

Growth crystallography and in-situ imaging of nucleation and growth dynamics of Al_8Mn_5 solidifying in AZ magnesium alloys.

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Abstract

Many magnesium-aluminium-based alloys contain a small manganese addition to improve corrosion resistance. However, this introduces Al-Mn intermetallics which add complexity to the phase transformations. Here we study the crystal growth of the most common Al-Mn phase, Al_8Mn_5 , in Mg-Al-Zn-Mn-based magnesium alloy solidification by combining electron microscopy of the faceted growth crystallography with in-situ synchrotron X-ray imaging of the Al_8Mn_5 nucleation and growth dynamics. Three Al_8Mn_5 morphologies, equiaxed, rod and plate, are shown to all come from cyclic twinned growth associated with the pseudo-cubic symmetry of rhombohedral Al_8Mn_5 . X-ray imaging revealed Al_8Mn_5 nucleated throughout the freezing range and grew with α -Mg dendrites over a wide temperature range by divorced eutectic solidification. This occurs because, in these alloys, Mn solute has little influence on the solute undercooling of growing α -Mg dendrites, although strongly affects the constitutional supercooling with respect to the Al_8Mn_5 liquidus. Rod/plate growth of Al_8Mn_5 is shown to be promoted by slow cooling rates and by divorced eutectic solidification. The findings provide new insights into the conditions that cause large, deleterious rods and plates, and explain why there is a large variation in Al_8Mn_5 growth morphology after solidification.

Keywords: nucleation and growth; intermetallic compounds; magnesium alloys; solidification microstructure; X-ray radiography

1 Introduction

Al_8Mn_5 is the most common Al-Mn intermetallic compound (IMC) in commercial Mg-Al-Mn (AM) and Mg-Al-Zn-Mn (AZ)-series magnesium alloys containing more than 3 wt.% Al, making up of more than 99 wt.% of all the Al-Mn IMCs after casting [1]. There has been a large body of research in AM and AZ series alloys on the role of Al_8Mn_5 on (i) magnesium grain refinement [2–9] and (ii) corrosion performance [10–13]. In such studies, the reported Al_8Mn_5 morphology varied from equiaxed particles [14–16] to rods/plates [2,15,17] in gravity castings and, at higher cooling rate in die castings, Al_8Mn_5 commonly grow as branched flower-like particles [18–21]. When Al_8Mn_5 grows as a large rod or a plate, it is usually detrimental to mechanical or corrosion performance due to their large interfaces with α -Mg. Therefore, it is important to understand the factors affecting the Al_8Mn_5 morphologies that form during solidification.

Of the different Al_8Mn_5 morphologies, equiaxed particles have been studied in most detail [15,16,22]. Zeng et al. [15] showed that the equiaxed morphology is generated by cyclic growth twinning, where four Al_8Mn_5 orientations are interrelated by $\sim 90^\circ$ rotations around the $\langle 1\bar{1}02 \rangle$ axes. They further showed that the cyclic twinned equiaxed morphology can nucleate heterogeneously on cubic B2-Al(Fe,Mn) (an impurity phase) where all four twinned Al_8Mn_5 share the same orientation relationship to one B2-Al(Fe,Mn) nucleant particle. The other two morphologies, rods and plates, have not been studied in detail and it is unclear how they relate to the equiaxed morphology and growth twinning.

Phase diagram calculations [23] show that adding typical concentrations of manganese to high purity AZ series magnesium alloys causes Al_8Mn_5 to form in two solidification reactions. First by the primary solidification reaction $L \rightarrow \text{Al}_8\text{Mn}_5$ and then by a eutectic-like reaction $L \rightarrow \alpha\text{-Mg} + \text{Al}_8\text{Mn}_5$. However, past work has not explored how Al_8Mn_5 crystallises in these different reactions nor how these reactions affect the growth morphology of Al_8Mn_5 . Indeed, currently, little is known of how the $L \rightarrow \alpha\text{-Mg} + \text{Al}_8\text{Mn}_5$ reaction proceeds in AZ-series alloys. To address these questions and understand the factors affecting the size and morphology of Al_8Mn_5 , it is useful to perform an in-situ study of microstructure evolution during solidification.

