonic bath for 10 mins to remove remaining OP				

Table 3.3 The parameters used in the PECS-II

Voltage (keV)	Operation time (min)	Beam angle (°)	Modulation	Stage rotation (rpm)
2	60	4	Dual Modulation	4
1	40			
0.5	20			

3.3.2. Electron microscopy characterisation

A Zeiss Sigma-300 was used for electron backscattered diffraction (EBSD) and SEM images under secondary electron (SE) and backscattered electron (BSE) modes. The parameters used for EBSD were under 20 keV electron beam and a 120-μm aperture with a 70° tilted stage in 15 mm working distance. Additionally, BRUKER e-FlashHR EBSD detector was set at 15 mm working distance to the tiled stage. For SEM images, the parameters were the same as EBSD

without the tiled angle. Zeiss Auriga field emission gun scanning electron microscope (FEG-SEM) was operated under 10 keV electron beam and a 60- μm aperture with 5 mm working distance for energy-dispersive X-ray spectroscopy (EDS). The Bruker Quanta Esprit 2.1 software was used and the indexing phase list for EBSD scanning is shown in Table 3.4. EBSD data was also analysed and visualised using the MTEX toolbox within Matlab. The TSL OIM data Collection 5 software was used to index Kikuchi bands to specific planes of the indexed phases. The crystal structures of indexed phases were extracted from ICSD as CIF format files and illustrated by CrystalMaker software. The presentation of some ORs in pole figures was illustrated using SingleCrystal software.

Table 3.4 The list of crystal structures for EBSD indexing [168,169,239,240,170,172–174,235–238]

Phase	Space group	Pearson symbol	Lattice parameters						Ref.
			a(nm)	b(nm)	c(nm)	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$	
α -Mg	P6 ₃ /mmc	hP2	0.3202	0.3202	0.5200	90	90	120	[168]
Al ₄ C ₃	R $\bar{3}$ mH	hR7	0.3335	0.3335	2.4967	90	90	120	[173]
T1-Al ₂ MgC ₂	P6 ₃ /mmc	hP10	0.3402	0.3402	1.2292	90	90	120	[174]
T2-Al ₂ MgC ₂	P $\bar{3}$ m1	hP5	0.3377	0.3376	0.5807	90	90	120	[169]
Al ₂ CO	P6 ₃ mc	hP4	0.3170	0.3170	0.5078	90	90	120	[172]
Al ₈ Mn ₅ (γ 2)	R3m	hR26	1.2667	1.2667	0.7942	90	90	120	[235]
Al ₁₁ Mn ₄	P $\bar{1}$	aP15	0.5095	0.8879	0.5051	89.35	100.47	105.08	[236]
Diamond	Fd $\bar{3}$ m	cF8	0.3567	0.3567	0.3567	90	90	90	[237]
α -SiC	P6 ₃ mc	hP12	0.3081	0.3081	1.512	90	90	120	[170]
Graphite*	P6 ₃ /mmc	hP4	0.2464	0.2464	0.6711	90	90	120	[238]
MgO	Fm $\bar{3}$ m	cF8	0.4217	0.4217	0.4217	90	90	90	[239]
Mg ₁₇ Al ₁₂	I $\bar{4}$ 3m	cI58	10.544	10.544	10.544	90	90	90	[240]

*Graphite could not produce any Kikuchi patterns from the experiment.

3.3.3. Grain size measurement

To reveal the α -Mg grain structure in Chapter 5 and Chapter 6, the samples were immersed in the etching solution shown in Table 3.5. After etching with an appropriate time, nitrogen gas

was used to dry the surface for a few seconds. Humid air was then applied for one second in the final step. For grain size measurement, optical micrographs were taken under polarised light using a Olympus BX51 optical microscope, and the low magnification macrographs of whole cross sections were taken by stereomicroscopy, Brunel Microzoom Stereomicroscope.

Table 3.5 The compositions of colour etching solution based on Ref. [241]

Solution	Volume (ml)
Distilled water	44
Absolute ethanol	156
Glacial acetic acid	1

The grain size measurement was calculated using the following steps [242]:

1. After the samples were colour etched, they were taken to the optical microscopy.
2. Images were firstly taken with cross polarised lenses.
3. ImageJ [243] was then used to adjust the white balance and contrast on the images.
4. Vertical and horizontal lines were then drawn from the beginning of one grain boundary to the end of another grain boundary. A demonstration is shown in Figure 3.3.
5. Two values were recorded from each line: (i) the length of the line in the actual scale and (ii) the number of grains across the line.
6. Each line could measure an average grain size from the length of the line divided by the number of crossing grains (intercepts). Each image gave eight values for the grain size.
7. At least 16 lines were calculated to average the grain size in each sample. The count of grains was at least 50.
8. The error bars for the grain sizes were taken from the 95% confidence interval Eq.(3.1).

In order to determine whether the average grain size was representative for each sample,

the relative accuracy was taken into account. The relative accuracy (RA) was calculated using Eq. (3.2) and measurements were continued until this value was lower than 10%.

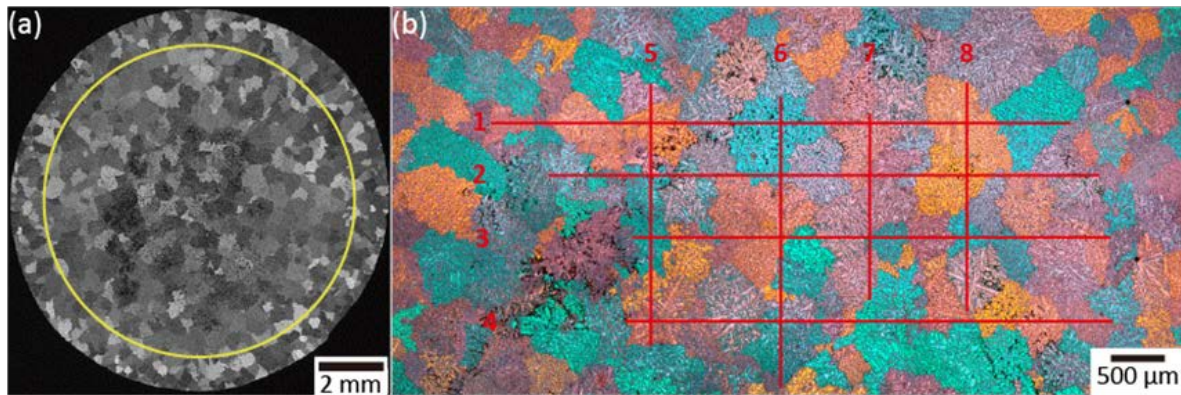


Figure 3.3 (a) A typical measured region in a gravity sample which excludes the chill zone (within the yellow circle). (b) An example of the linear intercept method used to measure grain size in (a) a typical region of gravity cast AZ91 within the yellow circle.

$$95\% \text{ confidence} = \frac{\text{standard deviation} * 95\% \text{ condient interval factor}}{\sqrt{\text{number of lines}}} \quad (3.1)$$

$$RA\% = \frac{95\% \text{ confidence}}{\text{Average grain size}} * 100\% \quad (3.2)$$

Chapter 4. Carbide formation in AZ91 after carbon inoculation

4.1 Introduction

Carbon inoculation is one of the well-known methods for grain refining Mg-Al based alloys. Most authors [48,50,148,154,161,51–53,58,62,63,70,75] agree that the mechanism involves the heterogenous nucleation of α -Mg on carbides. However, the carbon inoculation method has competing hypotheses about the detailed underlying mechanisms [106] and the extent to which carbides also play a role in grain refinement by superheating [29] and in the poisoning of native grain refinement [23]. Many works on the carbon inoculation of Al-bearing magnesium alloys mentioned Al_4C_3 [32,44,154,48–51,58,62,75,148] and, more recently, Al_2MgC_2 [52,53,70], but only a few have shown experimental evidence of these phases [51–53,70]. One reason is that these carbides hydrolyse easily [46,50–52,54,58,63,146,155,177] and so can react with water during sample preparation before microscopy and other forms of characterisation. For example, analysis of particles by EDS often yields a large oxygen peak.

Only tens of ppm of carbon are soluble in liquid Mg [244]. The typical amount of carbon in Al-bearing magnesium alloys is unclear but one study [151] found a T2- Al_2MgC_2 particle pre-existing in AZ91 that had not been inoculated with carbon.

An important body of information on carbides in Mg-Al based alloys comes from the metal matrix composites (MMCs) literature which has investigated interfacial reactions between carbon additions (e.g. graphite particles or carbon fibres) and Mg-Al based alloys [177–179]. Viala, Bosselet and co-workers [177,179] identified two ternary carbides, T1- Al_2MgC_2 and T2- Al_2MgC_2 . These two phases were considered to have certain metastable features between each other [178]. T1- Al_2MgC_2 is considered to form at lower temperatures than T2- Al_2MgC_2 . The weight percentage of T1- Al_2MgC_2 reached a maximum amount at 980K [179]. The authors [178] mentioned that T2- Al_2MgC_2 and Al_4C_3 can both form in the interfacial reaction between

Mg-Al alloys and carbon fibres at 1000K; which carbides forms depends on the Al content of the melt with threshold of 19 ± 2 wt% Al content in the Mg-Al alloy. When the Al content is below the threshold, Al_2MgC_2 is the dominant phase formed at 1000K. A recent investigation on the equilibrium phase diagram of the Al-Mg-C ternary system [245] calculated the Al-Mg-C liquidus projection and showed that Al_4C_3 forms at ≥ 18.5 wt% Al in the melt at 1000K. The same CALPHAD study [245] calculated that Scheil solidification of a Mg-9Al melt saturated with carbon at 1000 K will begin solidification with 0.021 mass fraction of Al_2MgC_2 , and then Al_4C_3 forms later from 535.5 °C after the growth of α -Mg dendrites increases the aluminium content of the melt. This implies that primary Al_2MgC_2 is probably the carbide which is responsible for nucleation and grain refinement of magnesium in Mg-9Al alloys. However, experiments have not yet tested the validity of the calculated solidification path or whether kinetic factors play a significant role in determining the sequence of carbide formation.

In order to further understand carbide formation in carbon inoculated Mg-Al-based alloys, this chapter presents a dedicated study on the carbides in AZ91 magnesium alloys after adding carbon sources. The main aims of this chapter are: (i) to investigate which carbide phases form at different stages of the solidification sequence; (ii) to identify the growth morphology and faceted growth mechanisms of the carbides; and (iii) to study the interactions between carbides and other phases during solidification including MgO, Al-Mn intermetallics, and $\text{Mg}_{17}\text{Al}_{12}$.

4.2 Methods

4.2.1. Materials and casting experiments

AZ91 was used with chemical compositions shown in Table 4.1. Two types of carbon-based additives were used in this experiment

1. synthetic diamond (purity >99%, particle size $1 < d < 2$ μm , Mozime Ltd.)
2. synthetic graphite (purity >99%, grain size $d < 50$ μm , Alfa Aesar).

First, the AZ91 alloy was heated to 685 °C covered by argon protective gas. Then, 4.5 wt% carbon additive (diamond or synthetic graphite) enveloped in aluminium foil (W: 8cm, L: 16cm, T: 13µm) was added into the melt. After the addition, the melt was stirred at 780 rpm for one hour. Finally, the melt was poured into a steel permanent mould which was coated with BN and preheated at 200 °C. The further detail on the casting method was given in Chapter 3.

Table 4.1 Chemical composition of AZ91 was analysed by ICP-OES.

Alloy	Composition (wt%)								
	Mg	Al	Zn	Mn	Cu	Si	Ni	Fe	Be
AZ91	Bal.	8.95	0.72	0.19	0.001	0.039	<0.001	<0.001	0.001

4.2.2. Growth of reaction product experiments

No.3 bar of the casting samples were sliced into 2 cm cylinders. The cylinders were then placed into alumina crucibles (internal diameter: 10mm, internal height: 25 mm) with lids and the whole alumina crucibles were encapsulated inside quartz tubes with argon gas as shown in Figure 4.1.

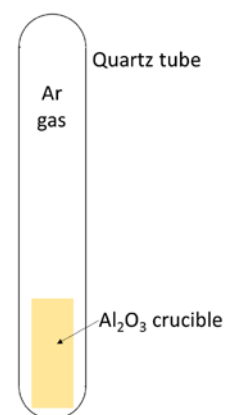


Figure 4.1 Illustration of enclosed system for high temperature heat treatment

The tubes were placed into a furnace preheated to a peak temperature and held for a set time, as listed in Table 4.2. One of two cooling methods was then applied: (i) fast cooling, where the quartz tube was taken out at the holding temperature and placed directly into the cylindrical hole in a room-temperature steel mould; and (ii) slow cooling, where the furnace was turned

off with the lid on until reaching 400°C, and the quartz tubes were then removed and placed directly into the cylindrical hole in the room-temperature steel mould. This second step in method (ii) was to minimise any solid-state transformations during slow cooling.

Table 4.2 Melt processing of AZ91+diamond and AZ91+graphite samples.

Sample	Holding temperature (°C)	Holding duration (hrs)	Cooling method
AZ91	700	4	Fast (4 K/s)
AZ91+diamond (1-2 µm)	900*	4	Fast (4 K/s)
	800	40	Slow (0.01 K/s)
	800	40	Fast (4 K/s)
	700	40	Fast (4 K/s)
	800	40	Slow (0.01 K/s)
AZ91+graphite (50 µm)	800	8	Fast (4 K/s)
	700	40	Fast (4 K/s)
	700	40	Fast (4 K/s)
	700	40	Fast (4 K/s)

*The sample was heated at 800 °C for 40 hours with fast cooling first and then held at 900 °C for 4 hours with fast cooling.

4.2.3. Characterisation

All samples were sliced with water-free oil before the cross-sections were mounted. Then, they were ground with absolute ethanol and polished with 20 vol% OP-S in ethanol solution. Further details of sample preparation and characterisation was described in Chapter 3.

4.3 Results and Discussion

4.3.1. Distinguishing the carbide phases by EBSD

The Kikuchi patterns collected by EBSD were auto-indexed by Bruker Esprit 2.1 using the Hough transform method with the given phase list (Table 3.4).

To further test for any misindexing of phases or their orientations, Bruker Esprit DynamicS software was used to perform dynamical simulations and to compare the measured patterns and the simulated patterns through a cross-correlation coefficient (CCC). Figure 4.2 overviews the

procedure using three carbides initially auto-indexed as T2-Al₂MgC₂, T1-Al₂MgC₂ and Al₄C₃. Figure 4.2 is arranged with the experimental Kikuchi patterns in the first column followed by a 3x3 matrix of dynamical simulation patterns. Each row compares the best-fit dynamical simulation for each candidate carbide to the experimental pattern. A CCC value closer to 1 indicates better pattern matching. The annotated CCC values show that the experimental pattern in row 1 is T2-Al₂MgC₂, the experimental pattern in row 2 is T1-Al₂MgC₂, and the experimental pattern in row 3 is Al₄C₃. This is in full agreement with the initial result from auto-indexing in Bruker Esprit 2.1. Importantly, there are large differences in CCC values between the correct phase and the other phases, and band-by-band inspection shows that the simulated patterns with the highest CCC are clearly the only suitable phase among the three candidate structures.

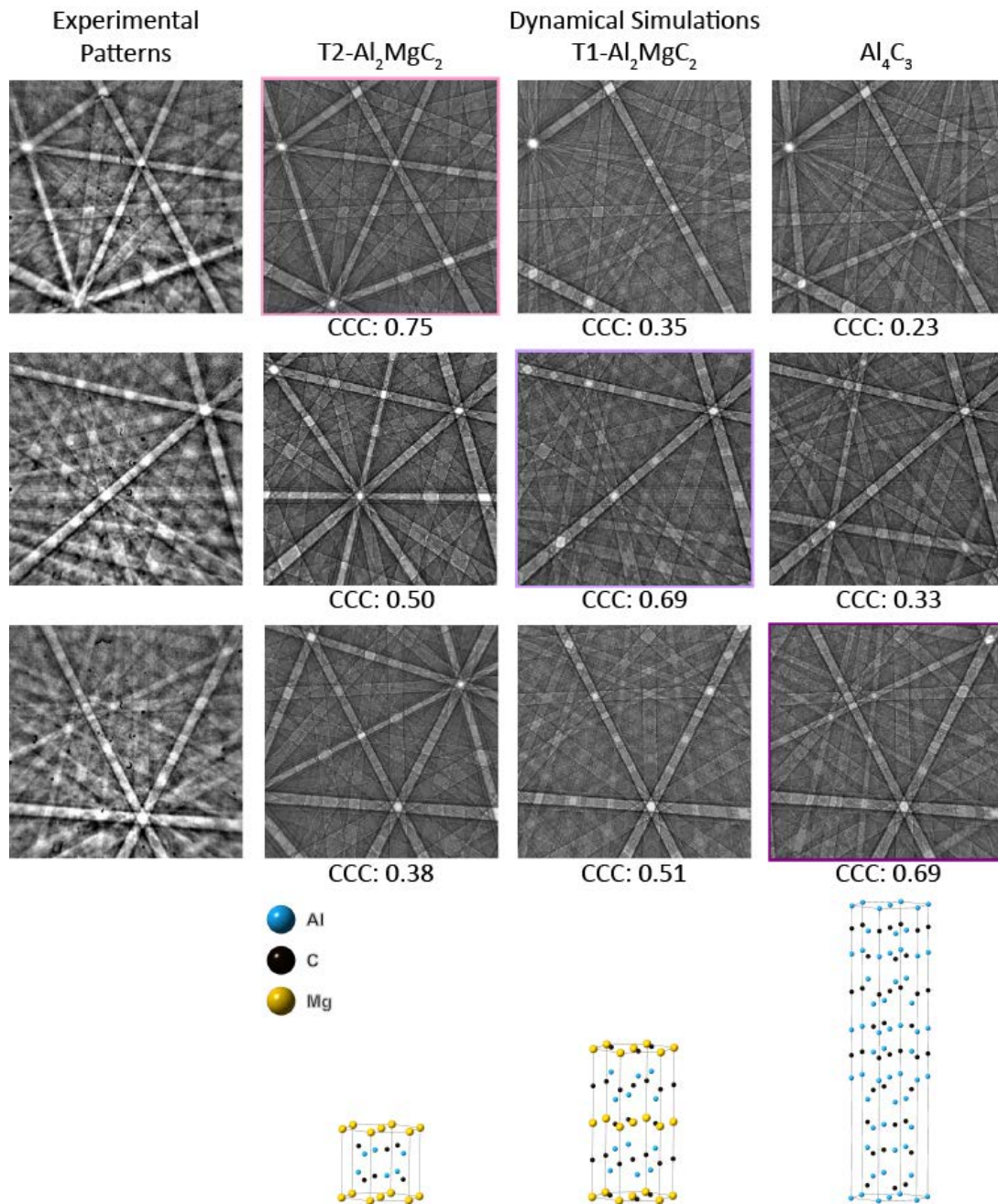


Figure 4.2 Distinguishing between carbides from the EBSD Kikuchi patterns. First column is the experimental EBSD patterns of different phases. The next three columns are dynamical simulations of Kikuchi patterns for T2-Al₂MgC₂, T1-Al₂MgC₂, and Al₄C₃. The best fit to the experimental pattern are boxed in colours in each row. ‘CCC’ = cross-correlation coefficient between the experimental and simulated patterns. The bottom row presents each unit cell for T2-Al₂MgC₂, T1-Al₂MgC₂ and Al₄C₃ in the 1:1 comparable ratio.

4.3.2. EDS analysis

EDS was used to reinforce the evidence of whether the phase list from EBSD was appropriate. EDS was performed under 10 keV so that the interaction volume could be minimised but 5 keV was applied specifically for the Al₄C₃ plates due to the relatively small

thickness of the phase. Also, the characteristic X-rays emitted from C and Al are less than the half of 5 keV which is more suitable to be applied than 10 keV to avoid additional signal noises.

Figure 4.3 shows two typical EDS elemental maps on regions containing Al_4C_3 and T1- Al_2MgC_2 (The two phases in Figure 4.3 were characterized by EBSD patterns in Figure 4.2 first.). The intensity scales show the relative the elemental content in the regions. For the EDS elemental maps in Figure 4.3(a), the plates contain Al, and C with minimal Mg content in the plate phase. In contrast, Figure 4.3(b) shows the multiple plates contain Al, Mg and C and the outer phase has high O content. These two EDS maps in Figure 4.3 also show: (i) Al_4C_3 phase attached to $\text{Mg}_{17}\text{Al}_{12}$ and (b) Al_2MgC_2 phase surrounded by MgO particles. To determine whether the ternary carbide in Figure 4.3(b) was T1- Al_2MgC_2 or T2- Al_2MgC_2 , EBSD characterisation was required.

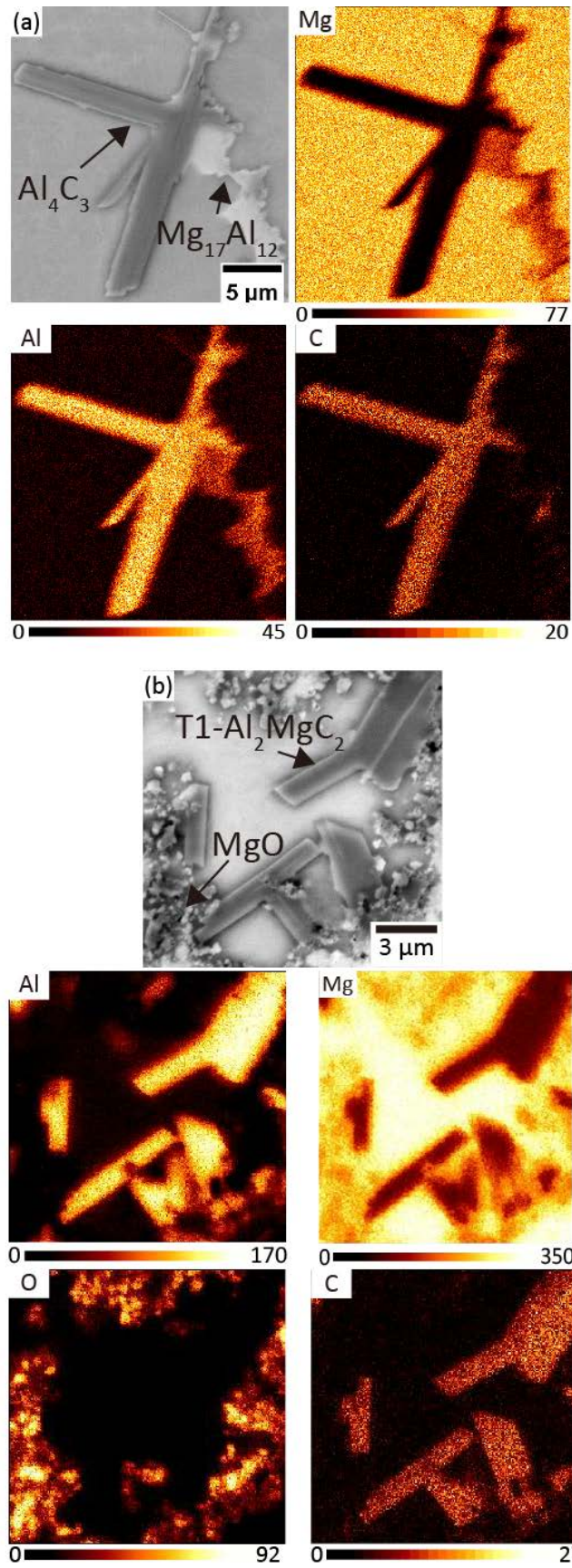


Figure 4.3 EDS elemental mapping on (a) Al_4C_3 and (b) T1- Al_2MgC_2 phase. The contrast shows the level of Al, Mg, and C contents.

The elemental maps in Figure 4.3 give a general view on what elements the phases contain. EDS spectra from point analysis were applied to collect quantitative data for analysing the chemical stoichiometries of the phases. The measured data are presented and compared with past literature in Table 4.3. The table shows that T2-Al₂MgC₂ and T1-Al₂MgC₂ have similar chemical compositions with past literature [177]. Al₄C₃ contained ~7 at% Mg which is consistent with past work that Al₄C₃ has some solubility from Mg as (Al,Mg)₄C₃ [245].

The Al₄C₃ phase was measured to contain 7 at% Mg (Table 4.3). Care was taken to perform measurements on the largest plates in the microstructures to minimise the chances of the α -Mg matrix being in the electron interaction volume. Solubility for Mg in Al₄C₃, with Mg substituting on the Al site, is also consistent with past work as summarised in Table 4.3. In the ternary Al-C-Mg phase diagram based on Viala et al. [178] and Deffrennes et al. [245], there is a window of Mg replacing Al atoms at different temperatures (Table 4.3). At 727 °C, Al₄C₃ has a maximum 5 at% Mg content and as the temperature increases to 1000 °C, the maximum increases to 7 at% Mg. Also, the calculation from Deffrennes et al. [245] shows that Al₄C₃ which transforms from Al₂MgC₂ contains 4 at% Mg at 536 °C. This indicates that when Al₄C₃ forms at lower temperature, the Mg content becomes less.

Table 4.3 The composition of T2-Al₂MgC₂, T1-Al₂MgC₂ and Al₄C₃ measured by SEM-EDS compared with prior work

Phase	Mg (at%)	Al (at%)	C (at%)	Target temperature (°C)	Ref.	Types
T2-Al ₂ MgC ₂	19.0 ± 1.0	37.0 ± 1.0	44.0 ± 2.0	700-900	Current	Experimental
T2-Al ₂ MgC ₂	16.7 ± 1.5	36.1 ± 3.0	47.2 ± 7.0	1000	[177]	Experimental
T2-Al ₂ MgC ₂	20.2 ± 0.4	40.5 ± 0.7	39.3 ± 0.7	1000	[169]	Experimental
T1-Al ₂ MgC ₂	24.0 ± 2.0	33.0 ± 1.0	43.0 ± 1.0	700	Current	Experimental
T1-Al ₂ MgC ₂	17.9 ± 1.5	36.5 ± 3	45.6 ± 7.0	727	[177]	Experimental
Al ₄ C ₃	7.0 ± 1.0	52.0 ± 2.0	41.0 ± 2.0	800	Current	Experimental
(Al,Mg) ₄ C ₃	5.4	52.0	42.6	727	[178]	Experimental
(Al,Mg) ₄ C ₃	6.8	50.4	42.8	1000	[245]	CALPHAD

4.3.3. Faceted growth morphology

T2-Al₂MgC₂ and Al₄C₃ were found in all AZ91+diamond samples and most of AZ91+graphite samples at all types of cooling rates (Table 4.2). In contrast, T1-Al₂MgC₂ was only observed in one AZ91+graphite sample. The morphologies of these three types of carbides are discussed in this section.

4.3.3.1 T2-Al₂MgC₂

Figure 4.4 overviews the reaction between a cluster of diamond particles and the AZ91 melt at 800 °C. The BSE image in Figure 4.4(a) shows two distinguishable regions: a grey phase surrounding a black phase. In the EDS elemental mapping in Figure 4.4(b), the dark region contains a high C content and the surrounding grey region contains Al, Mg and C. These EDS elemental maps correspond to the region indicated by the dashed box in the tilted SE image of Figure 4.4(c). EBSD phase mapping of the same region resulted in Figure 4.4(d) which confirms that the dark region is a cluster of diamond particles and the grey phase is T2-Al₂MgC₂. From the combined EBSD and EDS results, we see that T2-Al₂MgC₂ is the main reaction product between diamond particles and the AZ91 melt at 800 °C. The EBSD phase map in Figure 4.4(d) also contains MgO particles sharing interfaces with the diamond and T2-Al₂MgC₂. The EDS oxygen map confirms the presence of a high oxygen content in these locations.

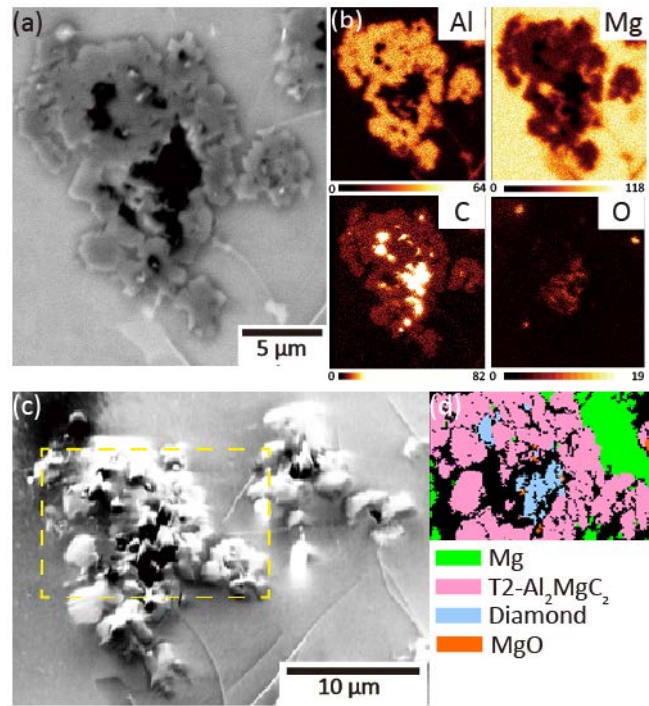


Figure 4.4 T2-Al₂MgC₂ clusters growing from a cluster of diamond particles in a sample held at 800 °C for 40 hours followed by slow cooling. (a)BSE image, (b)EDS elemental mapping of Al, Mg, C and O in the region of (a) and (c) tilted SE image for (d) EBSD phase mapping.

When T2-Al₂MgC₂ formed around diamond by chemical reaction, T2 often appeared as a cluster (e.g. Figure 4.4) and the growth morphology of the phase was not easily analysed. To obtain independent primary T2-Al₂MgC₂ crystals by the reaction $L \rightarrow T2-Al_2MgC_2$, a higher melt temperature of 900 °C was applied to increase the dissolved carbon content in the melt. However, increasing the holding temperature was found to greatly increase the chance of failure in the quartz tube. Therefore, an experiment was developed in which an AZ91+diamond sample was first held at 800 °C for 40 hours followed by fast cooling to avoid other carbide phases forming, and then held at 900 °C for 4 hours followed by fast cooling. The whole process was under the same encapsulation conditions. Figure 4.5 shows a primary T2-Al₂MgC₂ particle that grew using this procedure. Figure 4.5(a) is a BSE image showing that T2-Al₂MgC₂ grew as a faceted crystal. The EBSD IPF-X map in Figure 4.5(b) confirms that this T2-Al₂MgC₂ is a single crystal. The pole figures from the IPF-X map in Figure 4.5(c) show the growth facets

are consistent with $\{0001\}$ and $\{11\bar{2}0\}$. The growth facets are further illustrated in Figure 4.5(d) which is the unit cell wireframe plotted using the Euler angles measured by EBSD.

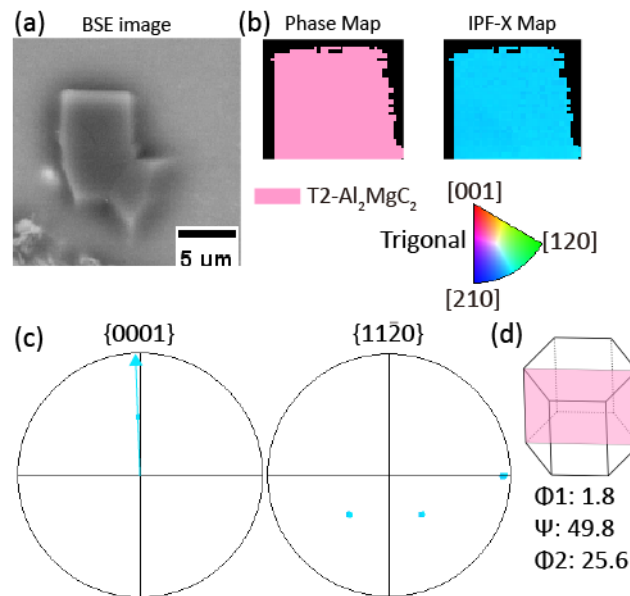


Figure 4.5 Standalone T2-Al₂MgC₂ in a sample held at 900 °C for 4 hours followed by fast cooling. (a) BSE image, (b) phase map and IPF-X map (c) pole figure of the facet growth (d) the orientation of the facet growth with labelled with $\{11\bar{2}0\}$ planes

4.3.3.2 T1-Al₂MgC₂

T1-Al₂MgC₂ was found in only one AZ91+graphite sample that was held at 700 °C for 40 hours and then fast cooled. This phase could not be reproduced in other samples using the same conditions or in other samples that changed the additive (graphite or diamond), the holding temperature or time, or the cooling rate. The melt temperature was set at 700 °C because other researchers [177,179] reported that the weight ratio of T1-Al₂MgC₂ to T2-Al₂MgC₂ was the highest at 990 ± 10 K based on the intensity of X-ray powder diffraction results. It is worth noting that T1-Al₂MgC₂ could only be found within the oxidised regions shown in Figure 4.6(a). This seems to be the same observed oxidised environment from Bosselet et al [179]. From their statement and the current experiment, both results show that the presence of T1-Al₂MgC₂ was free from Al₄C₃ but found to be attached with MgO. The BSE image in Figure 4.6(b) shows two faceted particles attached to the oxide particles. The EBSD phase mapping and IPF-X map in Figure 4.6(b) show that both particles are single crystal T1-Al₂MgC₂ plates. The pole figure

in Figure 4.6(c) indicates that the growth facets of the both T1-Al₂MgC₂ are consistent with {0001} planes.

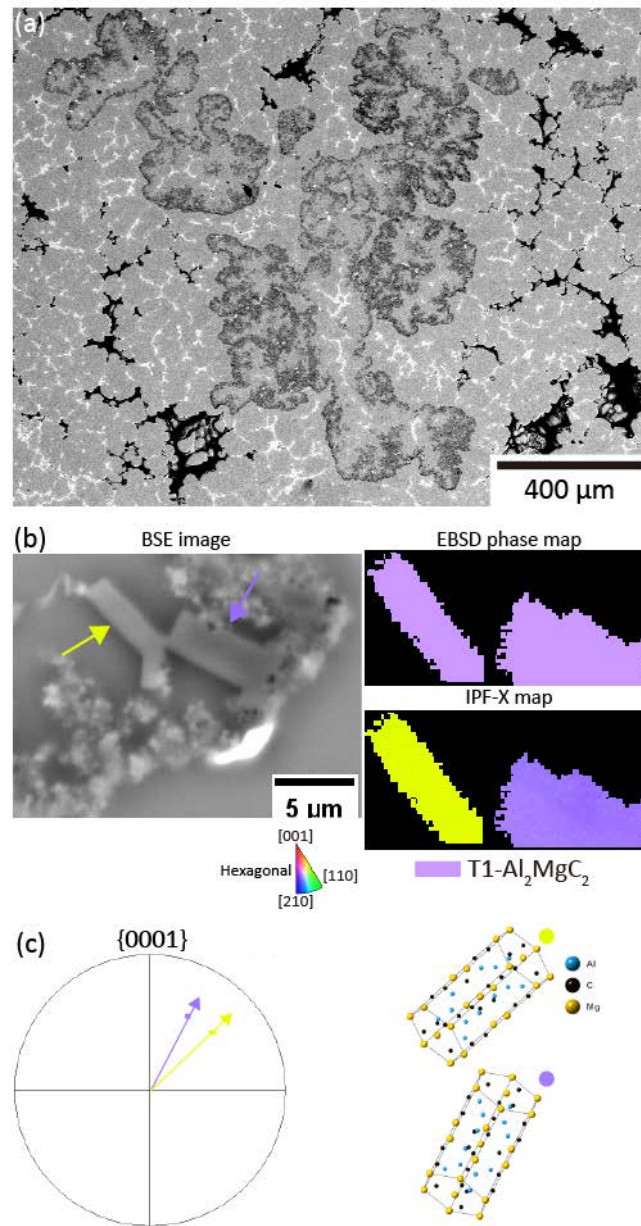


Figure 4.6 (a) BSE image of a general view on existence of T1-Al₂MgC₂ around oxides in the AZ91+graphite sample at 700 °C for 40 hours with fast cooling. (b) shows two single T1-Al₂MgC₂ crystals with EBSD phase map and IPF-X map. (b) {0001} pole figure shows the T1-Al₂MgC₂ growth facet and the crystal structures show the orientations of two T1-Al₂MgC₂ crystals

4.3.3.3 Al₄C₃

Al₄C₃ formed in samples held above 800 °C followed by either slow or fast cooling. Two types of growth twin were common for Al₄C₃ plates: penetration twins and contact twins.

4.3.3.3.1 Al₄C₃ penetration twin

Figure 4.7(a) overviews the morphology and structure of an Al₄C₃ penetration twin involving two interpenetrating plates. The IPF-X map in Figure 4.7(a) confirms that each plate has a single orientation and the pole figure of Figure 4.7(c) shows the main growth facet is {0001} in each case. The twin relationship between the penetrating Al₄C₃ plates can be seen from the Kikuchi patterns in Figure 4.7(b) where the {01 $\bar{1}$ 5} and {11 $\bar{2}$ 0} plane bands are parallel and intersect at a common <5 $\bar{5}$ 01> zone axis. This can be further confirmed from the overlapping spots in the pole figures in Figure 4.7(c) of {11 $\bar{2}$ 0}, {01 $\bar{1}$ 5}, {10 $\bar{1}$ 10} and <5 $\bar{5}$ 01>. The misorientation (MO) angle was measured as 98° in Figure 4.7(d). The twin is visualised using stereographic projections in Figure 4.7(d) which were created in SingleCrystal software by plotting the {11 $\bar{2}$ 0}, {01 $\bar{1}$ 5} and {10 $\bar{1}$ 10} planes of each plate orientation with the common (01 $\bar{1}$ 5) plane at the centre and the common <5 $\bar{5}$ 01> pointing west. A 98.1° rotation of orientation 1 around the (01 $\bar{1}$ 5) plane normal brings one {11 $\bar{2}$ 0}, two {01 $\bar{1}$ 5}, one {10 $\bar{1}$ 10} and one <5 $\bar{5}$ 01> into a coincident position.

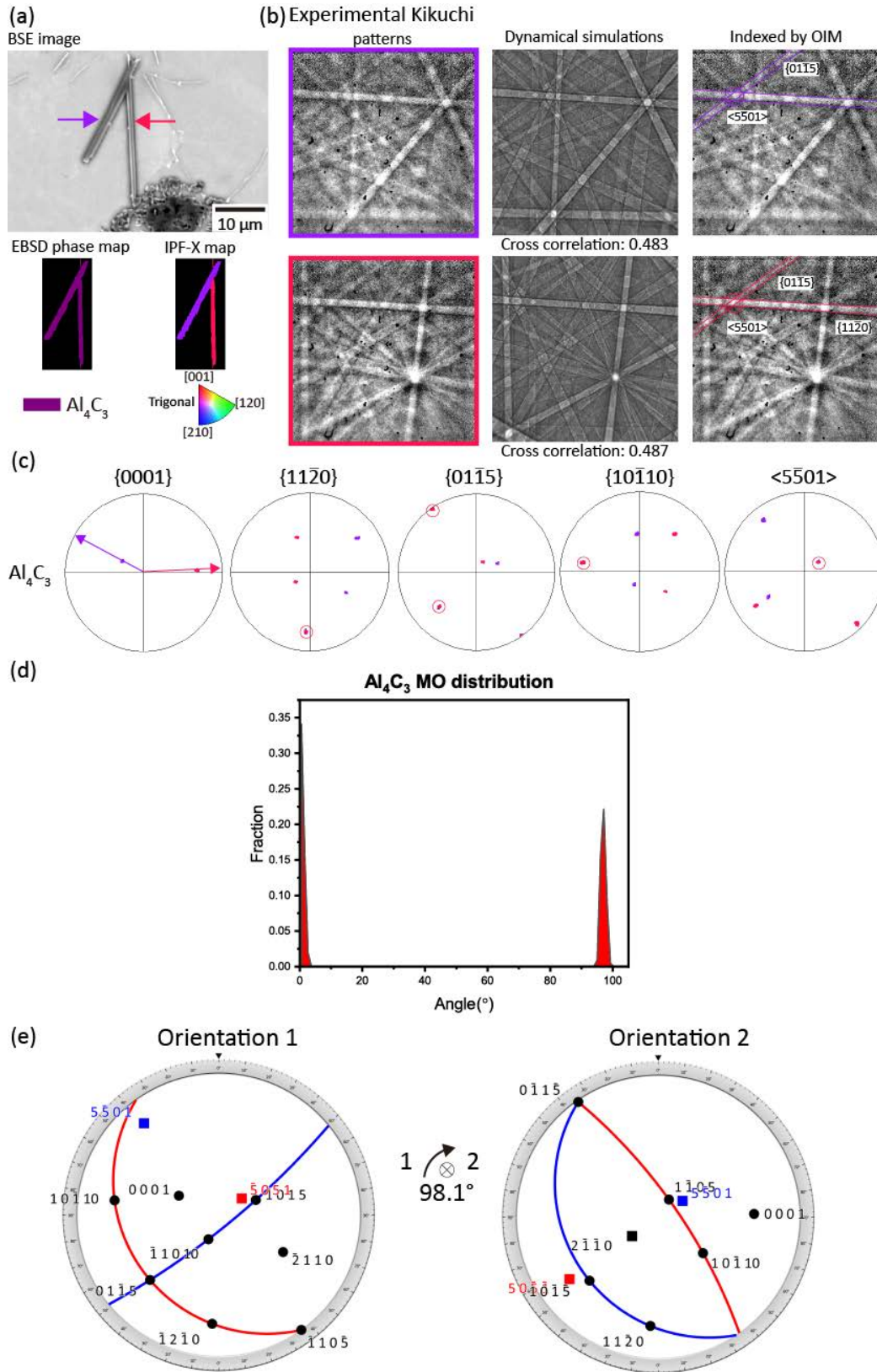


Figure 4.7 Penetration twin of Al_4C_3 in (a) BSE image, EBSD phase map, IPF-X orientation map and (b) Kikuchi patterns with comparison of simulation patterns. (c) Pole figures of IPF-X map in the $\{0001\}$, $\{11\bar{2}0\}$, $\{011\bar{5}\}$, $\{10\bar{1}10\}$, and $\langle 5501 \rangle$ family planes for the twin Al_4C_3 plates. (d) Misorientation angle (MO) of penetration twinning measured by Bruker Quantax Esprit 2.1 software. (e) The pole figures of two single crystal rotating at 98° .

Another example of this penetration twin type is given in Figure 4.8. The shape of the twinned crystal in Figure 4.8(a) is closer to an 'X' than in Figure 4.7 due to a different sectioning plane. Note that the common $\langle 11\bar{2}0 \rangle$ zone is present in the Kikuchi patterns but the common planes are not contained in the recorded region of the Kikuchi sphere.

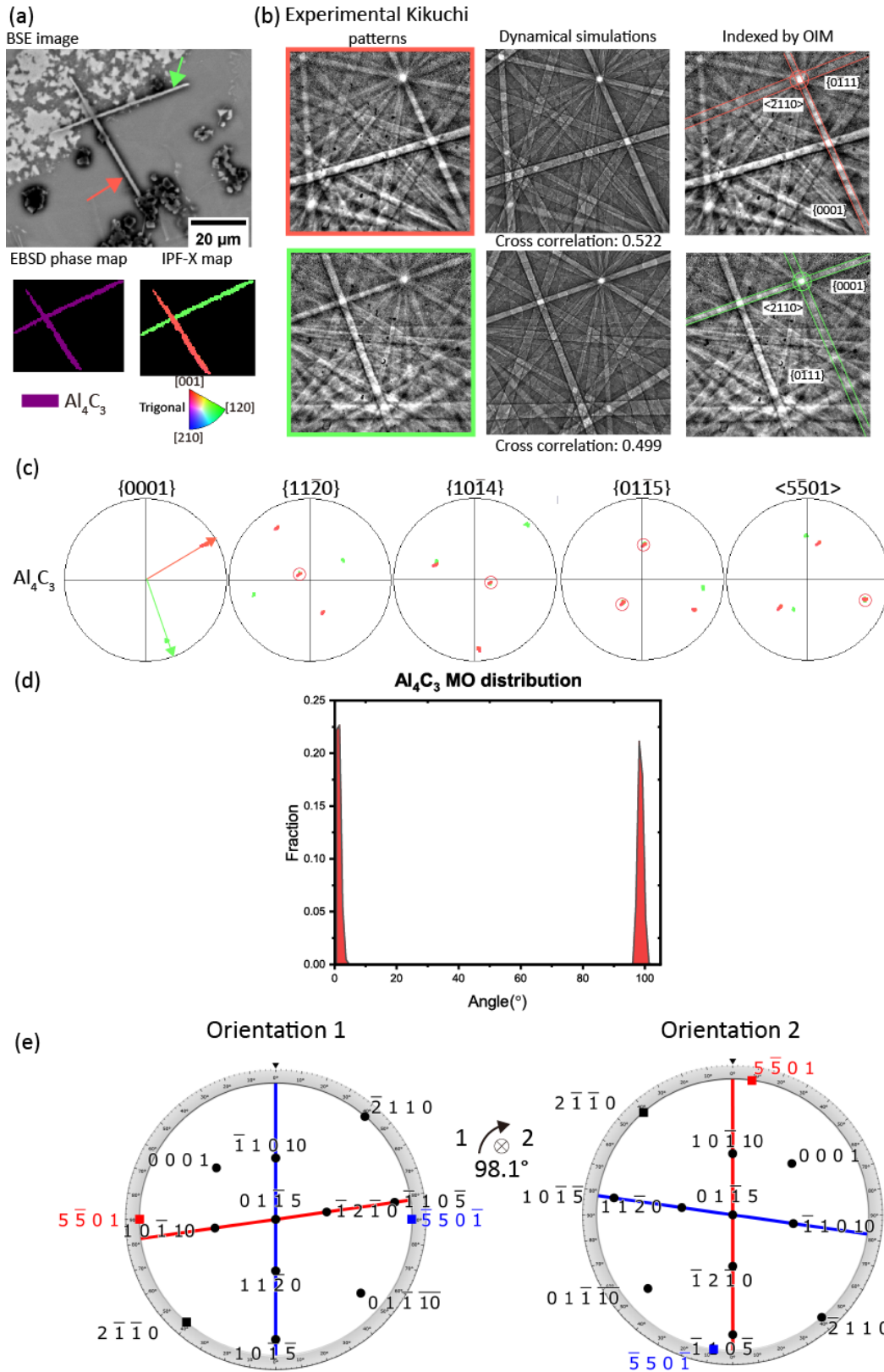


Figure 4.8 Another example of a penetration twin of Al_4C_3 in (a) BSE image, EBSD phase map, IPF-X orientation map and Kikuchi Patterns with comparison of simulation patterns. (b) Pole figures of IPF-X map in the $\{0001\}$, $\{11\bar{2}0\}$, $\{11\bar{1}5\}$, $\{10\bar{1}10\}$, and $\langle 5501 \rangle$ family planes for the twin Al_4C_3 plates. (c) Misorientation angle (MO) of penetration twinning measured by Bruker Quantax Esprit 2.1 software. The pole figures of two single crystal rotating at 98.1 $^\circ$.

4.3.3.3.2 Al_4C_3 contact twin

Al_4C_3 also commonly grew as contact twins. A typical example is shown in the BSE image of Figure 4.9(a). There is contrast between two twin domains sharing an interface that is parallel to the main facet. In Figure 4.9(a), the EBSD phase map shows that the plate was single-phase Al_4C_3 and the IPF-X map shows the plate contains two orientations. The experimental Kikuchi patterns of the two orientations in Figure 4.9(b) contain parallel bands of all $\{11\bar{2}0\}$ planes and a common $\langle 0001 \rangle$ zone yet the patterns are clearly different. This can also be seen in the pole figures of IPF-X map in Figure 4.9(c) where the two domains have parallel $\{0001\}$ and $\{11\bar{2}0\}$ planes and their $\{01\bar{1}5\}$ planes are in inequivalent positions. The twin relationship is illustrated by the crystal structures in Figure 4.9(c); each twin domain is 60° rotated around $\langle 0001 \rangle$ relative to the other. This is a common twin type in rhombohedral crystals and is known as an observe-reverse twin.