This paper first investigates the growth crystallography of the different morphologies of Al_8Mn_5 in AZ31 and AZ91, and how they are related to the cyclic twinning of Al_8Mn_5 . In-situ X-ray imaging is then applied on AZ91 to study the nucleation and growth dynamics of Al_8Mn_5

particles, gaining a deeper understanding of the divorced eutectic growth of Al_8Mn_5 and $\alpha\text{-Mg}$ and the development of Al_8Mn_5 particles with different morphologies.

2 Experimental Methods

2.1 Alloy composition and cooling rate

AZ31 and AZ91 alloys containing 0.1 – 0.5 wt.% Mn were studied, with compositions listed in Table 1 and plotted on the Mg-Al-Mn ternary liquidus projection in Figure 1. Note that the Zn concentration is neglected in Figure 1 for simplicity and, for Zn concentrations of ~1wt.%, the solidification paths of the Al-Mn intermetallics are not strongly different with and without Zn.

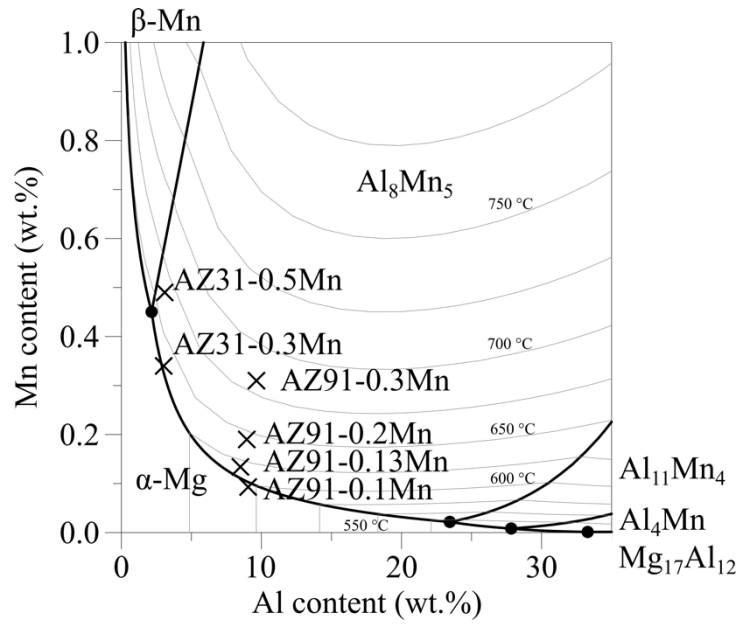


Figure 1. Alloy Al and Mn composition of AZ31-0.3Mn, AZ31-0.5Mn, AZ91-0.1Mn, AZ91-0.13Mn, AZ91-0.2Mn and AZ91-0.3Mn, superimposed on the liquidus projection of Mg-Al-Mn system at the rich corner.

The AZ31-0.5Mn, AZ91-0.13Mn and AZ91-0.2Mn were purchased as commercial ingots. The AZ91-0.1Mn and AZ91-0.3Mn were produced by melting the appropriate proportions of 99.9% Mg, 99.99%Al, 99.99% Zn and an Al-25 wt.% Mn master alloy and then gravity casting under argon into cylindrical rods. To produce AZ31-0.3Mn, some of the AZ31-0.5Mn ingot was remelted and held at 636 °C, 5 °C above its α -Mg liquidus, for four hours to allow the primary Al_8Mn_5 to settle down to the bottom the sample. Then the alloy was solidified and the bottom layer of settled primary Al_8Mn_5 was removed by grinding. This remaining alloy was then remelted at 800 °C and cast into an ingot.

Three solidification conditions were applied: (i) gravity casting, where the alloy was melted at ~660 °C and stirred at ~500 rpm for 5 min, then the temperature was raised to ~750 °C and,

after 1 h holding, the liquid was poured into a 200 °C steel mould coated with boron nitride; (ii) moderate cooling, where the ingots were machined into cylinders with diameter = 9 mm and height = 15 mm and placed into a cylindrical alumina crucible with similar inner diameter. This crucible was then encapsulated in a quartz tube with argon protective atmosphere and then placed into a furnace at the pre-set temperature of 800 °C for AZ31 and 850 °C for AZ91, to melt the samples. The quartz tube was then taken out and placed into a cylindrical hole in a room-temperature steel mould with similar diameter to the outer diameter of the quartz tube; and (iii) slow cooling, which was the same as method (ii) but the quartz tube was left in the furnace with the power-off and the lid-removed until 410 °C and was then placed into the hole of the steel mould to minimise the solid-state transformations. The cooling rates given by the three methods were (i) ~90 K/s, (ii) 4 K/s and (iii) 0.1 K/s, measured by a K-type thermocouple.

Table 1 Composition and cooling method of the alloys studied. The composition of alloys without superscripts were measured with ICP analysis. ¹=calculated from ThermoCalc2022 with TCMG6 database. For all alloys, Fe<0.003, Cu<0.002, Si<0.067 and Ni<0.001 in wt.%. 'g' = gravity casting; 'm' = moderate cooling; 's' = slow cooling and 'X' = synchrotron X-ray imaging.

	Mg	Al	Zn	Mn	Cooling Method
AZ31-0.3Mn ¹	Bal.	3.02	1.06	0.34	m
AZ31-0.5Mn	Bal.	3.09	1.06	0.49	g, m, s
AZ91-0.1Mn	Bal.	9.05	0.70	0.093	m
AZ91-0.2Mn	Bal.	8.95	0.72	0.19	m
AZ91-0.3Mn	Bal.	9.64	0.84	0.31	m
AZ91-0.13Mn	Bal.	8.495	0.505	0.134	X

2.2 Microscopy

Cross-sections were prepared using water-free metallographic procedures. To reveal the grain structure, colour etching was applied using a solution of 1 ml glacial acetic acid, 44 ml distilled water and 156 ml ethanol following the method in [24]. Etched samples were imaged using polarized light optical microscopy in an Olympus BX51 microscope. 10% nitric acid in ethanol was used to selectively etch α -Mg for observing the 3D microstructure of intermetallic particles.

Analytical scanning electron microscopy (SEM) was conducted using a Zeiss Sigma-300 and a Zeiss Auriga field emission gun (FEG) SEMs. Electron backscattered diffraction (EBSD) was conducted with a 20 keV electron beam and 120 μm aperture with a 70° tilted stage at 15 mm working distance on the Zeiss Sigma 300 with a Bruker e-FlashHR detector. Bruker Quantax Esprit 2.1 software was used for analysing EBSD datasets. MTEX 5.7 [25] within MATLAB 2020b (Mathworks, USA) was used to analyse and present the EBSD data.

A ThermoFisher Scientific Helios 5 CX dual-beam FIB-SEM with Ga ion source was used to site-specifically lift out lamellae containing a desired IMC particle, which were then investigated in transmission electron microscopy (TEM) using a JEOL 2100F operated at 200 kV. Gatan Microscopy suite 3 (GMS 3, AMETEK, Inc) and CrystTBox [26] software were used to analyse the TEM results. SingleCrystal 4 (CrystalMaker Software Ltd.) was used to simulate selected area electron diffraction (SAED) patterns.

The crystal structure of Al_8Mn_5 used to index EBSD and SAED patterns is summarised in Table 2 from reference [27]. Note that rhombohedral Al_8Mn_5 can be considered using various unit cells. Here we use both the hexagonal cell setting and a non-standard body centred rhombohedral (BCR) setting which is useful for showing the pseudo-cubic character of Al_8Mn_5 (the rhombohedral angle is $\alpha = 89.1^\circ$ in the BCR unit cell) as discussed by Zeng et al. [15].

Table 2 Crystallographic information of Al_8Mn_5 . S.D = Strukturbericht Designation. P.S. = Pearson Symbol. * = non-standard body centred rhombohedral (BCR) unit cell highlighting the link to BCC.