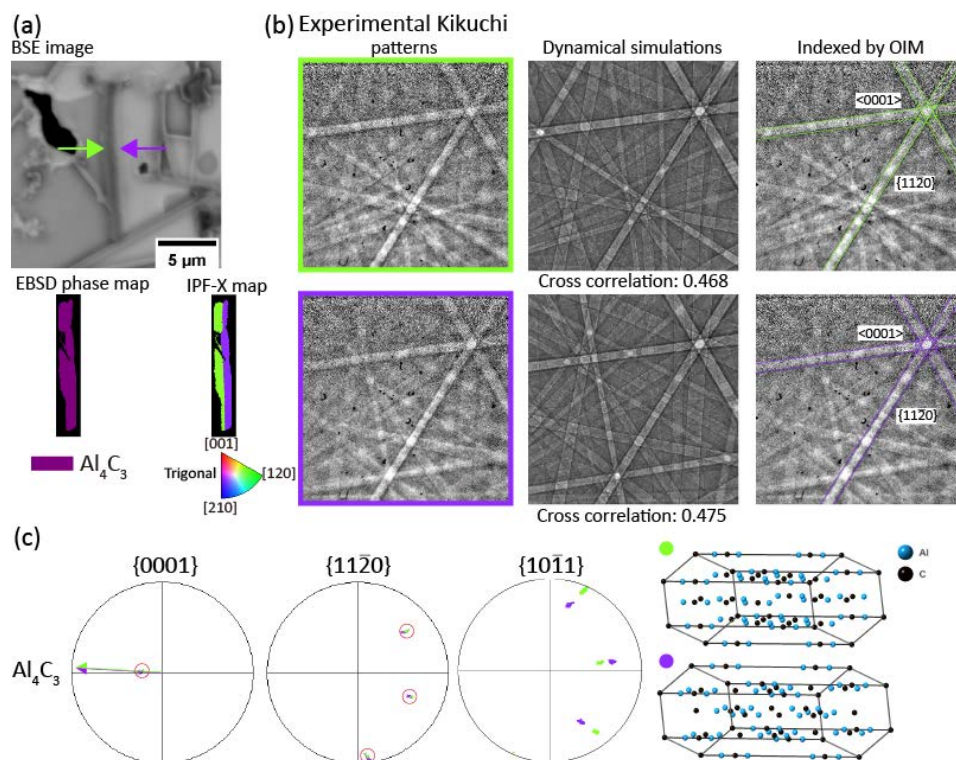


Figure 4.9 Contact twin of Al_4C_3 in (a) BSE image, EBSD phase map, IPF-X orientation map and (b) Kikuchi Patterns with comparison of simulation patterns. (c) Pole figures of IPF-X map in the $\{0001\}$, $\{11\bar{2}0\}$, and $\{01\bar{1}5\}$ family planes for the twin Al_4C_3 plates. The OR of the contacting twin shown by the crystal structures at 60° rotation to each other.

One important feature in single crystal Al_4C_3 and in Al_4C_3 with both types of growth twin was that they grew with the same growth facet in all cases: $\{0001\}$. Both types of Al_4C_3 twin plates were found in samples held above 800°C prior to solidification. This may indicate that Al_4C_3 plates form at high temperature when the Al-bearing magnesium alloys have higher dissolved carbon content although this is not expected from the phase diagram of Defferennes et al. [245]. Note that the samples heated to below 800°C did not contain any Al_4C_3 plates, but only Al_4C_3 flakes as described later in this Chapter.

4.3.4. Interactions between different carbides

In all the samples, several phases were commonly observed, including T2- Al_2MgC_2 , Al_4C_3 , diamond, $\text{Mg}_{17}\text{Al}_{12}$, Al-Mn particles and MgO. These phases can be seen in Figure 4.10 as typical regions surrounding the carbon additives.

T2- Al_2MgC_2 was often found as clusters around diamond particles or pores. In Figure 4.10(a), and (b), T2- Al_2MgC_2 is clustered around remaining diamond particles. In Figure 4.10(b) and (c) T2- Al_2MgC_2 is clustered in a chain around a pore (dark region). Al_4C_3 formed as flakes or plates beyond the T2- Al_2MgC_2 . The Al_4C_3 flakes were thin and often curved in cross-section and the Al_4C_3 plates (Figure 4.10(d)) were straight and thicker. The flakes were generally found in contact with T2- Al_2MgC_2 . The Al_4C_3 plates were found as: (i) standalone plate, (ii) two types of twins and (iii) within $\text{Mg}_{17}\text{Al}_{12}$.

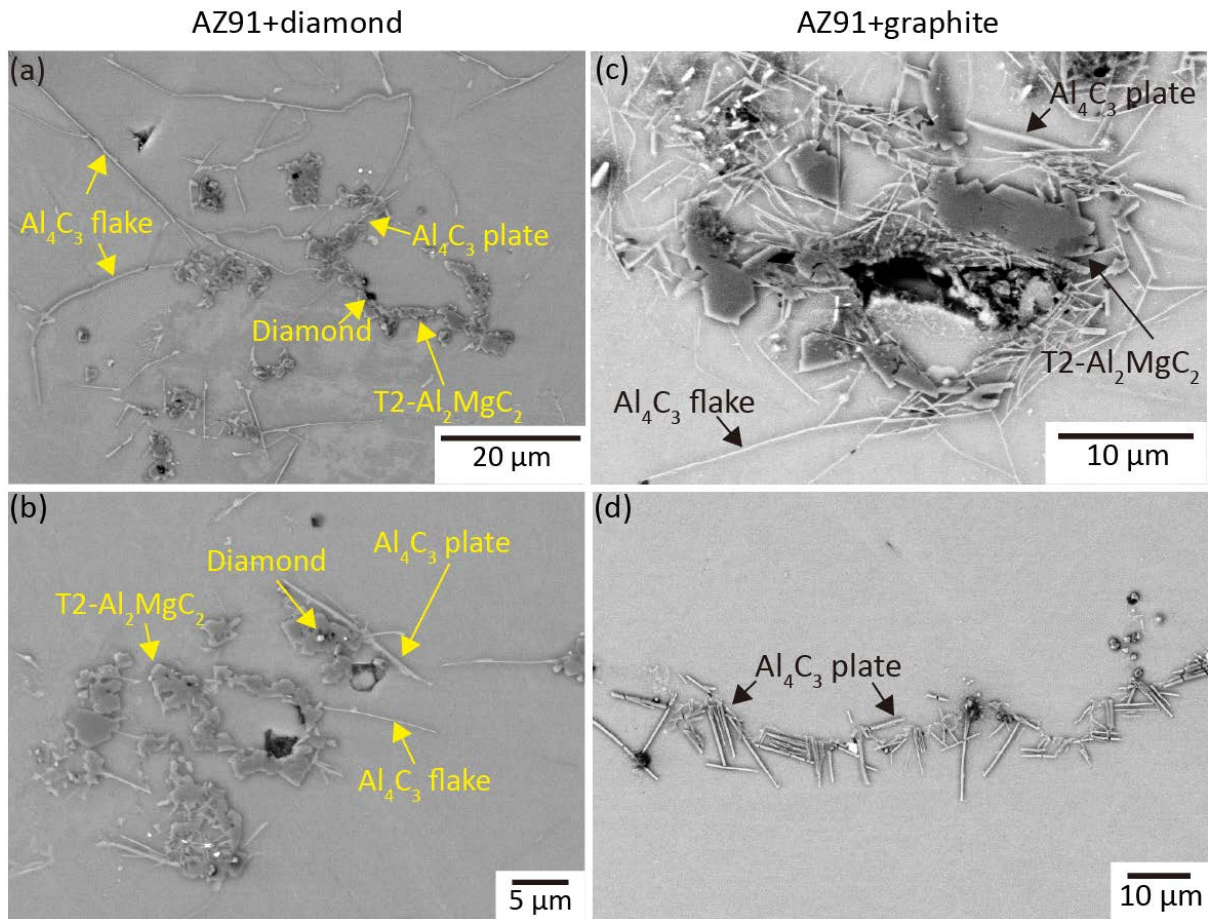


Figure 4.10 BSE images of remelted (a), (b) AZ91+diamond and (c), (d) AZ91+graphite at 800 °C for 40 hours followed by slow cooling.

T1-Al₂MgC₂ was usually a standalone phase without an interface with the other carbides. In contrast, there were commonly interfaces between T2-Al₂MgC₂ and Al₄C₃: (i) Al₄C₃ flakes attached to T2-Al₂MgC₂ and (ii) Al₄C₃ plates connecting to T2-Al₂MgC₂.

The first type involved thin and curved Al₄C₃ flakes growing out of T2-Al₂MgC₂ (Figure 4.10(a)). This is likely to be related to the transition reaction $L + Al_2MgC_2 \rightarrow (Mg) + Al_4C_3$ at 535 °C [245] that is discussed towards the end of this Chapter. This transformation was particularly stated as a slow reaction in reference [178].

The second type of interface between Al₄C₃ and T2-Al₂MgC₂ can be divided into two scenarios: (i) rare situations with a simple OR and (ii) the common situation with no simple or reproducible OR. An example of Al₄C₃ and T2-Al₂MgC₂ sharing an OR is given in Figure 4.11

from a sample held at 900 °C listed in Table 4.2. Here, both Al_4C_3 and $\text{T2-Al}_2\text{MgC}_2$ grew as single crystals and shared their $\{0001\}$ plane. The pole figures in Figure 4.11(c) show the two trigonal crystals had a simple basal-to-basal OR that can be expressed as Eq. (4.1). In this case it is likely that one carbide nucleated on the other.

$$\begin{aligned} \{0001\}_{\text{Al}_4\text{C}_3} // \{0001\}_{\text{T2-Al}_2\text{MgC}_2} \\ \langle 11\bar{2}0 \rangle_{\text{Al}_4\text{C}_3} // \langle 11\bar{2}0 \rangle_{\text{T2-Al}_2\text{MgC}_2} \end{aligned} \quad (4.1)$$

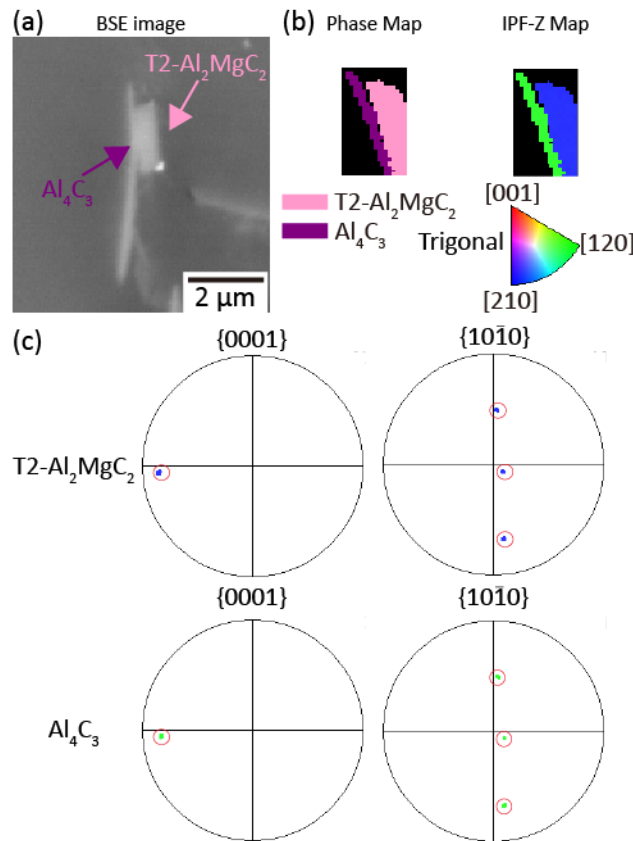


Figure 4.11 $\text{T2-Al}_2\text{MgC}_2$ and Al_4C_3 in a sample held at 800 °C for 40 hours with fast cooling and subsequently held at 900 °C for 4 hours with fast cooling. The contact of two phases shown in (a) BSE image, (b) phase map and IPF-Z map. (c) The pole figures of IPF-Z map of $\text{T2-Al}_2\text{MgC}_2$ and Al_4C_3 in parallel $\{0001\}$ and $\{10\bar{1}0\}$ family planes.

The second scenario of Al_4C_3 and $\text{T2-Al}_2\text{MgC}_2$ interfaces is shown in the BSE image of Figure 4.7(a). One of the Al_4C_3 crystals is in contact with $\text{T2-Al}_2\text{MgC}_2$, the darker phase in the bottom right corner of the BSE image. However, there was no simple OR between these crystals (EBSD not shown here). For this case in Figure 4.7(a), it is likely that the interface

was created by Al_4C_3 plate growth into the $\text{T2-Al}_2\text{MgC}_2$ because, in penetration twin growth, the two twin domains usually grow from a common centre.

The second scenario without any simple or reproducible OR was the most common type and happened in the 10 out of the 12 cases used for analysis. The single crystal Al_4C_3 plates usually contained one side of the twin attached with $\text{T2-Al}_2\text{MgC}_2$.

4.3.5. Interactions between carbides and other phases

4.3.5.1 Pores & Oxides

$\text{T2-Al}_2\text{MgC}_2$ and $\text{T1-Al}_2\text{MgC}_2$ were often attached to pores or oxides. In the example in Figure 4.12(a), $\text{T2-Al}_2\text{MgC}_2$ particles are present all around a pore and the dark spots in the BSE image are diamond particles. Within the pore, numerous hexagonal platelets of $\text{T2-Al}_2\text{MgC}_2$ can be observed revealing their 3D morphology. Figure 4.12(b) is an example of a single crystal $\text{T1-Al}_2\text{MgC}_2$ attached to the oxide particles. These consisted of MgO particles and possibly Al containing oxide as shown in Figure 4.12(c) EDS elemental mapping. The oxides in this sample were mentioned previously; they aggregated to form wide stain-like regions as shown in Figure 4.6(a). No particular ORs were found between the oxides and $\text{T2-Al}_2\text{MgC}_2$ or $\text{T1-Al}_2\text{MgC}_2$.

Al_4C_3 plates and flakes were less likely to be attached to oxides. One uncommon example can be seen in Figure 4.13: MgO particles are attached to the penetration twin of Al_4C_3 . Again, no simple OR exists between the phases.

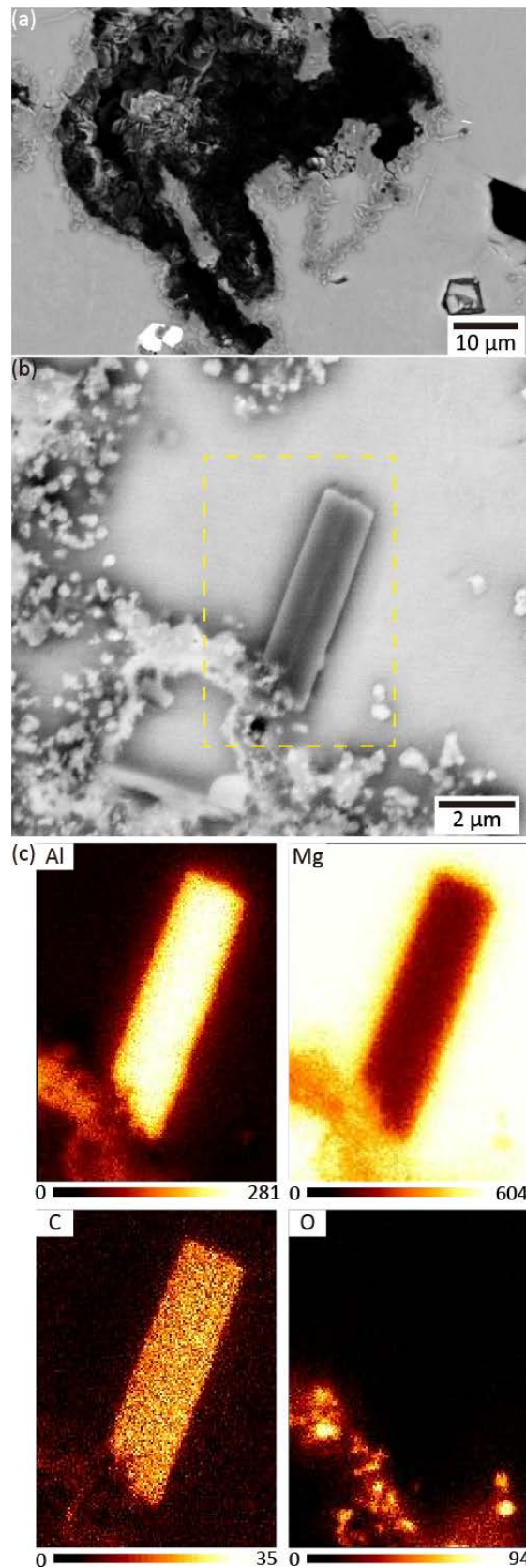


Figure 4.12 BSE images of (a) $T2-Al_2MgC_2$ clusters around pores in a sample of AZ91+diamond held at $800\ ^\circ C$ for 40 hours with slow cooling and (b) $T1-Al_2MgC_2$ attached to oxidised substances in a sample of AZ91+graphite held at $700\ ^\circ C$ for 40 hours with fast cooling. (c) EDS elemental mapping of Al, Mg, C and O in the yellow box in (b).

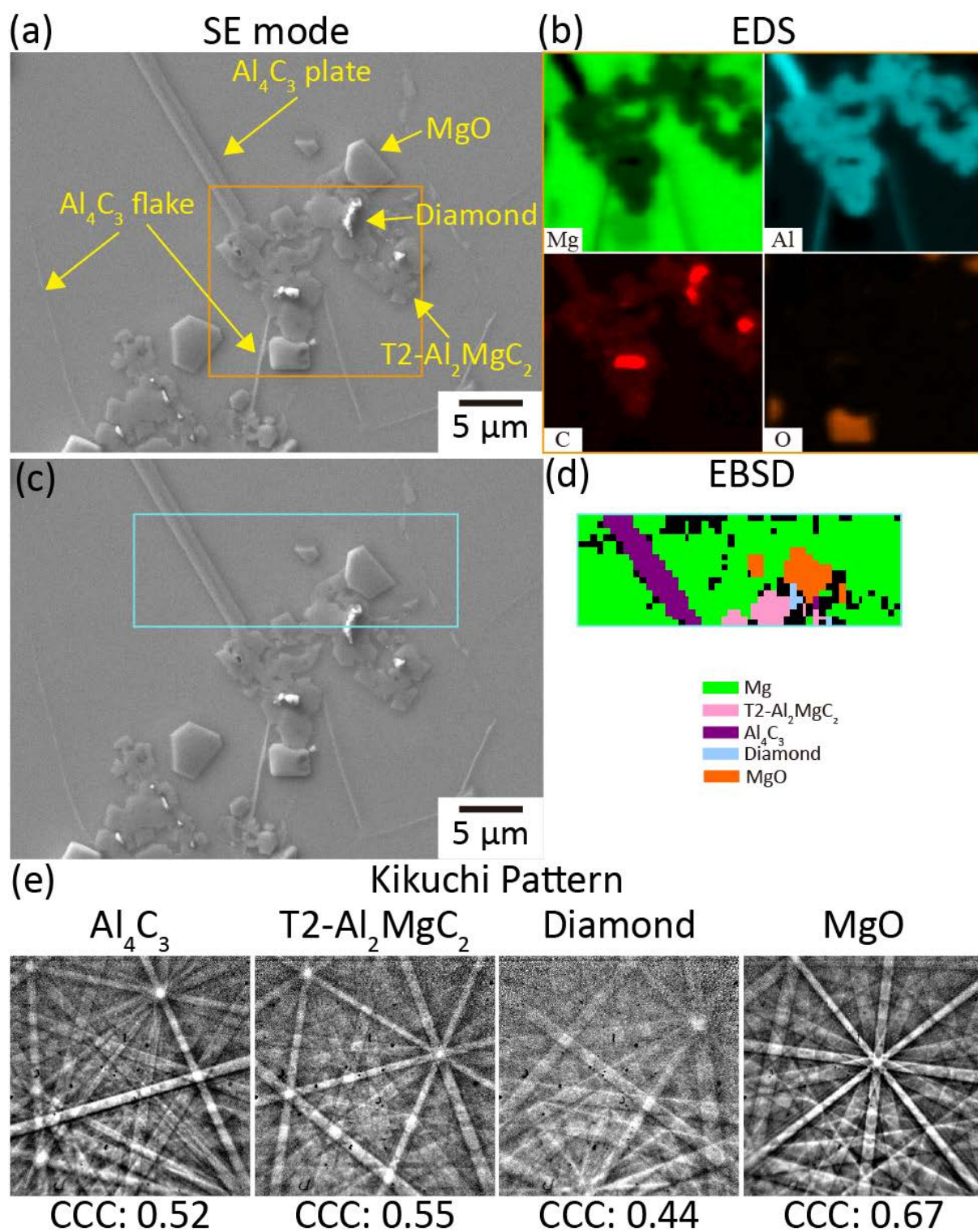


Figure 4.13 (a) SE mode of Al_4C_3 attached with $\text{T2-Al}_2\text{MgC}_2$ and (b) the EDS mapping is shown in the yellow box of (a). (d) EBSD phase map is shown the blue box in (c) the SE image. (e) The Kikuchi patterns of each phase were taken from the experiment.

4.3.5.2 Al-Mn Intermetallics

The past literature [44,48,51,57,66,69] has discussed how interactions between carbides and Al-Mn intermetallic particles affect the nucleation and grain refinement of magnesium. Various competing hypotheses have been put forward as summarised in Table 4.4. Some authors have suggested that Al_4C_3 nucleates on and coats the outside of Al-Mn particles. Some suggested Al-Mn particles attach to/nucleate on Al_4C_3 . Other authors [72,157] have suggested that Al_4C_3 would react with Al-Mn particles to form Al-C-Mn phases and that this Al-C-Mn phase is responsible for the grain refinement in carbon inoculation.

In this study, Al-Mn particles were often found in contact with clusters of carbides including $\text{Tl}_2\text{-Al}_2\text{MgC}_2$ (Figure 4.14(a),(b)) and Al_4C_3 (Figure 4.14(c)) and it was common for these clusters to be around pores (Figure 4.14(a)). Examining Figure 4.14(a)-(c), note that the bright Al-Mn intermetallics are on the outside of the carbide clusters indicating that the carbides were there first and the Al-Mn intermetallics grew on them. Note also that the Al-Mn intermetallics did not engulf/envelope the carbides and there is still a large area of carbide-liquid interface. No OR was detected between the Al-Mn particles and the carbides. No evidence of Al-C-Mn phases was found.

To compare Al-Mn intermetallics in samples with and without carbides, a normal (i.e. without carbon inoculation) AZ91 magnesium sample was held at 700 °C for 40 hours followed by fast cooling. Here too Al-Mn particles were often located around pores (Figure 4.14(d),(e),(f)). This shows that Al-Mn particles formed around pores irrespective of whether there were also carbides around the pores or not. Pores such as those in Figure 4.14(a) have the characteristics of entrainment defects. Past work [229,246] has shown that Al-Mn intermetallics are often clustered around entrained oxide and an in-situ X-ray imaging study [247] has shown that settling Al_8Mn_5 can become trapped in entrained oxide and that some Al_8Mn_5 particles also nucleate on oxide.

Table 4.4 Past literature commented on interaction between formation of Al_4C_3 with Al-Mn phase [44,48,51,57,69,72,157]

Comments	Refence
Al-Mn particles attach to/nucleate on Al_4C_3	[51,57,66,69]
Al_4C_3 coats around Al-Mn particles	[44,48]
Al_4C_3 reacts with Mn content to form Al-C-Mn (such as AlCMn_3)	[72,157]

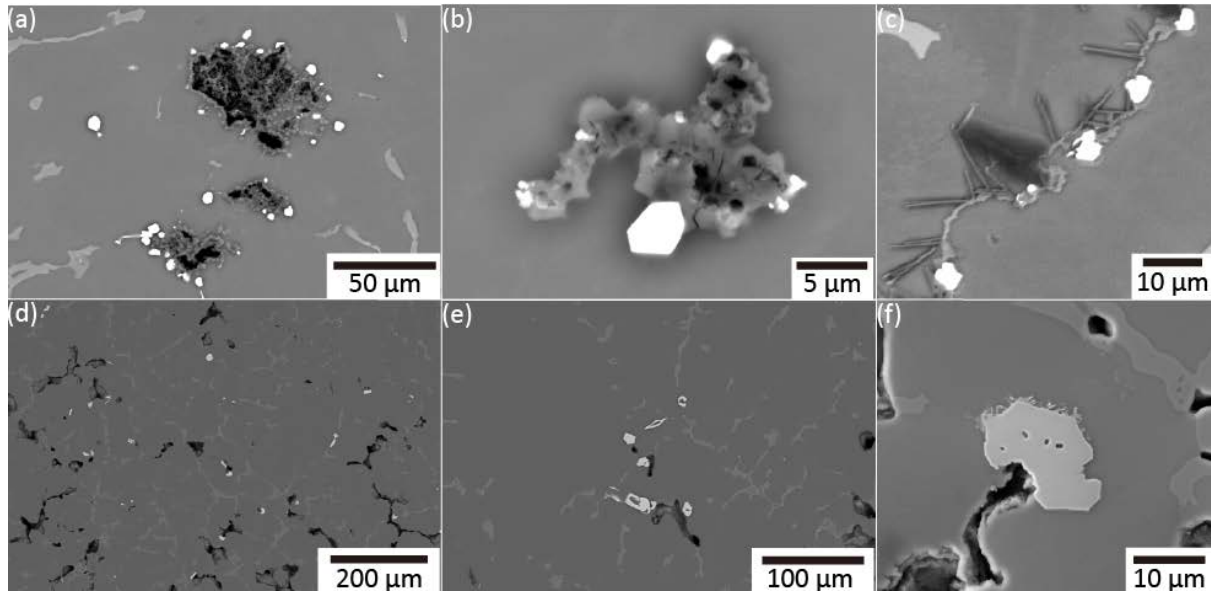


Figure 4.14 BSE images of (a) Al-Mn particles (white) attached to $\text{T2-Al}_2\text{MgC}_2$ (grey) which surround pores (black), (b) Al-Mn particles (white) attached to $\text{T2-Al}_2\text{MgC}_2$ clusters (grey) and diamonds (black) inside the cluster, (c) Al_4C_3 plates (dark grey) on $\text{Mg}_{17}\text{Al}_{12}$ (bright grey) with Al-Mn particles (white) attached in the AZ91+diamond sample at 800°C for 40 hours followed by slow cooling. (d)-(f): BSE images of Al-Mn compounds in an AZ91 sample without carbon inoculation held in Al_2O_3 crucible at 700°C for 4 hours with fast cooling: (d) general view showing many Al-Mn particles (white) touching pores, (e)-(f) higher magnification of Al-Mn particles (white) around pores (black).

4.3.5.3 $\text{Mg}_{17}\text{Al}_{12}$

$\text{Mg}_{17}\text{Al}_{12}$ is the last phase to form during the solidification of AZ91. After adding carbon, a carbide phase was observed within some regions of $\text{Mg}_{17}\text{Al}_{12}$ in the above 800°C remelted samples. An example is given in the BSE image of Figure 4.15(a). Note that this type of carbide with $\text{Mg}_{17}\text{Al}_{12}$ was typically found within α -Mg dendrite envelopes and not in the α -Mg grain boundaries. When the yellow box region (Figure 4.15(a)) was examined at higher magnification, the plates were clearly surrounded by $\text{Mg}_{17}\text{Al}_{12}$ as shown in Figure 4.15(b). The phases in the yellow box of Figure 4.15(b) were confirmed by the EBSD phase map in Figure

4.15(c) as Al_4C_3 plates within $\text{Mg}_{17}\text{Al}_{12}$. These Al_4C_3 plates in Figure 4.15(c) were characterised as individual single crystals within $\text{Mg}_{17}\text{Al}_{12}$ as shown in the IPF-X map Figure 4.15(d). These single crystals had the same growth morphology as all other types of carbides which grow along $\{0001\}$ plane as shown in Figure 4.15(e). In this case, there is no special OR between OR between the Al_4C_3 plates and no OR between the plates and $\text{Mg}_{17}\text{Al}_{12}$.

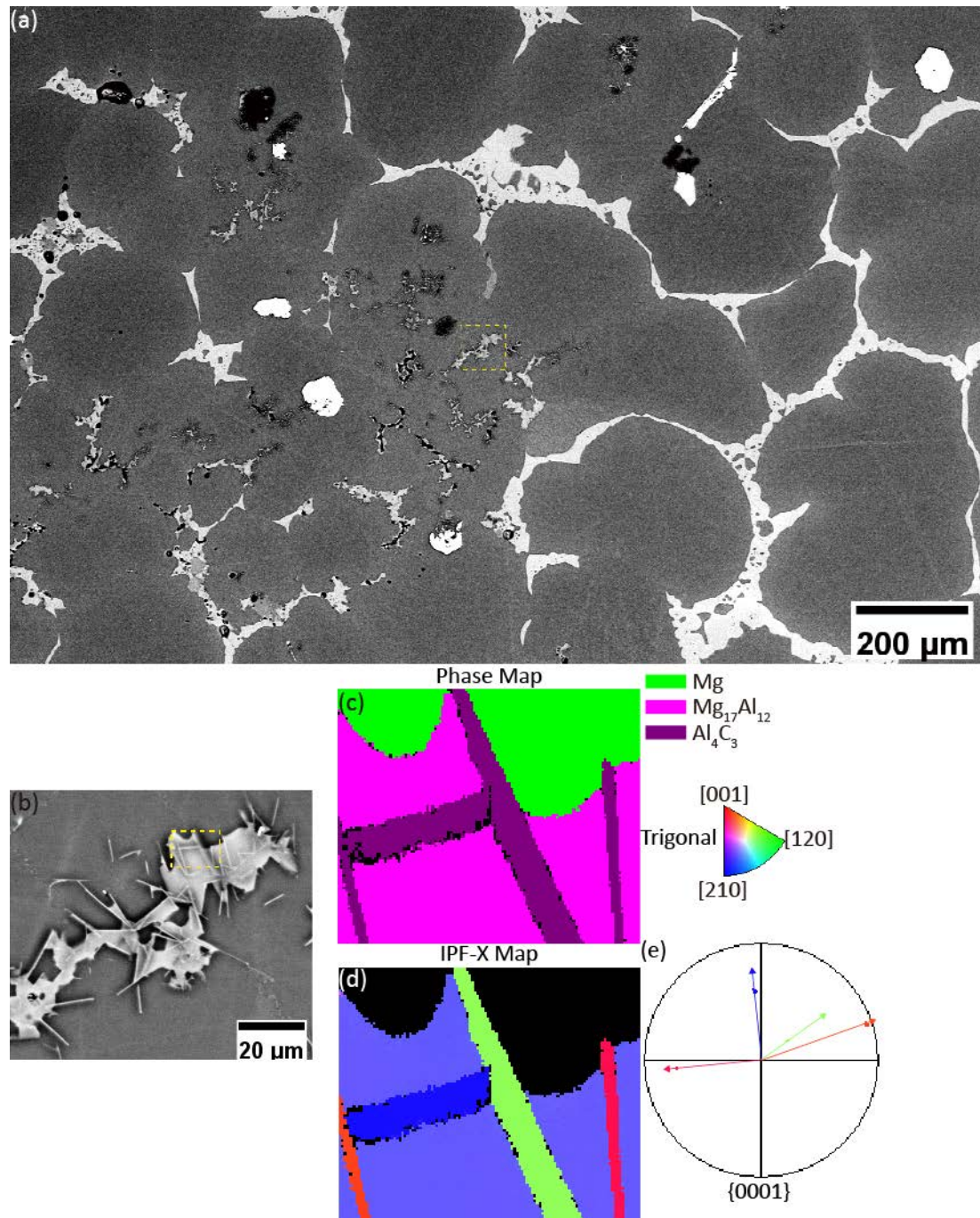


Figure 4.15 A typical region in a sample held at 800 °C for 40 hours with slow cooling where Al_4C_3 plates within $\text{Mg}_{17}\text{Al}_{12}$ are shown in BSE image of general view in (a) low magnification and (b) higher magnification. (c) EBSD phase mapping on a small region from (b). (d) is IPF-X Map of $\text{Mg}_{17}\text{Al}_{12}$ and Al_4C_3 phases. (e) shows the growth facet for Al_4C_3 in the $\{0001\}$ pole figure.

The calculated phase diagram from Deffrennes et al. [245] gives the series of solidification reactions during Scheil solidification as listed in Table 4.5. The table shows that Al_4C_3 is able to form in three stages: a transition reaction (quasi-peritectic) at 535°C , a eutectic reaction with $\alpha\text{-Mg}$ below 535°C , and a ternary eutectic reaction with $\alpha\text{-Mg}$ and $\text{Mg}_{17}\text{Al}_{12}$ at 436°C . The Al_4C_3 plates with $\text{Mg}_{17}\text{Al}_{12}$ and $\alpha\text{-Mg}$ in Figure 4.15 likely formed in this ternary eutectic reaction. However, the Al_4C_3 plates probably grew earlier and were pushed into the liquid spaces between the growing dendrite arms until the ternary eutectic reaction occurred there.

A feature of the reaction sequence in Table 4.5 from Figure 4.16 is the transition reaction $\text{L} + \text{Al}_2\text{MgC}_2 \rightarrow (\text{Mg}) + \text{Al}_4\text{C}_3$ at 535°C . It might be expected that this would cause a layer of Al_4C_3 to form around T2- Al_2MgC_2 particles since the reaction should occur at $\text{L} + \text{Al}_2\text{MgC}_2$ interfaces. However, this was not observed in this work.

Table 4.5 Scheil solidification sequence of a Mg-9Al-C alloy saturated in carbon at 800°C based on Ref. [245]. Here, the assumption is Mg-9Al-0.8 Zn with ~ 126 ppm saturated carbon content.

Temperature ($^\circ\text{C}$)	Reaction
800-600	$\text{L} \rightarrow \text{Al}_2\text{MgC}_2$
600-535	$\text{L} \rightarrow \text{Al}_2\text{MgC}_2 + (\text{Mg})$
535	$\text{L} + \text{Al}_2\text{MgC}_2 \rightarrow (\text{Mg}) + \text{Al}_4\text{C}_3$
535-436	$\text{L} \rightarrow (\text{Mg}) + \text{Al}_4\text{C}_3$
436	$\text{L} \rightarrow (\text{Mg}) + \text{Mg}_{17}\text{Al}_{12} + \text{Al}_4\text{C}_3$

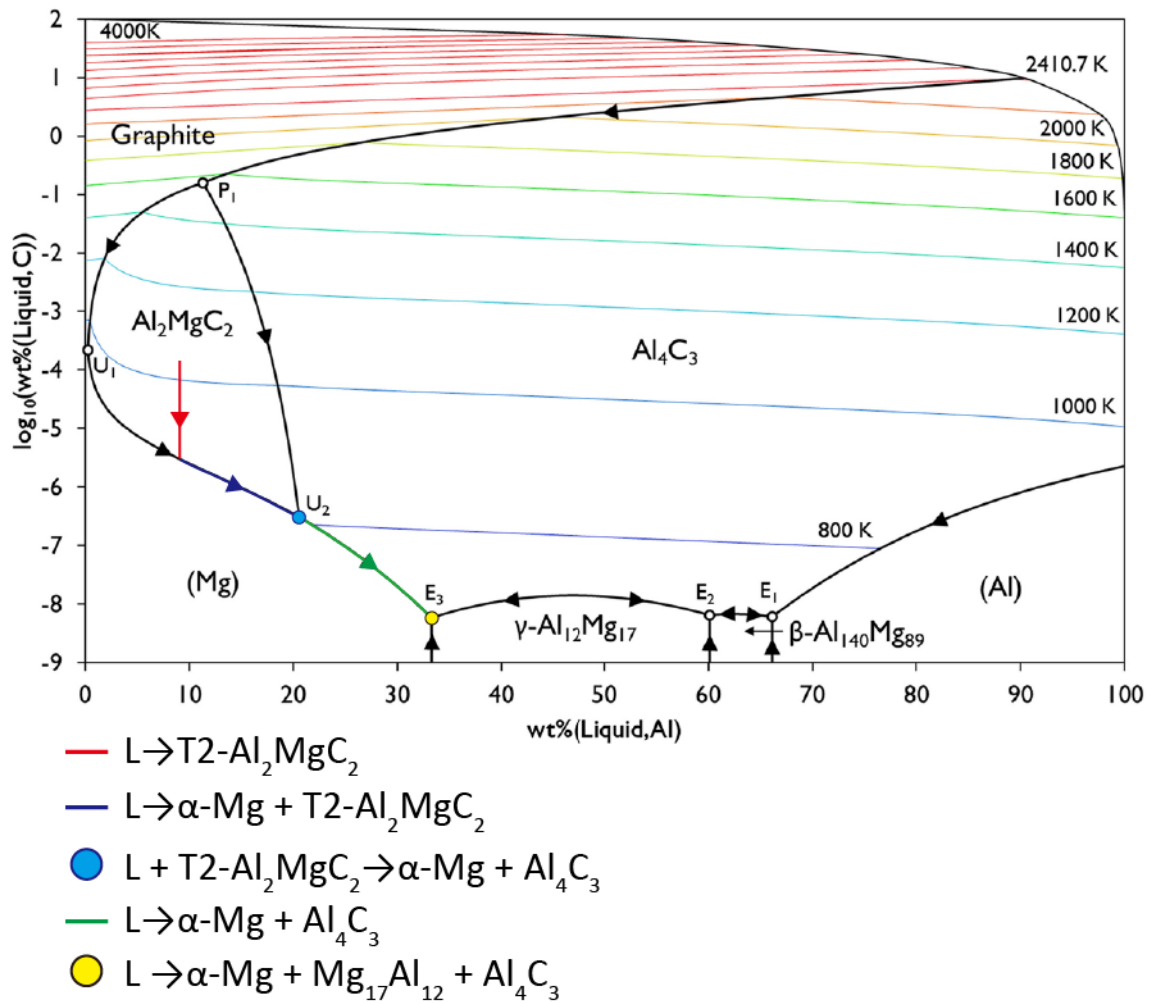


Figure 4.16 Calculated liquidus projection from Deffrennes et al. [245] superimposed with the approximate liquid composition path for a Mg-9Al-7Zn alloy saturated with C at 800 °C.

4.4 Conclusions

The formation of carbides has been studied in AZ91 after diamond or graphite powder was stirred into the melt prior to casting. Two key features of the experimental approach enabled new insights into carbide formation to be gained. First, samples were remelted and held for tens of hours at high melt temperatures to encourage the dissolution and reaction of the diamond and graphite with the AZ91 melt, followed by relatively slow cooling to generate large carbides during solidification for microstructural studies. Second, water-free sample preparation methods were developed which prevented the hydrolysis of carbides that has hampered previous studies.

Three carbide phases were detected due to interfacial reactions during isothermal holding and crystal growth during solidification on cooling: Al_4C_3 , $\text{T1-Al}_2\text{MgC}_2$ and $\text{T2-Al}_2\text{MgC}_2$. From characterisation of the carbide phases the following conclusions can be drawn:

- The various remelted samples with slow and fast cooling methods gave three types of carbide phases which are Al_4C_3 , $\text{T1-Al}_2\text{MgC}_2$ and $\text{T2-Al}_2\text{MgC}_2$. The Al_4C_3 twins have been only seen in the remelted above 800 °C samples. The observation implies that the Al_4C_3 twins might be high-temperature stable phases but the twinning growth mechanism here requires further investigation. $\text{T1-Al}_2\text{MgC}_2$ was only found to attach to oxide regions in one graphite sample held at 700°C. Note that $\text{T1-Al}_2\text{MgC}_2$ was not reproducible in this study and it was considered that the phase only formed in certain oxidised conditions. $\text{T2-Al}_2\text{MgC}_2$ formed as the reaction product between the carbon additives and the AZ91 melt.
- Al_4C_3 , $\text{T1-Al}_2\text{MgC}_2$ and $\text{T2-Al}_2\text{MgC}_2$ were successfully identified by EBSD and EDS characterisations. The Kikuchi patterns from the EBSD experimental data gave high CCC values of comparing to the simulated Kikuchi patterns for each phase. The high CCC values reinforced the evidence of production of three carbide phases.
- The growth morphologies of Al_4C_3 , $\text{T1-Al}_2\text{MgC}_2$ and $\text{T2-Al}_2\text{MgC}_2$ are faceted plates with $\{0001\}$ facets. Al_4C_3 grew with two types of twins and sometimes a simple OR with contacting $\text{T2-Al}_2\text{MgC}_2$:
 - (i) Penetration Al_4C_3 twins can be described as a 98.1° rotation around a common $\{01\bar{1}5\}$ plane normal. This twin type led to ‘X’ shaped crystals in cross-sections.
 - (ii) Contact Al_4C_3 twins have 60° rotation around a $\{0001\}$ shared interfacial plane.

- (iii) The OR between Al_4C_3 and $\text{T2-Al}_2\text{MgC}_2$ was found as a simple basal-to-basal relationship with $\{0001\}$ planes parallel to each other.
- $\text{T1-Al}_2\text{MgC}_2$, $\text{T2-Al}_2\text{MgC}_2$ and Al_4C_3 were observed to be close to other phases in the remelted samples. $\text{T1-Al}_2\text{MgC}_2$ and $\text{T2-Al}_2\text{MgC}_2$ were often found near the oxides and pores respectively in the cross section. $\text{T2-Al}_2\text{MgC}_2$ and Al_4C_3 could be found attached to Al-Mn particles but the phases did not envelope another. Some Al_4C_3 plates were found within $\text{Mg}_{17}\text{Al}_{12}$ which was predicted for the final eutectic reaction from the liquidus projection in the literature.

Chapter 5. Grain refinement of AZ91 by carbon inoculation

5.1 Introduction

Chapter 4 explored the different types of carbide formed during the solidification of AZ91 after carbon additions. Al_4C_3 , T1- Al_2MgC_2 and T2- Al_2MgC_2 were found after extended holding at 700 – 900 °C followed by relatively slow cooling. All types of carbides were located in regions close to Al-Mn intermetallics and, often, MgO oxide. No reproducible orientation relationships (ORs) were found between the carbides and the intermetallics or oxide.

The next step is to understand the role of carbides in the grain refinement of magnesium by carbon inoculation in Al-bearing magnesium alloys. Several different hypotheses have been proposed in the literature including the heterogenous nucleation of α -Mg on Al_4C_3 [36,48,49,51,66,146,148,154,157], Al_2MgC_2 [52–54,70,71,151,245], SiC [39–41,47,64,65], and Al_8Mn_5 [54,69,189] particles. In Chapter 4, T2- Al_2MgC_2 formed above the magnesium liquidus temperature which aligns with the past works on magnesium matrix composites [177–179], and Al_4C_3 also formed as expected from the calculated liquidus projection of Deffrennes et al. [245]. However, it was not clear which carbide (if any) is responsible for grain refinement during casting.

In this chapter, AZ91 melts were inoculated with graphite, diamond and α -SiC and gravity cast to explore the nucleant responsible for grain refinement by carbon inoculation in Al-bearing magnesium alloys. Three approaches were applied in this chapter: (i) investigate the reaction products around the carbon additives; (ii) use the holding and slow cooling method in Chapter 4 to study the reaction products; and (iii) evaluate the phase(s) that nucleate α -Mg.

5.2 Methods

5.2.1. Casting experiments

AZ91 was used with the chemical composition in Table 5.1. The three carbon-based additions shown in Table 5.2 were used for carbon inoculation. In each case, the addition was enveloped within aluminium foil (W: 8cm, L: 16cm, T: 13 μ m) and immersed into liquid AZ91 at 685°C. The melt was then stirred at 780 rpm for one hour before pouring into a pre-heated 200°C steel mould coated with BN. The detail casting procedure is in Chapter 3.

Table 5.1 Chemical compositions of AZ91 was analysed by ICP-OES.

Alloy	Composition (wt%)								
	Mg	Al	Zn	Mn	Cu	Si	Ni	Fe	Be
AZ91	Bal.	8.95	0.72	0.19	0.001	0.039	<0.001	<0.001	0.001

Table 5.2 Carbon-based additives added into AZ91 magnesium alloys

Carbon additives	Particle sizes	Weight percentage (wt%)	Stirring time (780 rpm)	Pouring temperature
Graphite (Alfa Aesar)	50 μ m	4.5	1 hour	685°C
Diamond (Mozime Ltd.)	50 μ m	4.5	1 hour	
Diamond (Mozime Ltd.)	1-2 μ m	4.5	1 hour	
α -SiC (Alfa Aesar)	50 μ m	4.5	1 hour	

5.2.2. Growth of reaction product experiments

For characterising the reaction products of all carbon-based additives, the remelting process was taken as the second stage of the experiment. The No.3 bar of each casting was used for the remelting process. The bar was cut into 2 cm cylinders to fit into alumina crucibles (internal diameter: 10mm, internal height: 25 mm) with a lid on the top of the crucible, which were then encapsulated in quartz under Ar atmosphere. The carbon-based additives casting (graphite, diamond and α -SiC) samples were then held in the melt at 800 °C for 40 hours and slow cooled

inside the furnace. The cooling rate was ~ 0.01 K/s. The illustration of the experiment is shown in Section 3.2.

5.2.3. Characterisation

All samples were sliced with water-free oil before the cross-sections were mounted. Then, they were ground with absolute ethanol and polished with 20 vol% OP-S in ethanol solution. Further details of sample preparation and characterisation was described in Chapter 3.

X-ray diffraction (XRD) was conducted on the carbon-based additions in Table 5.2 prior to their addition using a PANalytical MPD diffractometer with Cu-K α radiation ($\lambda = 1.5406$ Å). The diffraction data was collected in the 2θ angle range between 10° and 90° with an angular step size of 0.017° within 2-hour integration time. XRD patterns were analysed with HighScore Plus software with the PDF-4+2022 database.

For grain size measurement of gravity cast samples, colour etching was applied. The solution contained 1 ml acetic acid glacial, 44 ml distilled water and 156 ml absolute ethanol based on Ref. [241]. The polished samples were immersed into the etching solution for several minutes and then flushed with a large amount of ethanol. The samples were then dried with a nitrogen gas gun for several seconds. Finally, the surfaces were blown with humid air from a wet tissue covering a funnel for 1 second. The grain size measurement of etched samples was analysed using polarized light optical microscopy in an Olympus BX51. The grain size measurement is described in detail in Chapter 3. The etched microstructures were also imaged using a Brunel Microzoom stereomicroscope to produce low magnification macrographs of whole cross-sections.

5.3 Results and Discussion

5.3.1. Analysis of the additive particles

The morphologies of the original powder particles that were added for carbon inoculation are shown in Figure 5.1 combined with the XRD experimental results (red spectra) compared to the PDF-4+2022 database structures (blue peaks). The results confirm that the phases and particle sizes are consistent with Table 5.2.