Phase	S.D.	Crystal system	Space group	P.S.	Lattice parameters				Ref.
					a[Å]	c[Å]	$\alpha(^{\circ})$	$\gamma(^{\circ})$	
Al_8Mn_5	D8 ₁₀	rhombohedral	R3m	hR26	12.667	7.942	-	120	[27]
				*	9.029	-	89.09	-	

2.3 In-situ synchrotron imaging

In-situ X-ray imaging of the solidification of AZ91-0.13Mn was performed at the SPring-8 synchrotron radiation facility in Hyogo, Japan, on beamline BL20XU. A thin plate of AZ91-0.13Mn (0.127 mm thick before melting) was confined between two MgO plates and heated by a graphite heater in a chamber containing ~1 bar of argon gas. 150 μm thick single crystal MgO sheets were employed as confining sheets and spacers with cavities designed to house the sample, preventing melt reactions with the container. This assembly was then secured

within thicker boron nitride plates and integrated into a furnace setup on the beamline. Further details of the apparatus are provided in reference [28].

Cyclic heating and cooling experiments were conducted on the experimental cell during in-situ observation. In the first heating cycle, the solidification cell was heated to 655 °C and was held for ~10 mins to melt the sample. Then the sample was cooled at a constant rate of 30 K/min in a near isothermal condition. Some Al-Mn particles melted, and others remained as a settled sludge layer at the bottom of the crucible, resulting in a main body of liquid that was nearly free of Al-Mn(-Fe) particles. Observations were recorded after each heating segment to ensure the liquid was homogenised and saturated with Mn solute at the isothermal holding temperature in each experiment. To study the effect of cooling rate on the formation of Al-Mn IMCs, the same sample was then cyclically melted at 655 °C followed by ~10 minutes of isothermal holding for each experiment and then was cooled at 2 K/min, 5K/min and 15 K/min, respectively.

A monochromatic X-ray with 13 keV photon energy was used for imaging. The radiographs were recorded in 2048×2048 pixels with pixel size 0.51 μm and 2 frames per second. Background normalisation was applied to remove the influence of artefacts such as sample surface imperfections and heterogeneous background. Image alignment and subtraction were applied to minimise particle movement during solidification and to enhance contrast. ~~Examples of the same radiograph before and after image processing are shown in Figure SI.1.~~ Flat Field correction and particle-tracking analysis on X-ray radiographs was conducted using Image Processing Toolbox in MATLAB2023b to investigate the nucleation and growth dynamics of Al_8Mn_5 particles.

3 Results

3.1 Growth crystallography of Al_8Mn_5 in AZ-series alloys

The general microstructure of moderately cooled and slow cooled AZ31-0.5Mn and AZ91-0.2Mn are shown at low magnification in Figure 2(a)-(c), highlighting the α -Mg, $\text{Mg}_{17}\text{Al}_{12}$ and Al-Mn IMC phases. The majority of Al-Mn IMC particles in the microstructure were Al_8Mn_5 as expected from the Scheil model in ThermoCalc with the TCMG6 database and the liquidus projection in Figure 1.

The Al_8Mn_5 usually grew with one of three distinct morphologies as labelled in Figure 2(c): (i) equiaxed particles, similar to the morphology reported in [15,29]; (ii) rods, which were often multiple rods growing together as indicated by the yellow circle in Figure 2(b); and (iii) plates. Figure 2(d) is the same area as Figure 2(c) in polarised light microscopy after colour etching to reveal the α -Mg grains. Here, the equiaxed particle and rods are between dendrite arms within an α -Mg dendrite envelope while the plate was between dendrite arms at a dendritic grain boundary. Figure 2(e) shows an unusually long Al_8Mn_5 rod ($>350\text{ }\mu\text{m}$) from moderately cooled AZ91-0.2Mn to show how large rods can be.

Deep-etched 3D microstructures of the three morphologies are shown in Figure 2(f)-(h). All morphologies are faceted, often with hollows. In almost all cases, the rods and plates were found to be attached to an equiaxed particle, such as those indicated by white arrows in Figure 2(g)-(h). In Figure 2(g), note the equiaxed particle near the centre of the rod. In the rare cases where no attached equiaxed particle was observed, it is feasible that they were buried in the unetched α -Mg beneath or were occluded behind the rods/plates, but this could not be confirmed conclusively. When quantifying the fraction of particles with different morphologies later in this paper, we used shallow etched samples to reveal part of the 3D morphology, enabling particles to be distinguished from rods and plates.

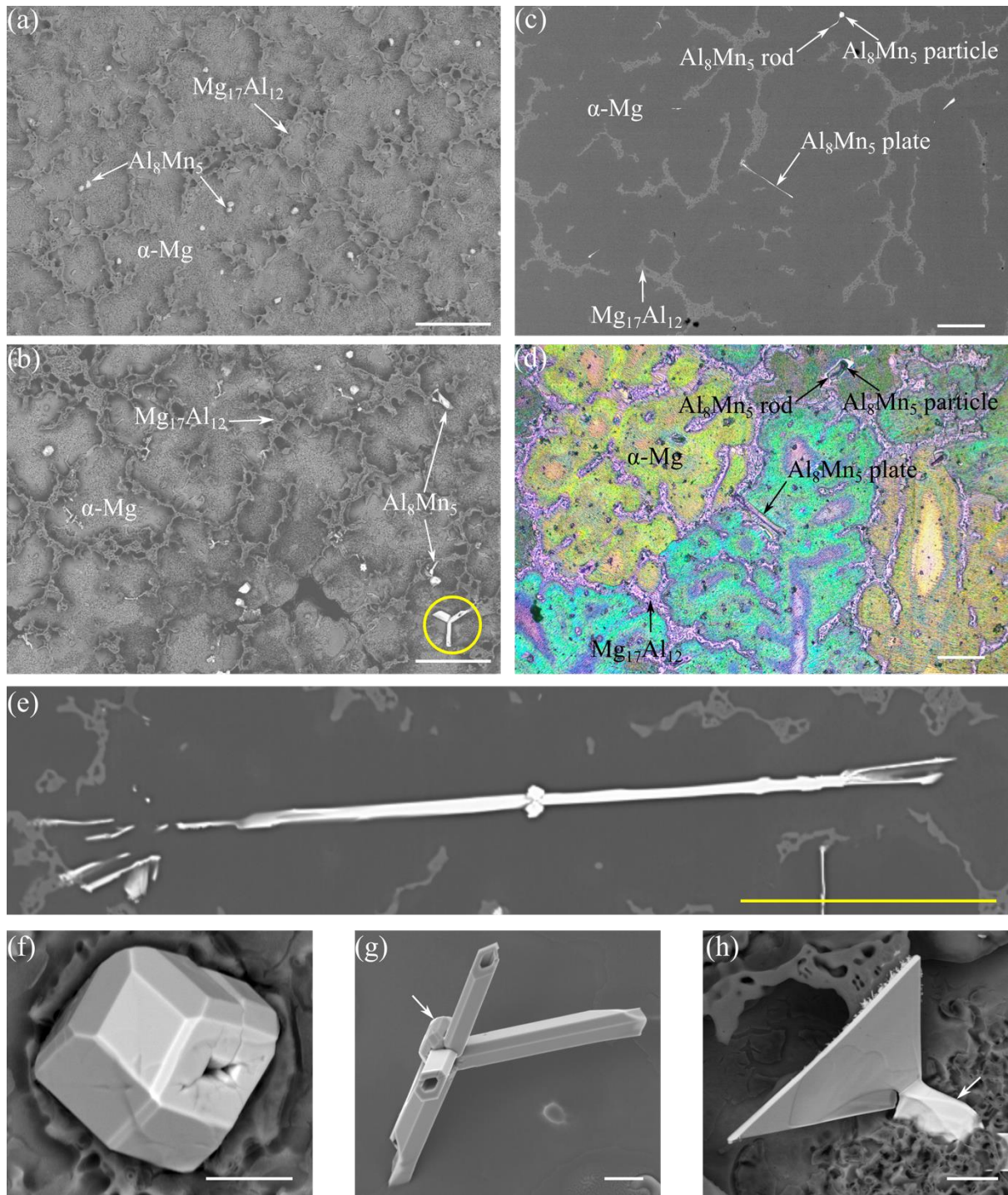


Figure 2 General microstructure of AZ31-0.5Mn and AZ91-0.2Mn and the morphology of Al_8Mn_5 . SEM-BSE images of moderately cooled samples after etching of α -Mg for (a) AZ31-0.5Mn and (b) AZ91-0.2Mn. (c) SEM-BSE microstructure of cross-section of slow cooled AZ31-0.5Mn. (d) Polarised optical microscopy of the identical area in (c) after colour etching to reveal α -Mg grain boundaries. (e) Abnormally long rod from moderately cooled AZ91-0.2Mn. Scale bars in (a)-(e) represent 100 μ m. (f) – (h) Three morphologies of Al_8Mn_5 – (e) equiaxed particle, (f) rods and (g) plate. Note in (g) and (h) that rods and plates grew from equiaxed particles indicated by white arrows. (f) and (g) are from AZ31-0.5Mn with moderate cooling and (h) is from AZ31-0.5Mn with slow cooling. Scale bars in (f)-(h) represent 5 μ m.