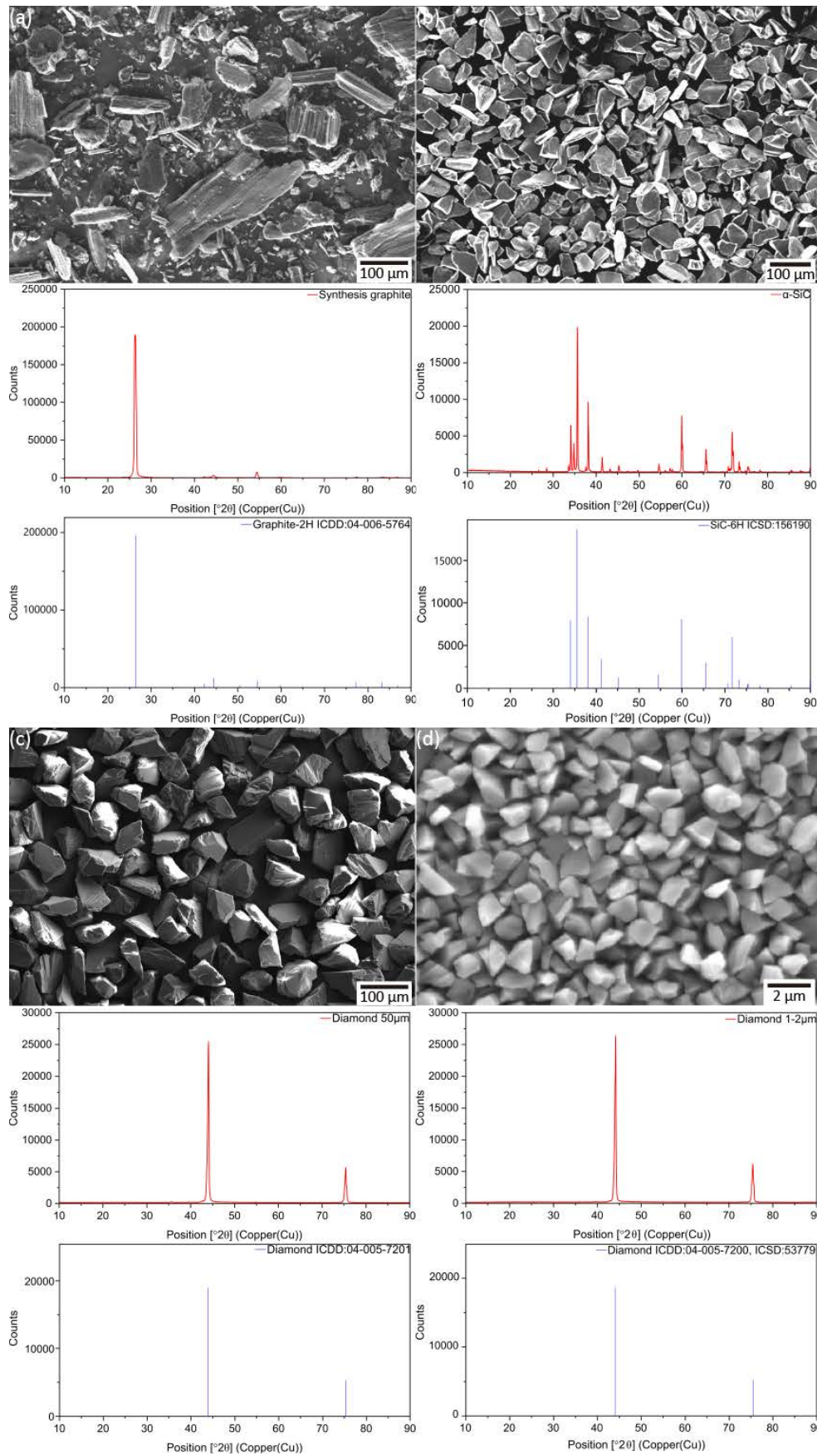


Figure 5.1 The microstructures of carbon-based additives include (a) synthetic graphite, (b) α -SiC, (c) 50 μm diamond and (d) 1-2 μm diamond with XRD analysis.

5.3.2. Optical and stereo microscopy of the magnesium grain structure

All carbon-based additions gave magnesium grain refinement after gravity casting, as shown in the stereomicroscope images in Figure 5.2(a)-(e). From higher magnification of polarised light optical micrographs (Figure 5.2(f)-(j)), the equiaxed dendrite α -Mg grains can be observed.

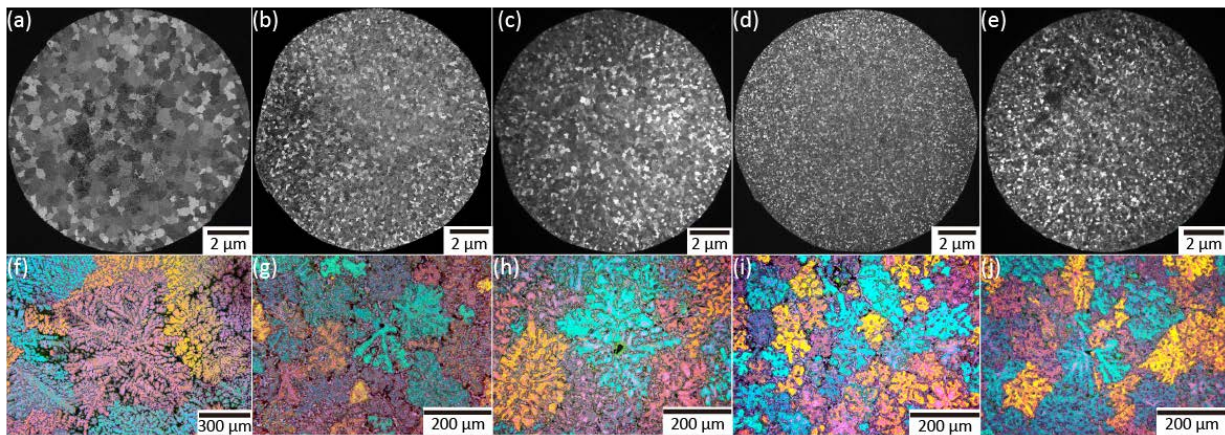


Figure 5.2 The stereomicroscopy of samples ((a)-(e)) reveals the grain size comparison between different carbon-based additives and the colour etching with higher magnification ((f)-(j)) presents the dendrite structures of α -Mg grains. These samples are (a),(f) normal AZ91 without any additions, (b),(g) AZ91+ 4.5wt% graphite, (c),(h) AZ91+4.5wt% α -SiC, (d),(i) AZ91+4.5wt% 50 μ m diamond and (e),(j) AZ91+4.5wt% 1-2 μ m diamond.

The colour contrast of grains was used to measure grain size using the method in Section 3.3.3 which excludes the chill zone. The grain size measurements in Figure 5.3 show that the grain sizes of carbon inoculated samples were reduced to at least 55% of the original gravity cast AZ91 sample. Note that the aim of this comparison is not to identify which carbon-based additive is the most effective nucleant for AZ91 because we did not optimise the particle size and volume fraction for each addition. The bar chart in Figure 5.3 simply demonstrates the successful grain refinement by carbon inoculation with each addition.

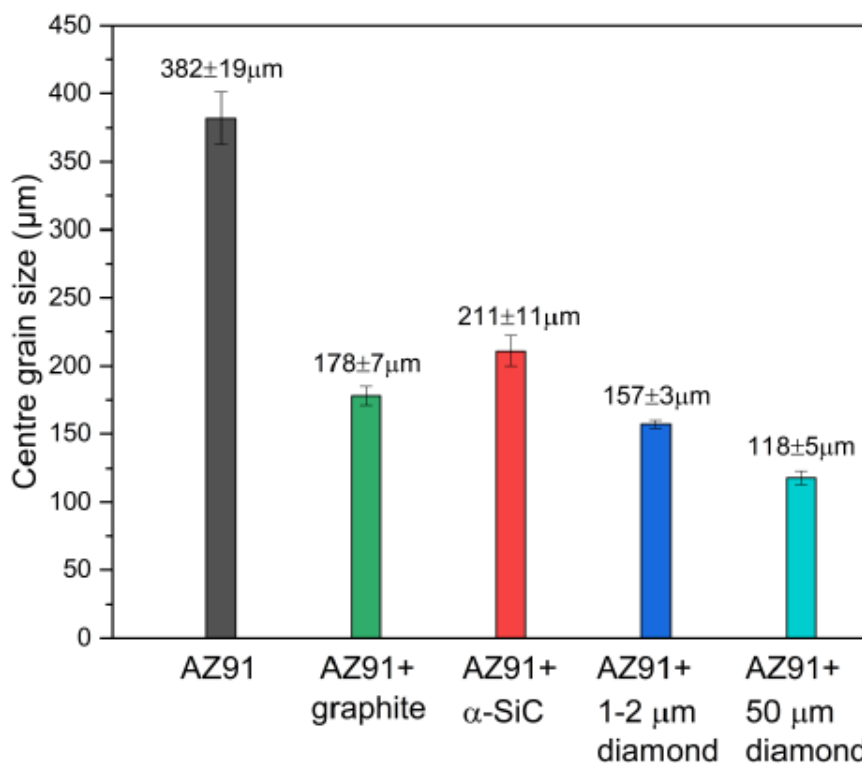


Figure 5.3 The grain size measurement was done by linear intercept procedure in multiple images. The bar chart shows the average grain size of all different carbon-based additive samples with 95% confident interval value as error bars.

5.3.3. AZ91 + graphite

5.3.3.1 Reaction products in gravity cast AZ91 inoculated with graphite

When 4.5 wt% graphite was added, the average grain size was reduced from 382 µm to 178 µm (Figure 5.3). Graphite and its reaction products were not easily found in gravity cast samples by SEM-based techniques. In Figure 5.4(a) and (b), the only captured example shows that a graphite particle (dark) surrounded by grey reaction product as well as $Mg_{17}Al_{12}$ (brighter) and Al_8Mn_5 (brightest). In the lower magnification EBSD phase map of Figure 5.4(c), only two phases, α -Mg and $Mg_{17}Al_{12}$ are detected. When the red box region in Figure 5.4(c) was mapped using a finer scan, the reaction product was identified as $T2-Al_2MgC_2$ (Figure 5.4(d)) and the graphite did not create any EBSD patterns. In Figure 5.4(e), the IPF-X map shows that the $T2-Al_2MgC_2$ particle is within an α -Mg grain but Figure 5.4(f) shows that this particular $T2-Al_2MgC_2$

Al_2MgC_2 particle and $\alpha\text{-Mg}$ do not have any simple orientation relationship (OR) and this particular particle probably did not trigger $\alpha\text{-Mg}$ nucleation.

The important result in Figure 5.4 is that the reaction product is T2- Al_2MgC_2 when graphite is added to liquid AZ91 prior to gravity casting. The case of Figure 5.4 is considered the saturation of carbon in the melt since the solubility of carbon in Mg is only about 20 ppm-w at 800°C [244,248] and around 2 ppm-w at 650 °C [248] which is close to the pouring temperature in this study.

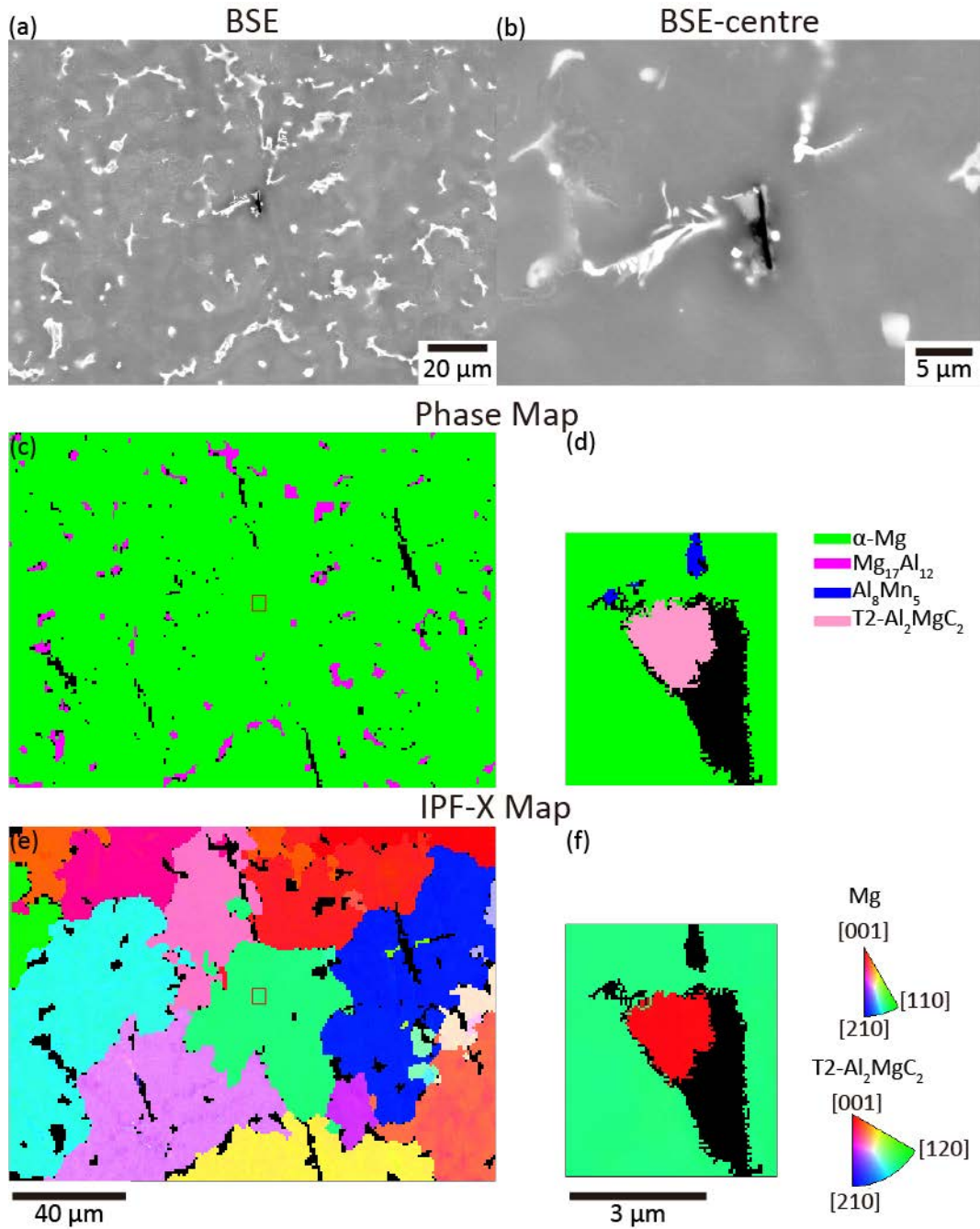


Figure 5.4 In the gravity cast AZ91+graphite sample, T2-Al₂MgC₂ (grey) around graphite (black) was observed under BSE mode in (a) lower magnification and (b) higher magnification. (c) EBSD phase mapping and (e) IPF-X map show the grains surrounding the grain enclosed T2-Al₂MgC₂ (Mg₁₇Al₁₂ and Al₈Mn₅ are off from the map). (d) EBSD phase mapping and (f) IPF-X map are the region of red box in (c) and (e) showing the no indexed graphite with T2-Al₂MgC₂ single crystal.

5.3.3.2 Reaction of graphite and AZ91 at 800 °C

The size of the T2-Al₂MgC₂ in the gravity cast sample was too small and low volume fraction to be found across the sample. To increase the reaction product, the remelting process in

Section 5.2.2 was used to provide time and temperature for reaction products to grow. By remelting the sample to 800°C for 40 hours with slow cooling, carbides formed in a characterisable size by SEM-based techniques. Before characterising by EBSD phase mapping, EDS was used to confirm the chemical composition of the product phase around graphite. A typical region of graphite surrounded by the reaction product is shown in Figure 5.5. The graphite region shows particularly high C content in the EDS elemental mapping and the reaction product contains Mg, Al, and C.

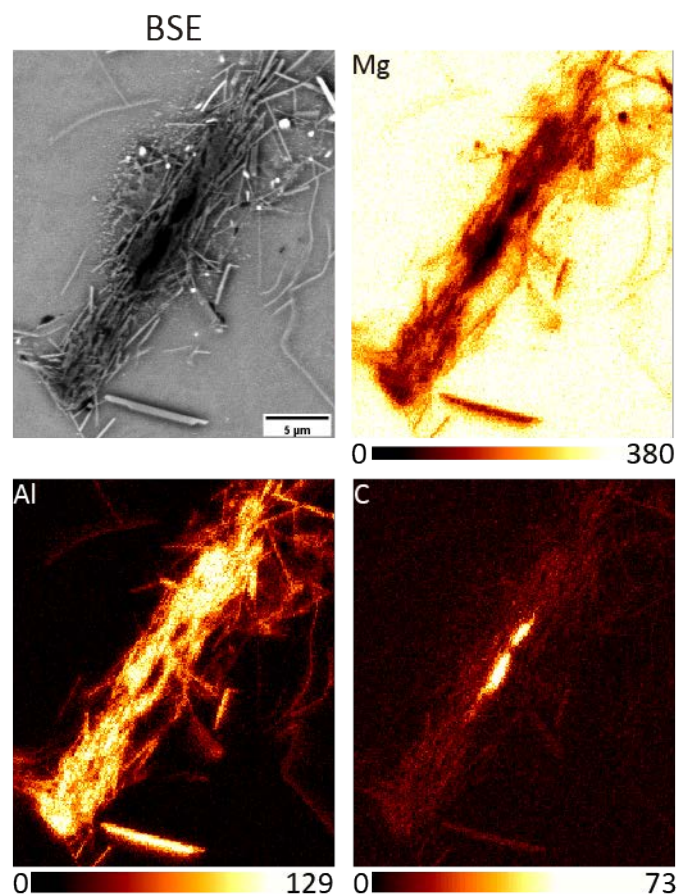


Figure 5.5 The reaction products around graphite (the dark region in BSE and the brightest region in elemental mapping of C) were formed under the remelting process at 800°C for 40 hours with slow cooling. The EDS elemental mapping shows the chemical compositions of Mg, Al and C.

Figure 5.6 gives two typical examples of reaction product growing around/near the graphite in samples held for 40 hours at 800°C. Figure 5.6(a) and (c) are BSE images which show graphite (the dark phase similar to Figure 5.4(b)) surrounded by faceted mid-grey phases.

EBSD mapping in Figure 5.6(b) and (d) confirms that T2-Al₂MgC₂ surrounds the graphite and Al₄C₃ formed in two locations: (i) attached to T2-Al₂MgC₂ in Figure 5.6(b) and (ii) close to Al-rich regions (Al-Mn particles or Mg₁₇Al₁₂) in Figure 5.6(d). Note that Al₄C₃ was never observed to form directly next to graphite. The plates of Al₄C₃ attached to the T2-Al₂MgC₂ near the top of the image/map in Figure 5.6(a) and (b) have the OR in Eq. (5.1), although this was unusual and was not found in most case of Al₄C₃ growing from T2-Al₂MgC₂. Figure 5.7 shows a closer look of Eq. (5.1) in Figure 5.6(a) and (b).

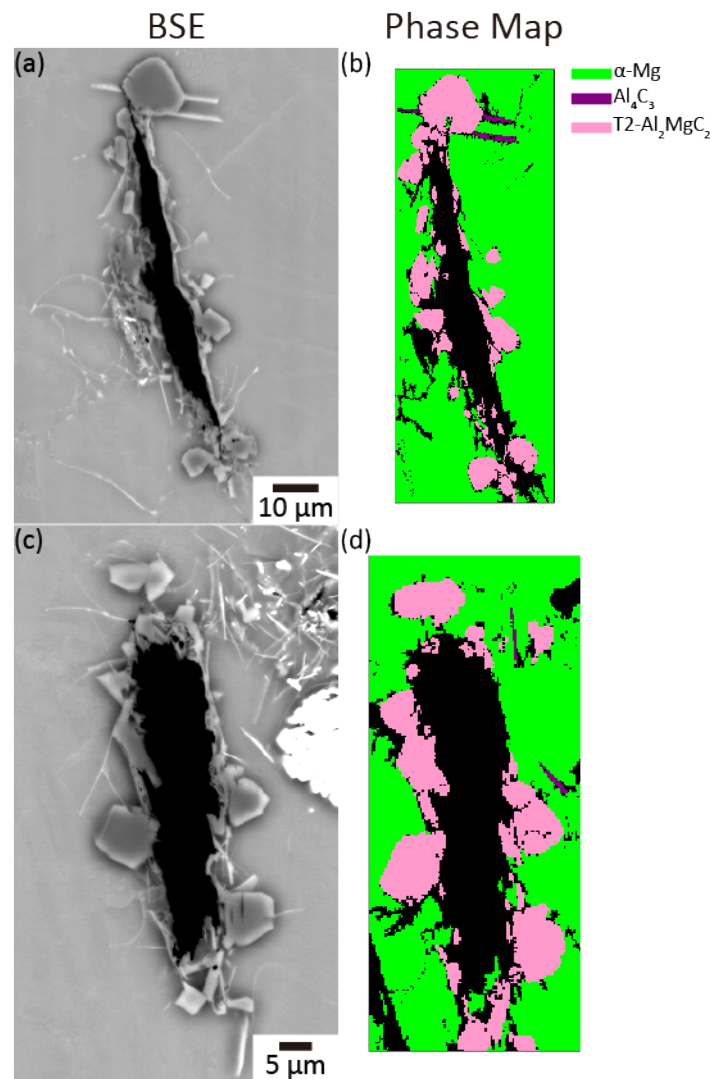


Figure 5.6 T2-Al₂MgC₂ is formed around graphite in the sample of being remelted at 800°C for 40 hours with slow cooling. (a), (c) BSE images and (b), (d) are the two typical examples of carbides formed around graphite.

$$\{1\bar{1}00\}_{\text{T2-Al}_2\text{MgC}_2} // \{0001\}_{\text{Al}_4\text{C}_3}$$

$$\langle\bar{1}\bar{1}20\rangle_{\text{T2-Al}_2\text{MgC}_2} // \langle\bar{1}2\bar{1}0\rangle_{\text{Al}_4\text{C}_3}$$

(5.1)

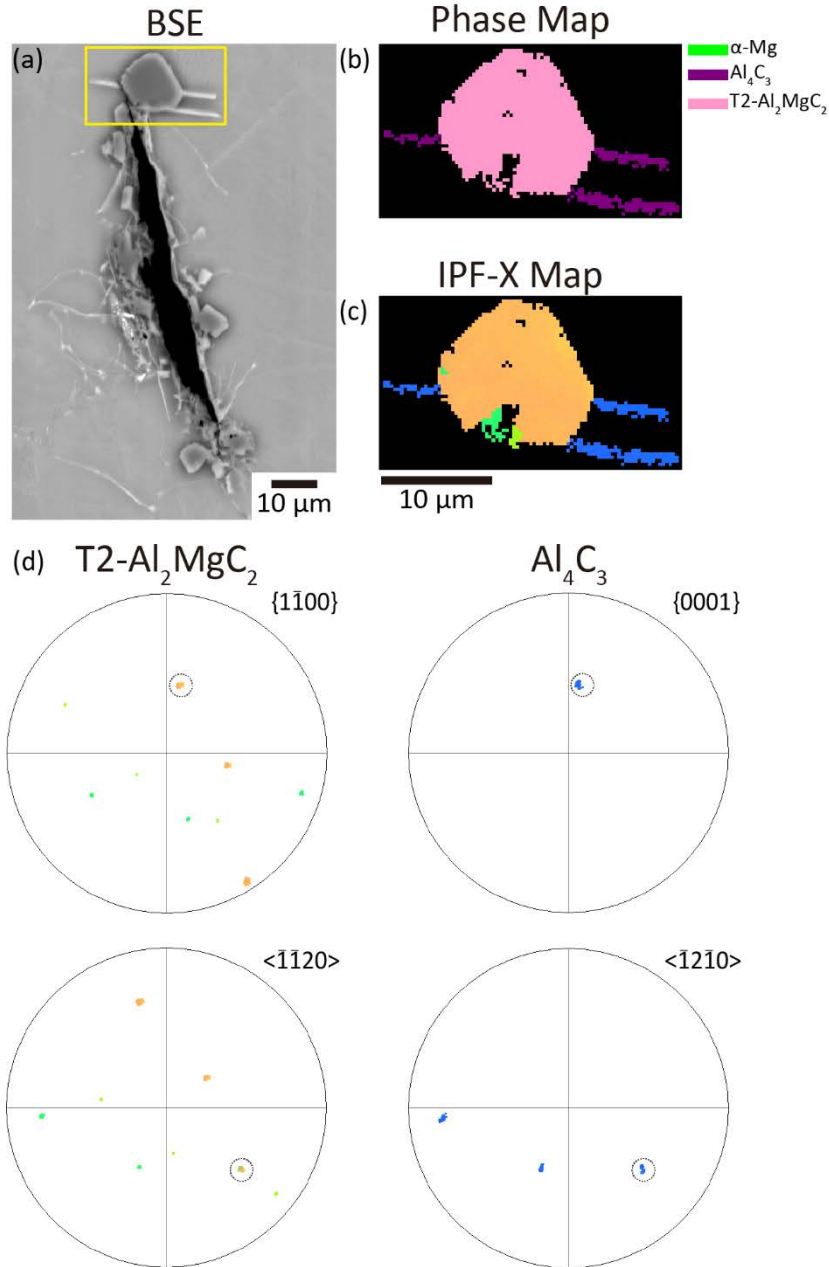


Figure 5.7 (a) A region of interest of BSE image in Figure 5.6(a) is boxed in yellow. (b) A higher magnification of (b) EBSD phase map and (b) IPF-X map of Al_4C_3 plates contacting $\text{T2-Al}_2\text{MgC}_2$. (d) The parallel planes and directions between $\text{T2-Al}_2\text{MgC}_2$ and Al_4C_3 .

5.3.4. AZ91 + diamond

Most microstructure analysis on diamond-containing samples was conducted on AZ91+1-2 μm diamond samples because the AZ91+50 μm diamond samples were difficult to polish well due to large protrusions of diamond and could not be used for EBSD scanning.

5.3.4.1 Reaction products in gravity cast AZ91 with diamond

Gravity cast AZ91+4.5wt% 1-2 μm diamond samples contained diamond particles throughout the cross section, in contrast to the difficulty of finding graphite particles in gravity cast AZ91+graphite samples in the previous subsection. Figure 5.8 shows a typical region of diamond particles surrounded by reaction products. In the tilted SE image in Figure 5.8(a), the protuberant particles are diamond which are the dark phase in the untilted BSE image in Figure 5.8(b). EBSD phase mapping (Figure 5.8(c)) shows two distinguishable diamond particles surrounded by $\text{T2-Al}_2\text{MgC}_2$. Note that the diamond phase produced good Kikuchi patterns unlike graphite which produced no EBSD patterns. The EDS elemental mapping (Figure 5.8(d)) additionally shows that the diamond particles contain only a high C content and the reaction product, $\text{T2-Al}_2\text{MgC}_2$, contains Mg, Al and C. From EBSD and EDS, both results confirm that the chemical reaction resulted in $\text{T2-Al}_2\text{MgC}_2$ growing from the diamond particles.

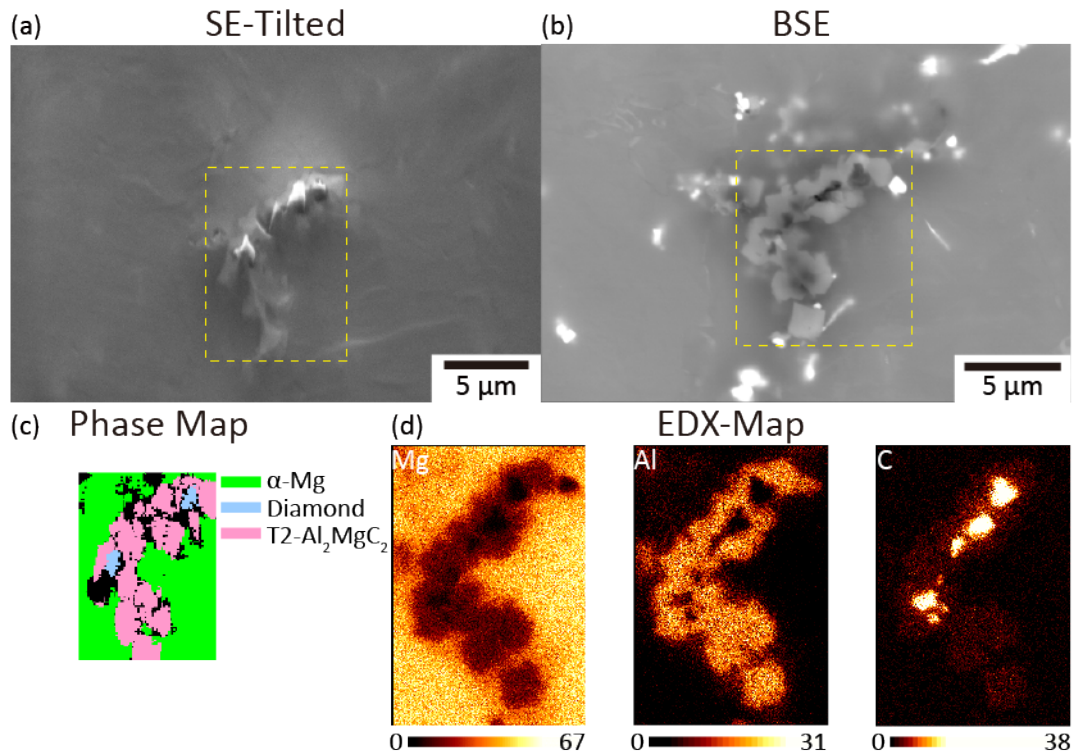


Figure 5.8 (a) Tilted SE image of protuberant diamonds surrounded by T2-Al₂MgC₂, and (b) untilted BSE mode image of diamonds and T2-Al₂MgC₂ present as dark and grey phases respectively. (c) EBSD phase mapping on the region shows diamond and T2-Al₂MgC₂ in α-Mg grain with (d) EDS elemental mapping of Mg, Al and C.

In gravity cast AZ91+diamond samples, the T2-Al₂MgC₂ phase was observed in two types of location: (i) near the diamond particles such as in Figure 5.8 and Figure 5.9; (ii) stand-alone particles without diamond in the cross-section such as in Figure 5.10. In both cases, there was sometimes an OR between the T2-Al₂MgC₂ and α-Mg as demonstrated in the next paragraphs.

Figure 5.9 is a case of T2-Al₂MgC₂ surrounding diamond particles. The T2-Al₂MgC₂ was aggregated in a cluster of particles close to the diamond as shown in Figure 5.9(a) and (b). From the same magnification of Figure 5.9(a), Figure 5.9(c) is an EBSD phase map containing T2-Al₂MgC₂ and diamond particles. The IPF-Y map in Figure 5.9(d) shows that these diamond and T2-Al₂MgC₂ particles were mostly located at/near α-Mg grain boundaries. Two T2-Al₂MgC₂ particles in this region are in different α-Mg grains and both have a simple OR with the surrounding α-Mg grain. Figure 5.9(e) and (f) presents the higher magnification finer EBSD scan of the red box region in Figure 5.9(c) and (d). The pole figures in Figure 5.9(g) from the

IPF-Y map (Figure 5.9(f)) show that T2-Al₂MgC₂ particles have a basal-to-basal OR with the surrounding α -Mg and that can be expressed as Eq. (5.2). The pole figures (Figure 5.9(g)) show the parallel planes of {0001}, {10 $\bar{1}$ 0} and {11 $\bar{2}$ 0} and the misorientation angles between T2-Al₂MgC₂ and α -Mg are within 2° measured by the Euler angles in Esprit 2.1.

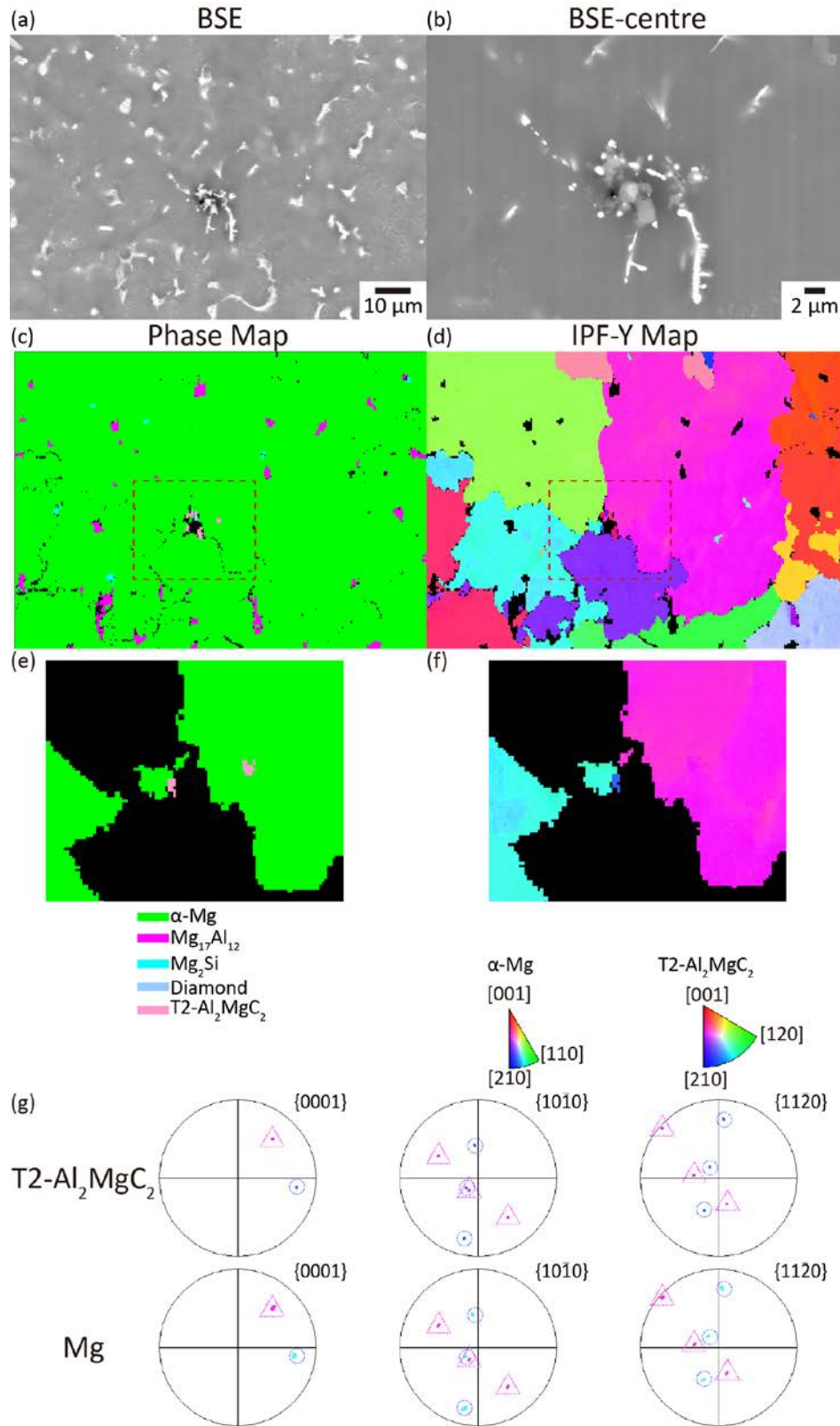


Figure 5.9 The observation of T2-Al₂MgC₂ around diamonds within α -Mg grains. (a) BSE mode image with (b) centre region. (c) EBSD phase mapping and (d) IPF-Y map show the T2-Al₂MgC₂ phase surrounded the central diamonds connecting to α -Mg and two of the T2-Al₂MgC₂ particles have ORs with the surrounded grain in (g) {0001}, {10 $\bar{1}$ 0} and {11 $\bar{2}$ 0} planes.

$$\begin{aligned} \{0001\}_{\text{T2-Al}_2\text{MgC}_2} // \{0001\}_{\alpha\text{-Mg}} \\ \langle 11\bar{2}0 \rangle_{\text{T2-Al}_2\text{MgC}_2} // \langle 11\bar{2}0 \rangle_{\alpha\text{-Mg}} \end{aligned} \quad (5.2)$$

A case of standalone T2-Al₂MgC₂ not attached to diamond particles is overviewed in Figure 5.10. The T2-Al₂MgC₂ particles in Figure 5.10(a), (b) and (c) are clustered together with both MgO (orange in the phase map in Figure 5.10(c)) and Al-Mn particles (not indexed in the phase map but can be seen as bright particles in the BSE image of Figure 5.10(a)). The IPF-X map of the same area in Figure 5.10(d) shows five main α -Mg grains. The small α -Mg orientations inside the major α -Mg grains in Figure 5.10(d) are deformation twins caused by grinding/polishing. In the selected region in Figure 5.10(e) and (f), a T2-Al₂MgC₂ particle has the basal-to-basal OR (Eq.(5.2)) with the surrounding α -Mg. Note that the MgO (Figure 5.10(g)) and Al₈Mn₅ particles indexed in Figure 5.10(c) do not have a simple or special OR with the surrounding α -Mg.

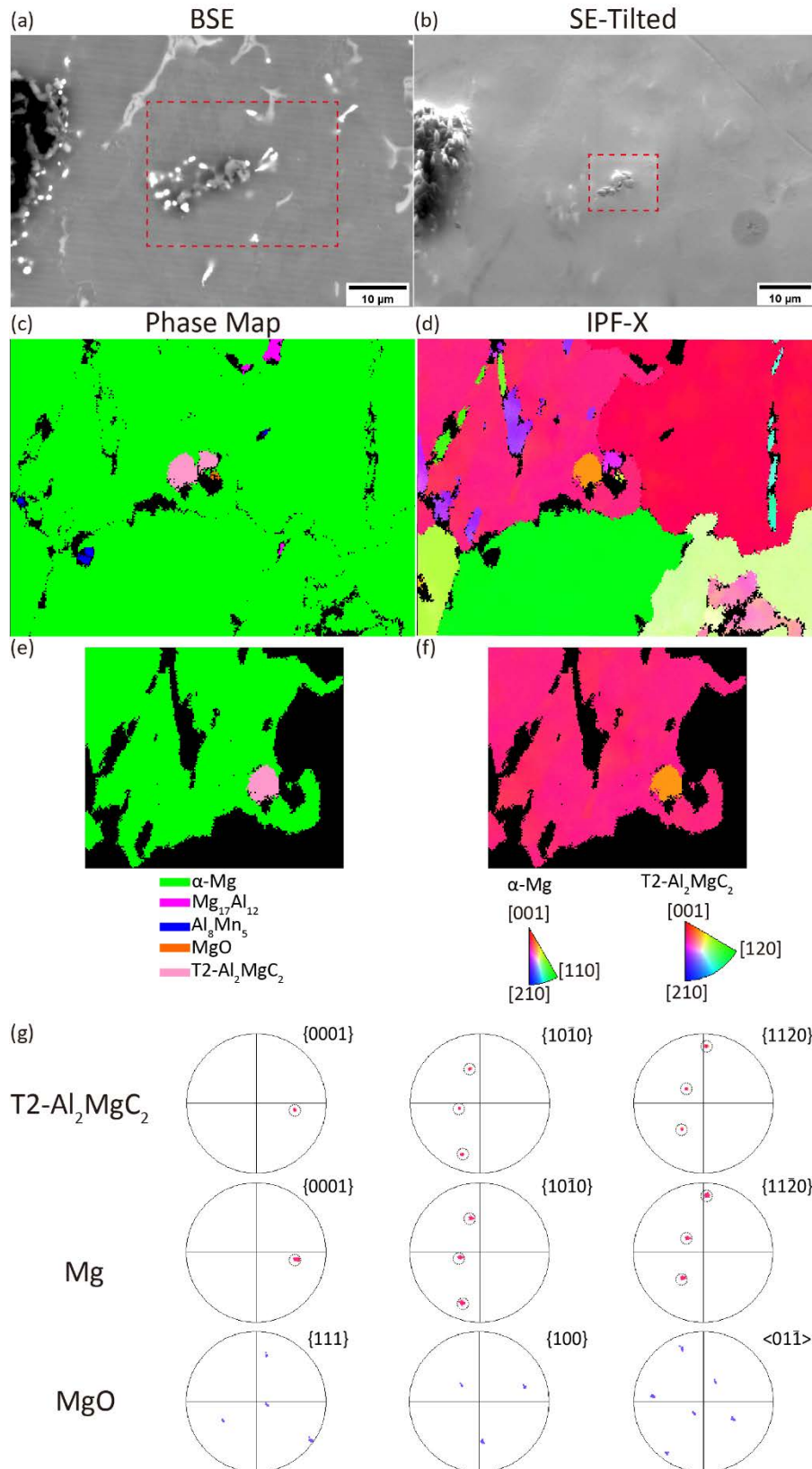


Figure 5.10 The observation of standalone T2-Al₂MgC₂ particles. (a) BSE mode image and (b) tilted SE image were analysed with (c) EBSD phase mapping and (d) IPF-X map. Both show the two standalone T2-Al₂MgC₂ particles. (e) and (f) show the T2-Al₂MgC₂ particle having OR with the surrounding α -Mg, and (g) this demonstrates on the pole figures of {0001}, {10 $\bar{1}$ 0} and {11 $\bar{2}$ 0} of T2-Al₂MgC₂ and α -Mg compared with {111}, {100} and <01 $\bar{1}$ > of MgO.

There are fifteen T2-Al₂MgC₂ particles in Figure 5.9(c) and Figure 5.10(c) and only three of them share the OR in Eq.(5.2) (or any other simple OR) with their surrounding α -Mg grain. This shows that although some T2-Al₂MgC₂ particles have an OR with the α -Mg matrix, most do not. This is consistent with past work on TiB₂ inoculant particles in aluminium alloys [134,139] which has shown that only a small fraction of TiB₂ particles trigger α -Al nucleation events. It is also evident in Figure 5.9 and Figure 5.10 that these three T2-Al₂MgC₂ particles with the OR are not located near the centre of the α -Mg grains. Therefore, these specific T2-Al₂MgC₂ particles may not have nucleated the α -Mg grains. Indeed, past work [249,250] has shown that solidification ORs can form by different mechanisms including by heterogenous nucleation and by the pushing and engulfment of particles by a growth front. The key point in Figure 5.9 and Figure 5.10 is that while many T2-Al₂MgC₂ particles had no special OR with the α -Mg, it was relatively easy to find T2-Al₂MgC₂ particles with the OR in Eq. (5.2) and ORs were not found between α -Mg and the MgO and Al₈Mn₅ particles in these maps. This indicates that there is a low energy interface between T2-Al₂MgC₂ particles and α -Mg and that this is likely to also be the heterogenous nucleation OR.

5.3.4.2 Reaction of diamond and AZ91 at 800 °C

Further information on the formation of carbides in AZ91+diamond samples was obtained by remelting the gravity cast sample at 800°C for 40 hours followed by slow cooling. This technique has the following desired effects to maximise the amount and size of carbides formed. (i) Increasing the melt temperature to 800 °C (compared with the peak temperature of 685 °C before gravity casting) increases the carbon solubility in the melt. (ii) Holding for 40 hours at this temperature gives more time for reaction between the diamond and liquid AZ91 and for carbon diffusion in the melt. (iii) Holding the suspension of denser diamond particles in the melt without stirring induces settling and causes an increased volume fraction of diamond particles near the bottom of samples where they can be easily found. (iv) Subsequent slow

cooling from 800 °C produces larger carbides by crystal growth on cooling. Figure 5.11 is a typical example from such an experiment. There a high-volume fraction of T2-Al₂MgC₂ surrounding clustered diamond particles. The linked chain in Figure 5.11(a) and (b) is made up of many individual T2-Al₂MgC₂ particles with different orientations, and some MgO. The carbide microstructures from 800 °C holding experiments such as Figure 5.11 had many similarities with the gravity cast AZ91+diamond experiment although the volume fraction of T2-Al₂MgC₂ was much higher and the carbides were larger. However, there was one significant difference: Al₄C₃ was found in these AZ91+diamond 800 °C holding experiments but not in gravity castings. For example, the thin plates extending from the T2-Al₂MgC₂ in Figure 5.11(a) are shown to be Al₄C₃ in the EBSD phase map in Figure 5.11(b).

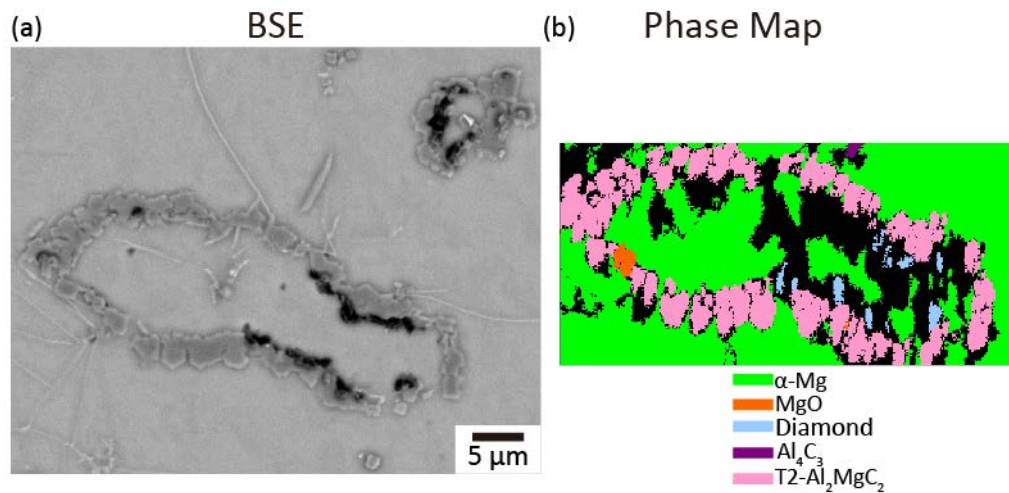


Figure 5.11 The reaction between diamond and AZ91 at 800°C for 40 hours with slow cooling. (a) BSE image with (b) EBSD phase mapping.

5.3.5. AZ91 + α -SiC

The last carbon-based additive used in this study was α -SiC since α -SiC has been frequently reported as an inoculant for Al-bearing magnesium alloys [39–41,47,64,65].

5.3.5.1 Reaction products in gravity cast AZ91 with α -SiC

α -SiC particles in the AZ91 caused challenges during grinding/polishing due to the large hardness difference between α -Mg and α -SiC which resulted in α -SiC protuberances. Note that

the added α -SiC particles were around 50 μm and a smaller particle size was not available from the manufacturer. The large size of the particles exacerbated the problem during sample preparation. The following characterisation results were generated after optimising the sample preparation method as much as possible.

Figure 5.12(a) is an SE image where the brightness and contrast between the α -SiC and α -Mg indicates the height difference. From the BSE image in Figure 5.12(b), the different phases are clearly seen and there is some reaction product on the top-left corner of the α -SiC particle and some bright Al-Mn intermetallics on the right side. In the EDS elemental mapping of Figure 5.12, it clearly shows the main particle contains Si and C, and the reaction product contains C, Mg and Al. Note in the Mg elemental mapping, that there is a shadow of Mg content on the right-hand side of the α -SiC particle caused by the protuberance.

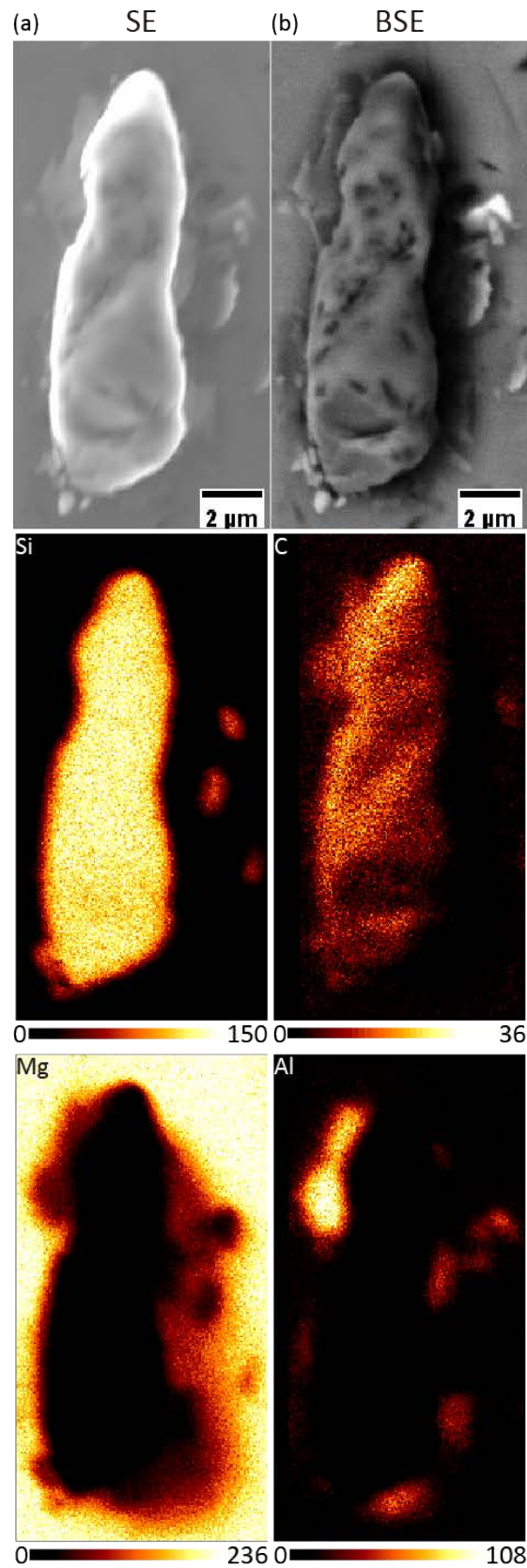


Figure 5.12 EDS elemental mapping on a region of α -SiC particle in the centre. (a) SE image shows the α -SiC particle protruded from α -Mg with different surrounding phases. (b) BSE image shows the α -SiC particle had clearly uneven surface and a plate (grey colour) next to the particle. The EDS elemental mapping contains the elements of Si, C, Mg and Al.

Figure 5.13(a) shows that there are some Al-Mn particles (bright) around the α -SiC and some small grey particles next to the α -SiC particle. The grey phase was indexed as T2-Al₂MgC₂ through its Kikuchi pattern by EBSD in Figure 5.13(c). Small regions of Mg₂Si close to the α -SiC particle imply that silicon was also released from the reaction between the α -SiC particle and the melt. Note that the zero-indexed region in Figure 5.13(c) is due to the height difference between the α -SiC particle and α -Mg shadowing the EBSD scanning. This effect can be clearly seen in Figure 5.13(b) which is a tilted SE image.

Similar examples of microstructure around α -SiC particles in gravity cast AZ91+ α -SiC are given in Figure 5.14 and Figure 5.15. In each case, there is a small amount of T2-Al₂MgC₂, Mg₂Si and Al₈Mn₅ around the partially reacted α -SiC particle. The reaction products were much smaller than the α -SiC particle indicating slow reaction kinetics during the 1 hour stirring at 685 °C prior to gravity casting.

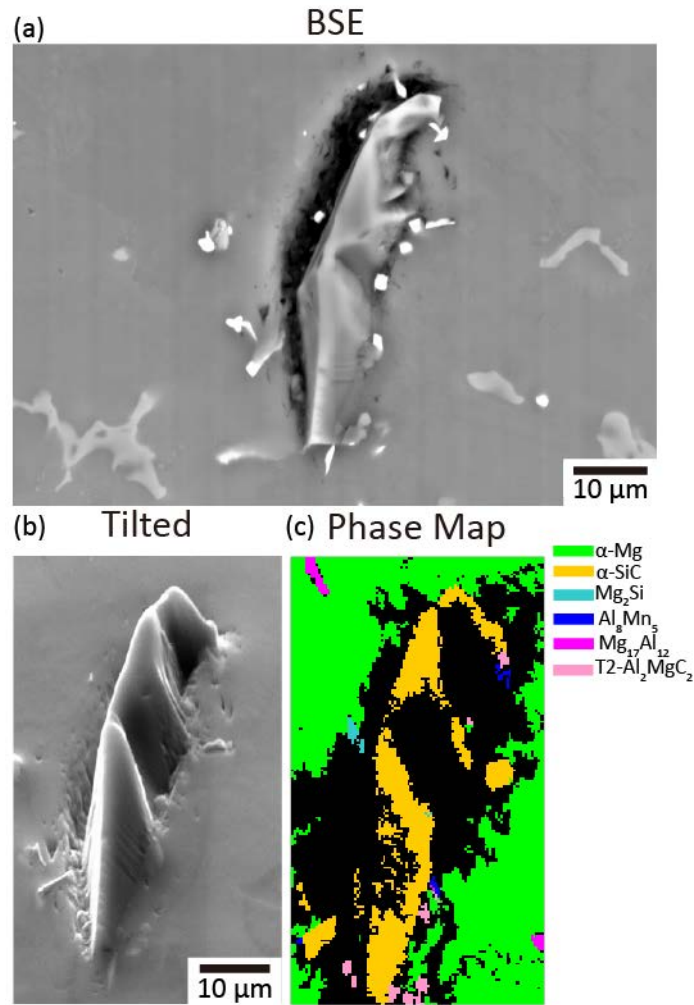


Figure 5.13 A typical region of an $\alpha\text{-SiC}$ particle in the gravity cast sample is shown in (a) BSE image, (b) tilted SE image with (c) EBSD phase mapping.

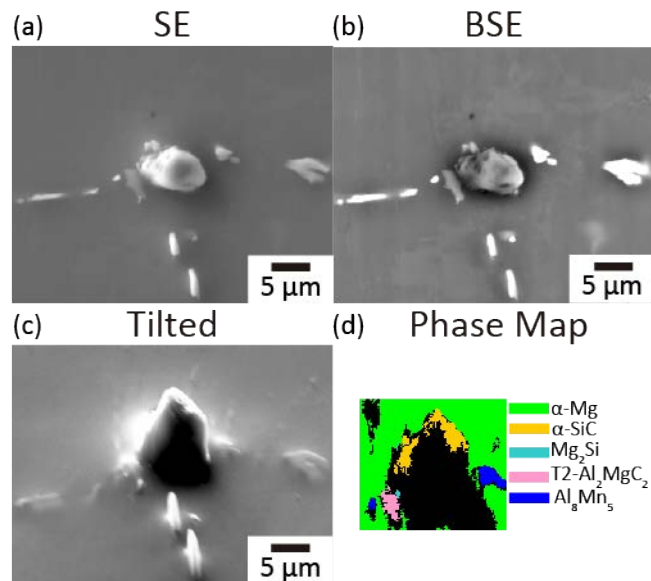


Figure 5.14 Another example of an $\alpha\text{-SiC}$ particle in the gravity cast sample is shown in (a) BSE image, (b) tilted SE image with (c) EBSD phase mapping.

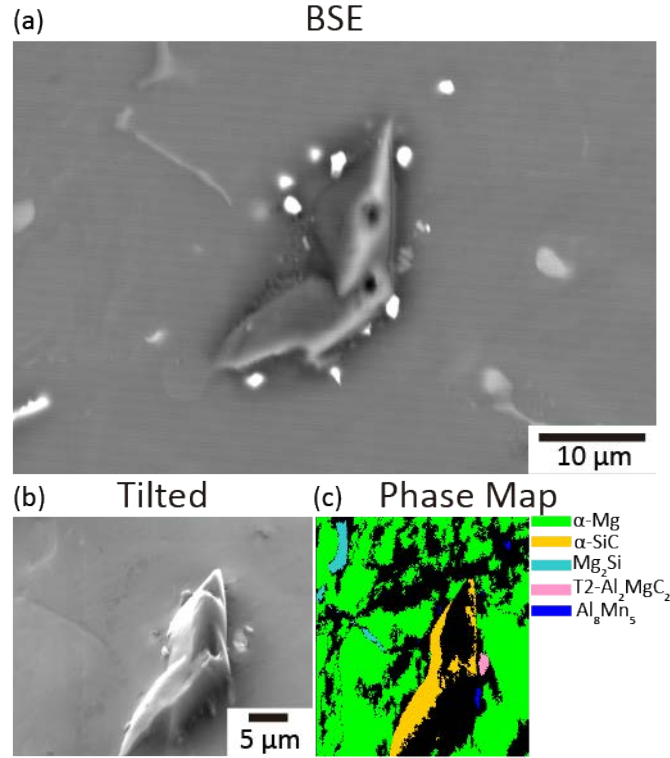


Figure 5.15 Another example of an α -SiC particle in the gravity cast sample is shown in (a) BSE image, (b) tilted SE image with (c) EBSD phase mapping.

No ORs were measured between $T2-Al_2MgC_2$ and α -Mg in gravity cast AZ91+ α -SiC. This is thought to be partly due to the very small amount of independent $T2-Al_2MgC_2$ and the fact that $T2-Al_2MgC_2$ around α -SiC tended to be shadowed by the protruding α -SiC during EBSD mapping. On one occasion, an OR was measured between α -SiC and α -Mg with the simple basal-to-basal OR in Eq. (5.3) as shown in Figure 5.16.

$$\begin{aligned} \{0001\}_{\alpha-SiC} // \{0001\}_{\alpha-Mg} \\ \langle 10\bar{1}0 \rangle_{\alpha-SiC} // \langle 10\bar{1}0 \rangle_{\alpha-Mg} \end{aligned} \quad (5.3)$$

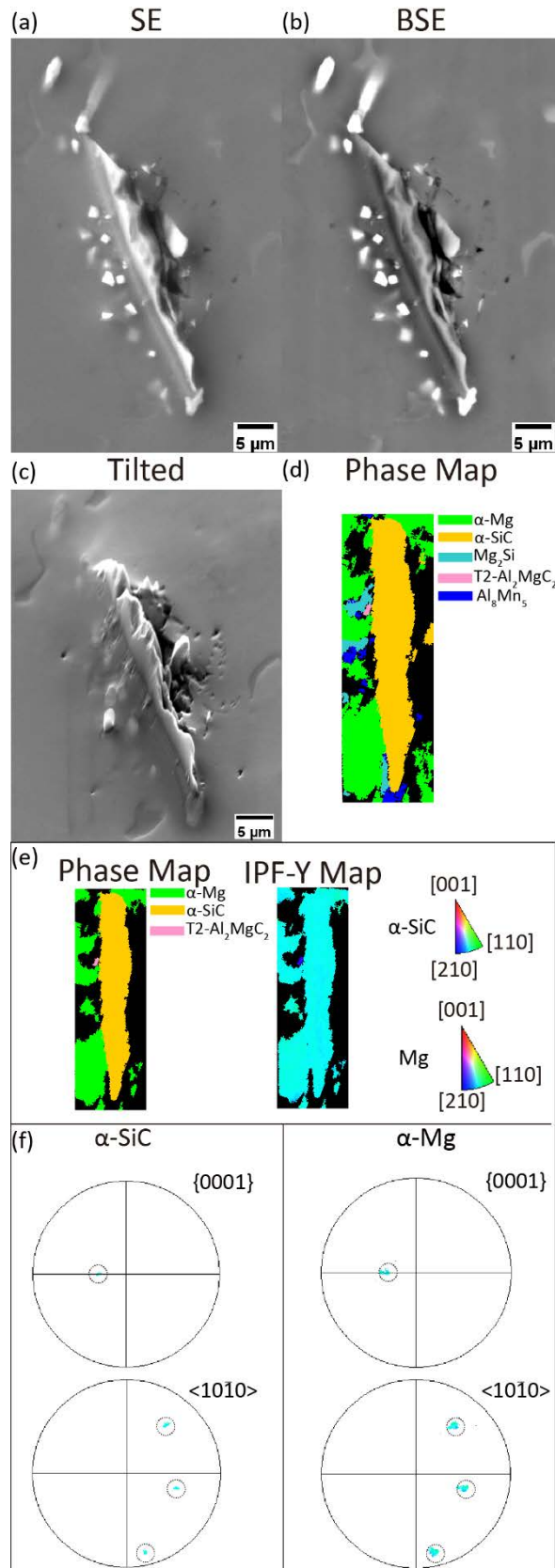


Figure 5.16 The observation of a T2-Al₂MgC₂ particle attaching with an α-SiC particle. (a) SE mode image and (b) BSE image. (c) Tilted SE image were analysed with (d) EBSD phase mapping. (e) EBSD phase map and IPF-Y map only include α-Mg, α-SiC and T2-Al₂MgC₂. (f) The IPF-Y pole figures of {0001}, <1010> for α-SiC and α-Mg.

However, it is suspected that this may actually be a double basal-to-basal OR of α -SiC // T2-Al₂MgC₂ // α -Mg with a combination of the α -SiC // α -Mg OR in Eq. (5.3) and the α -SiC // T2-Al₂MgC₂ in Eq. (5.4) in the next section. However, it was not possible to prove this suspicion here. Further TEM work is required to explore this question.

5.3.5.2 Reaction of α -SiC and AZ91 at 800 °C

An AZ91+ α -SiC gravity casting was remelted and held at 800 °C for 8 hours to obtain more extensive reaction between α -SiC and the AZ91 melt.

Figure 5.17 is a typical region where an α -SiC particle has almost completely reacted with the AZ91 melt. The EBSD phase map in Figure 5.17(b) matches with the BSE image in Figure 5.17(a). The EBSD phase map in Figure 5.17(b) shows T2-Al₂MgC₂ phase and a large faceted Mg₂Si crystal growing outside the remaining α -SiC. Figure 5.17(c) is a selected region of only α -SiC and T2-Al₂MgC₂. Some parts of this region have a simple OR which is shown by the pole figures in Figure 5.17(d) and demonstrated by the Kikuchi patterns in Figure 5.17(e) and plotted unit cell wireframes in Figure 5.17(f). The OR can be written as Eq. (5.4) and is a simple basal-to-basal OR.

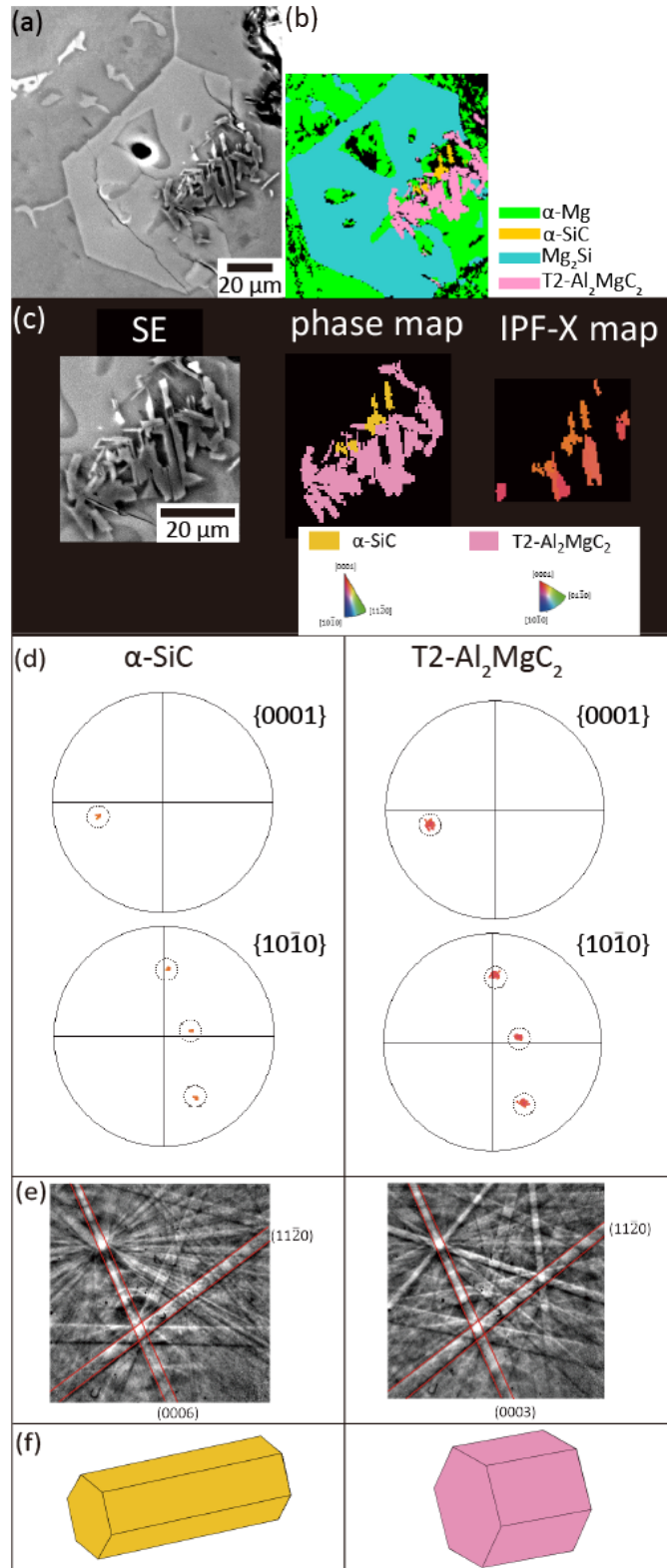


Figure 5.17 The reaction between α -SiC and AZ91 at 800°C for 8 hours with fast cooling. (a) SE and (b) BSE mode images of T2-Al₂MgC₂ formed around α -SiC. (c) Tilted SE mode image with (d) EBSD phase mapping. (e) EBSD phase mapping exclusive of α -Mg and Mg₁₇Al₁₂ and (f) IPF-X map of polycrystal T2-Al₂MgC₂ formation.

$$\begin{aligned} \{0001\}_{\text{T2-Al}_2\text{MgC}_2} // \{0001\}_{\alpha\text{-SiC}} \\ \langle 10\bar{1}0 \rangle_{\text{T2-Al}_2\text{MgC}_2} // \langle 10\bar{1}0 \rangle_{\alpha\text{-SiC}} \end{aligned} \quad (5.4)$$

However, in many regions, there was no special OR between α -SiC and T2-Al₂MgC₂. An example is shown in Figure 5.18 where multiple T2-Al₂MgC₂ orientations have grown around two α -SiC orientations without any simple or reproducible OR.

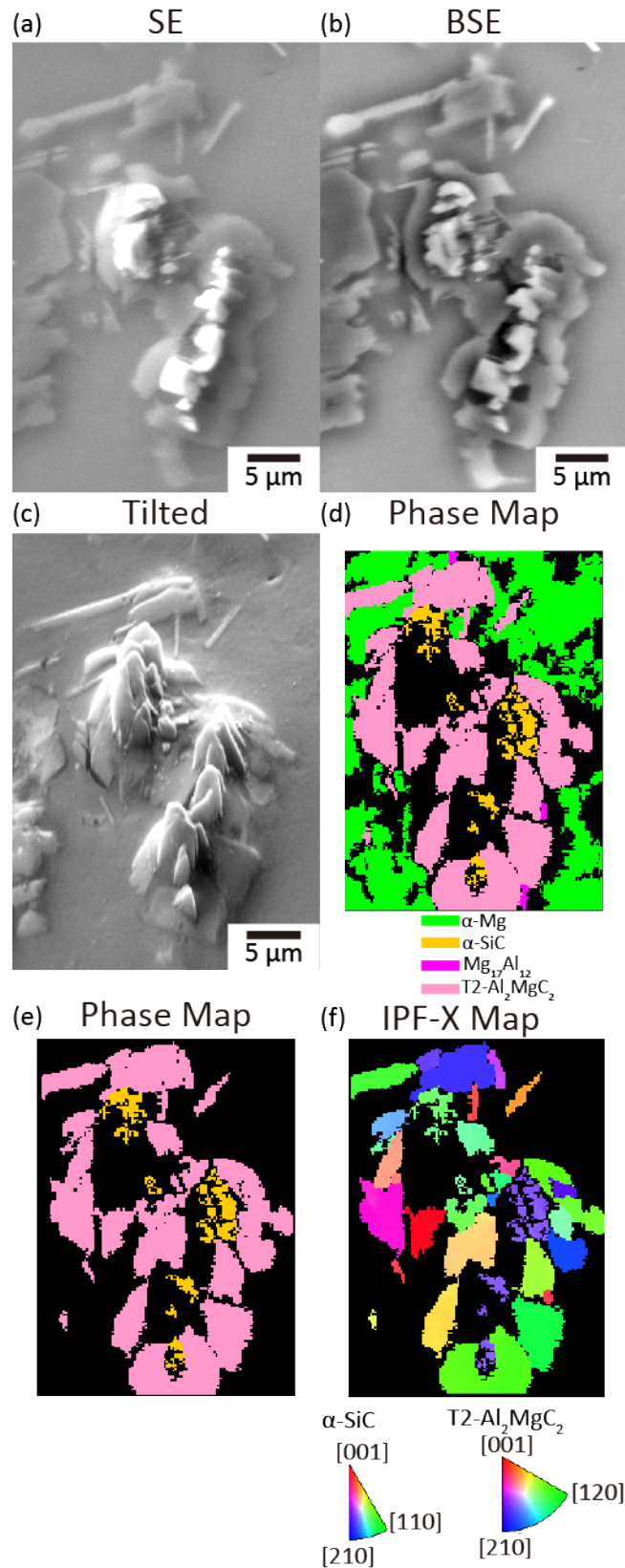
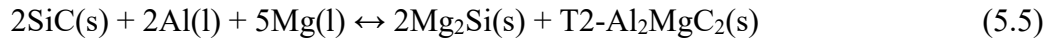


Figure 5.18 The reaction between two α -SiC particles and AZ91 at 800°C for 8 hours with slow cooling. (a) SE and (b) BSE images of $T2-Al_2MgC_2$ formed around α -SiC. (c) Tilted SE images with (d) EBSD phase mapping. (e) EBSD phase mapping and (f) IPF-X map show the two single crystal α -SiC and polycrystal $T2-Al_2MgC_2$.

Figure 5.12 to Figure 5.18 have demonstrated the chemical reaction between α -SiC and the AZ91 melt results in Mg_2Si and $\text{T2-Al}_2\text{MgC}_2$. This observed reaction is similar to the works in the past literature [52–54,70]. This chemical reaction can be written as Eq. (5.5).



The $\text{T2-Al}_2\text{MgC}_2$ phase from the reaction product is likely to be the phase responsible for grain refinement after adding α -SiC. However, note that $\text{T2-Al}_2\text{MgC}_2$ with an OR with α -Mg was difficult to find in the gravity cast samples because of the protuberant α -SiC particles.

5.3.6. Comparison of lattice disregistry between phases

Sections 5.3.3, 5.3.4, and 5.3.5 identified $\text{T2-Al}_2\text{MgC}_2$ as the reaction product between the carbon-based additives (graphite, diamond and α -SiC) and the AZ91 melt for the case of stirring at 685 °C followed by gravity casting. $\text{T2-Al}_2\text{MgC}_2$ was measured to have the basal-to-basal OR with α -Mg in Eq. (5.6) (repeated from earlier for ease of reading) in the AZ91+diamond samples.

$$\begin{aligned} \{0001\}_{\text{T2-Al}_2\text{MgC}_2} // \{0001\}_{\alpha\text{-Mg}} \\ \langle 11\bar{2}0 \rangle_{\text{T2-Al}_2\text{MgC}_2} // \langle 11\bar{2}0 \rangle_{\alpha\text{-Mg}} \end{aligned} \quad (5.6)$$

It is expected that the same OR probably existed in the AZ91+graphite and AZ91+ α -SiC casting but this was not proved here. Next, the potency of $\text{T2-Al}_2\text{MgC}_2$ as the nucleant for α -Mg compared with other potential phases is considered.

The nucleant for α -Mg in carbon inoculation has been proposed as Al_4C_3 [36,48,49,51,66,146,148,154,157], α -SiC [39–41,47,64,65], and $\text{T2-Al}_2\text{MgC}_2$ [52–54,70,71,151,245], and MgO has also been identified as a nucleant for magnesium in some cases [251–253]. Figure 5.19 illustrates the crystal structures of these phases compared with HCP α -Mg. The lattice parameters of the different phases were used to calculate the Bramfitt planar disregistry [108] with Eq. (5.7), assuming the interface plane is $\{111\}$ for the cubic and

$\{0001\}$ for the hexagonal or trigonal crystal structures, with closest packed rows set to be parallel in each case. Note that these interfaces have previously been suggested between α -SiC and α -Mg [65], calculated between T2-Al₂MgC₂ and α -Mg [182], and measured between MgO and α -Mg in AZ91 [251].

The results of the lattice disregistries are shown in Table 5.3. These results indicate the following points: (i) diamond particles are not possible to become potent nucleants; (ii) α -SiC particles have the lowest lattice disregistry but liquid+ α -SiC interfaces are unstable in liquid AZ91 and α -SiC particles are likely to have a layer of T2-Al₂MgC₂ on their surface; (iii) Al₄C₃ has lower lattice disregistry than T2-Al₂MgC₂ but Al₄C₃ was not found in any gravity cast samples (Al₄C₃ was only found after holding at 800 °C or higher followed by relatively slow cooling in Chapter 4). (iv) MgO has a slightly worse lattice match than T2-Al₂MgC₂. (v) T2-Al₂MgC₂ has an acceptably low lattice disregistry for it to be a nucleant for α -Mg. T2-Al₂MgC₂ seems to be the heterogenous nucleant based on the repeated measurement of this OR between T2-Al₂MgC₂ and α -Mg (eg. Figure 5.9 and Figure 5.10), and the measurement in Chapter 4 that T2-Al₂MgC₂ crystals grow with $\{0001\}$ as their largest facet which provides a scaffold for α -Mg nucleation.

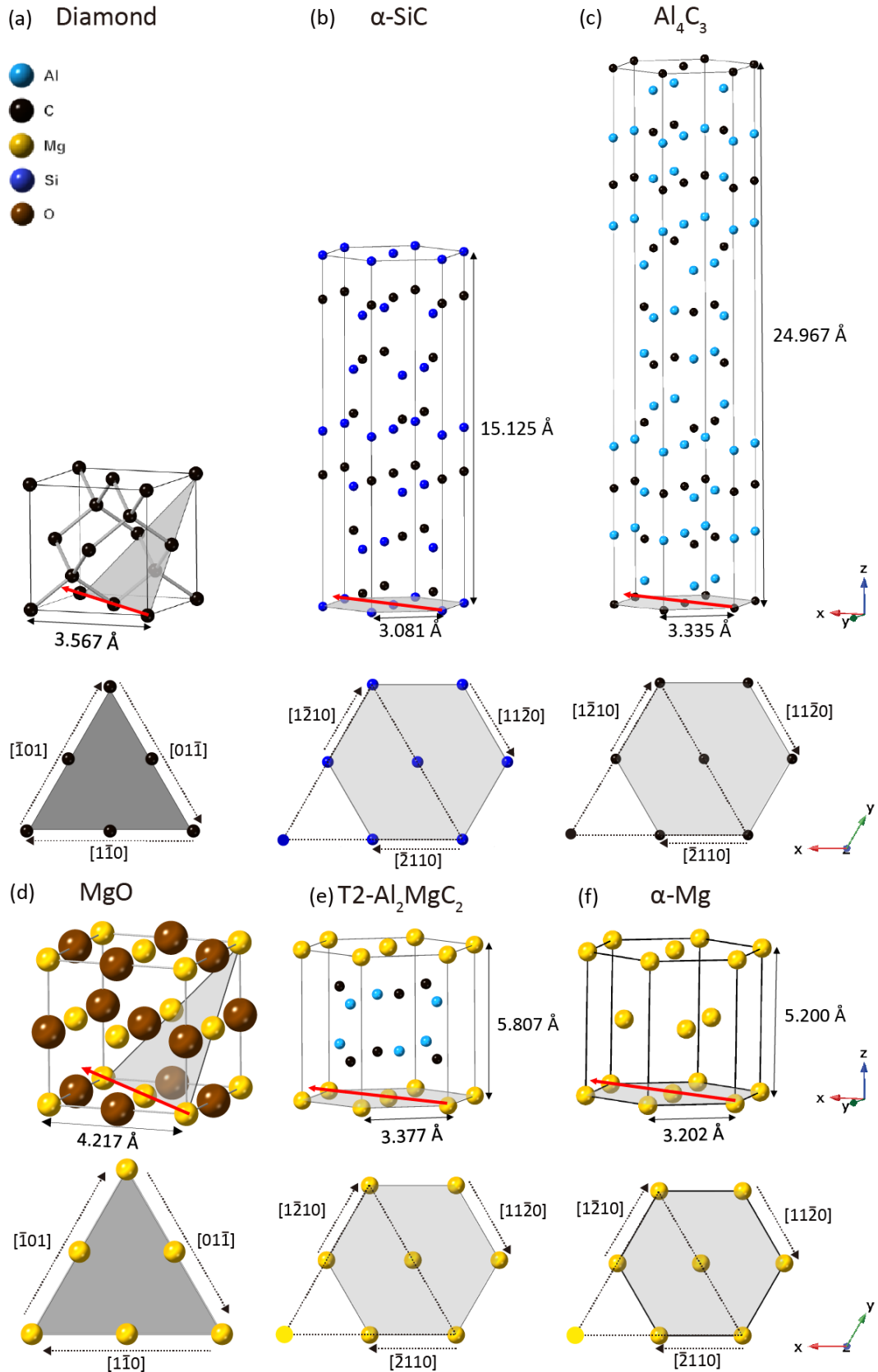


Figure 5.19 Two views of crystal structures in (a) general view and (111) plane of diamond, (b) general view and (0001) planes of α -SiC, (c) general view and (0001) planes of Al_4C_3 , (d) general view and (111) plane of MgO, (e) general view and (0001) planes of T2- Al_2MgC_2 , and (f) general view and (0001) planes of α -Mg

$$\delta_{(hkl)s}^{(hkl)n} = \frac{1}{3} \sum_{i=1}^3 \frac{|d[uvw]_n^i \cos \theta - d[uvw]_s^i|}{d[uvw]_s^i} \cdot 100\% \quad (5.7)$$

Table 5.3 The calculated lattice disregistry among the potential nucleants $\{111\}_{\text{diamond}}$, $\{0001\}_{\alpha\text{-SiC}}$, $\{0001\}_{\text{Al}_4\text{C}_3}$ and $\{0001\}_{\text{T2-Al}_2\text{MgC}_2}$ to $\{0001\}_{\alpha\text{-Mg}}$

Phase	Crystal system	Lattice parameters						Lattice disregistry with $\alpha\text{-Mg}$ (%)	Ref.
		a(nm)	b(nm)	c(nm)	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$		
$\alpha\text{-Mg}$	Hexagonal	0.3202	0.3202	0.5200	90	90	120	-	[168]
Diamond	Cubic	0.3567	0.3567	0.3567	90	90	90	21.23	[237]
$\alpha\text{-SiC}$	Hexagonal	0.3081	0.3081	1.512	90	90	120	3.78	[170]
Al_4C_3	Trigonal	0.3335	0.3335	2.4967	90	90	120	4.15	[173]
T1- Al_2MgC_2	Hexagonal	0.3402	0.3402	1.2292	90	90	120	6.25	[174,179]
T2- Al_2MgC_2	Trigonal	0.3377	0.3377	0.5807	90	90	120	5.46	[169,179]
MgO	Cubic	0.4217	0.4217	0.4217	90	90	90	6.87	[239]

Note that Zhang et al. [111] used their edge-to-edge model to predict nucleation ORs between Al_4C_3 and $\alpha\text{-Mg}$. They calculated the OR in Eq. (5.8). However, neither this OR nor any other OR between Al_4C_3 and $\alpha\text{-Mg}$ were measured in this work, so it is not considered further.

$$\begin{aligned} &\{0002\}_{\alpha\text{-Mg}} // \{10\bar{1}2\}_{\text{Al}_4\text{C}_3} \\ &\langle 11\bar{2}0 \rangle_{\alpha\text{-Mg}} // \langle 11\bar{2}0 \rangle_{\text{Al}_4\text{C}_3} \end{aligned} \quad (5.8)$$

5.4 Conclusions

The mechanisms of grain refinement by carbon inoculation have been studied in AZ91 after adding graphite, diamond or $\alpha\text{-SiC}$ powder to the melt prior to casting.

The following points can be concluded from this study:

- All three carbon inoculation methods (graphite, diamond and $\alpha\text{-SiC}$) gave good grain refinement. The grain size was reduced to at least 50% of the original grain size.

- T2-Al₂MgC₂ phase was found in all the gravity cast samples after carbon inoculation (graphite, diamond, and α -SiC).
- After gravity casting, the T2-Al₂MgC₂ phase was small and not easily characterised by the SEM-based techniques. Remelting and holding samples at 800 °C for 40 hours provided enough kinetics for the T2-Al₂MgC₂ phase to grow and be studied.
- In the gravity cast AZ91+diamond samples, multiple instances of the T2-Al₂MgC₂ phase having a simple basal-to-basal OR with α -Mg were measured. The measured OR has a planar lattice disregistry of ~5%. Therefore, T2-Al₂MgC₂ is probably the heterogenous nucleant responsible for grain refinement in the carbon inoculation method.

Chapter 6. Eutectic solidification of $\text{Mg}_{17}\text{Al}_{12}$ from divorced to coupled growth

6.1 Introduction

The previous two chapters explored how carbides form in AZ91 and the effects of carbides on the grain refinement magnesium. The grain refinement effect was caused by the $\text{T2-Al}_2\text{MgC}_2$ phase which led to a more than 50% reduction in grain size in carbon inoculated samples. As α -Mg grains grow during the solidification sequence, their morphology is determined by the combination of the grain size, branching and the secondary dendrite arm spacing (SDAS) [254]. In the absence of forced convection, the SDAS is driven by the local solidification time [194] and this has been studied in a number of past works for AZ91 [193,195–199]. When AZ91 reaches around 435°C , the $\text{L} \rightarrow \alpha\text{-Mg} + \text{Mg}_{17}\text{Al}_{12}$ eutectic reaction begins and the formation of $\text{Mg}_{17}\text{Al}_{12}$ is expected to depend on the microstructure of the pre-solidified α -Mg grains as well as on the local solidification conditions.

The $\text{Mg}_{17}\text{Al}_{12}$ morphology is known to depend on the Al content inside the alloy; $\text{Mg}_{17}\text{Al}_{12}$ in AZ91 usually presents as partially divorced eutectic morphology [210]. Past work has shown that the partially divorced morphology can be changed by the cooling rate, Al content and Zn content [78]. However, there is limited understanding of how the $\text{Mg}_{17}\text{Al}_{12}$ morphology depends on the pre-solidified α -Mg microstructure.

In this chapter, the $\alpha\text{-Mg} + \text{Mg}_{17}\text{Al}_{12}$ eutectic growth microstructure is investigated to determine how it depends on (i) the prior α -Mg dendrite morphology and (ii) the eutectic solidification condition.

6.2 Methods

6.2.1. Solidification experiments

Six casting/cooling methods were applied to study the dependence of the eutectic morphology on (i) the α -Mg grain size, (ii) the secondary dendrite arm spacing (SDAS), and (iii) the cooling rate during eutectic solidification. Methods 1 and 2 applied a relatively high cooling rate throughout solidification. Methods 3 and 5 applied two slower cooling rates throughout solidification. Methods 4 and 6 used two-stage solidification processes to decouple the cooling rate during α -Mg dendrite growth from the cooling rate during eutectic solidification.

- Method 1: gravity casting without grain refiner addition.
- Method 2: gravity casting with carbon inoculation (50 μm diamond particles used in Chapter 4 and 5) for grain refinement.
- Method 3: slow cooling by natural air cooling of liquid in a crucible. (no grain refiner)
- Method 4: interrupted solidification by first natural air cooling followed by an abrupt increase in cooling rate at 560 °C through immersion in water. (no grain refiner)
- Method 5: forced air cooling of liquid in a crucible using compressed air. (no grain refiner)
- Method 6: the edge of the sample from Method 3 was reheated to 450 °C for 30 minutes followed by an abrupt increase in cooling rate through immersion in water. (no grain refiner)

Methods 1 and 2 used gravity cast bars from Chapters 4 and 5, whose method is described in detail in Chapter 3. For the carbon inoculated sample in Method 2, the 50 μm diamond (Mozime Ltd.) casting was used as it had the smallest grain size of all grain refiner additions

in this thesis. To obtain a cooling curve for the gravity cast specimens, an additional casting was produced in which a K-type thermocouple was placed in the centre of the mould cavity at 5 cm above the bottom of the cavity prior to casting with the same casting parameters. All subsequent microstructure analysis was performed at the same position.

In Methods 3 to 5, 90 g of AZ91 was melted in a boron nitride (BN) coated mild steel cylindrical crucible with 55 mm height, 40 mm diameter and 2 mm thickness under a cover gas of tetrafluoroethane with CO₂. A K-type thermocouple was inserted near the centre height of the melt and the alloy was then held at 700 °C for 20 minutes. Temperature data was recorded at 10 datapoints per second. Three types of cooling were then imposed. In Method 3, cooling was initiated by removing the furnace and allowing the sample to cool naturally in air, giving a cooling rate of $\sim 1 \text{ Ks}^{-1}$ in the liquid prior to nucleation of α -Mg. In Method 4, the furnace was removed and the sample cooled naturally in air until 560 °C was reached (in the α -Mg plus liquid two-phase region) and the cooling rate was then abruptly increased by immersing the crucible into an ice-water bath. In Method 5, the furnace was removed and compressed air cooling was applied around the crucible, giving a cooling rate of $\sim 3 \text{ Ks}^{-1}$ in the liquid prior to nucleation of the α -Mg.

In Method 6, a small cuboid (5x5x5 mm) was cut from the edge of a slow cooling sample in Method 3, painted in boron nitride paste to reduce oxidation, and was then partially remelted and held isothermally at 450 °C for 30 minutes. The sample was then quenched abruptly from 450 °C directly into water to achieve a high cooling rate throughout eutectic solidification. The small sample volume and quench from 450 °C was selected to promote a higher eutectic cooling rate than in any of the samples with methods 1-5.

Different batches of AZ91 were used for methods 1-2 and methods 3-5. The compositions are given in Table 6.1.

Table 6.1 Chemical compositions of the AZ91 magnesium alloys used in this study were analysed by ICP-OES.

Method	Alloy	Composition (wt%)									
		Mg	Al	Zn	Mn	Cu	Si	Ni	Fe	Be	Sr
1-2	AZ91	Bal.	8.95 ±0.55	0.72 ±0.16	0.19 ±0.02	0.001	0.039	<0.001	<0.001	0.007 ± 0.002	-
3-6	AZ91	Bal.	8.57	0.74	0.15	<0.002	0.01	0.003	0.002	-	<0.001

6.2.2. Characterisation

Cross-sections were prepared by grinding with 2000 and 4000 grit size SiC papers followed by polishing with colloidal silica suspension in ethanol as a lubricant. Analytical scanning electron microscopy (SEM) was performed using a Zeiss Sigma-300. For secondary electron (SE) and backscattered electron (BSE) images, an accelerating voltage of 20 kV and a working distance of 12 mm were used. Electron backscattered diffraction (EBSD) was conducted with a BRUKER e-FlashHR EBSD detector using 20 kV accelerating voltage, 15 mm working distance, a 120 µm aperture and the sample tilted to 70°. EBSD data was analysed and visualised using Bruker Esprit 2.1 software and the MTEX toolbox in Matlab.

Samples were selectively etched to reveal the 3-D morphology of Mg₁₇Al₁₂ using a solution of 9 vol% acetic acid in water for 10-20 min similar to Ref. [34]. These samples were imaged in SE mode.

To reveal the α-Mg grain structure, samples were etched with a solution containing 1 ml glacial acetic acid, 44 ml distilled water and 156 ml absolute ethanol similar to Ref. [241]. After etching, nitrogen gas was used to dry the surface for a few seconds. Humid air was then applied for one second in the final step. Microstructures were imaged using polarised light optical microscopy (Olympus BX51). The α-Mg grain size (Chapter 3) and SDAS

measurements (6.2.3) were taken near the same radial and height position as the thermocouple in all samples.

6.2.3. Secondary dendrite arm spacing (SDAS) measurement

The SDAS was measured based on Ref. [255] using the following steps:

1. Polarised light optical microscopy images came from the same source as measuring grain size but with higher magnification.
2. From the images, first select grains with distinguishable dendrite structures (Figure 6.1) so that the average SDAS can be calculated reliably.
3. Figure 6.2 shows a schematic image of measuring SDAS. In Figure 6.2(a), the labelled distance is the definition of SDAS. However, it is not easy to measure SDAS from each middle of one arm to the middle of another arm so Figure 6.2(b) is the measurement method used in this thesis. The length of the measurement is taken from the beginning of one arm to the beginning of the boundary in another arm.
4. The average SDAS is calculated from the length of drawn lines divided by the number of arms crossed. At least 20 lines were drawn in each sample and the error bars were calculated from 95% confidence interval (Eq.(3.1)). Measurements were continued until the RA value was lower than 10% (Eq. (3.2)).

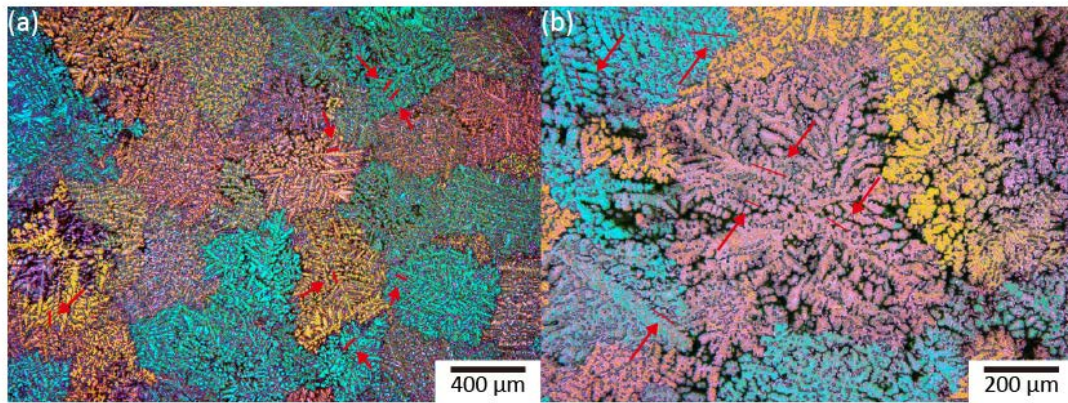


Figure 6.1 (a) Example of SDAS measurement on a typical region of gravity cast AZ91 and (b) a higher magnification on the measurement of SDAS.

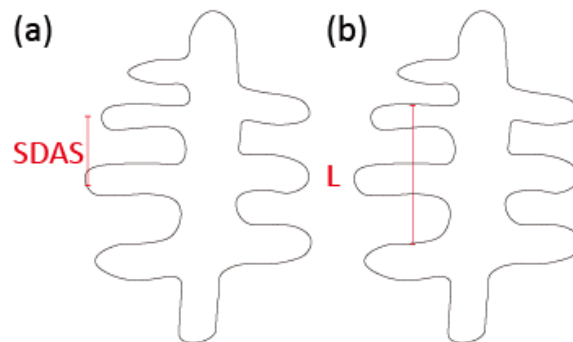


Figure 6.2 (a) The definition of SDAS and (b) an example of measuring average SDAS as taking length, L , divided by the number of secondary dendrite arms, n . Here $n=2$ but would typically be 2 to 6.

6.2.4. Eutectic spacing measurement

The measurement of eutectic spacing in the complex partially-divorced α -Mg+Mg₁₇Al₁₂ eutectic is more difficult to define and measure than in a regular rod or lamellar eutectic [256] because the morphology and spacing of Mg₁₇Al₁₂ in AZ91 does not have regular shapes. Therefore, a definition of eutectic spacing is required for the partially-divorced Mg+Mg₁₇Al₁₂ eutectic. The following approach was used here:

1. BSE SEM images were taken at high magnification of at least 1000x with working distance of 11 mm.

2. Lines were drawn across partially divorced regions as shown in Figure 6.3. Due to the irregular shapes of $\text{Mg}_{17}\text{Al}_{12}$, the lines were drawn with a direction across the width of the eutectic region unless they were in the conjunction region of $\text{Mg}_{17}\text{Al}_{12}$ between three α -Mg grains. An example of a conjunction region is shown in Figure 6.3. Here, multiple lines are drawn crossing each other due to the undetermined width directions. Multiple lines were drawn with a 1 μm gap in between which created at least 50 lines in each image of every sample. Two eutectic morphologies were considered here: (1) when the line crossed the divorced eutectic region (no α -Mg islands), the number of α -Mg would be zero so the eutectic spacing was equal to the length of the line, and (2) if the line crossed the partially divorced eutectic region such as three α -Mg islands, then the eutectic spacing would be the length of the line divided by four (Eq. (6.1)).
3. The lengths of each line were measured by ImageJ. The average eutectic spacing of each line was calculated from Eq. (6.1). The overall average eutectic spacing was the mean of more than 50 lines of eutectic spacing. Error bars were calculated from the 95% confidence interval (Eq. (3.1)).

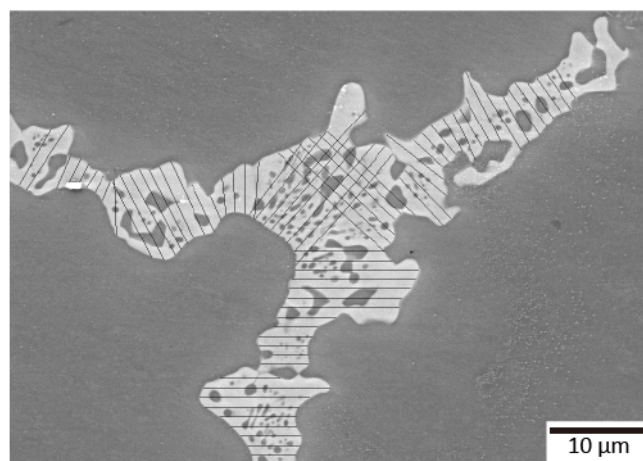


Figure 6.3 Eutectic spacing measurement on a typical partially divorced $\text{Mg}_{17}\text{Al}_{12}$ in an interrupted solidification sample.

$$\text{Average eutectic spacing} = \frac{\text{Length of the line}}{\text{number of } \alpha\text{-Mg islands} + 1} \quad (6.1)$$

6.2.5. Measurement of volume fraction of α -Mg embedded inside $\text{Mg}_{17}\text{Al}_{12}$

The volume fraction of α -Mg embedded inside $\text{Mg}_{17}\text{Al}_{12}$ was measured on SEM-BSE image using ImageJ [243]. The area fraction of $\text{Mg}_{17}\text{Al}_{12}$ in 2D microstructure can be considered as the volume fraction of the sample in 3D due to the stereology [257] (provided the measurement area spans many α -Mg grains) since the equiaxed morphology results in no significant directionality in the microstructure. The method of measuring the volume fraction involved the following steps:

1. Image processing of the BSE images was done in ImageJ. First, the outer boundary of the $\text{Mg}_{17}\text{Al}_{12}$ was selected by the tracing tool, and the brush tool was used to make sure the boundary was inclusive (Figure 6.4(a)).
2. When only $\text{Mg}_{17}\text{Al}_{12}$ and embedded α -Mg were selected, the area of $\text{Mg}_{17}\text{Al}_{12}$ could be distinguished by thresholding in a binary image as shown in Figure 6.4(b). The area of the $\text{Mg}_{17}\text{Al}_{12}$ was measured from the selected area.
3. The selection of the embedded α -Mg was done by the same method. However, the boundary of the $\text{Mg}_{17}\text{Al}_{12}$ was included due to the same grey value range (Figure 6.4(c) which required further processing steps).
4. Thus, the area of the α -Mg was defined manually and the α -Mg in the final image (Figure 6.4(d)) was measured.
5. At least 20 images were analysed in each sample. The volume fraction of α -Mg embedded inside $\text{Mg}_{17}\text{Al}_{12}$ was the weighted average of volume fraction from each image.