3.1.1 Equiaxed particles

The growth crystallography of equiaxed particles is overviewed in Figure 3. Figure 3(a) is an equiaxed particle with a rod growing off. The EBSD IPF-Z map shows the equiaxed particle contains four orientations and the rod is a single crystal of one of the orientations in the equiaxed particle. The four orientations are cyclic twinned in the way described by Zeng et al. [15] for rhombohedral Al_8Mn_5 , by repeated $\sim 90^\circ$ rotations around the common $\langle 1\bar{1}02 \rangle_{\text{HEX}} / \langle 100 \rangle_{\text{BCR}}$ with $\{2\bar{2}01\}_{\text{HEX}} / \{100\}_{\text{BCR}}$ interfaces. The unit cell wireframes are plotted from the measured Euler angles for both hexagonal and BCR settings. In the hexagonal setting, the cyclic twinning results in the four orientations sharing $\langle 11\bar{2}0 \rangle$ axes with their neighbours and, in the BCR setting, the four orientations share common $\langle 100 \rangle$ axes and $\{100\}$ planes. This is consistent with the $\{2\bar{2}01\}_{\text{HEX}} / \{100\}_{\text{BCR}}$ pole figure – each grain has six members of $\{2\bar{2}01\}_{\text{HEX}} / \{100\}_{\text{BCR}}$ resulting in three spots in the pole figure (northern hemisphere) and, at each spot, there are four orientations overlapping. Clear and straight twin boundaries can be seen between the four orientations in the EBSD IPF-Z map. To deduce the interface plane of the twin boundaries, the 2D vectors formed where the twin boundaries intersect the polished section were measured and plotted in a inverse pole figure with respect to the crystallographic orientation of the Al_8Mn_5 on both sides of the boundary. With this method, 40 twin boundaries from AZ31-0.5Mn (black dots) and 10 twin boundaries from AZ91-0.2Mn (black circles) are summarised in the inverse pole figure in Figure 3(b). The twin boundaries are in good consistency with the trace of $\{2\bar{2}01\}_{\text{HEX}} / \{100\}_{\text{BCR}}$, showing the cyclic twin boundaries are $\{2\bar{2}01\}_{\text{HEX}} / \{100\}_{\text{BCR}}$. All the Al_8Mn_5 equiaxed particles studied in this work were cyclic twinned.