6. In order to minimise measurement bias [258], the error bar of the volume fraction of α -Mg embedded within $\text{Mg}_{17}\text{Al}_{12}$ was calculated by the 95% confidence in Eq. (3.1).

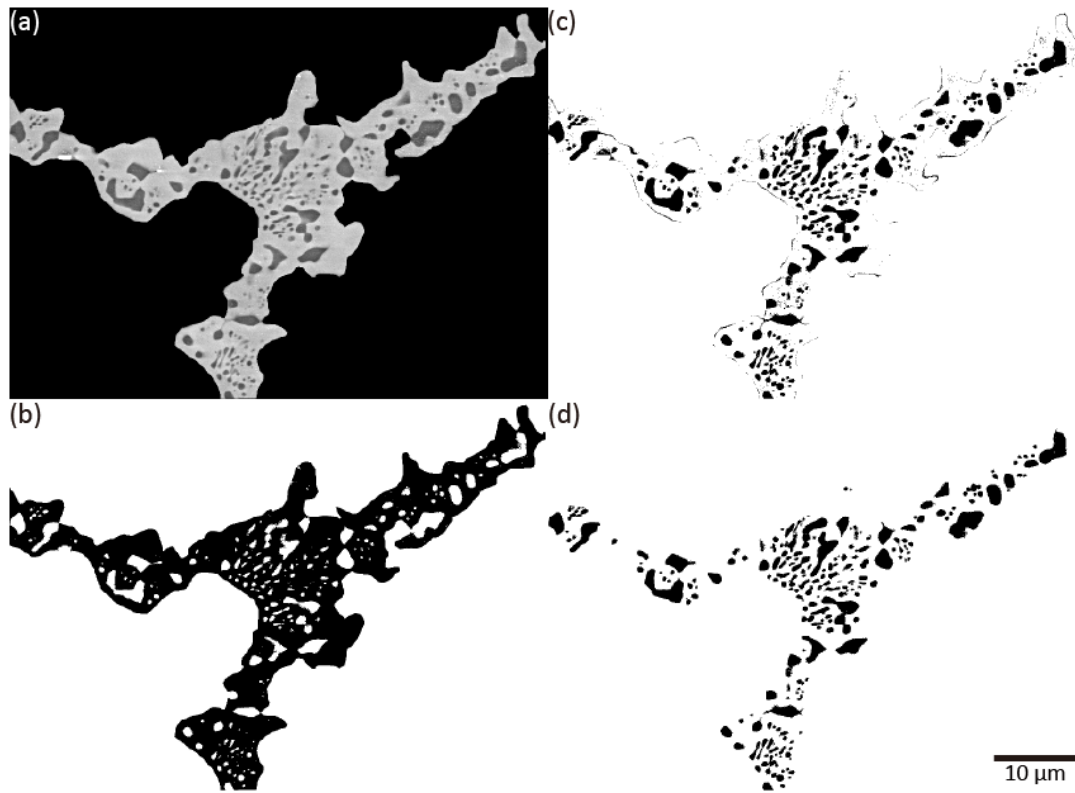


Figure 6.4 Steps in measuring the volume fraction of α -Mg embedded within $\text{Mg}_{17}\text{Al}_{12}$. (a) BSE image of a typical extracted region of an interrupted solidification sample. (b) The area of $\text{Mg}_{17}\text{Al}_{12}$ was measured through after binary thresholding. (c) The opposite of binary values of (b) in the remaining area. (d) is the clear α -Mg without any boundary of $\text{Mg}_{17}\text{Al}_{12}$.

6.3 Results and Discussion

6.3.1. α -Mg dendrite morphology

The different cooling conditions and grain refinement in this work generated a wide range of equiaxed α -Mg microstructures. The morphology of equiaxed grains produced by solidification can be described by the ratio between the grain size and the SDAS [254], where ratios greater than four have equiaxed dendritic morphology, ratios between four and two have rosette morphology, and a ratio less than two can be defined as a globular shape [254]. In this work, the combined grain sizes and SDAS (Figure 6.5) resulted in morphologies in the equiaxed dendritic and rosette shape regimes. The morphologies from gravity casting, slow

cooling, and interrupted solidification produced the equiaxed dendrites in Figure 6.5(1), (2), (3i), (3ii), (4i). The fast-cooling method produced the rosette shaped morphology in Figure 6.5(5i).

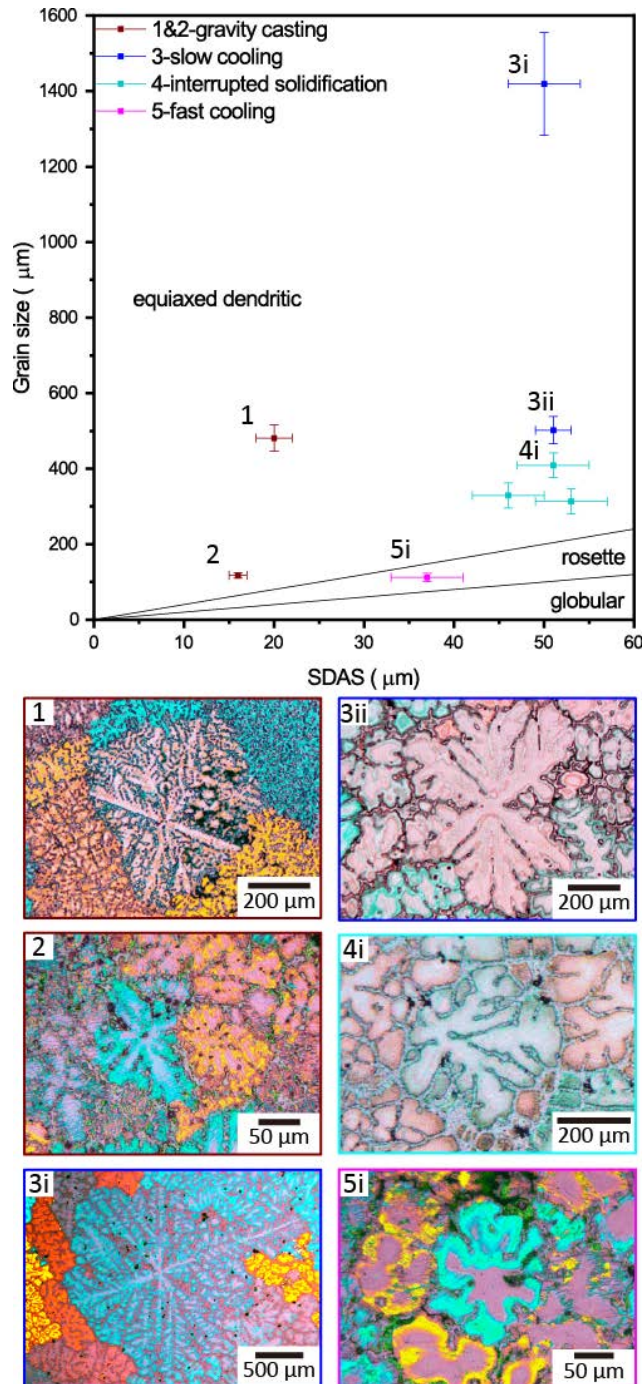


Figure 6.5 Equiaxed α -Mg grain morphologies plotted in a grain size vs SDAS map, and colour etched optical micrographs of six samples. (1) gravity cast. (2) gravity cast with grain refinement. (3i) slow cooled with large grain size. (3ii) slow cooled with smaller grain size. (4i) interrupted solidification sample. (5i) forced air cooled.

Typical cooling curves from the four cooling methods are plotted in Figure 6.6(a). Three cooling rates were measured from each curve as shown in Figure 6.6(b) and given in Table 6.2. The liquid cooling rate ($\dot{T}_L$) was defined as the mean value from 650-630°C shortly before α -Mg nucleates, and the eutectic cooling rate ($\dot{T}_E$) was defined as the mean value from 450-430°C shortly before the start of the eutectic reaction, and the average cooling rate during α -Mg solidification ($\Delta T/\Delta t$) was defined as the α -Mg freezing range ($T_i - T_E$) divided by the α -Mg freezing time ($t_i - t_E$) as shown in Figure 6.6(b). This definition was used for the average cooling rate during solidification partly because the actual end of solidification (t_f , T_f) is difficult to identify accurately [194] and because the use of other definitions including from (t_i , T_i) until the end of eutectic recalescence gave similar average cooling rate values.

From Table 6.2, it can be seen that the five casting/cooling methods gave liquid cooling rates spanning two orders of magnitude from 0.88 – 94K s⁻¹ and average cooling rates ranging from 0.5 – 20.5 Ks⁻¹. A key feature of the experimental approach is that interrupted solidification decoupled the liquid cooling rate (which plays an important role in the α -Mg grain size) from the eutectic cooling rate (which affects the α -Mg+Mg₁₇Al₁₂ eutectic reaction). For example, the interrupted solidification samples in Table 6.2 had significantly lower liquid cooling rates than the forced-air cooled sample but higher eutectic cooling rates. This feature of the experiment will be used later to explore the dependence of the partially divorced eutectic morphology on the pre-existing α -Mg microstructure and the eutectic cooling conditions.

Table 6.2 Summary of cooling rates, grain size and SDAS from the five casting/cooling: methods: 1-5. $\Delta T/\Delta t$ =average cooling rate, $\dot{T}_L$ =liquid cooling rate, and $\dot{T}_E$ =eutectic cooling rate each defined in Figure 6.6(b)

Cooling method		$\Delta T/\Delta t$	$\dot{T}_L$	$\dot{T}_E$	α -Mg grain size	α -Mg SDAS	Solidification study	Heat treatment study
		[Ks ⁻¹]	[Ks ⁻¹]	[Ks ⁻¹]	[μ m]	[μ m]		
Gravity casting	1	20.5	93.5	16.88	481±35	20±2	✓	✓
Gravity casting + GR	2	20.5	93.5	16.88	117±7	16±1	✓	✓
Slow cooling	3i	0.49	1.06	0.54	1419±136	50±4	✓	✓
Slow cooling	3ii	0.49	1.12	0.54	502±36	51±2	✓	✓
Interrupted	4i	1.11	0.88	3.89	409±33	51±4	✓	✓
Interrupted	4ii	1.27	0.92	4.19	313±33	53±4	✓	–
Interrupted	4iii	0.85	0.91	4.65	329±33	46±4	✓	–
Interrupted	4iv	1.33	0.77	1.33	423±26	49±5	✓	–
Interrupted	4v	0.91	0.84	0.91	653±80	41±2	✓	–
Fast cooling	5i	2.16	3.55	2.34	112±11	37±4	✓	✓
Fast cooling	5ii	2.30	3.24	2.30	148±10	38±2	✓	–

The SDAS data in Table 6.2 was investigated with the widely used relationship between SDAS and the local freezing time (t_E - t_i) in Eq. (6.2) [194].

$$\lambda_2 = 5.5(M(\Delta t))^{1/3} \quad (6.2)$$

where λ_2 is the SDAS and Δt is the local freezing time. M can be expressed as Eq. (6.3a)

[194] for binary alloys and as Eq. (6.3b) [259] for multicomponent alloys such as Mg-Al-Zn.

$$M = \frac{-\Gamma D \ln \left(\frac{C_f}{C_0} \right)}{m(1 - k)(C_f - C_0)} \quad (6.3a)$$

$$M = \frac{-\Gamma}{\sum_{j=1}^n m_j(1 - k_j)(c_{f,j} - c_{o,j})/D_j} \ln \left[\frac{\sum_{j=1}^n m_j(1 - k_j)c_{f,j}/D_j}{\sum_{j=1}^n m_j(1 - k_j)c_{o,j}/D_j} \right] \quad (6.3b)$$

Where Γ is the Gibbs-Thomson coefficient, D is the diffusion coefficient of solute in the liquid, C_f is the final liquid composition, C_0 is the initial liquid composition, m is the liquidus slope, k is the partition coefficient, and the subscript j indicates the type of solute (Al or Zn here).

Eq. (6.2) can be restated in terms of the average cooling rate during solidification using Eq. (6.4) [201] where ΔT is the freezing range for Scheil solidification.

$$\lambda_2 = 5.5(M\Delta T)^{\frac{1}{3}}\left(\frac{\Delta T}{\Delta t}\right)^{\frac{-1}{3}} \quad (6.4)$$

Using the parameters in Table 6.3 with Eq. (6.3b)(6.3a), the value of M can be calculated as $3.78 \times 10^{-18} \text{ m}^3 \text{ s}^{-1}$ for AZ91. With the known freezing range, Eq. (6.4) can be calculated as

$$\lambda_2 = 47.28\left(\frac{\Delta T}{\Delta t}\right)^{\frac{-1}{3}} \text{ with slope in } \mu\text{m s}^{\frac{-1}{3}} \text{ K}^{\frac{1}{3}}.$$

Table 6.3 Thermophysical property parameters used for the solidification of AZ91

Parameter	Symbol	Value	Unit	Ref.
Solid-liquid interfacial energy	γ	0.065	Jm^{-2}	[260]
Heat of fusion	ΔH_v	5.5×10^8	Jm^{-3}	[260]
Melting point of pure Mg	T_m	923	K	-
Gibbs-Thomson coefficient	Γ	1.09×10^{-7}	Km	
Diffusion coefficient for Al in liquid	D_{Al}	3×10^{-9}	$\text{m}^2 \text{s}^{-1}$	[261]
Diffusion coefficient for Zn in liquid	D_{Zn}	8×10^{-9}	$\text{m}^2 \text{s}^{-1}$	[262,263]
Liquidus slope for Al in Mg-Al	m_{Al}	-6.87	$\text{K wt}\%^{-1}$	[264]
Liquidus slope for Zn in Mg-Zn	m_{Zn}	-6.04	$\text{K wt}\%^{-1}$	[264]
Partition coefficient for Al in Mg-Al	k_{Al}	0.31	$\text{wt}\%/\text{wt}\%$	[202]
Partition coefficient for Zn in Mg-Zn	k_{Zn}	0.12	$\text{wt}\%/\text{wt}\%$	[265]
Initial composition of Al in liquid	$C_{0,Al}$	8.95	$\text{wt}\%$	-
Initial composition of Zn in liquid	$C_{0,Zn}$	0.72	$\text{wt}\%$	-
Final composition of Al in liquid	$C_{f,Al}$	30.77	$\text{wt}\%$	[202]
Final composition of Zn in liquid	$C_{f,Zn}$	3.6	$\text{wt}\%$	[202]
Freezing range (Scheil)	ΔT	170	K	[202]
Volume fraction of eutectic	g_e	0.137	$\text{vol}\%$	[202]

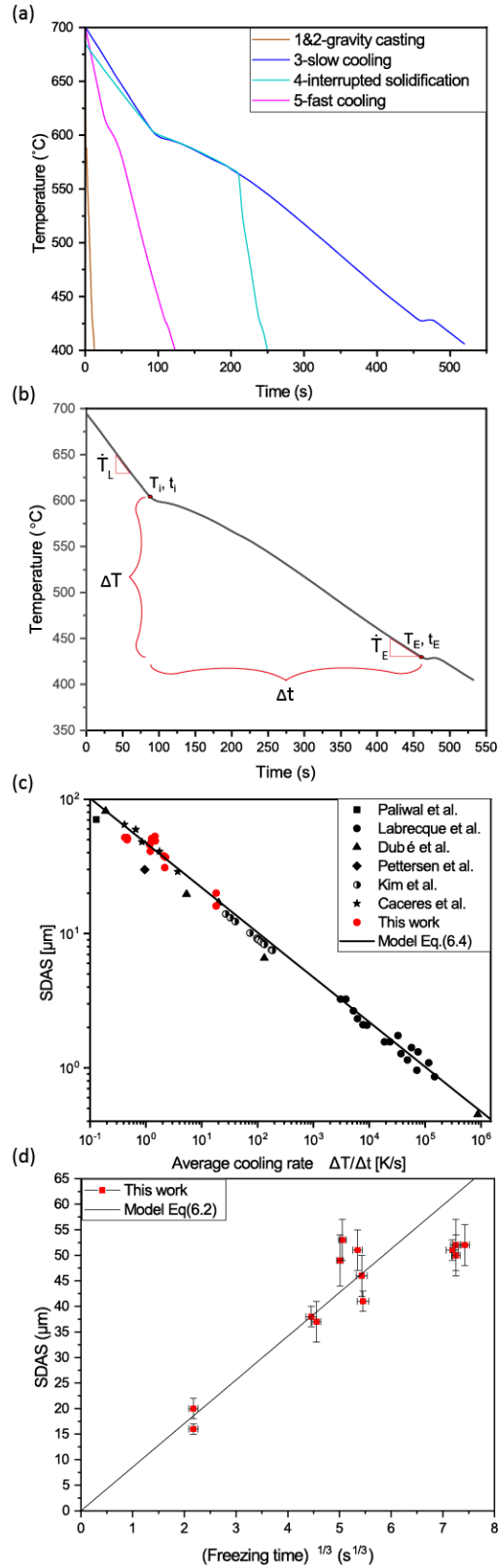


Figure 6.6 (a) cooling curves from four casting/cooling methods. (b) definitions used when extracting data from cooling curves. (c) measured SDAS versus the average cooling rate during solidification (red) compared with literature data (black) and analytical Eq. (6.4). (d) measured SDAS versus $(\text{the freezing time})^{1/3}$ and analytical Eq.(6.2).

The four casting/cooling conditions generated microstructures with α -Mg SDAS varying from 15 to 55 μm . The analytical model in Eq. (6.4) linking SDAS to the average cooling rate is plotted in Figure 6.6(c) on a log-log scale using the calculated value for M along with the experimental data from Table 6.2 and past literature values [193,195–199]. In Figure 6.6(c), the analytical model is in a good agreement with the combination of all measured SDAS values. Figure 6.6(d) is a plot of the analytical model in Eq.(6.2) linking SDAS to the freezing time compared with the experimental data from Table 6.2. The analytical model used the calculated value for M without any fitting parameters. The model is in reasonable agreement with the measurements over the range studied: 15 to 55 μm . In Figure 6.6(d), the horizontal error bars show the difference between two definitions ($\frac{T_i-T_E}{t_i-t_E}$ and $\frac{T_i-T_f}{t_i-t_f}$) for the solidification time, highlighting that this does not have a significant influence.

While the SDAS measurements could be reasonably explained from the local freezing time, the factors affecting the α -Mg grain size were more complex. Referring to the samples labelled as 1-5i in Figure 6.5, the grain refinement in the gravity castings from 1 to 2 was due to carbon inoculation, and the small grain size of 5i was due to the relatively fast cooling rate. However, sample 3i and 3ii had the same applied solidification conditions and similar SDAS but resulted in very different grain sizes. The origin of this is unclear, but it is useful for this study as it provided a wide range of α -Mg grain size and morphology for study.

6.3.2. Crystallographic aspects of eutectic nucleation and growth

Figure 6.7(a)-(h) overviews typical results on the crystallographic relationship between α -Mg and $\text{Mg}_{17}\text{Al}_{12}$ in gravity cast samples at low magnification. Figure 6.7(a)-(d) was cast without grain refiner and Figure 6.7(e)-(h) was grain refined by carbon inoculation. In these two cases, the number density of growing α -Mg dendrites differs substantially (Figure 6.5) but the heat flow conditions (temperature gradients and isotherm velocities) are similar during the eutectic reaction.

Figure 6.7(a) and (e) are backscattered electron (BSE) images where the $\text{Mg}_{17}\text{Al}_{12}$ (bright) and $\alpha\text{-Mg}$ (darker) can be clearly distinguished but the $\alpha\text{-Mg}$ grain structure is not clear. Figure 6.7(b)-(c) and (f)-(g) are EBSD inverse pole figure orientation maps from the same areas as the BSE images in Figure 6.7(a) and (e). Figure 6.7(b) and (f) show clear $\alpha\text{-Mg}$ grain refinement. In the orientation maps of $\text{Mg}_{17}\text{Al}_{12}$ in Figure 6.7(c) and (g), note that a dilation filter has been applied to the $\text{Mg}_{17}\text{Al}_{12}$ maps to increase the size of each region of $\text{Mg}_{17}\text{Al}_{12}$ for improved visualisation. The function of the dilation filter from ImageJ was to increase each pixel size in the images such as 1x1 pixel size spot could be increased to 2x2 pixel size spot. The original and dilated maps are shown side by side in the Figure 6.8 for comparison. In Figure 6.7(c) and (g), there are domains of near-constant $\text{Mg}_{17}\text{Al}_{12}$ orientation, and the white lines have been superimposed on the maps to highlight the approximate boundaries of the $\text{Mg}_{17}\text{Al}_{12}$ orientation domains. The same domain boundaries have been superimposed with the black lines on the $\alpha\text{-Mg}$ orientation maps in Figure 6.7(b) and (f). Comparing Figure 6.7(b)-(c) and (f)-(g), the $\text{Mg}_{17}\text{Al}_{12}$ orientation domain boundaries do not correlate with the $\alpha\text{-Mg}$ grain boundaries, and many $\text{Mg}_{17}\text{Al}_{12}$ domains span multiple $\alpha\text{-Mg}$ grains.

Figure 6.7(d) and (h) are SEM images in SE mode after the $\alpha\text{-Mg}$ had been selectively removed by deep etching. Note that these two images are from different regions but in the same samples, and they are at a similar magnification to Figure 6.7(a) and (e). Figure 6.7(d) and (h) confirm that the eutectic $\text{Mg}_{17}\text{Al}_{12}$ grew with an interconnected 3D skeleton which is consistent with the presence of large $\text{Mg}_{17}\text{Al}_{12}$ orientation domains in Figure 6.7(c) and (g). The shapes of the holes left by the etched $\alpha\text{-Mg}$ dendrites indicate that the $\text{Mg}_{17}\text{Al}_{12}$ has retained its 3D structure after the $\alpha\text{-Mg}$ was removed and did not fracture or collapse inwards. This interconnected 3D $\text{Mg}_{17}\text{Al}_{12}$ structure is similar to that reported previously in high pressure die cast (HPDC) AZ91 [266] but, in the present study, the $\text{Mg}_{17}\text{Al}_{12}$ microstructure is more uniform due to the simpler cooling and solidification conditions than in HPDC.

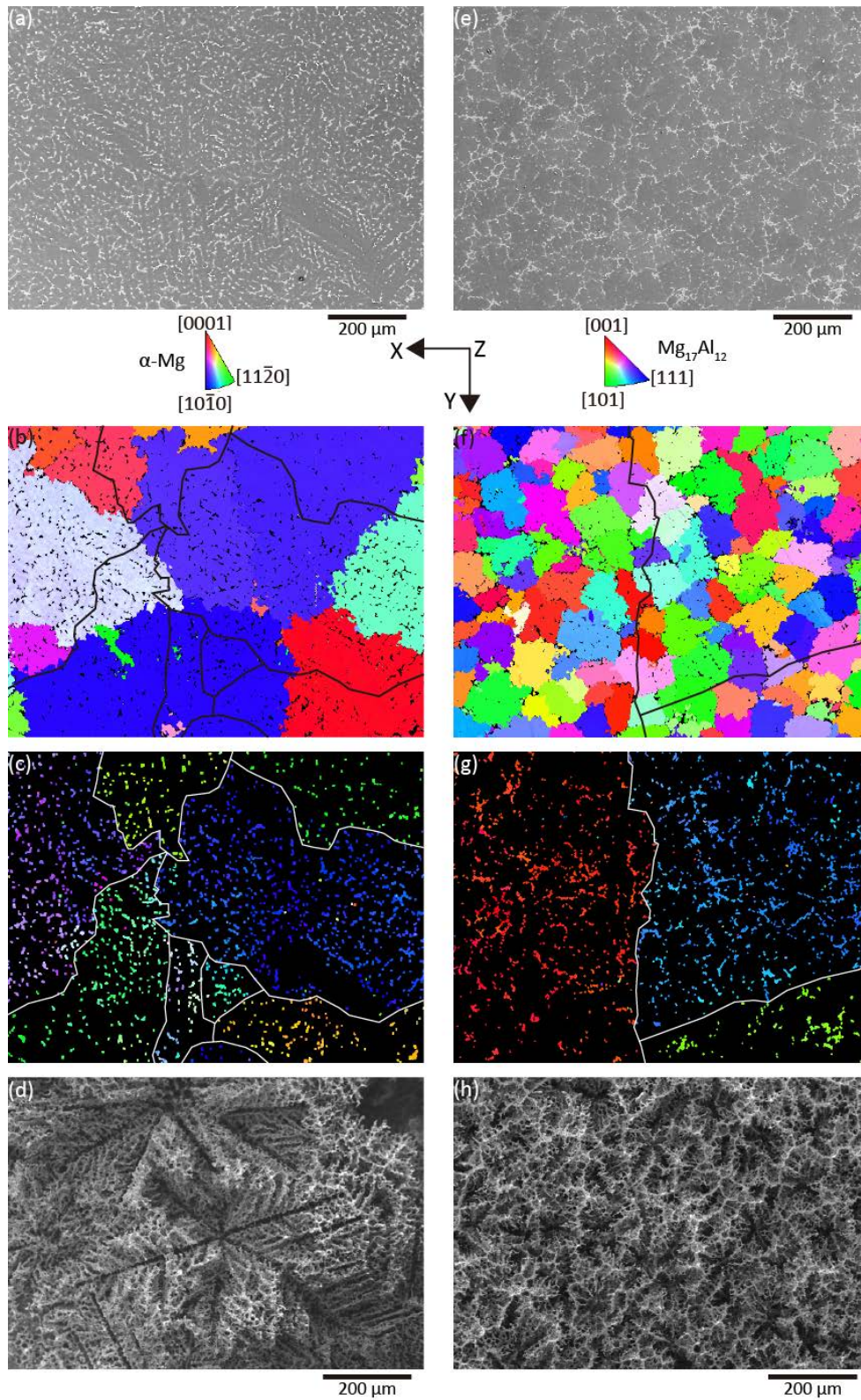


Figure 6.7 Crystallographic mapping of α -Mg grains and $\text{Mg}_{17}\text{Al}_{12}$ orientation domains. Left column: gravity cast without grain refiner. Right column: gravity cast with grain refiner. (a)&(e) BSE-SEM images. (b)&(f) EBSD IPF orientation maps of the α -Mg phase. (c)&(g) EBSD IPF orientation maps of the $\text{Mg}_{17}\text{Al}_{12}$ phase. (d)&(h) SE-SEM images after deep etching to reveal the 3D $\text{Mg}_{17}\text{Al}_{12}$ microstructure. (a-c) and (e-g) are each from the same area.

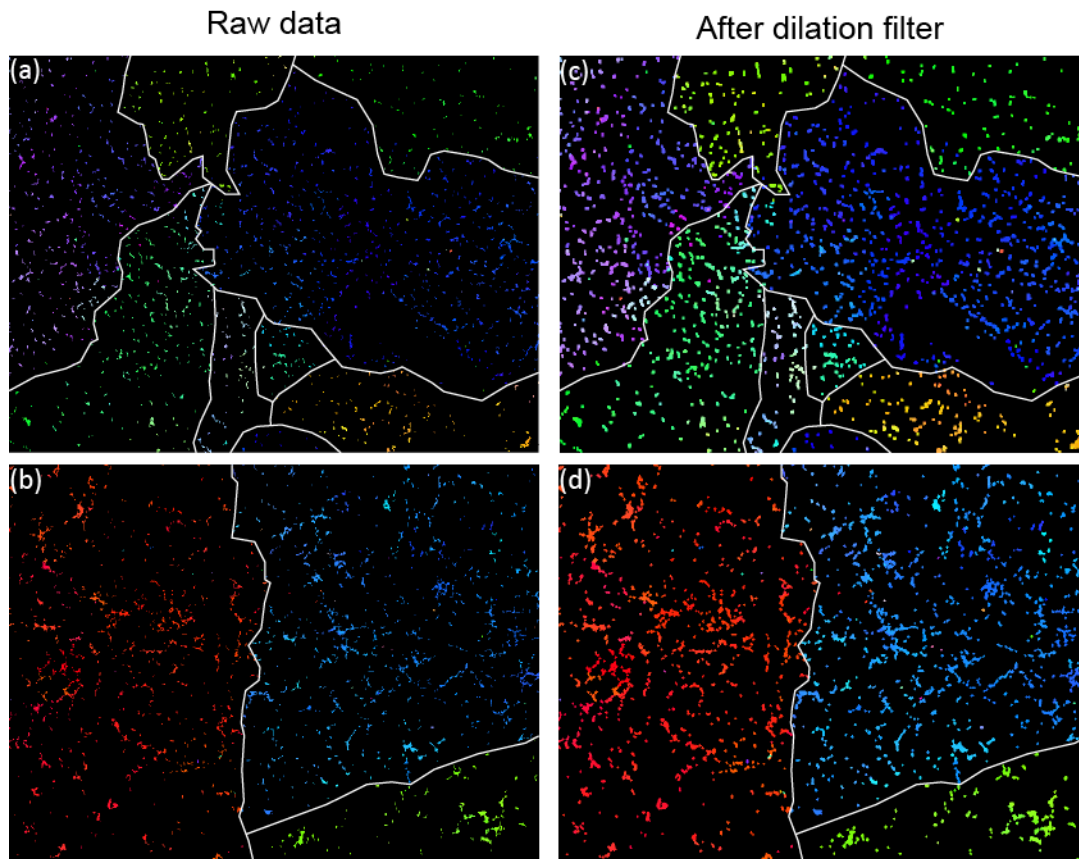


Figure 6.8 Comparison of the original and dilated EBSD IPF orientation maps of the $\text{Mg}_{17}\text{Al}_{12}$ phase shown in Figure 6.7. (a)-(b) original maps and (c)-(d) maps after the application of a dilation filter in Image J.

Figure 6.9 overviews EBSD analysis on the crystallography of partially divorced eutectic growth at higher magnification in the gravity cast samples. Both with and without grain refiner addition, the $\text{Mg}_{17}\text{Al}_{12}$ had a partially divorced eutectic morphology as shown in Figure 6.9(a) and (d) with α -Mg embedded within $\text{Mg}_{17}\text{Al}_{12}$. Note that, after equiaxed dendritic α -Mg solidification, some of the eutectic $\text{Mg}_{17}\text{Al}_{12}$ grows within dendrite envelopes and some grows between dendritic grains (Figure 6.7). Examples of both are given in Figure 6.9. Taking an example from the gravity cast AZ91 (without grain refiner), the IPF-X orientation map in Figure 6.9(c) shows a typical region of $\text{Mg}_{17}\text{Al}_{12}$ in a single dendritic α -Mg grain. The α -Mg embedded within $\text{Mg}_{17}\text{Al}_{12}$ has the same crystallographic orientation as the surrounding α -Mg dendrite. Taking an example from the carbon inoculated gravity cast AZ91, the IPF-Y orientation map in Figure 6.9(f) shows a typical region where the $\text{Mg}_{17}\text{Al}_{12}$ is at the boundary

between two dendritic α -Mg grains. Here, some embedded α -Mg regions have the orientation of one of the α -Mg grains (e.g. the purple grain) and other regions of embedded α -Mg have the orientation of the other α -Mg grain (e.g. the red grain). Additional examples are given in Figure 6.10 and Figure 6.11 of EBSD analysis on α -Mg embedded in $\text{Mg}_{17}\text{Al}_{12}$ in partially divorced eutectic regions. These show very similar results as Figure 6.9. From all EBSD maps from this study, it can be inferred that the eutectic α -Mg embedded within $\text{Mg}_{17}\text{Al}_{12}$ grew from the primary α -Mg dendrites, the eutectic α -Mg did not nucleate individually and is interconnected in 3D.

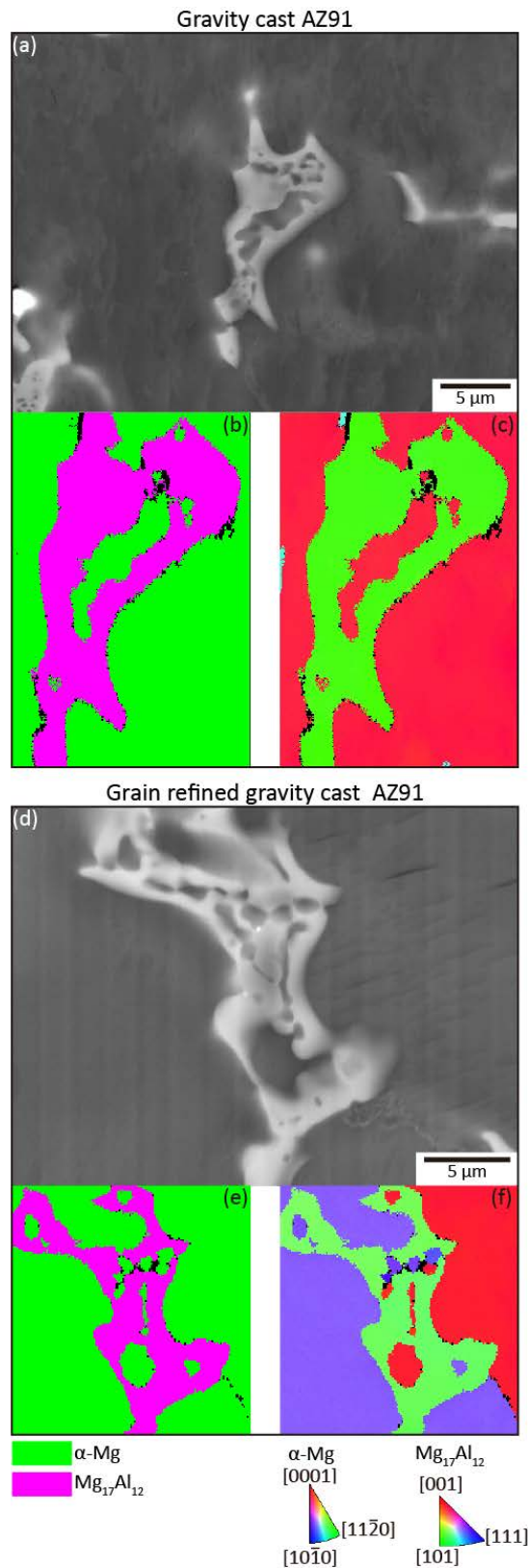


Figure 6.9 EBSD analysis of partially divorced eutectic. (a)-(c) a region between dendrite arms within a $\alpha\text{-Mg}$ grain in a gravity cast sample (Method 1). (d)-(f) a region between two $\alpha\text{-Mg}$ grains in a sample gravity cast with grain refiner (Method 2). (a)&(d) BSE-SEM images. (b)&(e) EBSD phase maps. (c)-(f): EBSD IPF orientation maps.

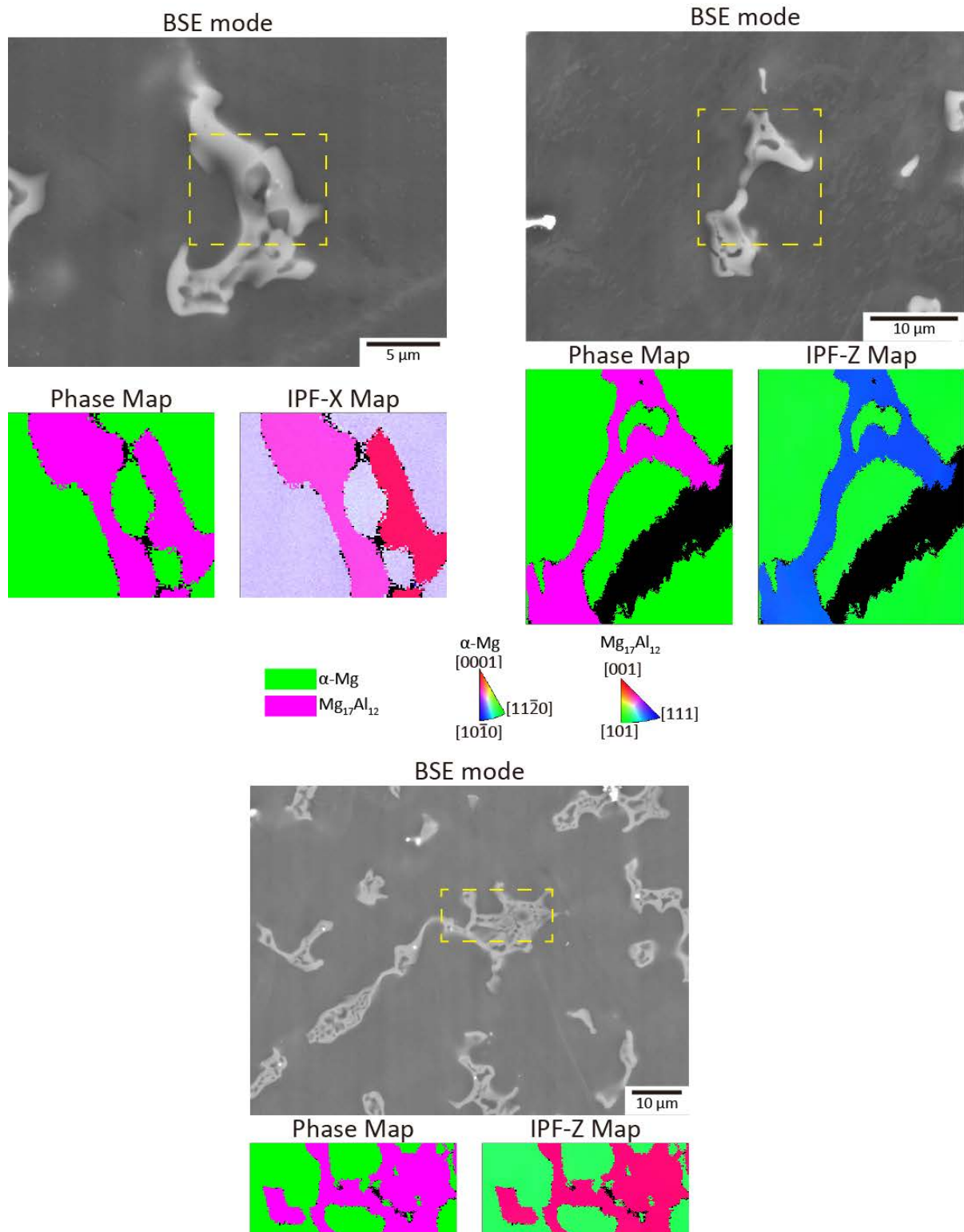


Figure 6.10 EBSD analysis of partially divorced $\text{Mg}_{17}\text{Al}_{12}$ morphologies in gravity cast AZ91 without grain refinement (Method 1).

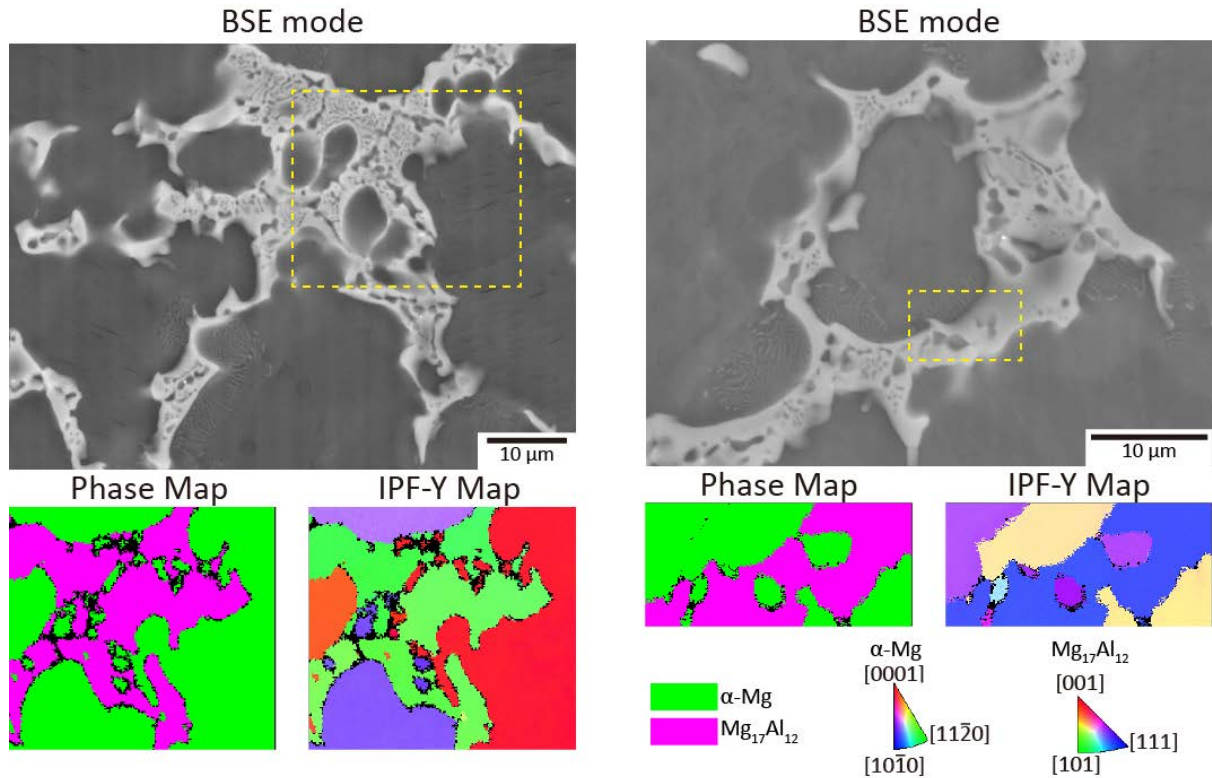


Figure 6.11 EBSD analysis of partially divorced $\text{Mg}_{17}\text{Al}_{12}$ morphologies in grain refined gravity cast AZ91 (Method 2).

At least 13 orientation relationships (ORs) have been reported between $\alpha\text{-Mg}$ and $\text{Mg}_{17}\text{Al}_{12}$ [217,218,275–277,267–274], mostly after solid state precipitation. To test for any reproducible orientation relationships (ORs) between $\alpha\text{-Mg}$ and $\text{Mg}_{17}\text{Al}_{12}$ in partially divorced eutectic growth, an approach similar to Deng et al. [278] was applied which searches for reproducible angle(s) that exist between predefined axes of the two crystals. The minimum angle between $\langle 0001 \rangle_{\alpha\text{-Mg}}$ and $\langle 100 \rangle_{\text{Mg}_{17}\text{Al}_{12}}$ and between $\langle 0001 \rangle_{\alpha\text{-Mg}}$ and $\langle 110 \rangle_{\text{Mg}_{17}\text{Al}_{12}}$ was calculated for each region of contacting $\alpha\text{-Mg}$ and $\text{Mg}_{17}\text{Al}_{12}$ using the Euler angles extracted from EBSD maps such as those in Figure 6.7 and Figure 6.9. This minimum angle was then plotted as histograms in Figure 6.12 which compiles data of contacting $\alpha\text{-Mg}$ and $\text{Mg}_{17}\text{Al}_{12}$ from 68 regions in the gravity cast sample and 406 regions in the grain refined gravity casting. Figure 6.12 also plots the distribution of misorientation angles expected of randomly oriented $\alpha\text{-Mg}$ and $\text{Mg}_{17}\text{Al}_{12}$ as datapoints at the centre of each bin. This random distribution was obtained by starting with uniform distributions of orientations on a sphere in MTEX for both $\alpha\text{-Mg}$ and

Mg₁₇Al₁₂, calculating the misorientation between 1072 randomly selected pairs of these orientations, and binning the data with the same bin width as the experimental histograms.

In Figure 6.12, there is no indication of a preferred OR between α -Mg and most regions of eutectic Mg₁₇Al₁₂ and, in the grain refined sample which has more datapoints, the experimental distribution is close to the random distribution between $\langle 0001 \rangle_{\alpha\text{-Mg}}$ and both $\langle 100 \rangle_{\text{Mg}_{17}\text{Al}_{12}}$, and $\langle 110 \rangle_{\text{Mg}_{17}\text{Al}_{12}}$ (Figure 6.12(c) and (d)). This shows that most eutectic Mg₁₇Al₁₂ does not share any reproducible OR with the surrounding α -Mg.

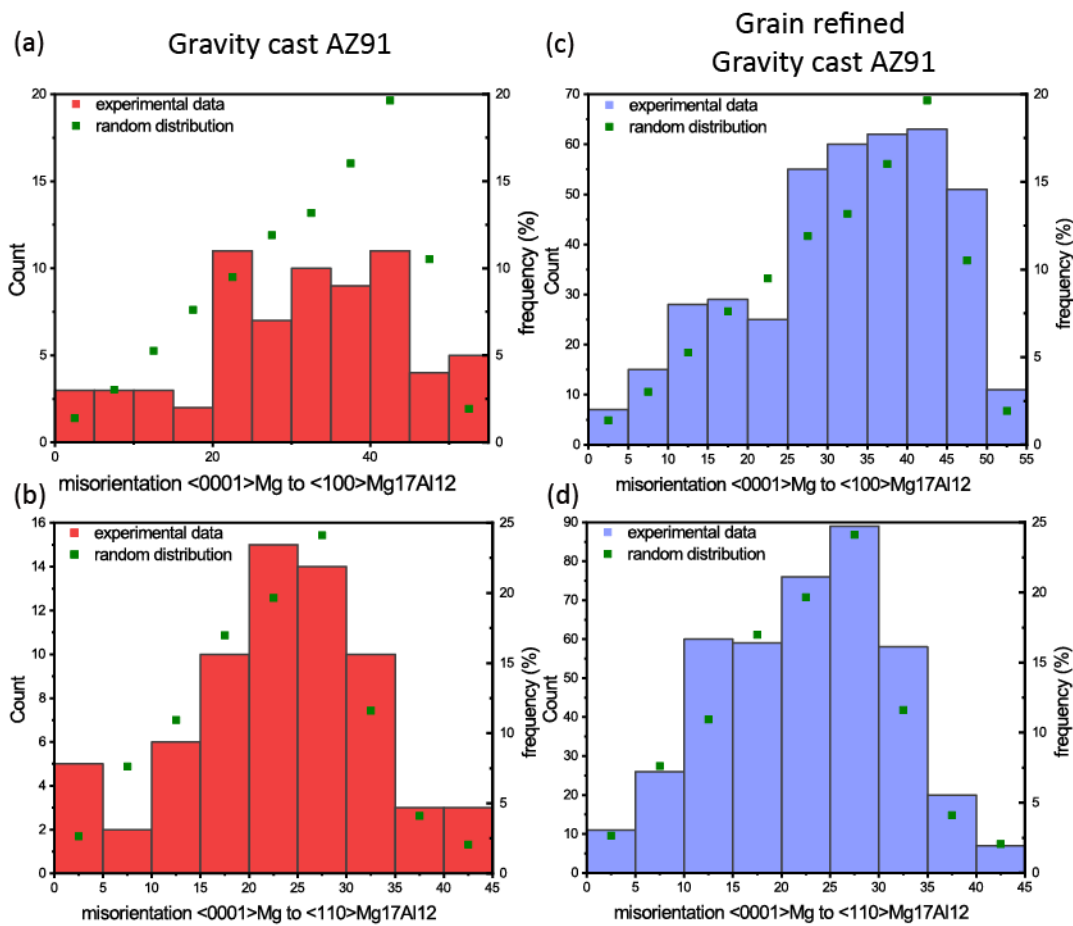


Figure 6.12 Misorientation analysis between contacting α -Mg and Mg₁₇Al₁₂ using EBSD datasets. Histograms plot the frequency of the measured minimum angle between predefined axes in the two phases: (a)&(c) $\langle 0001 \rangle_{\text{Mg}}$ to $\langle 100 \rangle_{\text{Mg}_{17}\text{Al}_{12}}$, (b)&(d) $\langle 0001 \rangle_{\text{Mg}}$ to $\langle 110 \rangle_{\text{Mg}_{17}\text{Al}_{12}}$. Green symbols are the distribution of misorientation angles for randomly oriented α -Mg and Mg₁₇Al₁₂. (a)-(b): gravity cast (Method 1) using 68 pairs of contacting α -Mg and Mg₁₇Al₁₂ (red). (c)-(d) grain refined gravity cast (Method 2) using 406 pairs of contacting phases.

At the same time, there were a small number of regions of contacting eutectic $\text{Mg}_{17}\text{Al}_{12}$ and $\alpha\text{-Mg}$ that had an OR. For example, there are five cases in the $0\text{-}5^\circ$ histogram bin of the $\langle 0001 \rangle_{\alpha\text{-Mg}}$ to $\langle 110 \rangle_{\text{Mg}_{17}\text{Al}_{12}}$ distribution in Figure 6.12(b), which is higher than random. Of these five cases, three had contacting $\text{Mg}_{17}\text{Al}_{12}$ and $\alpha\text{-Mg}$ orientations that are close to the Burgers and/or Potter ORs (Table 6.4) [217,267]. Similarly, in the grain refined gravity cast AZ91, one case of a region with a Burgers/Potter OR was found.

Table 6.4 The Burgers and Potter orientation relationships (ORs)

Name	OR	Ref.
Burgers OR	$(0001)_{\text{Mg}} // (110)_{\text{Mg}_{17}\text{Al}_{12}}$ $[2\bar{1}\bar{1}0]_{\text{Mg}} // [11\bar{1}]_{\text{Mg}_{17}\text{Al}_{12}}$ $[0\bar{1}10]_{\text{Mg}} // [2\bar{1}1]_{\text{Mg}_{17}\text{Al}_{12}}$	[217,268– 271,279– 281]
Potter OR	$(0001)_{\text{Mg}} 2^\circ \text{ from } (011)_{\text{Mg}_{17}\text{Al}_{12}}$ $[2\bar{1}\bar{1}0]_{\text{Mg}} // [1\bar{1}1]_{\text{Mg}_{17}\text{Al}_{12}}$ $(01\bar{1}1)_{\text{Mg}} // (110)_{\text{Mg}_{17}\text{Al}_{12}}$	[216– 218]

An example is given in Figure 6.13 of a region where most eutectic $\text{Mg}_{17}\text{Al}_{12}$ within one $\alpha\text{-Mg}$ dendrite envelope has the Burgers OR with the surrounding $\alpha\text{-Mg}$. The circled spots in the pole figures in Figure 6.13(c) highlight the near-parallel nature of the $\{0001\}_{\text{Mg}}$ and $\{110\}_{\text{Mg}_{17}\text{Al}_{12}}$, $\langle 2\bar{1}\bar{1}0 \rangle_{\text{Mg}}$ and $\langle 111 \rangle_{\text{Mg}_{17}\text{Al}_{12}}$, and between $\langle 0\bar{1}10 \rangle_{\text{Mg}}$ and $\langle 2\bar{1}1 \rangle_{\text{Mg}_{17}\text{Al}_{12}}$. In this particular case, the $\text{Mg}_{17}\text{Al}_{12}$ near the centre of the $\alpha\text{-Mg}$ dendrite (marked with a red arrow) has a MO $< 0.2^\circ$ from the Burgers OR to the contacting $\alpha\text{-Mg}$. This can be confirmed from the misorientation angles in Table 6.5 that were calculated from the measured Euler angles. However, note also that there is spread in the orientations in the pole figures in Figure 6.13, and some contacting $\text{Mg}_{17}\text{Al}_{12}$ and $\alpha\text{-Mg}$ in other parts of this dendrite are misoriented by up to $\sim 4^\circ$ from the Burgers OR. Thus, while the $\text{Mg}_{17}\text{Al}_{12}$ near the centre of this dendrite is very close to (MO $< 0.2^\circ$ from) the Burgers OR, other regions of $\text{Mg}_{17}\text{Al}_{12}$ in this dendrite only have an approximate Burgers OR that cannot be distinguished from near-Burgers ORs or the Potter OR. Note also in Figure 6.13 that, while the green $\text{Mg}_{17}\text{Al}_{12}$ has the Burgers OR with the blue

α -Mg grain, the same green $\text{Mg}_{17}\text{Al}_{12}$ orientation is at grain boundaries with surrounding α -Mg grains with which it has no special OR.

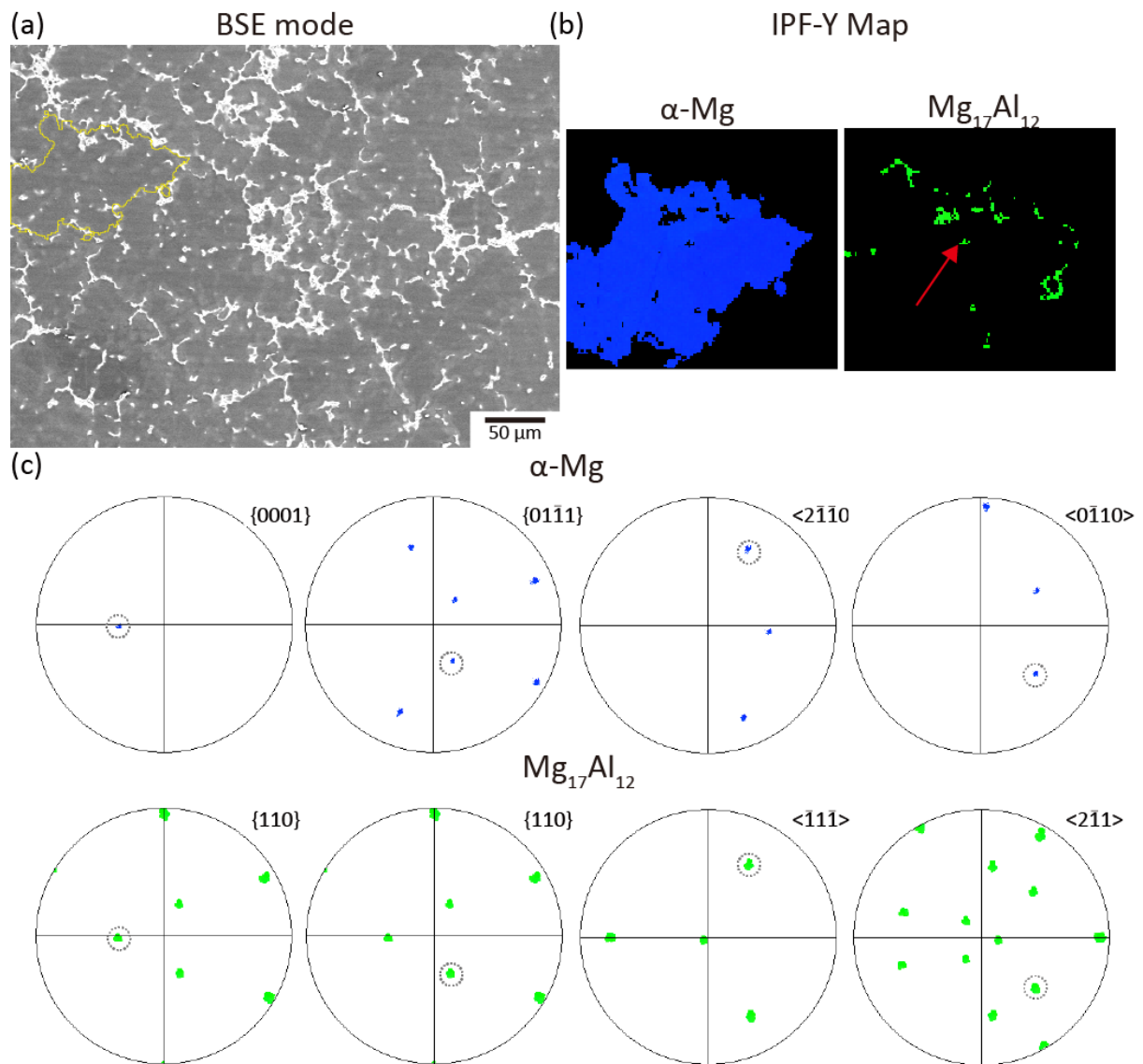


Figure 6.13 A rare example of a region of eutectic α -Mg and $\text{Mg}_{17}\text{Al}_{12}$ with the Burgers OR. (a) BSE-SEM image with an α -Mg grain outlined in yellow. (b) EBSD IPF-Y maps of the α -Mg and $\text{Mg}_{17}\text{Al}_{12}$ phases separately. The red arrow points at the region used for Table 6.5. (c) selected pole figures. Circles (c) highlight the near parallelism between one pair of planes and two pairs of directions.

Table 6.5 Misorientation angles between selected planes and directions for the $\text{Mg}_{17}\text{Al}_{12}$ indicated with an arrow in Figure 6.13-Figure 6.16 and surrounding $\alpha\text{-Mg}$.

Near-parallel planes and directions	Figure 6.13 (Mg-blue $\text{Mg}_{17}\text{Al}_{12}$ -green)	Figure 6.14 (Mg-red $\text{Mg}_{17}\text{Al}_{12}$ -green)	Figure 6.15 (Mg-green $\text{Mg}_{17}\text{Al}_{12}$ -green)	Figure 6.16 (Mg-pearl $\text{Mg}_{17}\text{Al}_{12}$ -pink)
$\{0001\}_{\text{Mg}} // \{110\}_{\text{Mg}_{17}\text{Al}_{12}}$	0.14°	1.36°	1.58°	1.12°
$\{01\bar{1}1\}_{\text{Mg}} // \{110\}_{\text{Mg}_{17}\text{Al}_{12}}$	1.92°	0.69°	0.99°	1.16°
$\langle 2\bar{1}\bar{1}0 \rangle_{\text{Mg}} // \langle \bar{1}1\bar{1} \rangle_{\text{Mg}_{17}\text{Al}_{12}}$	0.15°	0.55°	1.66°	0.65°
$\langle 0\bar{1}10 \rangle_{\text{Mg}} // \langle 2\bar{1}1 \rangle_{\text{Mg}_{17}\text{Al}_{12}}$	0.06°	1.26°	1.19°	0.91°
Euler angles of $\alpha\text{-Mg}$	(92.7;38.2;292)	(351.5;33.8;18.3)	(246.2;559;109)	(131.5;38.9;229.1)
Euler angles of $\text{Mg}_{17}\text{Al}_{12}$	(32.7;54.8;311)	(265.2;33.8;129.8)	(307.4;36.9;89.1)	(222.9;23.6;151)

Figure 6.13-Figure 6.16 present other examples of regions of contacting $\text{Mg}_{17}\text{Al}_{12}$ and $\alpha\text{-Mg}$ with a near-Burgers OR. In each case, there is a spread in the orientations in the pole figures and there is only a general approximate Burgers OR that cannot be distinguished from near-Burgers ORs or the Potter OR. Table 6.5 shows misorientation from selected pairs of orientations from neighbouring regions of $\text{Mg}_{17}\text{Al}_{12}$ and $\alpha\text{-Mg}$ in contact; some are closer to the Burgers OR and others to the Potter OR.

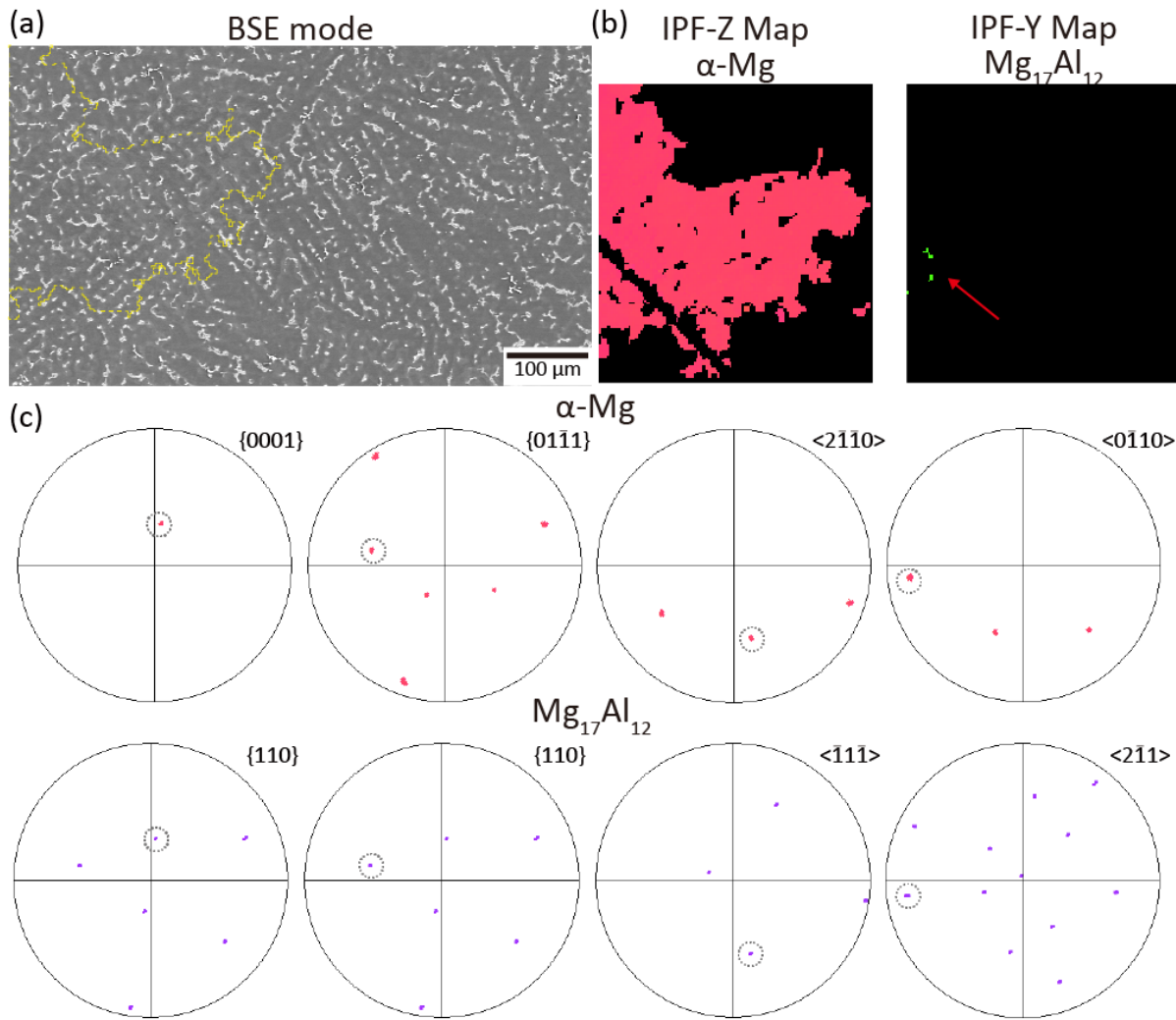


Figure 6.14 An example of a region of eutectic α -Mg and $\text{Mg}_{17}\text{Al}_{12}$ with a near-Burgers OR in a sample gravity cast without grain refinement (Method 1). (a) BSE-SEM image with an α -Mg grain outlined in yellow. (b) EBSD IPF maps of the α -Mg and $\text{Mg}_{17}\text{Al}_{12}$ phases separately. (c) selected pole figures. Circles have been added to highlight the near-parallelism between two pairs of planes and two pairs of directions.

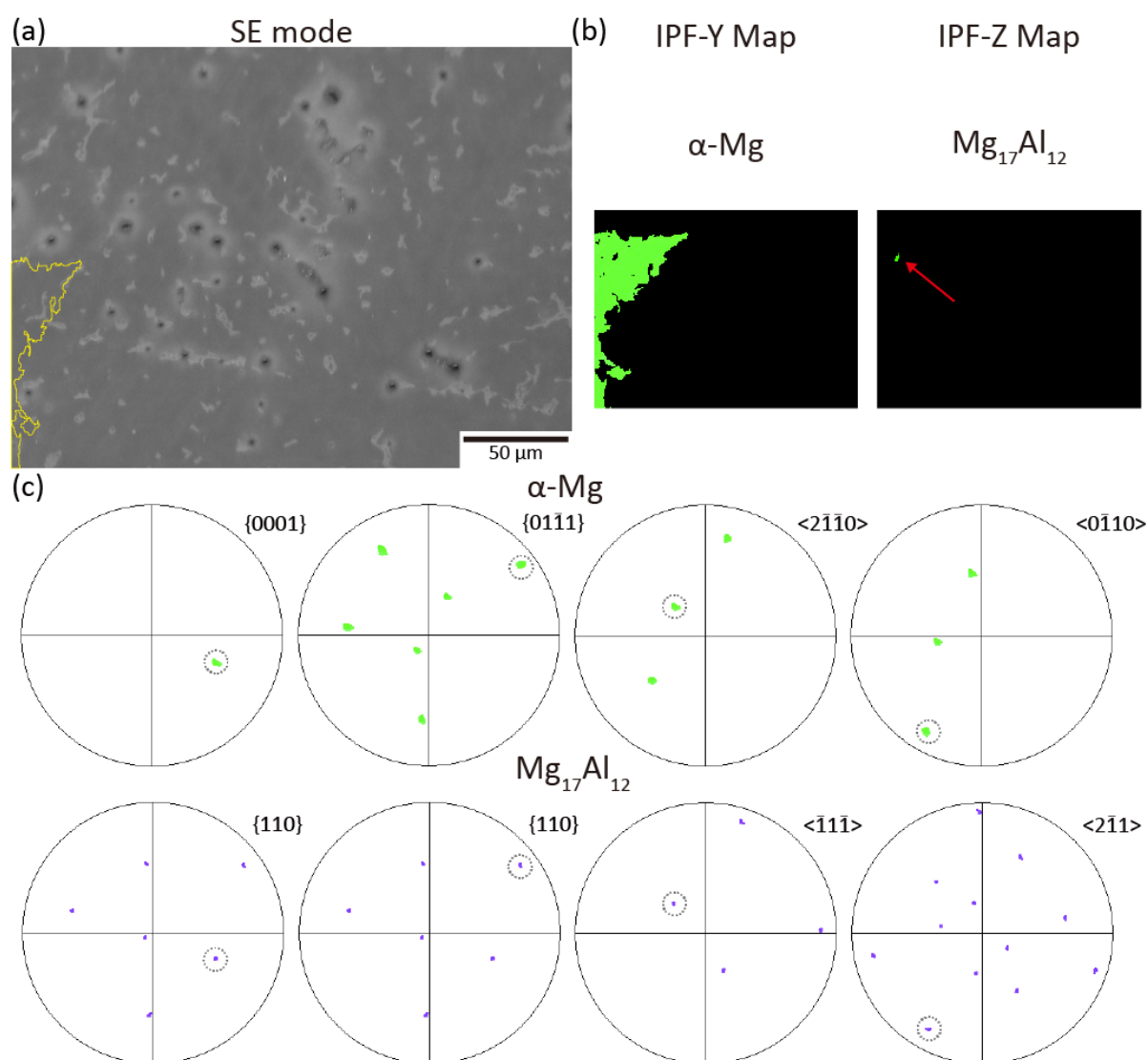


Figure 6.15 An example of a region of eutectic α -Mg and $\text{Mg}_{17}\text{Al}_{12}$ with a near-Burgers OR in a sample gravity cast without grain refinement (Method 1). (a) SE-SEM image with an α -Mg grain outlined in yellow. (b) EBSD IPF maps of the α -Mg and $\text{Mg}_{17}\text{Al}_{12}$ phases separately. (c) selected pole figures. Circles have been added to highlight the near-parallelism between two pairs of planes and two pairs of directions.

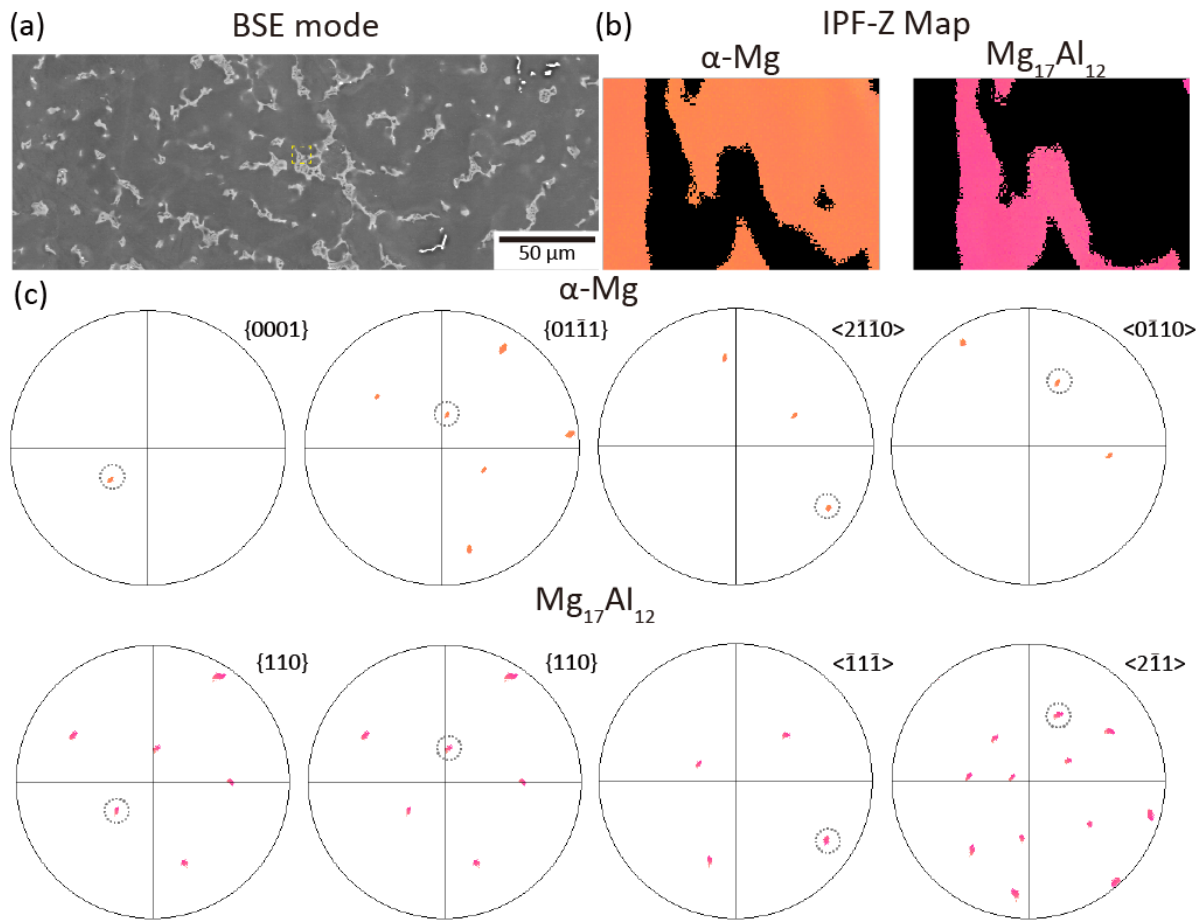


Figure 6.16 An example of a region of eutectic α -Mg and $\text{Mg}_{17}\text{Al}_{12}$ with a near-Burgers OR in a sample gravity cast without grain refinement (Method 1). (a) BSE-SEM image with an α -Mg grain outlined in yellow. (b) EBSD IPF maps of the α -Mg and $\text{Mg}_{17}\text{Al}_{12}$ phases separately. (c) selected pole figures. Circles have been added to highlight the near-parallelism between two pairs of planes and two pairs of directions.

The lack of a preferred OR in most regions of partially divorced eutectic after equiaxed solidification in Figure 6.12 is what would be expected from the observation in Figure 6.7 that $\text{Mg}_{17}\text{Al}_{12}$ forms large orientation domains that grow through multiple equiaxed α -Mg dendrite envelopes, and the finding in Figure 6.9 that regions of embedded eutectic α -Mg share the same orientation as their neighbouring α -Mg dendrite. The measurement of a small number of regions with Burgers OR (Figure 6.13) may be due to the heterogeneous nucleation of $\text{Mg}_{17}\text{Al}_{12}$ on α -Mg dendrites in some locations. Indeed, the reduced frequency of finding an OR in the grain refined sample (1 vs 3 without grain refinement) is consistent with this interpretation since, in a cross-section of fixed area where $\text{Mg}_{17}\text{Al}_{12}$ orientation domains span many α -Mg

grains such as in Figure 6.7(c) and (g), a smaller α -Mg grain size makes it less likely that the α -Mg grain that caused $\text{Mg}_{17}\text{Al}_{12}$ nucleation will be in the cross-section. However, there is significant uncertainty on the nucleation of $\text{Mg}_{17}\text{Al}_{12}$ here and further work is required to prove where $\text{Mg}_{17}\text{Al}_{12}$ nucleates.

While the lack of a preferred OR in most regions is generally consistent with past work on Mg-Al alloys that found no OR [88,278], we additionally discovered a small number of eutectic regions with the Burgers OR. The reason this was found here and not in references [88,278] seems to be that a larger area of microstructure was analysed here, increasing the chances of finding the small number of regions with an OR.

Combining the crystallographic orientation mapping results in Figure 6.7-Figure 6.16 provides new insights into the nucleation and growth of the partially divorced α -Mg+ $\text{Mg}_{17}\text{Al}_{12}$ eutectic in gravity cast samples. The key feature is that eutectic $\text{Mg}_{17}\text{Al}_{12}$ grew in contiguous liquid between the arms of multiple α -Mg dendrites forming relatively large $\text{Mg}_{17}\text{Al}_{12}$ orientation domains, while the eutectic α -Mg grew from each surrounding dendrite, even in partially coupled regions where the α -Mg was embedded within $\text{Mg}_{17}\text{Al}_{12}$, resulting in no preferred OR in most regions. The interconnected 3D skeleton of $\text{Mg}_{17}\text{Al}_{12}$ indicates that it grew mostly in contiguous liquid and not in isolated liquid pockets. The relatively large $\text{Mg}_{17}\text{Al}_{12}$ orientation domains spanning multiple α -Mg grains indicates that $\text{Mg}_{17}\text{Al}_{12}$ nucleation events were relatively infrequent. The occasional region where the eutectic had the Burgers OR indicates that eutectic $\text{Mg}_{17}\text{Al}_{12}$ nucleated on primary α -Mg in at least some cases.

6.3.3. Factors affecting the eutectic morphology

Figure 6.17 shows the typical $\text{Mg}_{17}\text{Al}_{12}$ morphologies from casting/cooling methods 1-5. It is split into three columns: SE SEM images after deep etching revealing the 3D morphology of $\text{Mg}_{17}\text{Al}_{12}$ (left column Figure 6.17(a)-(e)); lower magnification BSE SEM images of polished cross-sections (middle column Figure 6.17(f)-(j)); and higher magnification BSE SEM images of similar polished cross-sections overviewing the partially divorced $\text{Mg}_{17}\text{Al}_{12}$ morphologies (right column Figure 6.17(k)-(o)). The images have been scaled by the average SDAS in each sample to enable a better comparison of the morphology. In the first two columns, the scale bar represents one average SDAS; in the third column, the scale bar represents half of the average SDAS.

From the deep etched microstructures in the left column (Figure 6.17(a)-(e)), all samples have an interconnected network of $\text{Mg}_{17}\text{Al}_{12}$, indicating that most $\text{Mg}_{17}\text{Al}_{12}$ grew from contiguous liquid and not from isolated liquid pockets in AZ91 under all casting/cooling conditions studied. The holes left after etching away the α -Mg have the shapes of the dendrites. From this, the $\text{Mg}_{17}\text{Al}_{12}$ has grown both (i) through the liquid spaces between α -Mg dendrite arms within dendritic grains and (ii) through the liquid between dendritic grains. At the solid fraction when the eutectic started growing (~ 84 vol% of α -Mg for Scheil solidification [202]), the relative amount of liquid in locations (i) and (ii) will depend on the grain size-to-SDAS ratio, and therefore the α -Mg morphology in Figure 6.5. A large ratio corresponds to more of the remaining liquid being within dendritic grains; a smaller ratio corresponds to more of the remaining liquid being between grains. Consistent with this, in the samples with equiaxed dendritic morphology, most of the $\text{Mg}_{17}\text{Al}_{12}$ occupies the SDAS. In contrast, in the fast cooled sample which has rosette morphology (Figure 6.5(D) and Figure 6.17(c)), the shape of the $\text{Mg}_{17}\text{Al}_{12}$ shows that it grew more between the grains with less $\text{Mg}_{17}\text{Al}_{12}$ growing between the arms inside the grains. A further striking feature in the deep-etched microstructures is that,

while in most samples the $Mg_{17}Al_{12}$ microstructure was a framework of struts, interrupted solidification samples (Figure 6.17(b)) also had some $Mg_{17}Al_{12}$ spanning the gaps between struts. This ‘strut and membrane’ $Mg_{17}Al_{12}$ microstructure only formed in the interrupted solidification samples.

The polished sections in the middle column (Figure 6.17(f)-(j)) show the appearance of the $Mg_{17}Al_{12}$ networks in 2D section. In most cases, the $Mg_{17}Al_{12}$ between dendrite arms can be clearly seen. The higher magnification images in the last column (Figure 6.17(k)-(o)) show that $Mg_{17}Al_{12}$ formed partially divorced eutectic morphologies in all samples where casting/cooling methods 1-5 were applied, but the degree of divorced growth depended on the casting/cooling method. It can be seen qualitatively in Figure 6.17 that the $Mg_{17}Al_{12}$ in the slow (Figure 6.17(k)) and fast (Figure 6.17(m)) cooled samples were the most divorced, both the gravity cast samples (Figure 6.17(n) and (o)) were less divorced, and the interrupted solidification samples (Figure 6.17(l)) were the least divorced.

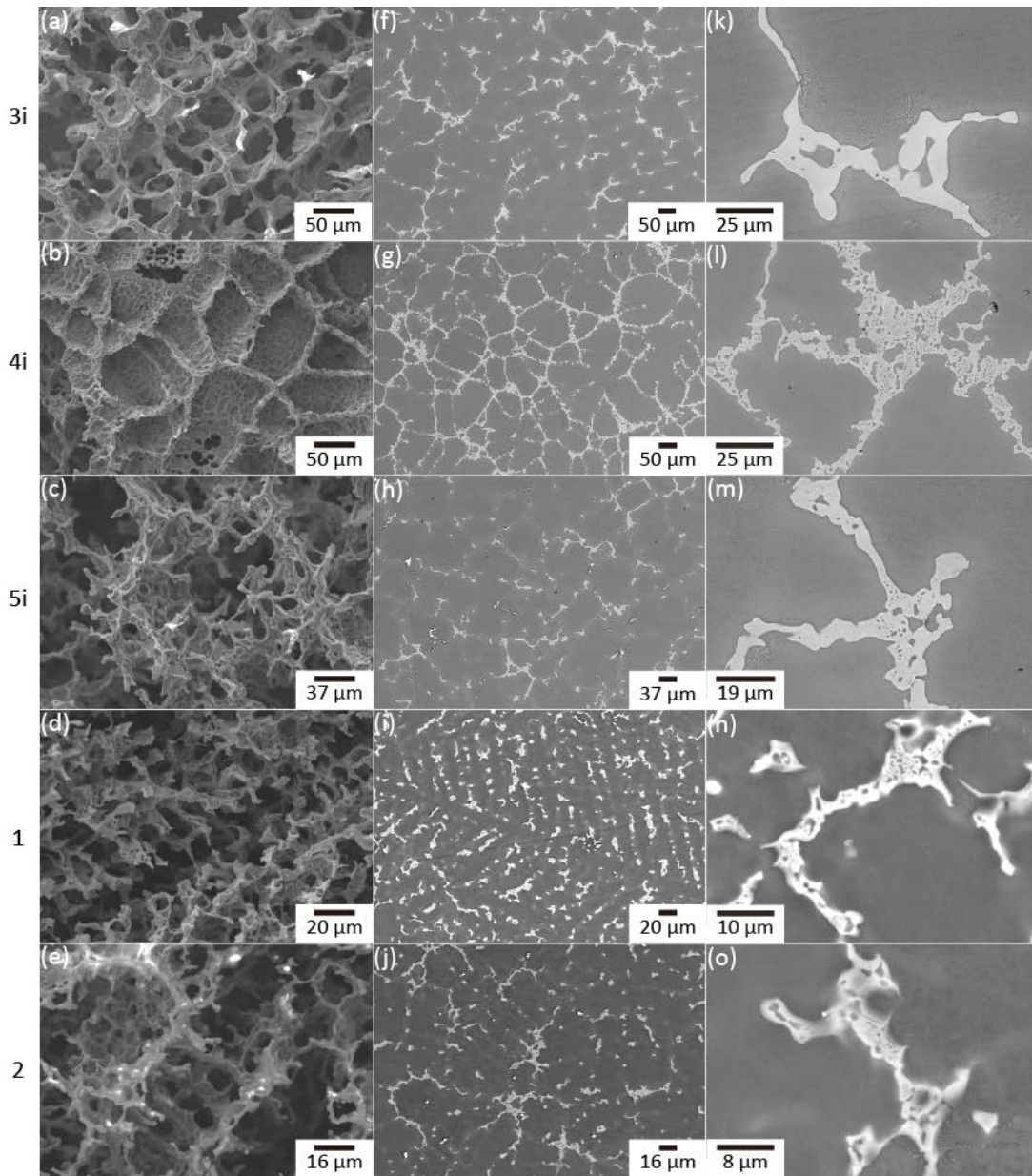


Figure 6.17 $\text{Mg}_{17}\text{Al}_{12}$ microstructures from each casting/cooling method. (a)-(e) SE-SEM images of the 3D $\text{Mg}_{17}\text{Al}_{12}$ network after deep etching. (f)-(o) BSE-SEM images of polished sections scaled such that the scale bars equal the average SDAS (a-j) and half the average SDAS (k-o). (a, f, k) slow cooled. (b, g, l) interrupted solidification. (c, h, m) fast cooled. (d, i, n) gravity casting without grain refinement. (e, j, o) gravity casting with grain refiner.

The level of eutectic divorce of the eutectic was defined and quantified here by measuring the average volume fraction of α -Mg embedded inside $\text{Mg}_{17}\text{Al}_{12}$ in 2D cross-sections. With this definition, a fully divorced eutectic has 0 vol% α -Mg embedded inside $\text{Mg}_{17}\text{Al}_{12}$, and the eutectic becomes less divorced as the vol% of embedded α -Mg increases. Note in the right-hand column of Figure 6.17 that the degree of divorced growth often varied from location to

location in the same micrograph and, generally, thinner interdendritic spaces were more divorced and thicker interdendritic spaces had a higher fraction of embedded α -Mg. Therefore, here, mean values are plotted from at least 20 micrographs in each sample. The samples from cooling/casting methods 1-5 had between 2-30 vol% of α -Mg embedded inside $\text{Mg}_{17}\text{Al}_{12}$. The lower value is almost fully divorced. The upper value is slightly below the calculated volume fraction for fully coupled eutectic growth (34 vol% α -Mg) calculated from the mass fraction of phases on the eutectic tie line [202] and the densities of the phases [168,240].

As can be seen in Figure 6.5 and Table 6.2, five samples had a similar SDAS of $50 \pm 4 \mu\text{m}$ and came from two different cooling methods, slow cooling and interrupted solidification, which had similar liquid cooling rate but significantly different eutectic cooling rate (Table 6.2). This resulted in strong differences in the degree of divorced growth as shown in the micrographs inside the blue and cyan boxes in Figure 6.18(a). The vol% of α -Mg embedded inside $\text{Mg}_{17}\text{Al}_{12}$ is plotted against eutectic cooling rate for the samples with SDAS of $50 \pm 4 \mu\text{m}$ in Figure 6.18(b). The embedded α -Mg increased near-linearly with increasing eutectic cooling rate. However, note that this was only true when comparing samples with a similar SDAS whereas samples with significantly different SDAS did not follow this simple trend. For example, the gravity castings (not plotted) would be far to the right of all datapoints in Figure 6.18(b).

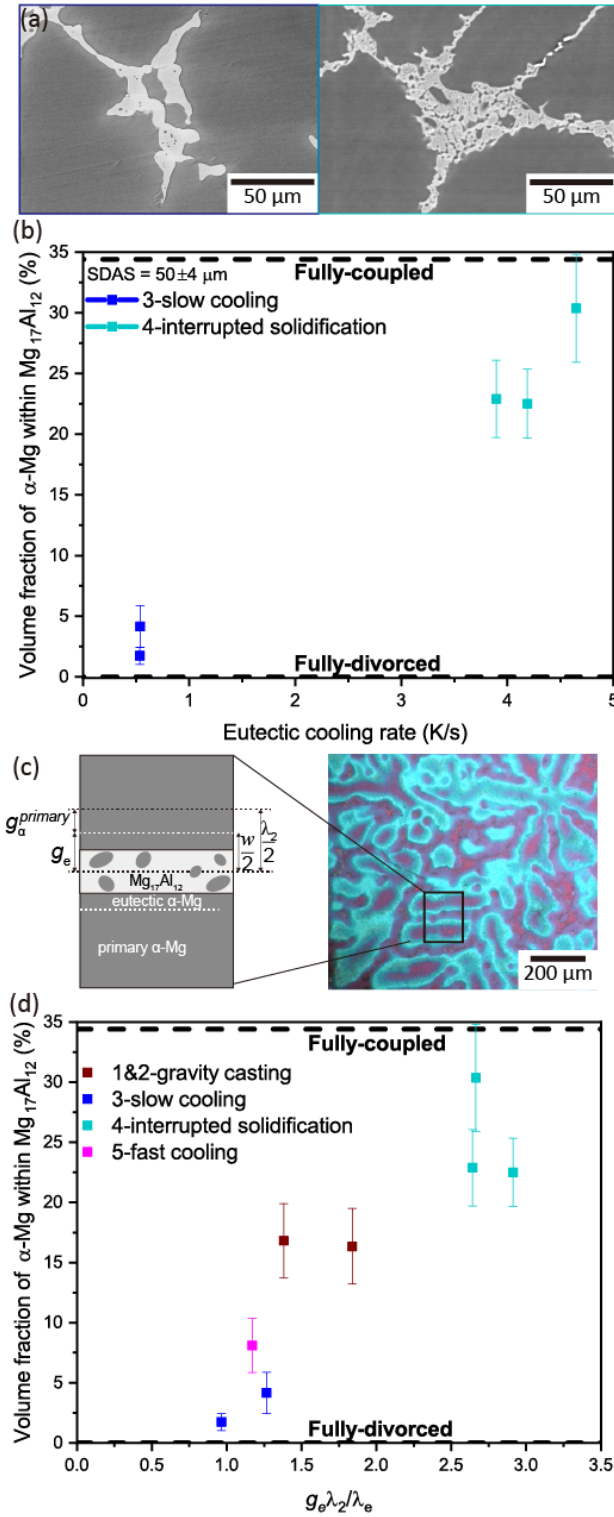


Figure 6.18 (a) The BSE images of near-fully divorced (blue) and coupled $Mg_{17}Al_{12}$ (cyan). (b) Plot of the volume fraction of α -Mg within $Mg_{17}Al_{12}$ versus the eutectic cooling rate (450-430°C) for samples with similar SDAS of $50 \pm 4 \mu m$. N.B. this simple relationship was not valid for other values of SDAS. (c) The illustration of primary Mg and eutectic phase distribution between a Mg dendrite with an etched optical image. (d) Plot of the volume fraction of α -Mg within $Mg_{17}Al_{12}$ versus $g_e \lambda_2 / \lambda_e$, the ratio of the liquid channel width to the eutectic spacing (g_e : mean volume fraction of eutectic, λ_2 : mean SDAS; λ_e : mean eutectic spacing). Terms are defined in the schematic diagram. Data are from cooling methods 1-5.

To compare samples with different SDAS, we consider the geometrical factors affecting the divorcedness of eutectic growth: the width of liquid channels between dendrite arms (w in the schematic in Figure 6.18(c)) and the local eutectic spacing, λ_e . In Figure 6.18(c), the image illustrates how the eutectic channel width is related to the average SDAS, λ_2 , and the average volume fraction of eutectic region, g_e , where the eutectic region includes $\text{Mg}_{17}\text{Al}_{12}$ and the α -Mg formed during the eutectic reaction. From the same schematic sketch, it can be seen that the average liquid channel width at the start of the eutectic reaction can be expressed as $w = g_e \lambda_2$. The ratio of the channel width to the eutectic spacing, $g_e \lambda_2 / \lambda_e$, is the number of mean eutectic spacings across the eutectic channel width. $g_e \lambda_2 / \lambda_e$ was calculated using $g_e = 0.137$ assuming Scheil solidification [202] and the measured values of SDAS, λ_2 , and eutectic spacing, λ_e . The resulting values of $g_e \lambda_2 / \lambda_e$ are plotted against the volume fraction of α -Mg within $\text{Mg}_{17}\text{Al}_{12}$ in Figure 6.18(d).

The plot shows reasonable agreement with the following expectations: (i) when the channel width ($g_e \lambda_2$) is smaller than or equal to the required eutectic spacing (λ_e), i.e. $g_e \lambda_2 / \lambda_e \leq 1$, the eutectic should be fully divorced since the α -Mg does not need to grow within the $\text{Mg}_{17}\text{Al}_{12}$ to optimise lateral diffusive mixing of solute; (ii) as the $g_e \lambda_2 / \lambda_e$ increases, an increasing fraction of α -Mg becomes embedded within $\text{Mg}_{17}\text{Al}_{12}$; and (iii) when the channel width ($g_e \lambda_2$) becomes much larger than the required eutectic spacing (λ_e), fully coupled growth may be expected. The samples with the highest $g_e \lambda_2 / \lambda_e$ values measured in this study had a volume fraction of α -Mg embedded within $\text{Mg}_{17}\text{Al}_{12}$ slightly below the fraction expected of coupled growth (34 vol%). This indicates that all of these samples in Figure 6.18(d) were partially divorced and none became fully coupled.

Although the data points in Figure 6.18(d) do not fit tightly on a curve, an approximate extrapolation to when $g_e \lambda_2 / \lambda_e$ equals the calculated coupled growth value of 34 vol% indicates

that the channel width would need to be approximately 3 to 5 times the eutectic spacing for fully coupled growth to occur.

Nave et al. [90] reported that the α -Mg+Mg₁₇Al₁₂ eutectic was more divorced at higher cooling rate. This is opposite to the findings in Figure 6.18(b), indicating that cooling rate is not causally linked to how divorced the eutectic is. Dargusch et al. [79] reported a more complex relationship between the dendrite morphology, the cooling rate and the Mg₁₇Al₁₂ morphology. From Figure 6.18(d), we see that this relationship can be stated simply using $g_e\lambda_2/\lambda_e$. The cooling rate will affect all three of these terms in different ways such that different dependencies of cooling rate on level of eutectic divorce can be obtained.

6.3.4. Coupled eutectic growth in Mg-9Al-0.7Zn-0.2Mn

We next consider solidification conditions that yield fully coupled eutectic growth in this alloy. From Figure 6.18(d), coupled growth is expected when the ratio of the SDAS to eutectic spacing is large enough that $g_e\lambda_2/\lambda_e$ exceeds ~ 3 -5. Since λ_2 depends on the time the dendrites are surrounded by liquid (Figure 6.6(d)) and λ_e depends mostly on the eutectic growth velocity [282,283], a large value of λ_2/λ_e requires solidification conditions that maximise the time the dendrites are surrounded by liquid and maximise the heat extraction rate during the eutectic reaction. To achieve this, we developed casting/cooling Method 6 which is described in the Methods section. This had two key features. First, to start with a sample with one of the largest λ_2 values and increase λ_2 further through solid-liquid coarsening. Second, to use a small sample volume so that quenching from 450 °C produced the highest eutectic cooling rate of all Methods applied here. We note that increasing the time the dendrites are surrounded by liquid will provide time for back diffusion and, therefore, reduce the fraction of eutectic, g_e , that subsequently forms on cooling. Thus, we held for only 30 minutes at 450 °C.

It was found that Method 6 resulted in fully coupled α -Mg+Mg₁₇Al₁₂ eutectic growth in all spaces between dendrite arms. Typical examples are given in Figure 6.19. Coupled growth can be confirmed from the growth morphology where eutectic cells exist with the minor phase (α -Mg) fanning out within a matrix of the major phase (Mg₁₇Al₁₂).

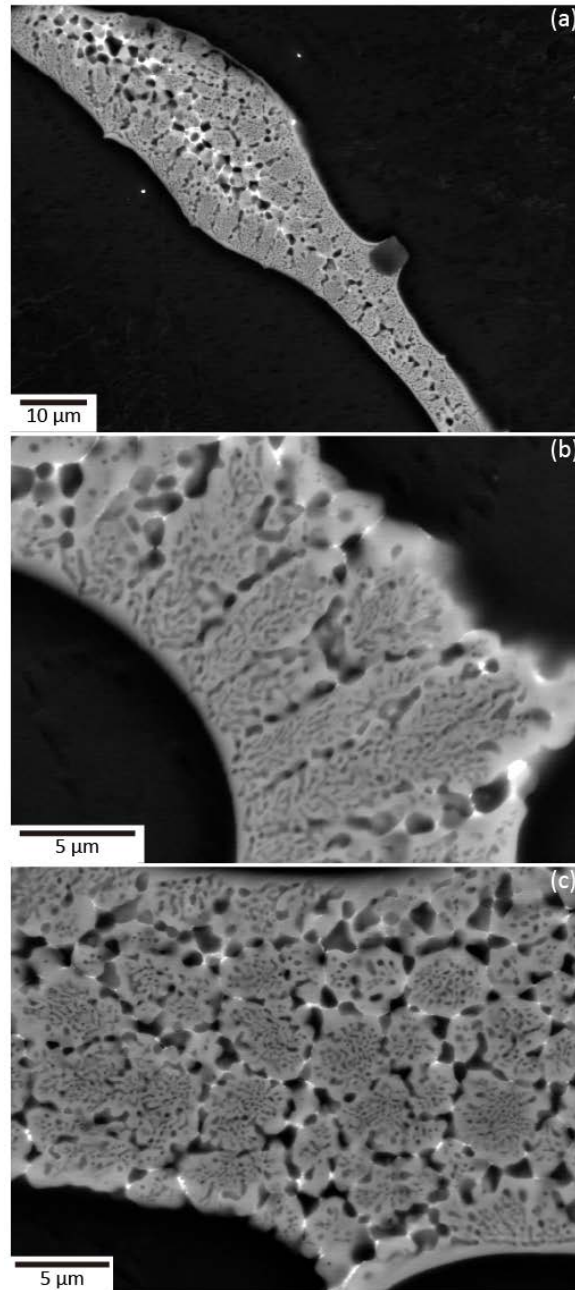


Figure 6.19 Coupled α -Mg+Mg₁₇Al₁₂ eutectic growth in cooling Method 6. (a) and (b): cross-sections with the eutectic cell growth direction approximately in the plane of the screen. (c) Cross-section with eutectic cells growing approximately in/out of the screen. Dark = α -Mg, mid-grey = Mg₁₇Al₁₂, small bright = Mg-Al-Zn ternary intermetallics.