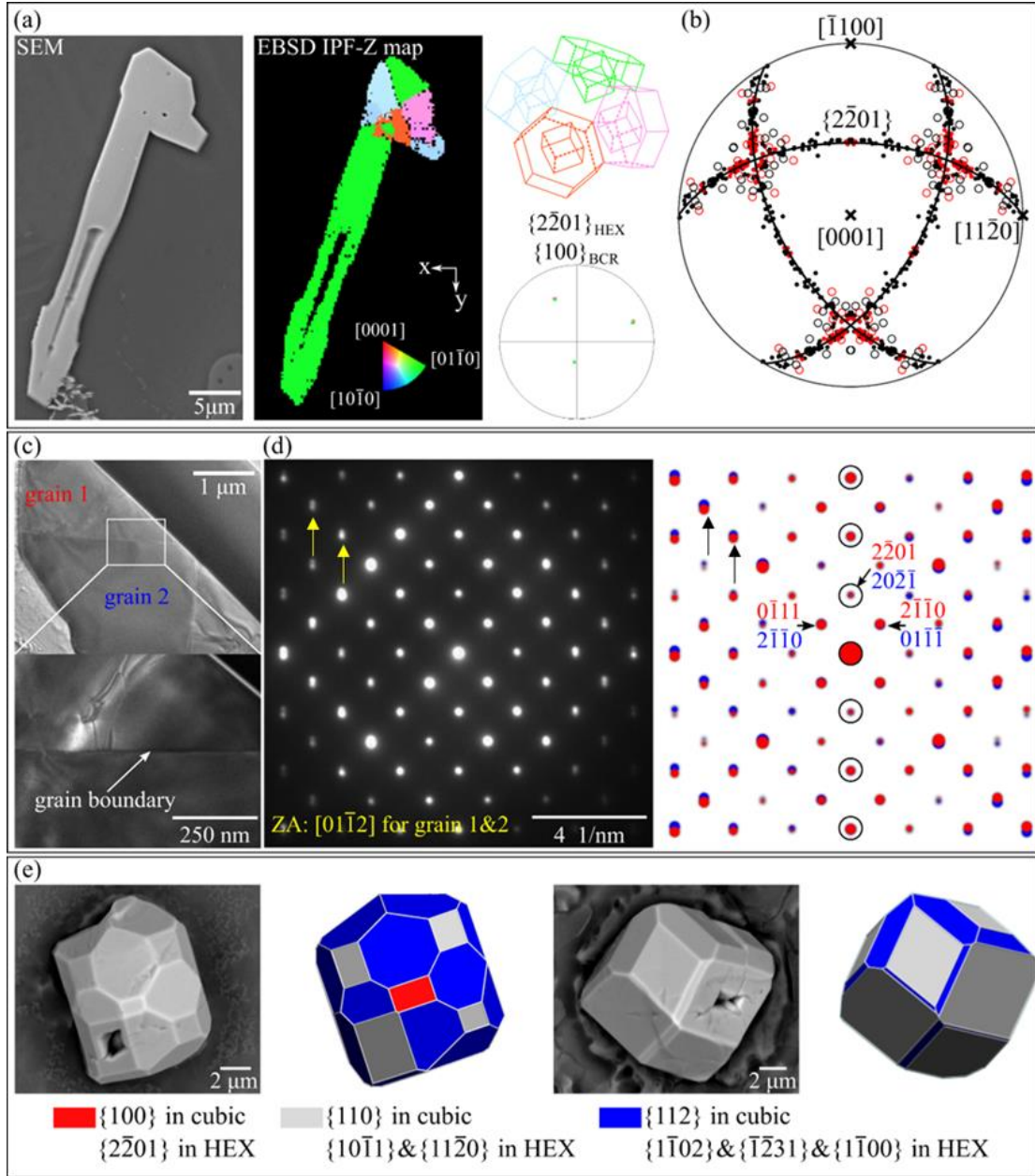


Figure 3 Growth crystallography of cyclic twinned Al_8Mn_9 equiaxed particles from moderately cooled AZ31-0.5Mn. (a) SEM-BSE image and EBSD IPF-Z map of an equiaxed particle with a rod growing off. Hexagonal and BCR unit cell wire frames that are plotted based on measured Euler angles and $\{2\bar{2}01\}$ pole figure. (b) Inverse pole figure of twin boundaries of Al_8Mn_9 , including 40 twin boundaries from equiaxed particles in moderately cooled AZ31-0.5Mn (black dots), 15 boundaries from plates from slow cooled AZ31-0.5Mn (red dots), 10 twin boundaries from equiaxed particles from moderately cooled AZ91-0.2Mn (black circles) and 5 twin boundaries from plates in slow cooled AZ91-0.2Mn (red circles). (c) BF-TEM of a $\{2\bar{2}01\}$ twin boundary in an equiaxed particle from moderately cooled AZ31-0.5Mn. (d) Corresponding experimental and simulated SAED from an area containing two twinned orientations. The yellow arrows on the left side of each pattern indicate where partially overlapping spots can be distinguished. (e) facet indexing on two equiaxed particles using facet models.