Examining regions where the local cell growth direction lies close to the sectioning plane (e.g. Figure 6.19(a)-(b)), we see that each eutectic cell grew inwards from the surrounding α -Mg, sometimes from the dendrite arms on both sides of an interdendritic space (Figure 6.19(a)) and sometimes only from one side (e.g. Figure 6.19(b)). In regions where the sectioning plane is near-perpendicular to the local cell growth direction (e.g. Figure 6.19(c)), we see that the cells are approximately cylindrical and the cell diameter is similar in longitudinal sections (Figure 6.19(b)) and transverse sections (Figure 6.19(c)) at $3.2 \pm 0.4 \mu\text{m}$. The mean eutectic spacing within cells is $0.47 \pm 0.09 \mu\text{m}$ and the mean SDAS is $38.1 \pm 3.7 \mu\text{m}$ giving $g_e \lambda_2 / \lambda_e \sim 11$. Combining this result with Figure 6.18(d) supports the idea that the degree of eutectic divorce depends on the size of interdendritic spaces compared with the eutectic spacing and shows that fully coupled eutectic growth is possible in interdendritic spaces when $g_e \lambda_2 / \lambda_e$ is sufficiently high.

The growth of α -Mg+Mg₁₇Al₁₂ eutectic cells in the interdendritic spaces can be understood from the liquidus projection in Figure 6.20(a) which shows the liquid composition path and the solidification reaction sequence assuming the Scheil model, calculated using the TCMG4 database with Thermo-Calc [202]. Note that, although the Zn content in the alloy is only 0.7 wt%, zinc is rejected into the liquid ahead of growing α -Mg+L dendrite interfaces and, when the liquid composition reaches the α -Mg+Mg₁₇Al₁₂ eutectic groove, the Zn content in the liquid has increased to Mg-31Al-3.5Zn-0.001Mn (wt%) [202]. Subsequent eutectic growth along the eutectic groove occurs over a temperature range (Figure 6.20(a) and (b)) and Zn is rejected ahead of both α -Mg+L and Mg₁₇Al₁₂+L interfaces as the coupled eutectic growth front advances. This, in combination with the high growth rate, results in constitutional supercooling ahead of the eutectic front which causes morphological instability and the breakdown into eutectic cells. A schematic diagram of α -Mg+Mg₁₇Al₁₂ eutectic cell growth in an interdendritic space is drawn in Figure 6.20(c).

Figure 6.20(a) also shows that the α -Mg+Mg₁₇Al₁₂ eutectic groove passes a quasi-peritectic point and continues downwards with a reaction $L \rightarrow \alpha\text{-Mg} + \phi\text{-Mg}_{21}(\text{Al,Zn})_{17}$. Therefore, the Scheil model predicts that Mg-9Al-0.7Zn-0.2Mn will solidify with some $\phi\text{-Mg}_{21}(\text{Al,Zn})_{17}$ in the last stages of solidification (Figure 6.20(b)). In Figure 6.19, there are traces of a nanoscale phase between adjacent or impinging cells that are bright in backscatter electron images. These may be the Zn-rich phase $\phi\text{-Mg}_{21}(\text{Al,Zn})_{17}$ or, possibly $\tau\text{-Mg}_{32}(\text{Al,Zn})_{49}$ which is not predicted by the Scheil model but has been reported to form instead of $\phi\text{-Mg}_{21}(\text{Al,Zn})_{17}$ in other Mg-Al-Zn alloys [278]. The details of this phase were not characterised further here. Similar bright particles were not found in samples with lower eutectic cooling rate, probably because back diffusion in the solid phases terminated solidification earlier along the eutectic groove. In Figure 6.20(a), the dashed portion of the red line indicates a liquid path for very limited back solidification.

This work has shown that, in AZ91, the late-forming α -Mg+Mg₁₇Al₁₂ eutectic can be fully divorced, partially divorced or fully coupled. The dominant determining factor seems to be how the width of the remaining liquid channels at the start of the eutectic reaction compares with the eutectic spacing that forms during eutectic growth. This can be described simply by $g_e \lambda_2 / \lambda_e$. From this, we see that AZ91 is usually fully or partially divorced because g_e is low in this alloy (0.137 or less) and the ratio λ_2 / λ_e does not vary widely between casting processes. We have shown that, if the solidification time and the eutectic cooling rate are decoupled using interrupted solidification or by quenching small samples from just above the eutectic temperature then a wide range of $g_e \lambda_2 / \lambda_e$ values can be obtained, enabling the degree of eutectic divorce to be controlled and fully coupled eutectic growth to be generated.

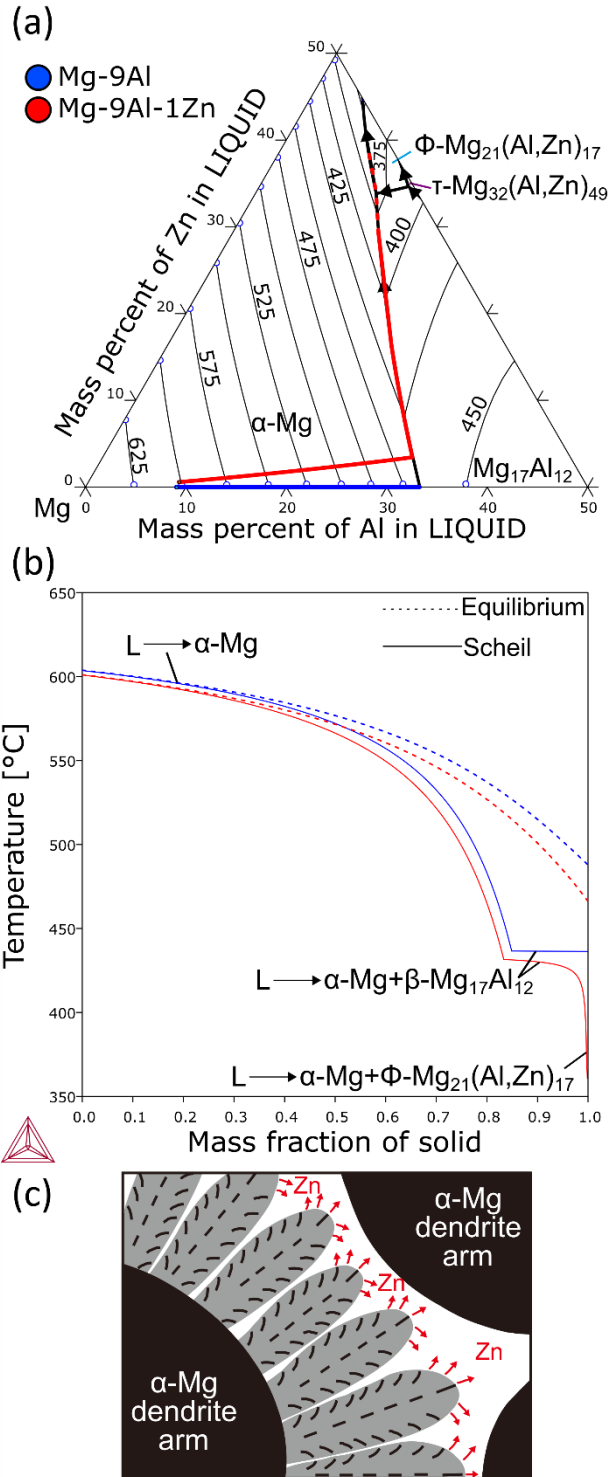


Figure 6.20 (a) Mg-rich corner of the Mg-Al-Zn liquidus projection with the liquid composition paths overlaid for two alloy compositions, assuming the Scheil model [202]. (b) Temperature-solid fraction plot for the same alloy compositions, with three reactions highlighted. N.B. the lowest temperature reaction requires very limited back diffusion. (c) Schematic representation of eutectic cell growth between α -Mg dendrite arms in AZ91.

6.4 Conclusions

This Chapter has explored the nucleation, growth and morphology of the $\text{Mg}_{17}\text{Al}_{12}$ phase during equiaxed solidification of magnesium alloy AZ91. The key findings are:

1. For all solidification conditions studied here, $\text{Mg}_{17}\text{Al}_{12}$ formed an interconnected skeleton in 3D, indicating that $\text{Mg}_{17}\text{Al}_{12}$ grew mostly or completely in contiguous liquid rather than in isolated liquid pockets.
2. $\text{Mg}_{17}\text{Al}_{12}$ domains ($\text{Mg}_{17}\text{Al}_{12}$ regions with the same crystallographic orientation) were significantly larger than α -Mg grains in gravity cast samples. Thus, $\text{Mg}_{17}\text{Al}_{12}$ nucleation events were relatively infrequent and the growth of a single $\text{Mg}_{17}\text{Al}_{12}$ orientation occurred through and between multiple α -Mg dendrite envelopes.
3. In most regions, no preferred orientation relationship (OR) developed during partially divorced eutectic growth. However, in a small number of cases, the Burgers OR and/or Potter OR was measured between eutectic $\text{Mg}_{17}\text{Al}_{12}$ and the surrounding α -Mg dendrite which may be due to the nucleation of $\text{Mg}_{17}\text{Al}_{12}$ on α -Mg during solidification.
4. The eutectic divorce depended on the space available for eutectic growth. A simple geometrical expression for the ratio of the liquid channel width between dendrite arms to the preferred eutectic spacing, $g_e\lambda_2/\lambda_e$, is a reasonable predictor of the eutectic divorce. When this ratio was close to unity, the eutectic was nearly fully divorced. As the ratio increased, the eutectic became less divorced. The results indicate that fully coupled eutectic growth requires a minimum $g_e\lambda_2/\lambda_e$ of approximately 3-5.
5. While AZ91 usually solidifies with a low value of $g_e\lambda_2/\lambda_e$, it was shown that a wide range of $g_e\lambda_2/\lambda_e$ values could be generated by decoupling the solidification time and the eutectic cooling rate using two-stage solidification methods. This enabled the full range of eutectic growth morphologies to be obtained in AZ91, including fully coupled eutectic growth. Potentially, this can be tested whether the different types of $\text{Mg}_{17}\text{Al}_{12}$

morphologies have effects on corrosion resistance of Mg-Al alloys for the industrial usage.

6. Coupled growth in AZ91 occurred with the morphology of eutectic cells due to Zn segregation ahead of the α -Mg + Mg₁₇Al₁₂ eutectic front and the high eutectic growth rate.

Chapter 7. Dissolution kinetics of $\text{Mg}_{17}\text{Al}_{12}$

7.1 Introduction

In industry, as well as using AZ91 as as-cast components, it is common to perform a solution heat treatment to dissolve $\text{Mg}_{17}\text{Al}_{12}$ into the α -Mg matrix prior to deformation processing such as forging of AZ80 (which has similar composition to AZ91) [15], to improve toughness for machining [91], and/or prior to a precipitation heat treatment. Therefore, it is important to understand how the as-cast microstructure affects the dissolution kinetics of $\text{Mg}_{17}\text{Al}_{12}$ during solution heat treatment.

This chapter explores the influence of the α -Mg dendrite and $\text{Mg}_{17}\text{Al}_{12}$ microstructure on the kinetics of $\text{Mg}_{17}\text{Al}_{12}$ dissolution during solution heat treatment.

7.2 Methods

Six samples were selected from the five casting/cooling methods used in Chapter 6 for a solution heat treatment study (Table 6.2): One gravity casting without grain refinement, one gravity casting with grain refinement, two slow cooled samples with different grain sizes, one interrupted solidification sample and one fast cooled sample. For the gravity castings (methods 1 and 2), the cut section was a 12 mm diameter and 20 mm height cylinder from 55 mm above the bottom, sliced into eight semi-cylinders. For method 3, 4, 5 samples, specimens were cut from the annular region that contained the thermocouple, sliced into eight cuboids with 10 mm width, 5 mm length and 5 mm height (methods 3 and 4) or 10 mm width, 4 mm length and 10 mm height (Method 5). All sliced samples were then placed into a forced air convection oven at 410°C and were removed after 0, 1, 3, 6, 9, 24, 72 and 144 hours and quenched into a bucket of water. The sample preparation and electron microscopy characterisation were given in Chapter 6.

Phase stability at 410 °C was investigated by X-ray diffraction (XRD) on the secondary phases in the as-cast condition and after long term (10 day) holding at 410 °C. The secondary phases were first extracted by selectively etching in a solution of 9% acetic acid in water for 12 hours to completely remove the α -Mg matrix, followed by dilution with ethanol five times. The resulting powder was then transferred to a flat silicon holder for XRD. Phase analysis was conducted in a PANalytical MPD diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). Due to a relatively small number of particles, an automatic divergence slit was adopted to maintain the background to a similar level for all angles. The diffraction data were collected in the 2θ range of 10–90° with an angular step size of 0.017° and 1500 s integration time. XRD patterns were analysed within HighScore Plus with the PDF-4+ 2022 database.

7.2.1. Measurement of volume fraction of $\text{Mg}_{17}\text{Al}_{12}$

The six selected samples with five cooling/casting methods were solution heat-treated. The volume fraction of $\text{Mg}_{17}\text{Al}_{12}$ at different heat-treatment time was measured using the following steps:

1. BSE images such as Figure 7.1(a) were taken for image processing with magnification of 300x and 10 mm working distance. However, $\text{Mg}_{17}\text{Al}_{12}$ in the longer than one day heat-treatment samples was difficult to observe so the magnification needed to be increased to reveal the $\text{Mg}_{17}\text{Al}_{12}$. To maintain a similar analysis area in all different heat-treatment samples, five extra images were taken in the longer heat-treatment samples.
2. In BSE images, three phases presented as three different levels of brightness: α -Mg in dark grey, $\text{Mg}_{17}\text{Al}_{12}$ in mid grey and Al-Mn phase(s) as bright particles. Thus, the threshold function in ImageJ was applied to exclude the α -Mg and Al-Mn phases as shown in Figure 7.1(b).

3. When all regions with the same grey values as $\text{Mg}_{17}\text{Al}_{12}$ were selected, binary images such as Figure 7.1(c) were obtained, but some boundaries of Al-Mn particles were included as well.
4. The final step of image processing was to remove all the bright Al-Mn inclusions. In the particle analysis function of ImageJ, the threshold of particle sizes was set to be $2\text{ }\mu\text{m}^2$ so that only $\text{Mg}_{17}\text{Al}_{12}$ was counted in the analysis (Figure 7.1(d)). In the measurement in ImageJ, the area fraction of $\text{Mg}_{17}\text{Al}_{12}$ was calculated as a percentage and this can be considered as the volume fraction (percentage) due to the stereology. That is to say, since the area of microstructure in each micrograph contained multiple α -Mg dendritic grains and the equiaxed growth mode had no significant directionality, the average area fraction from multiple micrographs is a good approximation of the volume fraction. At least 25 micrographs were taken in each sample under each heat treatment condition.

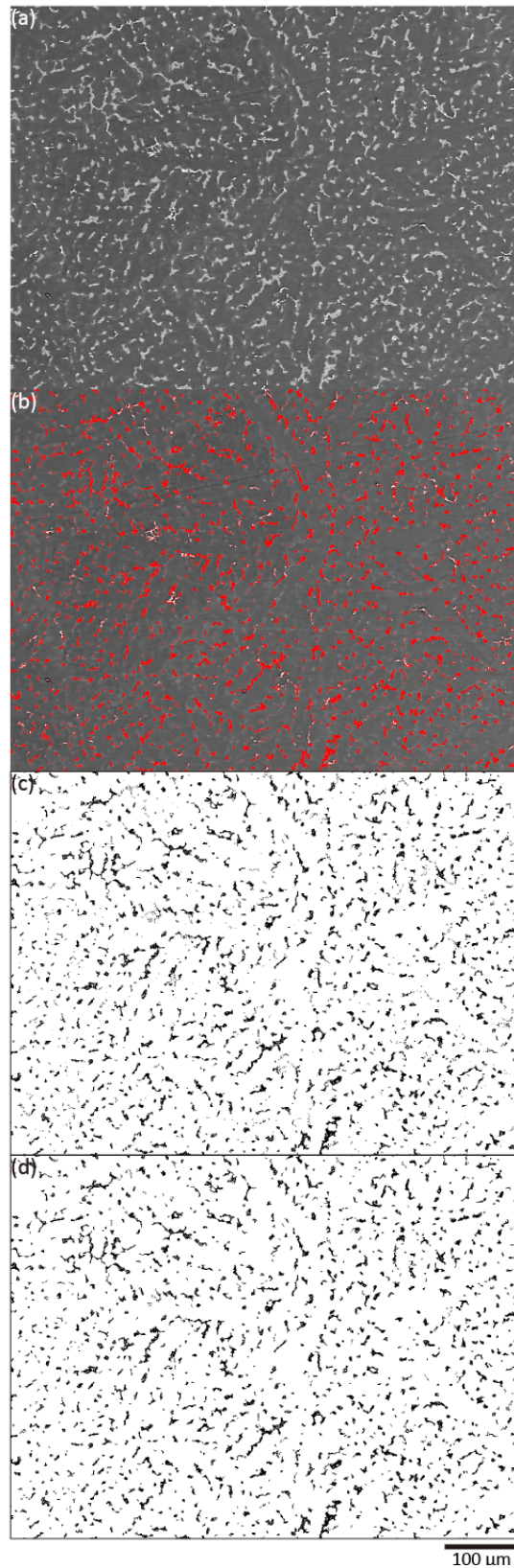


Figure 7.1 The typical image processing steps before measuring volume fraction of $\text{Mg}_{17}\text{Al}_{12}$. (a) an original BSE image. (b) mid-grey identified in red after thresholding. (c) a mixture of $\text{Mg}_{17}\text{Al}_{12}$ and the boundaries of some Al-Mn intermetallics from (b). (d) A final image for quantification after removing non- $\text{Mg}_{17}\text{Al}_{12}$ phases.

7.3 Results and Discussion

7.3.1. Intermetallic compounds before and after solution heat treatment

Typical microstructures after casting and after long-term holding at 410°C are shown in Figure 7.2(a) and (c). After casting, intermetallics were distributed between dendrite arms and between dendritic grains. After six days of solution heat treatment, most intermetallics had dissolved but some bright particles remained. To identify the intermetallic compounds present before and after long-term heat treatment, the extracted intermetallics were analysed with XRD and identified with the PDF-4+ 2022 database in HighScore Plus. Figure 7.2(b) and (d) show that, in the as-cast condition, $\text{Mg}_{17}\text{Al}_{12}$ and Al_8Mn_5 were present (ICDD 04-003-2934 [284] and ICDD 04-024-1009 [285] respectively). After 10-day solution heat treatment, the only IMC identified was LT- $\text{Al}_{11}\text{Mn}_4$ (ICDD 01-073-8903) [236]. Thus, during heat treatment at 410°C, two phenomena occurred involving the intermetallic compounds: (i) the $\text{Mg}_{17}\text{Al}_{12}$ dissolved into the α -Mg and (ii) the Al_8Mn_5 transformed into LT- $\text{Al}_{11}\text{Mn}_4$. The transformation involving Al-Mn compounds has been studied in detail elsewhere [229,230,286,287] and is not considered further in this study. Fortunately, the Al-Mn intermetallics could be easily distinguished from $\text{Mg}_{17}\text{Al}_{12}$ by their brightness in backscatter electron images, enabling the fraction of $\text{Mg}_{17}\text{Al}_{12}$ to be measured without interference from the transforming Al-Mn intermetallics.

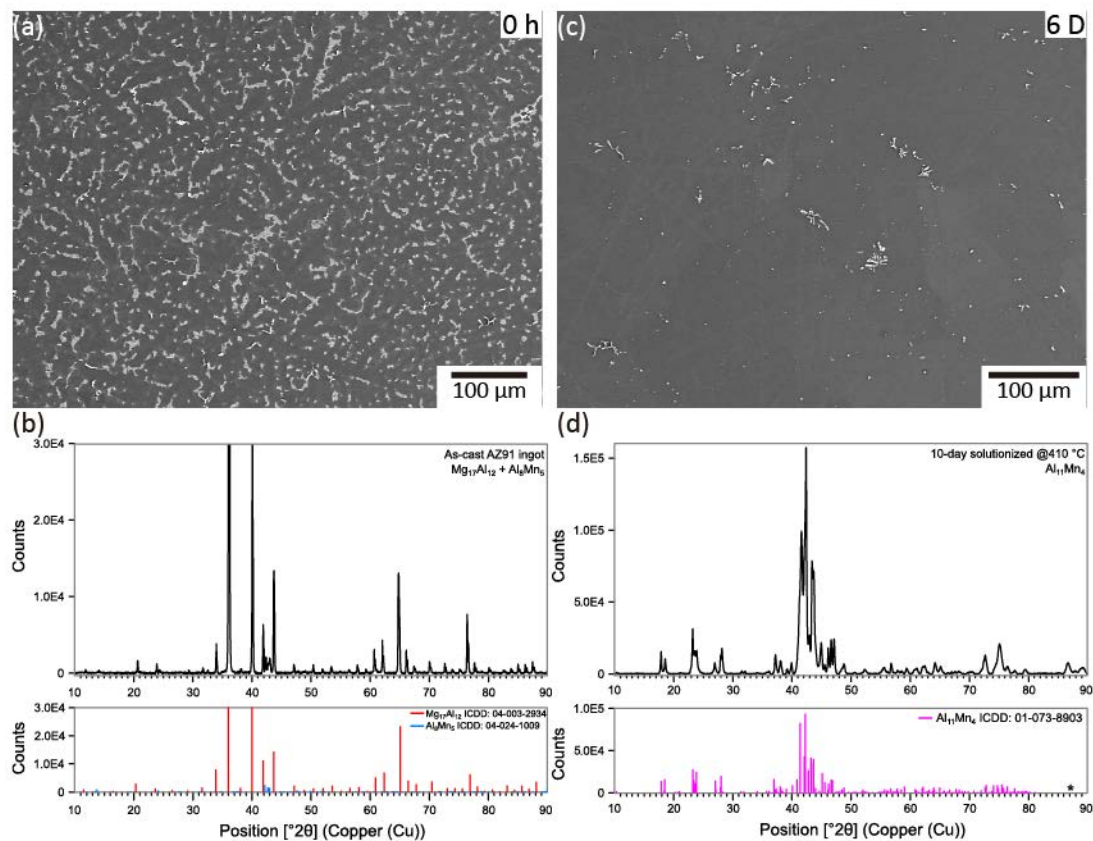


Figure 7.2 (a) BSE image of typical region of as-cast AZ91 (dark: α -Mg, grey: $\text{Mg}_{17}\text{Al}_{12}$ and bright: Al_8Mn_5) with (b) XRD patterns of extracted secondary phases from 0 hour heat-treated AZ91 containing $\text{Mg}_{17}\text{Al}_{12}$ and Al_8Mn_5 and (c) BSE 6-day solutionized AZ91 with (d) a longer 10-day solutionized AZ91 containing only $\text{Al}_{11}\text{Mn}_4$. The reference patterns with calculated intensity are attached, indexed with PDF-4+ 2022 database in HighScore Plus. Note that the peaks of $\text{Mg}_{17}\text{Al}_{12}$ in (a) are truncated to scale the XRD patterns for a better visual recognition of small peaks. *The reference pattern of $\text{Al}_{11}\text{Mn}_4$ (ICDD: 01-073-8903) only shows up to $82^\circ(2\theta)$.

7.3.2. Microstructure evolution during solutionising

Figure 7.3 overviews colour-etched optical micrographs of the changes in α -Mg grain morphology during solutionising in three samples: a gravity cast, gravity cast with grain refiner, and a slow cooled sample. In each case the dendritic structure can be clearly seen in the as-cast condition (Figure 7.3(a), (e), and (i)). As the heat treatment time increased, the dendritic structure was gradually lost (Figure 7.3(c)-(d), (f)-(h) and (k)-(l)) due to $\text{Mg}_{17}\text{Al}_{12}$ dissolution between α -Mg dendrite arms and the reduction of coring by Al diffusion. It is also apparent in each sample in Figure 7.3 that the grain boundaries straighten with increasing solutionising time causing the shape of α -Mg grains to become more polygonal. This is particularly

noticeable when comparing the as-cast condition (Figure 7.3(a), (e), and (i)) and the 6-day heat treated condition (Figure 7.3(d), (h), and (l)) and after 6 days, is at the most advanced stage in the grain refined cast samples (Figure 7.3(h)).

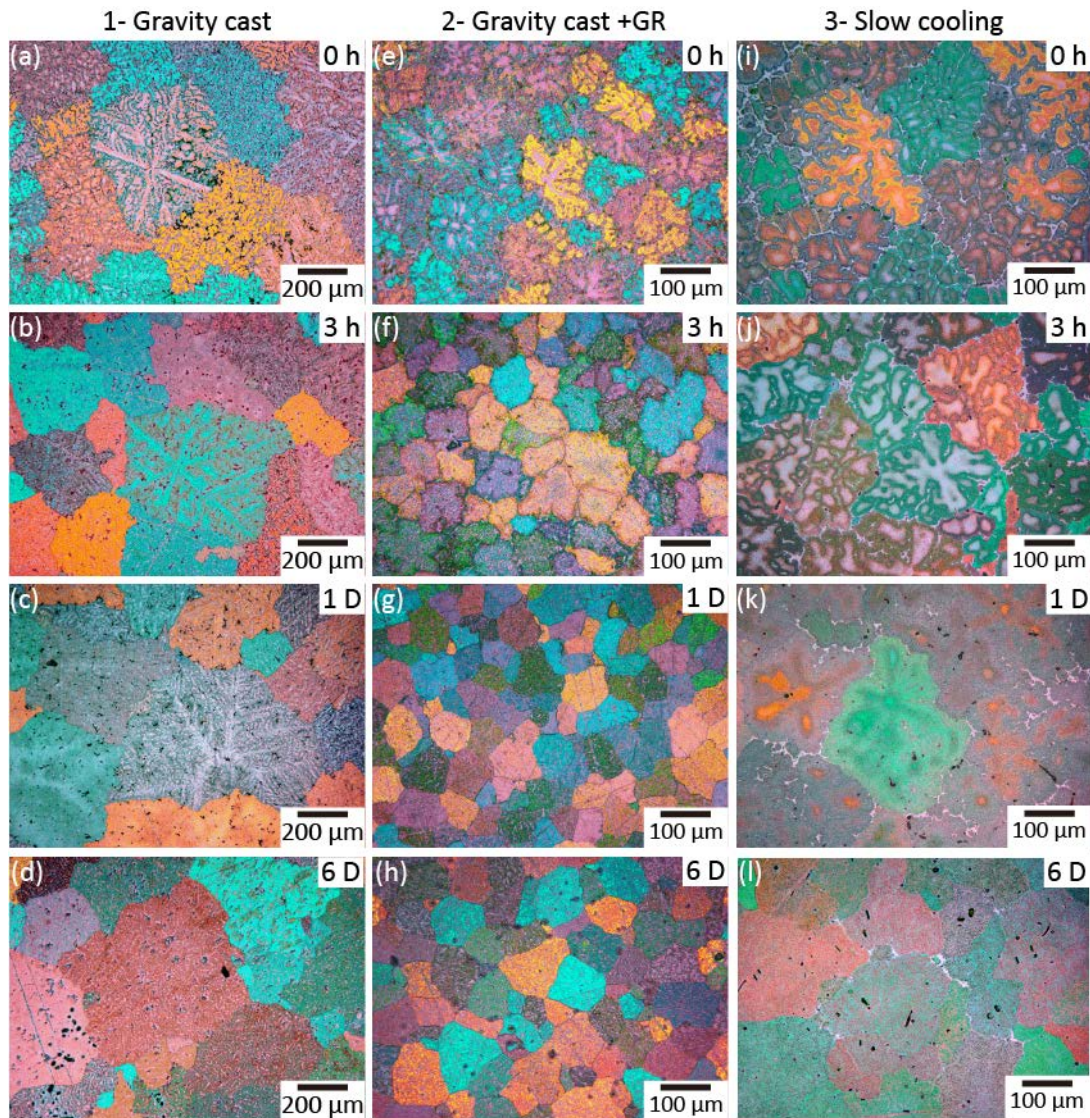


Figure 7.3 Colour etching reveals α -Mg morphologies through heat treatment at 410°C for 0, 3, 24, 144 hours. (a)-(d) in gravity cast AZ91, (e)-(h) gravity cast AZ91 with grain refinement and (i)-(l) slow cooling sample with a smaller grain size shown in Table 6.2.

Figure 7.4 overviews typical low magnification BSE-SEM images from each casting/cooling method at four heat treatment times. The magnification has been selected to show the volume fraction of $\text{Mg}_{17}\text{Al}_{12}$ and its location in the microstructure. The volume fraction of $\text{Mg}_{17}\text{Al}_{12}$ gradually dissolves in all samples. As the heat treatment reaches 6 days, most $\text{Mg}_{17}\text{Al}_{12}$ was

dissolved but, importantly, it was not fully dissolved. From the orientation contrast of BSE images [288,289], different α -Mg grains can be seen allowing the location of the undissolved $\text{Mg}_{17}\text{Al}_{12}$ to be identified in the 3-hour and 1-day heat treatment samples. In Figure 7.4(f)-(j) and (k)-(o), the remaining $\text{Mg}_{17}\text{Al}_{12}$ was often located at α -Mg grain boundaries and the largest amount of remaining $\text{Mg}_{17}\text{Al}_{12}$ appeared in the junction regions between three or more α -Mg grains. A similar result can be seen in the colour etched micrographs of Figure 7.4(i)-(l) where the remaining $\text{Mg}_{17}\text{Al}_{12}$ (white) is located mostly at α -Mg grain boundaries after 1 and 6 days.

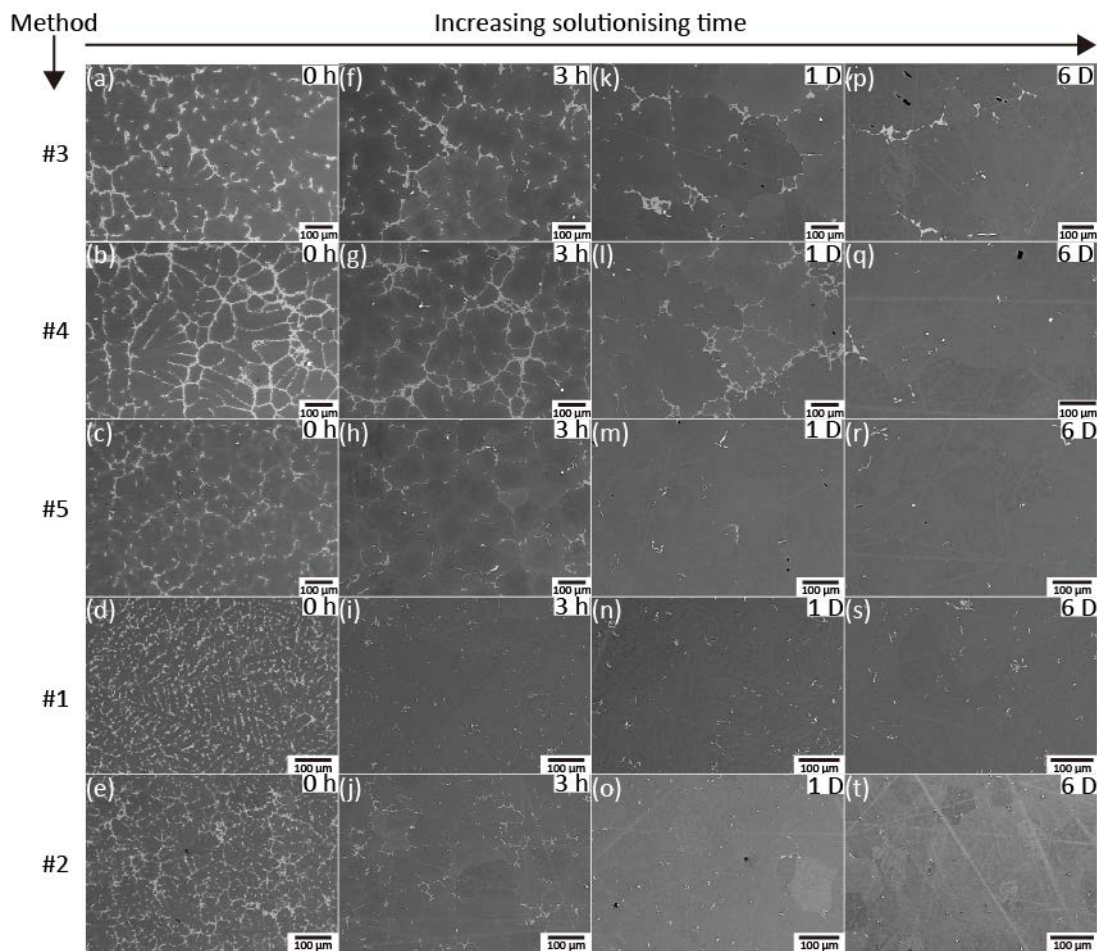


Figure 7.4 Typical regions of five different samples in three different heat treatment time: (a)-(e) 0 hour, (f)-(j) 3 hours, (k)-(o) 1 day and (p)-(t) 6 days. These five samples are (a),(f),(k),(p) slow cooling, (b),(g),(l),(q) interrupted solidification, (c),(h),(m),(r) fast cooling, (d),(i),(n),(s) gravity cast without grain refinement, and (e),(j),(o),(t) gravity cast with grain refinement.

For completeness, typical example micrographs at all seven times during solutionising are given for all sample in Figure 7.5-Figure 7.9. These show the same story as Figure 7.10.

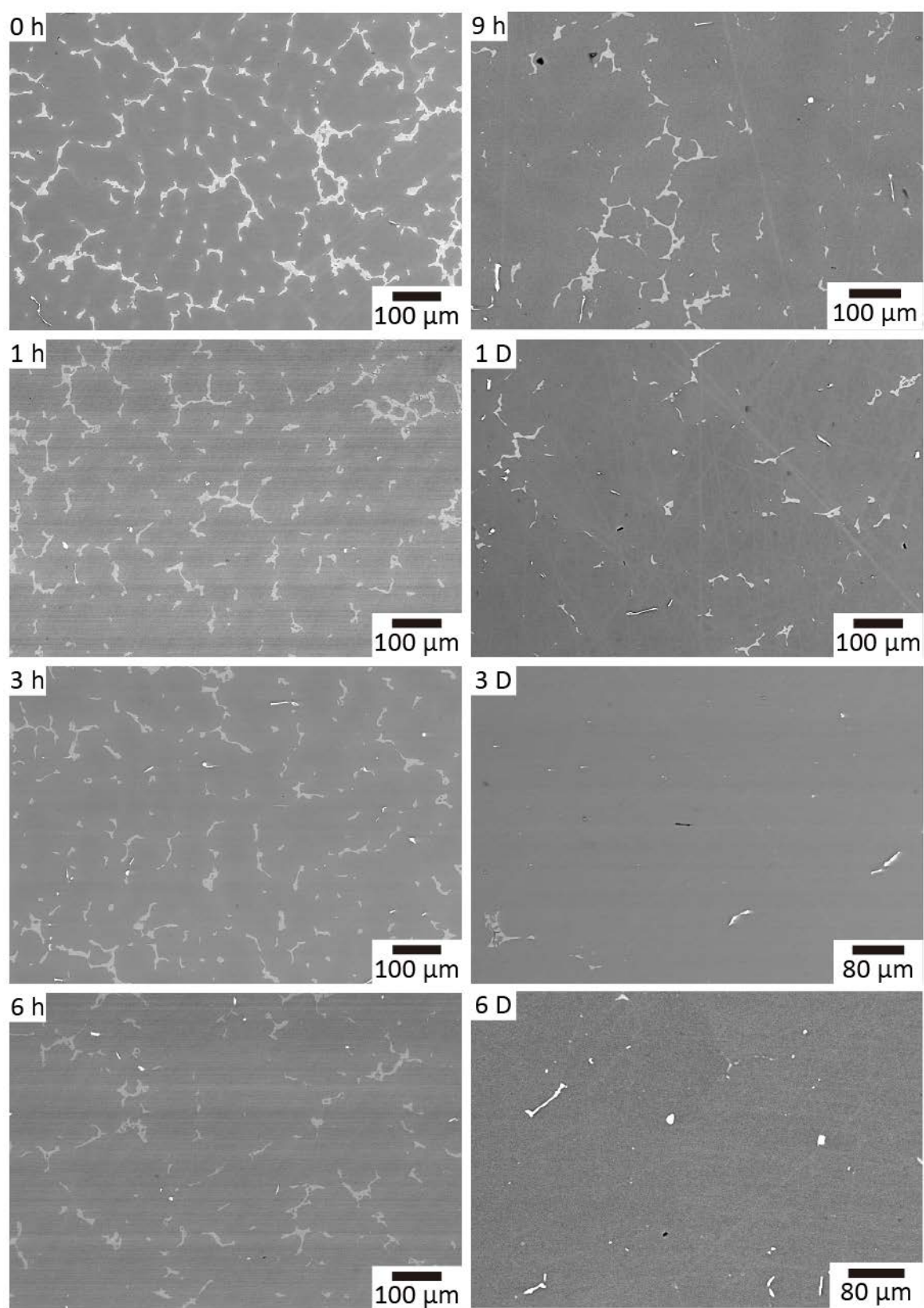


Figure 7.5 The BSE images for volume fraction of $\text{Mg}_{17}\text{Al}_{12}$ on the slow cooling sample through heat treatment of 0, 1, 3, 6, 9, 24, 72, 144 hours.

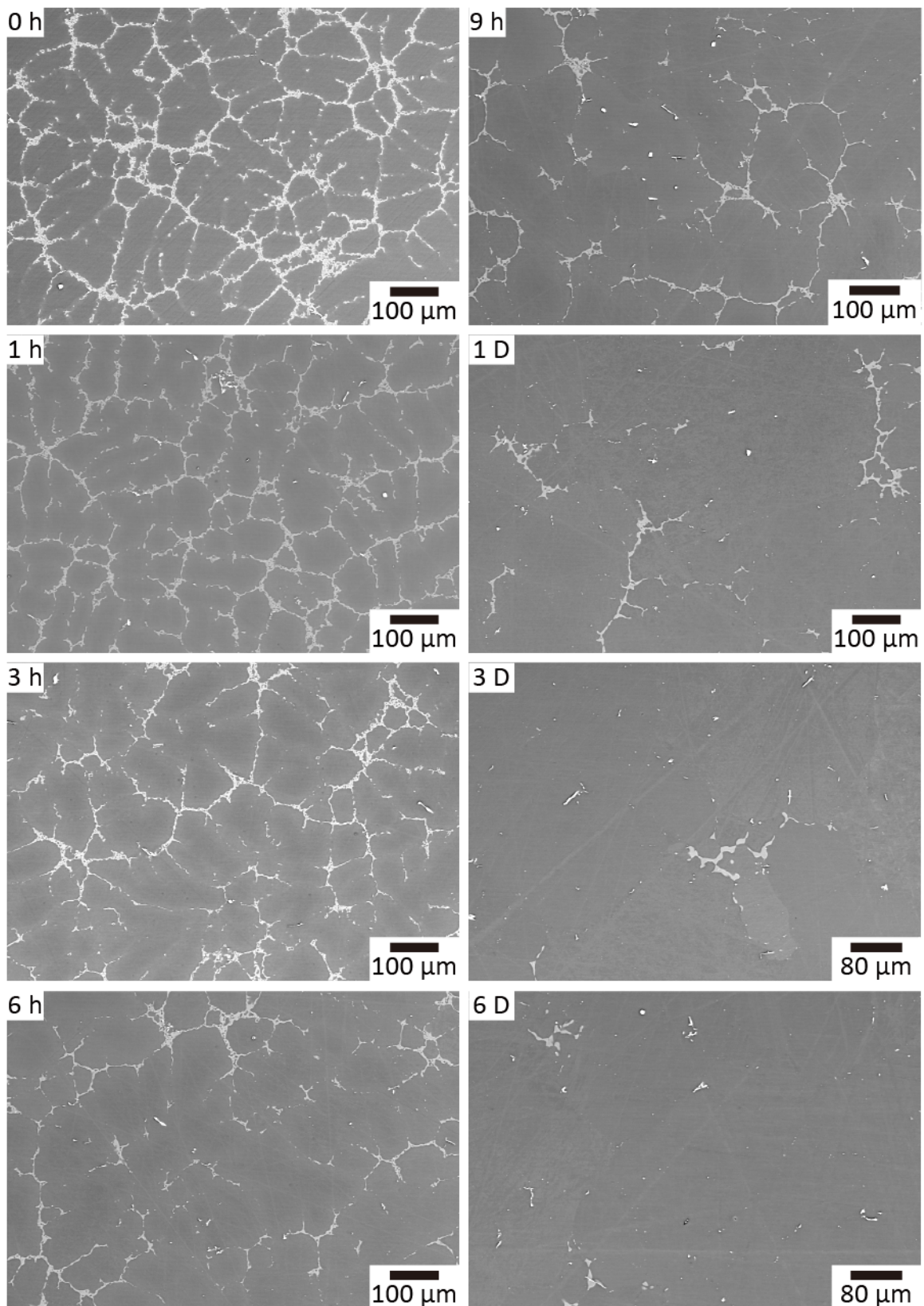


Figure 7.6 The BSE images for volume fraction of $\text{Mg}_{17}\text{Al}_{12}$ on the interrupted solidification sample through heat treatment of 0, 1, 3, 6, 9, 24, 72, 144 hours.

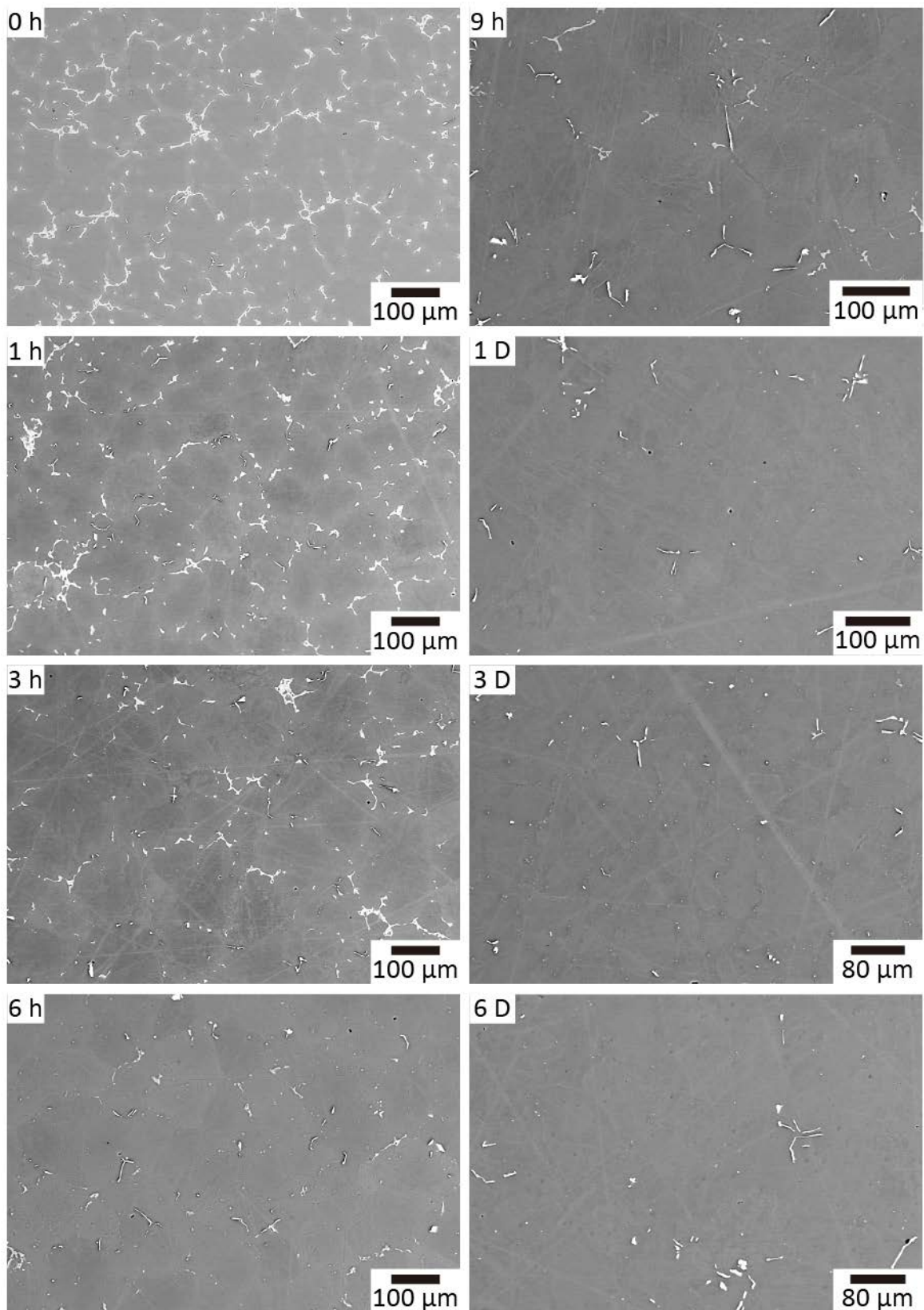


Figure 7.7 The BSE images for volume fraction of $\text{Mg}_{17}\text{Al}_{12}$ on the fast cooling sample through heat treatment of 0, 1, 3, 6, 9, 24, 72, 144 hours.

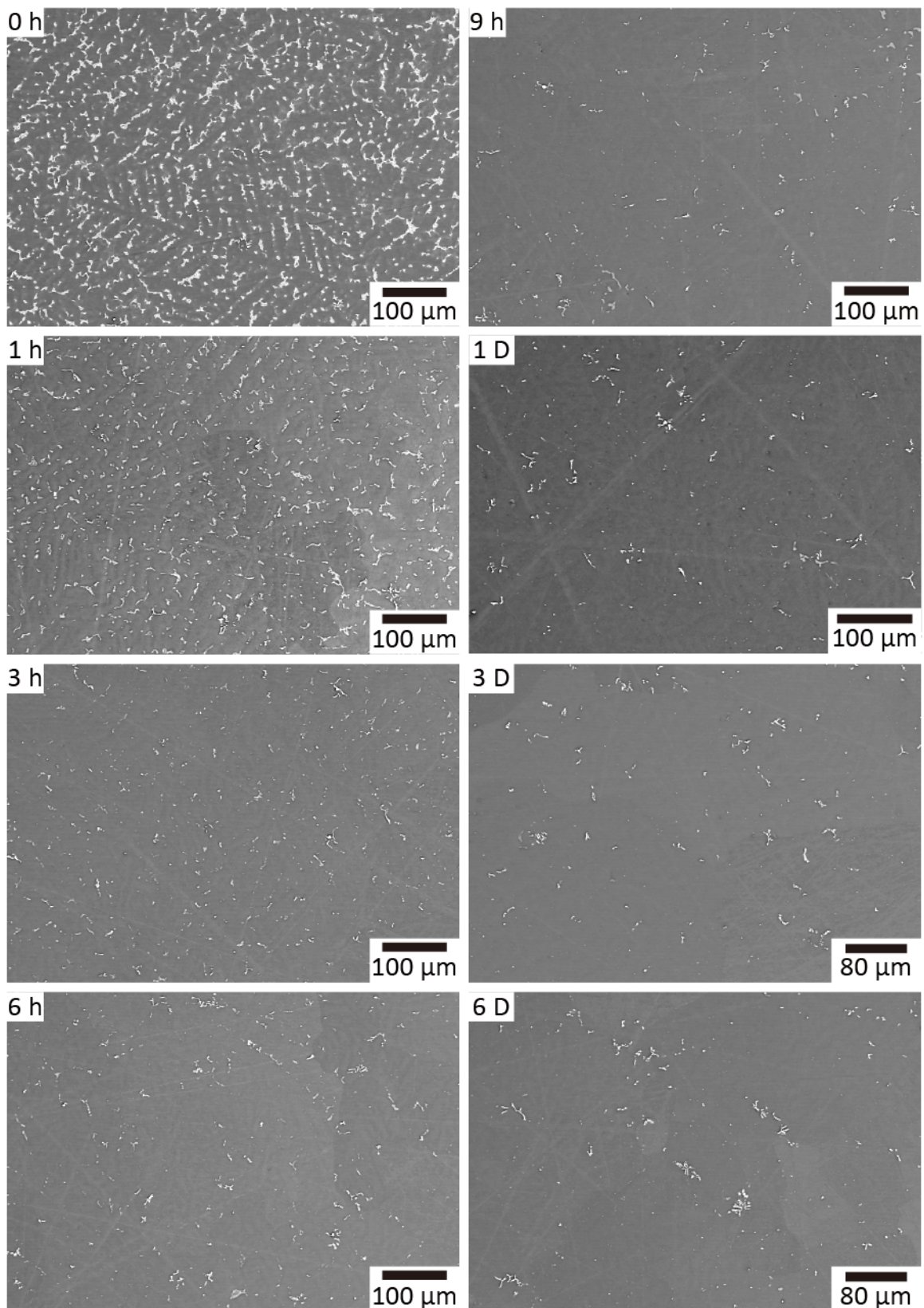


Figure 7.8 The BSE images for volume fraction of $\text{Mg}_{17}\text{Al}_{12}$ on the gravity cast without grain refinement sample through heat treatment of 0, 1, 3, 6, 9, 24, 72, 144 hours.

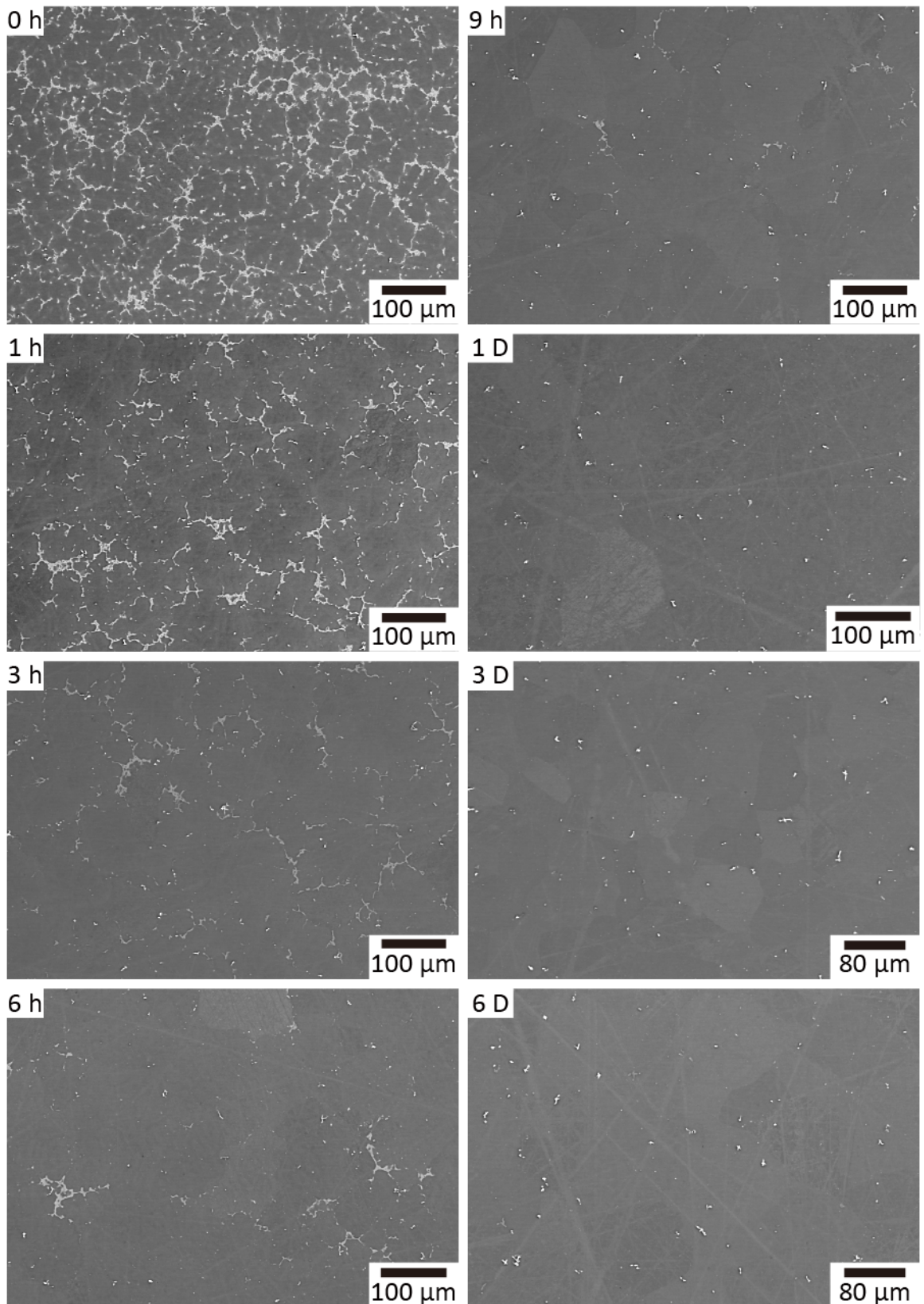


Figure 7.9 The BSE images for volume fraction of $\text{Mg}_{17}\text{Al}_{12}$ on the gravity cast with grain refinement sample through heat treatment of 0, 1, 3, 6, 9, 24, 72, 144 hours

Higher magnification BSE images of the five samples are shown in Figure 7.10, where further details of the $\text{Mg}_{17}\text{Al}_{12}$ dissolution process can be observed. Note that, with these partially divorced eutectic microstructures, the eutectic α -Mg embedded inside $\text{Mg}_{17}\text{Al}_{12}$ remained through most of the heat treatment while the outer parts of the $\text{Mg}_{17}\text{Al}_{12}$ dissolved. This is clearest in the slow cooled sample in Figure 7.10(a),(f),(k),(p) where the eutectic α -Mg still remained after 6-day heat treatment until the surrounding $\text{Mg}_{17}\text{Al}_{12}$ dissolved into the α -Mg.

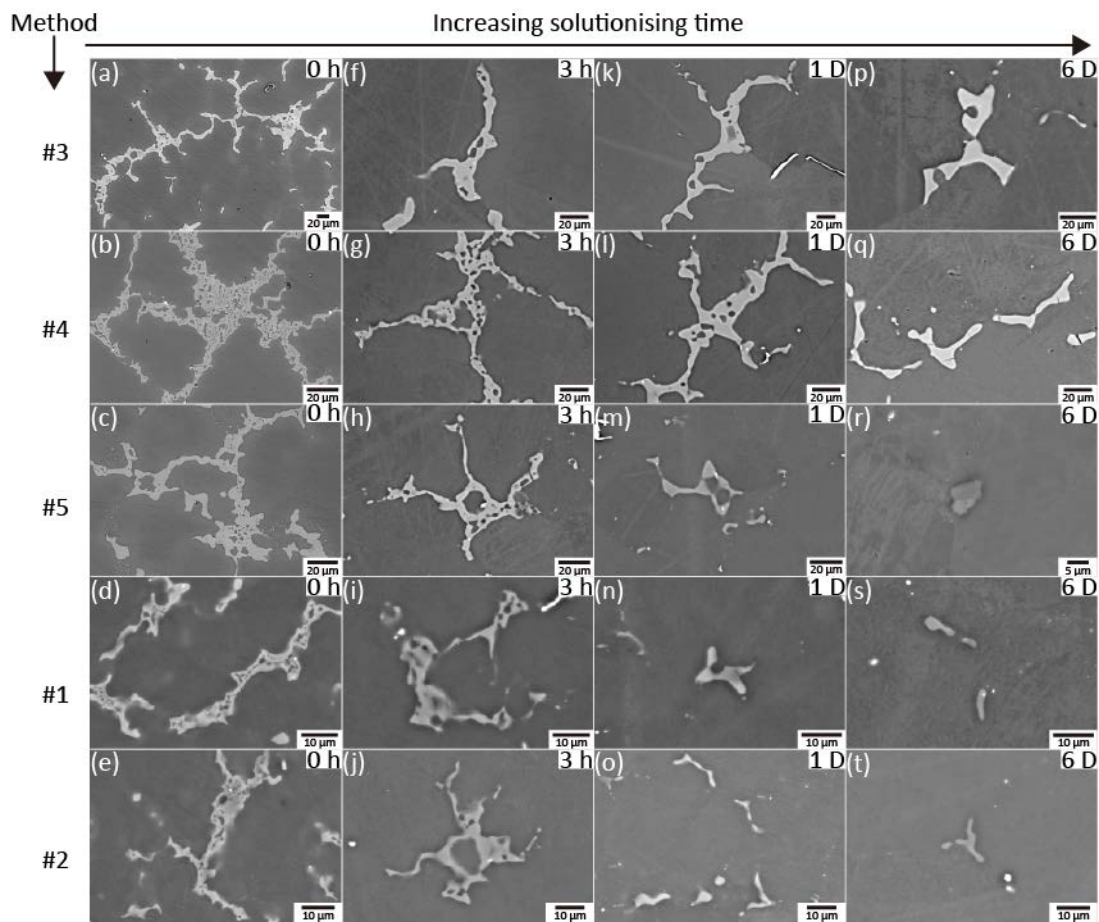


Figure 7.10 Higher magnification BSE images on partially divorced $\text{Mg}_{17}\text{Al}_{12}$ in five different samples during the heat treatment of (a)-(e) 0 hour, (f)-(j) 3 hours, (k)-(o) 1 day and (p)-(t) 6 days. These five samples are (a),(f),(k),(p) slow cooling, (b),(g),(l),(q) solidification interrupted, (c),(h),(m),(r) fast cooling, (d),(i),(n),(s) gravity cast AZ91 without grain refinement and (e),(j),(o),(t) gravity cast AZ91 with grain refinement.

7.3.3. Influence of microstructure on dissolution kinetics

Figure 7.11(a) is a plot of the changing volume fraction of $\text{Mg}_{17}\text{Al}_{12}$ during solution heat treatment of the six samples (1-5i) in Figure 6.5. The data were obtained by quantifying a fraction of $\text{Mg}_{17}\text{Al}_{12}$ in at least 22 micrographs for each sample at the same magnification as in Figure 7.5-Figure 7.9 using ImageJ. In Figure 7.11(a), all samples have a similar shaped curve with a long tail after 1 day heat treatment. This tail can be confirmed in the microstructures of Figure 7.5-Figure 7.9 where $\text{Mg}_{17}\text{Al}_{12}$ was not completely dissolved even after 6-day heat treatment. The data in Figure 7.11(a) fall into two groups: the slow cooling and interrupted solidification samples having larger SDAS of $\sim 50 \mu\text{m}$ dissolved $\text{Mg}_{17}\text{Al}_{12}$ slower than other three sample having smaller SDAS (Table 6.2). Note that Table 2.15 shows various $\text{Mg}_{17}\text{Al}_{12}$ dissolution times but Figure 7.11(a) shows most $\text{Mg}_{17}\text{Al}_{12}$ in the gravity cast samples is dissolved into $\alpha\text{-Mg}$ within a day and the time differences were governed by the SDAS (λ_2) values and other factors. Thus, the gravity samples were generally recommended to be heat treated within the range of 400 to 420 °C for 24 hours to achieve low volume fraction of $\text{Mg}_{17}\text{Al}_{12}$.

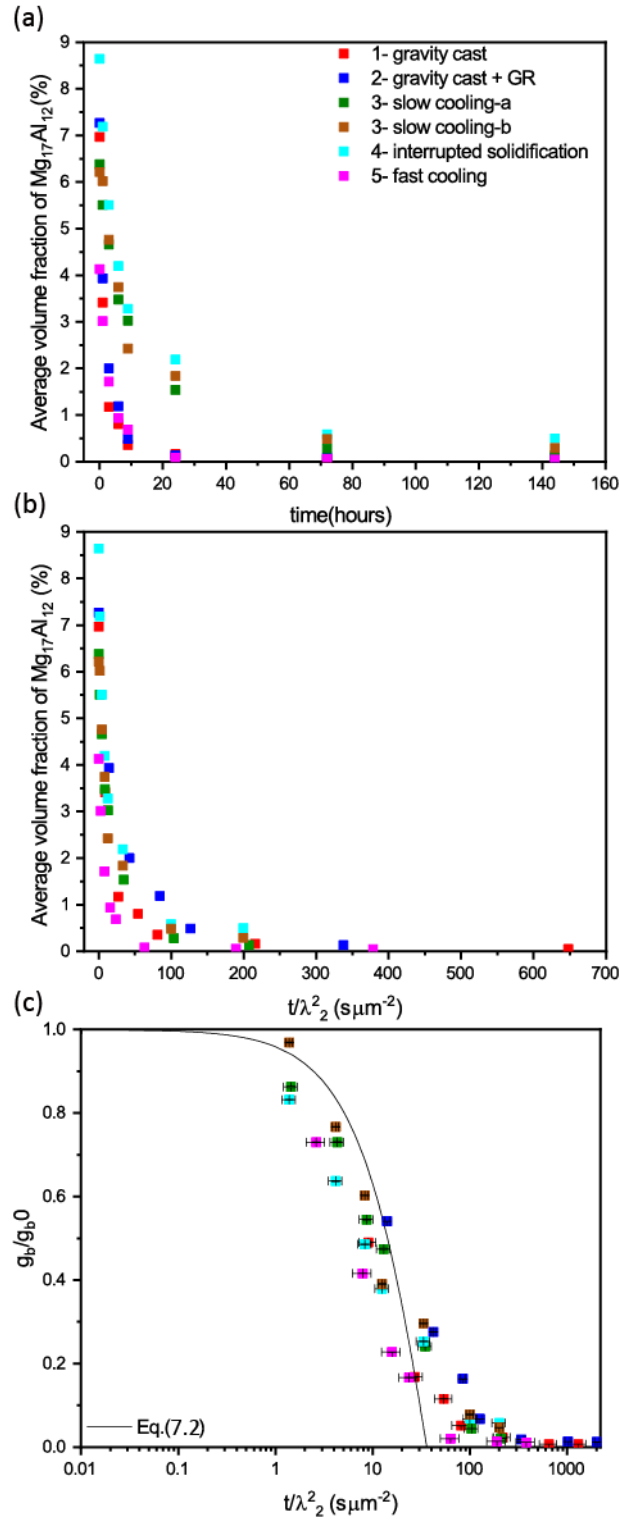


Figure 7.11 (a) Experimental data of the average volume fraction of $Mg_{17}Al_{12}$ in the six samples versus heat treatment time. (b) The average volume fraction of $Mg_{17}Al_{12}$ in the six samples through heat treatment time over square of SDAS as x-axis. (c) The ratio of $Mg_{17}Al_{12}$ volume fraction during heat treatment to original $Mg_{17}Al_{12}$ volume fraction with time over square of SDAS as x-axis, fitted with a analytical model based on Ref [228].

Considering diffusion across half a SDAS, Singh and Flemings [228,290] derived an analytical model for the dissolution kinetics during solution heat treatment of a divorced eutectic. For a given alloy, their model predicts that the volume fraction of remaining intermetallic, g_β , should scale with t/λ_2^2 where t is time and λ_2 is the SDAS. That is to say, irrespective of the lengthscale of the dendritic microstructure, the model predicts that all data should fall on a common curve when plotted as g_β versus t/λ_2^2 . This is done in Figure 7.11(b) and the data are much closer to a single curve in Figure 7.11(b) than Figure 7.11(a) in reasonable agreement with the model [228,290], although still with some scatter.

To compare the g_β versus t/λ_2^2 data with an analytical model, we use the expression of Dantzig and Rappaz [225] in Eq. (7.1) which is a modification of the Singh and Flemings [228,290] model. This can be rearranged into Eq. (7.2) to make g_β the subject of the equation.

$$\frac{g_\beta + (C_\alpha^{410} - C_0)/(C_\beta^{410} - C_\alpha^{410})}{g_\beta^0 + (C_\alpha^{410} - C_0)/(C_\beta^{410} - C_\alpha^{410})} = e^{-\left(\frac{\pi^2 D_s}{g_\alpha^2}\right) \frac{t}{\lambda_2^2}} \quad (7.1)$$

$$g_\beta = \left[\left(g_\beta^0 + \frac{(C_\alpha^{410} - C_0)}{(C_\beta^{410} - C_\alpha^{410})} \right) e^{-\left(\frac{\pi^2 D_s}{g_\alpha^2}\right) \frac{t}{\lambda_2^2}} \right] - \frac{(C_\alpha^{410} - C_0)}{(C_\beta^{410} - C_\alpha^{410})} \quad (7.2)$$

Eq. (7.2) is plotted in Figure 7.11(c) as g_β/g_β^0 versus t/λ_2^2 using the parameters in Table 7.1, along with the experimental data from Figure 7.11(a). Figure 7.11(c) uses a log scale for the horizontal axis to allow better comparison between the model and experiments at short times.

Table 7.1 Thermophysical property parameters used for analytical model of AZ91 heat treatment [202,291]

Parameter	Symbol	Value	Unit	Ref.
Initial volume fraction of $Mg_{17}Al_{12}$	g_β^0	9.4	vol%	[202]
Composition of α -Mg at 410°C	C_α^{410}	11.4	wt% Al	[202]
Composition of $Mg_{17}Al_{12}$ at 410°C	C_β^{410}	42.7	wt% Al	[202]
Alloy composition	C_0	9	wt% Al	-
Diffusion coefficient at 410°C	D_s	1.95×10^{-3}	$\mu m^2 s^{-1}$	[291]
Initial volume fraction of α -Mg	g_α	90.6	vol%	[202]

In Figure 7.11(c), Eq. (7.2) is in reasonable agreement with the experiment data down to $g_\beta/g_\beta^0 \sim 0.15$ beyond which the measured dissolution rate of $Mg_{17}Al_{12}$ becomes much slower than that calculated by the analytical model in Eq. (7.2). Comparing with past work on this alloy, we note that Zhu et al.[98] did not consider dissolution beyond $g_\beta/g_\beta^0 < 0.15$ when comparing their diffusion-based dissolution model with their $Mg_{17}Al_{12}$ dissolution data.

The finding that all data follow a similar curve when time is corrected for the SDAS through t/λ_2^2 (Figure 7.11(b)) and that all data are reasonably described by Eq. (7.2) up to $g_\beta/g_\beta^0 \sim 0.15$ shows that $Mg_{17}Al_{12}$ dissolution is governed by solute diffusion in α -Mg across half the SDAS until the $Mg_{17}Al_{12}$ within dendrite arms is dissolved in all cases. Interestingly, this scaling by the SDAS is valid even in the rosette microstructure (the fast cooled sample) with grain size to SDAS ratio ~ 3 (Figure 6.5) where more of the $Mg_{17}Al_{12}$ was located between α -Mg grains before dissolution began.

The discrepancy towards the end of dissolution (at $g_\beta/g_\beta^0 < \sim 0.15$) between experiments and analytical models derived assuming diffusion across half of a SDAS has been reported and discussed by various researchers in aluminium alloys [225,228,292,293]. It has been argued that, towards the end of dissolution, the intermetallic between most secondary dendrite arms has dissolved and the majority of remaining intermetallic is at grain boundaries which increases the diffusion length and slows dissolution significantly [225,228,293]. This phenomenon can be understood based on the Fick's 2nd law of flattening the concentration of Al content in the Mg matrix. Additionally, Roósz et al. [292] showed that the end of dissolution is determined by the largest dendrite arm, and the tail in the experimental data can be better matched by considering the distribution of λ_2 rather than the average λ_2 .

The observation that the remaining $Mg_{17}Al_{12}$ after 1 and 6 days heat treatment was mostly located at α -Mg grain boundaries in Figure 7.4(k)-(o) and (p)-(t) indicates that the increasing

diffusion length in the late stages of dissolution is also active in magnesium alloys. A further factor that seems to be important in AZ91 is the variation in thickness of $\text{Mg}_{17}\text{Al}_{12}$ from one region to another (e.g. in Figure 7.4) which results in thicker regions remaining in the late stages of dissolution when the diffusion profile has become shallower.

To demonstrate the effects of a locally thicker region of $\text{Mg}_{17}\text{Al}_{12}$, Figure 7.12 considers three dendrite arms with the same SDAS = 50 μm but differing $\text{Mg}_{17}\text{Al}_{12}$ thickness. The two middle $\text{Mg}_{17}\text{Al}_{12}$ regions have the correct $\text{Mg}_{17}\text{Al}_{12}$ thickness for the SDAS assuming the Scheil model. The right-most $\text{Mg}_{17}\text{Al}_{12}$ region is thicker and the left-most $\text{Mg}_{17}\text{Al}_{12}$ region is thinner such that the solute balance occurs over multiple SDAS rather than just half a SDAS. In practice, this could occur by shrinkage-driven liquid flow creating a locally non-uniform alloy composition. In Figure 7.12, the Al solute diffusion profile in the α -Mg phase has been plotted at four times using the 1-D analytical solutionising model from Dantzig & Rappaz [225] in Eq. (7.3) with the parameters in Table 7.1. Eq. (7.3) is based on an approximate solution to the diffusion equation (Fick's 2nd law) that starts with a diffusion profile similar to the Scheil equation and maintains an overall solute balance throughout dissolution. The other assumptions are local equilibrium at α -Mg+ $\text{Mg}_{17}\text{Al}_{12}$ interfaces and that interface motion (into the $\text{Mg}_{17}\text{Al}_{12}$ phase) is governed by solute diffusion in the α -Mg phase.

$$C_s(x, t) \approx C_\alpha^{410} + A_0 \cos \left(\frac{\pi x}{\lambda_2 g_\alpha} \right) e^{-\left(\frac{\pi^2 D_s}{g_\alpha^2} \right) \frac{t}{\lambda_2^2}} \quad (7.3)$$

Where x in Eq. (7.3) is the distance from the centre of a secondary dendrite arm and other terms are defined in Table 7.1. A_0 was selected to give the correct solute balance.

In Figure 7.12, at $t = 8.9$ hours the thinner (left-most) $\text{Mg}_{17}\text{Al}_{12}$ region has dissolved and the other $\text{Mg}_{17}\text{Al}_{12}$ regions are still dissolving. By 22.9 hours, only the thickest (right-most) $\text{Mg}_{17}\text{Al}_{12}$ region is still dissolving. At a later time such as the plot labelled $\gg 22.9$ hours, any remaining $\text{Mg}_{17}\text{Al}_{12}$ will have a concentration gradient at its α -Mg+ $\text{Mg}_{17}\text{Al}_{12}$ interface that is

shallower than at earlier times so the Al diffusion flux becomes slower, resulting in a continuously slowing dissolution rate. From Figure 7.12, we see how local variations in $\text{Mg}_{17}\text{Al}_{12}$ thickness and, particularly, local regions of thicker $\text{Mg}_{17}\text{Al}_{12}$ play an important role in the long tail in the dissolution kinetics in Figure 7.11(c).

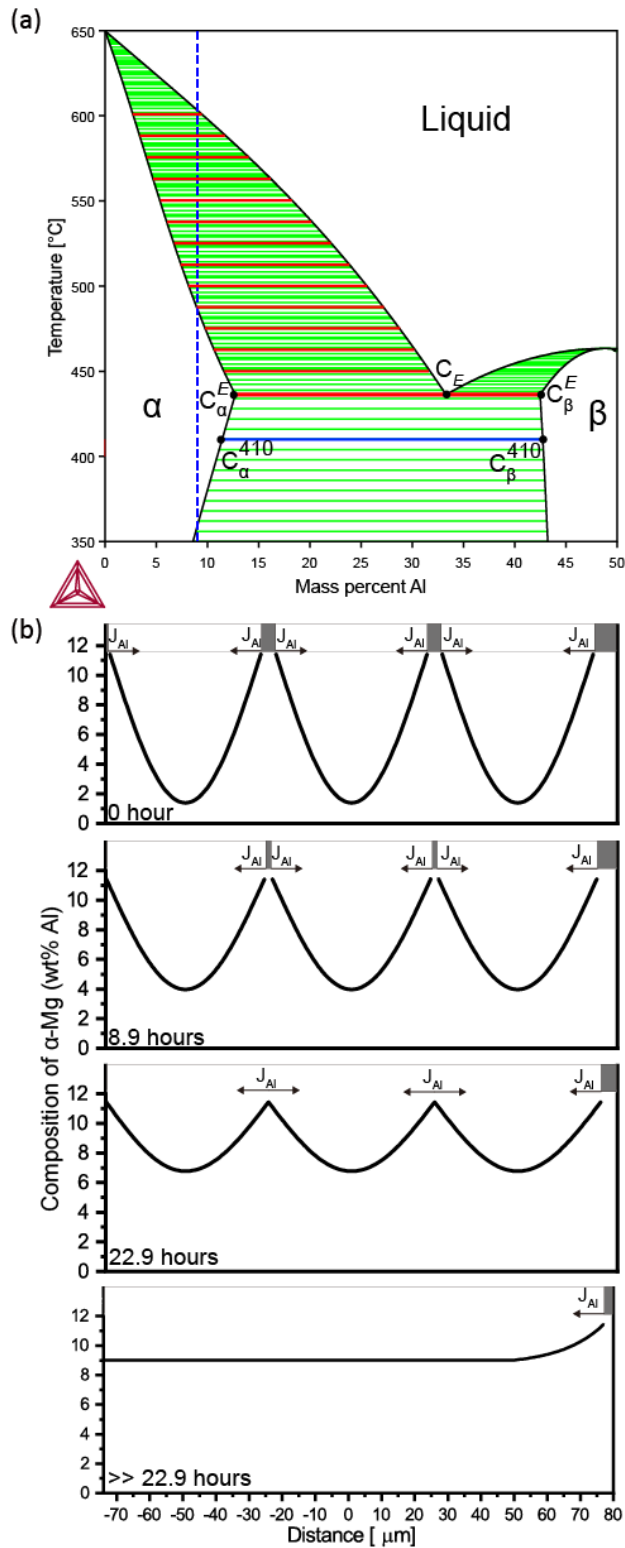


Figure 7.12 (a) The phase diagram of Mg-Al system between 0 to 50 wt% with tie lines labelled at 435 °C and 410 °C. The contact line of 9 wt% Al is drawn in the blue dashed line. (b) The solute profile demonstrates the concentration of Al content in α -Mg varies through solution heat treatment. The original thickness of the $\text{Mg}_{17}\text{Al}_{12}$ (grey) was calculated by Eq. (7.3) in the middle two sections. The thicker and thinner $\text{Mg}_{17}\text{Al}_{12}$ sections were deliberated on multiplying an integer and fraction to the complete dissolution time calculated by Eq. (7.3) for varying the thicknesses respectively.

Since the remaining $\text{Mg}_{17}\text{Al}_{12}$ in the late stages of dissolution is located at grain boundaries, it might be expected that the grain size would affect the end of dissolution. However, this was not found here. For example, the two slow cooling samples with similar SDAS and very different grain size showed similar dissolution kinetics (Figure 7.11(a)), suggesting that any effect of α -Mg grain size is masked by the scatter in the data.

Examining Figure 7.11(b) and (c), note that the interrupted solidification and grain refined gravity cast samples have closely overlapping data yet the former had the least divorced eutectic and the latter the most divorced eutectic among the alloys (Figure 6.18(d)). This shows that the degree of eutectic divorcedness had no significant effect on the dissolution kinetics in this study.

Some past studies on the dissolution of $\text{Mg}_{17}\text{Al}_{12}$ in AZ80 [101,294] (which has similar composition to AZ91 [229]) have investigated the dissolution kinetics with the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation [295–297] in Eq. (7.4).

$$f = 1 - \exp(-k(t)^n) \quad (7.4)$$

Where f is the volume fraction of $\text{Mg}_{17}\text{Al}_{12}$ dissolved, k is a temperature-dependent rate constant [298] and n is an exponential time constant.

They found best fit exponents of $n = 0.37\text{--}0.39$ [294] and $n = 0.61$ [101] and noted that a value of $n < 1$ indicates a dissolution rate that decreases with time. As discussed above with Figure 7.11(c) and Figure 7.12, a decreasing dissolution rate with increasing time is expected due to both the flattening concentration gradients in α -Mg during back diffusion and, the increasing diffusion length in the late stages of dissolution.

To link further with this prior work, the data in Figure 7.11(a) were reanalysed using the JMAK equation by plotting $\ln[\ln(1/1 - f)]$ versus $\ln(t)$ and finding the best fit slope (n) and intercept ($\ln(k)$) An example is shown in Figure 7.13 where the data are approximately linear

indicating the data can be approximated reasonably with the JMAK equation. The best fit values of n and k for each sample are listed in Table 7.2. The samples of this study had $n = 0.37 - 0.84$ similar to past work [294]. The procedure was then repeated using t/λ_2^2 rather than t since all data approximate to a common curve with this scaling in Figure 7.11(b). These best fit values are also listed in Table 7.2; note that using t/λ_2^2 rather than t does not affect the values of the time exponent, n nor the R^2 values.

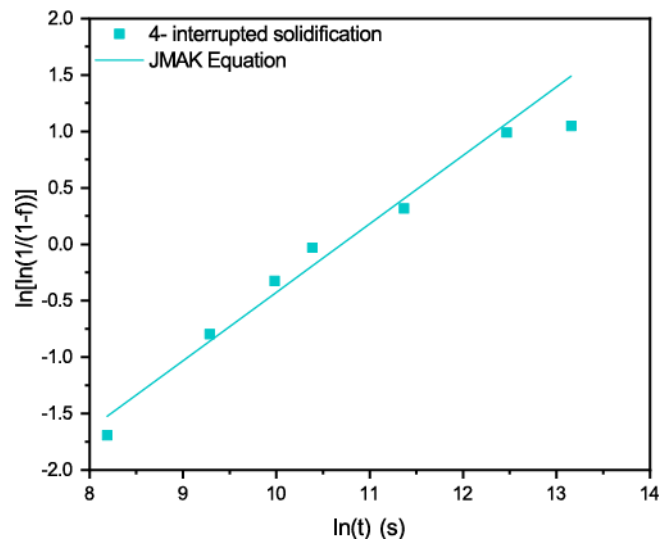


Figure 7.13 An example of plotting $\ln[\ln(1/(1 - f))]$ versus $\ln(t)$ to find the best fit values of n and k in the JMAK equation. This example is an interrupted solidification sample.

Table 7.2 Fitting parameters to the JMAK equation in Eq. (7.4) using either time (t) or the lengthscale-corrected time (t/λ_2^2)

Casting/cooling method	n	Using t	R^2	n	Using t/λ_2^2	R^2
	(-)	$\ln(k)$ (s^{-1})	(-)	(-)	$\ln(k)$ (s^{-1})	(-)
Gravity cast	0.37	-3.01	0.89	0.37	-0.79	0.89
Gravity cast + GR	0.40	-3.43	0.89	0.40	-1.22	0.89
Slow cooling 1	0.67	-7.32	0.99	0.67	-2.07	0.99
Slow cooling 2	0.84	-9.46	0.88	0.84	-2.85	0.88
Fast cooling	0.53	-5.10	0.90	0.53	-1.27	0.90
Interrupted solidification	0.61	-6.49	0.98	0.61	-0.41	0.98

Since all the dissolution data approximate to a common g_β/g_β^0 versus t/λ_2^2 curve when data is plotted in terms of t/λ_2^2 (Figure 7.11(b) & (c)), it was also possible to find the best-fit JMAK

equation through the dissolution data of all samples. In practical situations, we are most interested in times when a high fraction of $\text{Mg}_{17}\text{Al}_{12}$ has dissolved, so $\ln[\ln(1/1-f)]$ versus $\ln(t/\lambda_2^2)$ was plotted using data from all samples only for data with $\ln(t/\lambda_2^2) > 3$, giving best fit values of $n = 0.31$ and $\ln(k) = -0.49$ (where k is $0.61 \text{ s}^{-1} \text{ m}^2$). The best fit curve is plotted with all datasets in Figure 7.14(b). This empirical fit may be useful in practice to estimate the time to dissolve a chosen high fraction (e.g. 95%) of $\text{Mg}_{17}\text{Al}_{12}$ at 410°C when the analytical model deviates significantly from reality (Figure 7.11(b) & (c)). To use this empirical equation, the SDAS needs to be known which could either be measured or calculated with reasonable accuracy using Eq. (6.2) & (6.4) as was shown in Figure 6.6(c) & (d).

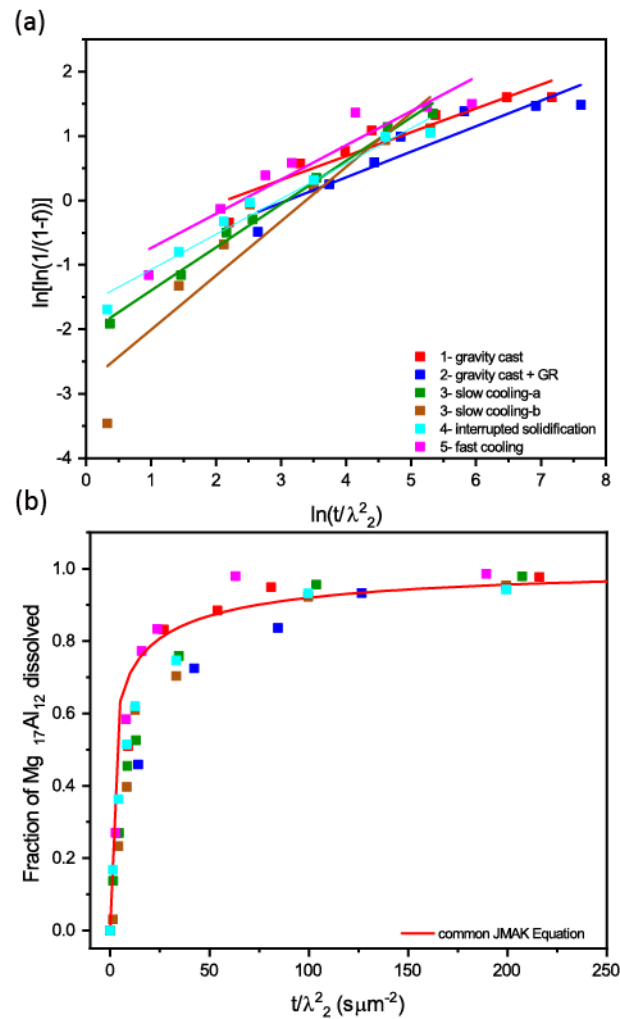


Figure 7.14 The reanalysed data based on Figure 7.11(a) plotted by the JMAK equation of (a) $\ln[\ln(1/1-f)]$ versus $\ln(t/\lambda_2^2)$ and (b) the fraction of $\text{Mg}_{17}\text{Al}_{12}$ dissolved into $\alpha\text{-Mg}$ versus t/λ_2^2 .

7.4 Conclusions

Six as-cast samples of AZ91 with a wide range of α -Mg grain size, SDAS and eutectic morphology have been used to study the effects of microstructure on the dissolution kinetics of $\text{Mg}_{17}\text{Al}_{12}$ at 410 °C. The key findings are:

- Two phase transformations occurred during solutionising at 410°C: the $\text{Mg}_{17}\text{Al}_{12}$ dissolved into α -Mg and Al_8Mn_5 transformed into $\text{LT-Al}_{11}\text{Mn}_4$.
- The $\text{Mg}_{17}\text{Al}_{12}$ dissolution kinetics were not significantly affected by the grain size nor the extent to which the eutectic was divorced or partially divorced. In contrast, the dissolution kinetics depended significantly on the SDAS, and when plotting volume fraction of $\text{Mg}_{17}\text{Al}_{12}$ versus t/λ_2^2 the data for all samples approximately fell onto a common curve.
- Use of an analytical model [225] for $\text{Mg}_{17}\text{Al}_{12}$ dissolution, governed by solute diffusion in α -Mg across half the SDAS, was in reasonable agreement with the measured dissolution data of all five types of samples up to the time when ~15% of the initial $\text{Mg}_{17}\text{Al}_{12}$ remained. This confirms that solute diffusion within α -Mg dendrite arms governs dissolution for the first ~85% of dissolution.
- When less than ~15% of the initial $\text{Mg}_{17}\text{Al}_{12}$ remained, the measured dissolution kinetics were much slower than calculated by the analytical model based on the SDAS. Small regions of $\text{Mg}_{17}\text{Al}_{12}$ remained even after 6 days at 410 °C. Microscopy revealed that, in the latter stages of dissolution, the remaining $\text{Mg}_{17}\text{Al}_{12}$ was mostly located at α -Mg grain boundaries indicating that the slowing dissolution kinetics was due to the complete dissolution of $\text{Mg}_{17}\text{Al}_{12}$ between dendrite arms which increased the diffusion length between the remaining $\text{Mg}_{17}\text{Al}_{12}$ in the late stages of dissolution. It was further shown that local regions of initially thicker $\text{Mg}_{17}\text{Al}_{12}$ play a role in the slowing the final dissolution rate.

- Fitting the dissolution data to the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation yielded exponential time constant values of $n = 0.37 - 0.84$ similar to past work. This indicates a dissolution rate that decreases with time and is consistent with the increased diffusion length between $\text{Mg}_{17}\text{Al}_{12}$ in the late stages of dissolution.
- A common JMAK equation was fit through all data using the lengthscale-corrected time, t/λ_2^2 . This may be useful for estimating the time required for a high degree of dissolution in practical situations.

Chapter 8. Conclusions and Future work

8.1 Conclusion

The result chapters (Chapter 4 - Chapter 7) have built new understanding of microstructure formation throughout the solidification sequence and solution heat treatment of the widely used magnesium alloy, Mg-9Al-0.7Zn-0.2Mn (wt% AZ91). The focus has been on how carbon inoculation affects the magnesium dendrite microstructure, how this subsequently affects $\text{Mg}_{17}\text{Al}_{12}$ development in the eutectic reaction, and $\text{Mg}_{17}\text{Al}_{12}$ dissolution during heat treatment. Chapter 4 - Chapter 7 have addressed each question in turn: (i) Chapter 4 was to understand carbide formation during the solidification of AZ91 after carbon inoculation. (ii) Based on the understanding from Chapter 4, Chapter 5 investigated the carbide responsible for magnesium grain refinement caused by carbon inoculation. (iii) Chapter 6 was to understand how the magnesium dendrite microstructure affects eutectic solidification and the morphology of $\text{Mg}_{17}\text{Al}_{12}$. (iv) Chapter 7 was to understand how the microstructure affects the dissolution kinetics of $\text{Mg}_{17}\text{Al}_{12}$ during solution heat treatment. The main findings from each chapter can be drawn into the following overall conclusions:

- Water-free sample preparation techniques are necessary to avoid carbides being oxidised from hydrolysis. This advance enabled the study of carbides in AZ91 and the mechanism of carbon inoculation in the grain refinement of Al-bearing magnesium alloys.
- Al_4C_3 , T1- Al_2MgC_2 , and T2- Al_2MgC_2 were successfully produced through extended holding at 700-900 °C (~100-300 K above the α -Mg liquidus temperature) followed by relatively slow cooling (≤ 4 K/s) to provide sufficient kinetics for carbide growth. Al_4C_3 was mainly found in the solidification process of samples held above 800 °C. T1- Al_2MgC_2 , unfortunately, was only found in one AZ91+graphite sample which was held

at 700 °C and contained a large amount of entrained oxide. The formation of T1- Al_2MgC_2 was considered to be related to the special oxidised environment. T2- Al_2MgC_2 , in contrast, was reproducibly found in all types of casting and all holding samples.

- The three carbide phases, Al_4C_3 , T1- Al_2MgC_2 , and T2- Al_2MgC_2 , had a similar faceted growth morphology with the $\{0001\}$ plane as the largest facet in each case. Among the three carbide phases, Al_4C_3 was found to have two types of twinings: (i) X-shaped penetration twins with 98.1° rotation around a common $\{01\bar{1}5\}$ plane normal between the two crystals. (ii) Contact twins which have 60° rotation around the $\{0001\}$ shared interfacial plane. Al_4C_3 was found to have simple basal-to-basal OR with primary T2- Al_2MgC_2 with $\{0001\}$ planes in both phases are parallel to each other.
- In the extended melt holding samples, Al_4C_3 , T1- Al_2MgC_2 , and T2- Al_2MgC_2 were often attached to other phases including Al-Mn particles, $\text{Mg}_{17}\text{Al}_{12}$ and oxides. Al-Mn particles were found in contact with Al_4C_3 and T2- Al_2MgC_2 but there was no engulfment or encapsulation effect between Al-Mn particles and carbides and no ORs were found among the phases. Al_4C_3 plates were frequently found within $\text{Mg}_{17}\text{Al}_{12}$ and this indicates that Al_4C_3 was surrounded by liquid in the last stages of solidification when the reaction $\text{L} \rightarrow \alpha\text{-Mg} + \text{Mg}_{17}\text{Al}_{12} + \text{Al}_4\text{C}_3$ occurred. T1- Al_2MgC_2 and T2- Al_2MgC_2 were commonly found closed to oxides and pores.
- In gravity cast sample, the reaction product between each carbon additives (graphite, diamond and $\alpha\text{-SiC}$) and liquid AZ91 was T2- Al_2MgC_2 , and additionally Mg_2Si in the case of $\alpha\text{-SiC}$. Each additive gave a good level of grain refinement.
- Multiple T2- Al_2MgC_2 particles were found in the gravity cast AZ91+diamond samples that had a simple basal-to-basal OR between T2- Al_2MgC_2 and $\alpha\text{-Mg}$:

$$\{0001\}_{\text{T2-Al}_2\text{MgC}_2} // \{0001\}_{\alpha\text{-Mg}}$$

$$\langle 11\bar{2}0 \rangle_{\text{T2-Al}_2\text{MgC}_2} // \langle 11\bar{2}0 \rangle_{\alpha\text{-Mg}}$$

- The ~5% lattice disregistry between the two phases for this OR indicates that T2-Al₂MgC₂ is probably the heterogenous nucleant in the carbon inoculation method.
- Eutectic solidification was studied using four different cooling rate methods, gravity cast, slow cooling, interrupted solidification, and fast cooling. In all cases, Mg₁₇Al₁₂ formed a 3D interconnected skeleton. Mg₁₇Al₁₂ orientation domains were found to have no correlation with the α-Mg grain boundaries. Mostly, no preferred OR developed during the partially divorced eutectic growth. However, the Potter and/or Burgers OR was found in a small number of cases which indicate the nucleation of Mg₁₇Al₁₂ on α-Mg.
- The ‘divorcedness’ of the eutectic was shown to correlate well with the ratio of the liquid channel width between dendrite arms to the preferred eutectic spacing, $g_e \lambda_2 / \lambda_e$. Fully divorced growth occurred when the value was ~1. Fully coupled eutectic growth required a value greater than 3-5. Fully coupled eutectic growth in AZ91 was demonstrated in a sample that decoupled the solidification time and the eutectic cooling rate.
- The Mg₁₇Al₁₂ dissolution kinetics were not significantly affected by the magnesium grain size nor the extent to which the eutectic was divorced or partially divorced. In contrast, it depended significantly on the SDAS. An analytical model [225] for Mg₁₇Al₁₂ dissolution, governed by solute diffusion in α-Mg across half the SDAS, was in reasonable agreement with the measured dissolution data of all samples up to the time when ~15% of the initial Mg₁₇Al₁₂ remained.

- When less than ~15% of the initial $\text{Mg}_{17}\text{Al}_{12}$ remained, the dissolution kinetics were much slower than the calculation from the analytical model based on the SDAS. The SEM images showed that the remaining $\text{Mg}_{17}\text{Al}_{12}$ was mostly located at α -Mg grain boundaries which indicates the complete dissolution of $\text{Mg}_{17}\text{Al}_{12}$ increased the diffusion length between the remaining $\text{Mg}_{17}\text{Al}_{12}$ in the late stage of dissolution. The local thickness of $\text{Mg}_{17}\text{Al}_{12}$ also played a role in the slowing of the final dissolution rate.
- The dissolution data could be empirically fit to the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation yielding values for the exponent $n = 0.37 - 0.84$. $n < 1$ indicates a decrease in the dissolution rate with time, consistent with the increased diffusion length between $\text{Mg}_{17}\text{Al}_{12}$ in the late stages of dissolution. A common JMAK equation could be reasonably fit to all starting microstructures using the lengthscale-corrected time, t/λ_2^2 , in place of the usual time, t . This may help estimate the time required for a high degree of $\text{Mg}_{17}\text{Al}_{12}$ dissolution in practical situations for any starting microstructure.

8.2 Suggestions for future research

This thesis has developed the fundamental understanding of carbides formation, the responsible nucleant and the effect of grain morphology on $\text{Mg}_{17}\text{Al}_{12}$. However, there are still some detailed further works which can be recommended as follows

Solidification sequences of Al_4C_3 twinning plates

In Chapter 4, three carbides grew in extended melt holding AZ91 samples. In all remelted samples, large Al_4C_3 twinned plates only formed when the samples were remelted above 800 °C followed by either fast or slow cooling. From the existing liquidus projection [245], only T2- Al_2MgC_2 is expected as a primary phase (i.e. before α -Mg nucleation) irrespective of the carbon content, and Al_4C_3 should only form later in the solidification sequence which usually

grew as flakes. This raises the question of when the Al_4C_3 twinning plates formed during solidification. In addition, the liquidus projection contains a transition reaction from T2- Al_2MgC_2 to Al_4C_3 but this reaction (Al_4C_3 surrounding T2- Al_2MgC_2) was hardly seen in the remelted samples. Therefore, further detail of Al_4C_3 formation and the competition with T2- Al_2MgC_2 formation is still required to be understood. The suggested experiment for observing the twinned plate formation and the transition reaction is to increase the cooling rate with temperature from 800 °C to 600 °C under shorter remelting time. The transition reaction could also be testified from changing the Al content to observe the formation of Al_4C_3 .

Formation condition of T1- Al_2MgC_2

The T1- Al_2MgC_2 phase was found in Chapter 4 but it was not reproducible. The sample containing T1- Al_2MgC_2 was highly oxidised and T1- Al_2MgC_2 was considered as a metastable phase of T2- Al_2MgC_2 [178]. Thus, future work could explore whether and how oxides affect the nucleation and growth of carbides. For example, a synthetic oxidised environment can be made from adding oxides into the carbon inoculation samples keeping the remelting temperature at 700 °C to optimise the ratio between T1- Al_2MgC_2 and T2- Al_2MgC_2 .

Development of a T2- Al_2MgC_2 based grain refiner

The T2- Al_2MgC_2 phase was characterised as the nucleant responsible for the grain refinement effect in carbon inoculated Al-bearing magnesium alloys. In the gravity cast samples, only a relatively small amount of T2- Al_2MgC_2 formed due to the slow reaction kinetics of the carbon-based additives with the melt. The remelted samples produced more T2- Al_2MgC_2 due to the higher temperature and times for reaction. However, those T2- Al_2MgC_2 were all settled down in the bottom of the remelted samples. It would be interesting to test if an effective grain refiner could be made in which the additive had fully transformed into T2-

Al_2MgC_2 before being added and stirred in the melt. After that, the grain size reduction in the gravity cast samples can be measured to compare with the normal AZ91.

The long decay of dissolving $\text{Mg}_{17}\text{Al}_{12}$

Chapter 7 has discussed how the dissolution of $\text{Mg}_{17}\text{Al}_{12}$ could be explained by an analytical model [225] up to ~15% of remaining $\text{Mg}_{17}\text{Al}_{12}$ and the solute profile [228,290] could explain the long decay of dissolving $\text{Mg}_{17}\text{Al}_{12}$ for the final 15% of dissolution. However, further microstructural detail of how the tail develops would require detailed analyses of how the local microstructure and local Al composition profile in α -Mg affects the local dissolution of $\text{Mg}_{17}\text{Al}_{12}$. Techniques that would be suitable here include coupling (i) EDS scanning of the composition and (ii) forescatter electron (FSE) imaging of the location of the remaining $\text{Mg}_{17}\text{Al}_{12}$ relative to the α -Mg microstructure.

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