TEM analysis of a cyclic twinned particle is overviewed in Figure 3(c)-(d). FIB lift-out was performed to produce the sample imaged by BF-TEM in Figure 3(c), where two twinned grains are oriented such that they both have $\langle 01\bar{1}2 \rangle$ in the incident beam direction with clear straight twin boundaries in the image. The SAED pattern in (d) was obtained across the twin boundary containing both grain 1 and grain 2. Note in Figure 3(d) that the measured diffraction spots on

the left and right-side split into two separate spots when they are far away from the centre (transmitted beam), showing this is not a pattern from a single crystal but from multiple crystals. Simulated patterns of grain 1 (red) and grain 2 (blue) are given in Figure 3(d) to show the twinning. Grain 1 and grain 2 are related by an 89.1° rotation around the common $[01\bar{1}2]$ axis. The patterns are also related by mirror reflection across $\{2\bar{2}01\}$ and the two grains share common $\{2\bar{2}01\}$ spots, as highlighted by black circles. For the planes in all the other directions, their spots are close to each other but are not overlapping; they are almost overlapping near the centre of the pattern (transmitted beam) where they are difficult to distinguish in both the measured and simulated patterns, but the spots become more separated further away from the centre, enabling them to be distinguished. These TEM results are consistent with the EBSD analysis in Figure 3(a)-(b).

The overall shape of cyclic twinned equiaxed particles consisting of four Al_8Mn_5 orientations usually had cubic symmetry which is not consistent with the rhombohedral point group symmetry of Al_8Mn_5 . For example, the facet models of the equiaxed particles in Figure 3(e) were made based on the Al_8Mn_5 facets reported by Zeng et al. [15]: $\{100\}$, $\{110\}$ and $\{112\}$ in the pseudo-cubic symmetry. This shows that the four rhombohedral orientations grew together to produce a multigrain particle with their combined cubic pseudosymmetry as is common during faceted growth of cyclic twinned crystals (e.g. in minerals [30]).

In Ref. [15], it was shown that an origin of cyclic twinning in this system is that Al_8Mn_5 can nucleate on the cubic impurity phase, B2-Al(Fe,Mn), and the four rhombohedral orientations in the cyclic twin are the four variants of the orientation relationship between Al_8Mn_5 and B2-Al(Fe,Mn). No B2-Al(Fe,Mn) phase was found in the current paper because we used higher purity alloy than in [15], although we cannot rule out the possibility that nano-sized B2-Al(Fe,Mn) nucleants were missed. A similar ‘higher symmetry nucleant’ mechanism has been reported for twinned growth during solidification of other low symmetry intermetallics including multiply twinned Al_3Ti growing from cubic TiC in [31]. Further work is required to test if other mechanisms can also operate.

3.1.2 Al_8Mn_5 rods and plates

The growth crystallography of Al_8Mn_5 rods is overviewed in Figure 3(a) and Figure 4(a)-(f). In Figure 3(a), there is a rod growing from the equiaxed particle. The EBSD IPF-Z map shows it has the same orientation as one of the twin orientations (green), indicating that the rod grew

out epitaxially from the cyclic twinned particle. Further transverse and longitudinal cross sections of rods are given in Figure 4(a) and (b) showing that rods are single crystals. The rods grew along $[0001]_{\text{HEX}}/[111]_{\text{BCR}}$ as can be seen from the green unit cell wireframe in Figure 3(a) and the wireframes in Figure 4(b).

In many cases, Al_8Mn_5 rods existed as multiple rods growing off an equiaxed particle, as shown in Figure 4(c) and (e). In Figure 4(e), six rods can be seen growing off a central particle and EBSD was done on the cross section of one rod indicated by the red spot. (Mis)indexing the EBSD patterns as cubic $\text{D}_{82}\text{-Al}_8\text{Mn}_5$ allows the pseudo-cubic symmetry to be plotted in pole figures such as the pseudo-cubic $\langle 111 \rangle$ pole figure in Figure 4(e). Arrows are drawn through the centre of the $\langle 111 \rangle$ pole figure to the four $\langle 111 \rangle$ spots and are replicated in the SEM micrograph, illustrating that each rod grew along one of the $\langle 111 \rangle$ pseudo-cubic directions. Rods 1 and 1' grew antiparallel with each other, corresponding to the $\langle 111 \rangle$ directions in the northern and southern hemispheres respectively. The same is true for rods 2 and 2'. Theoretically, there can be up to eight rods growing along the eight $\langle 111 \rangle$ directions from the central equiaxed particle using pseudo-cubic symmetry. Considering the four twinned rhombohedral orientations, each rod grows parallel and antiparallel with the $[0001]$ direction of each of the four twinned orientations. Crystallographic facet models of the rods are plotted in Figure 4(f). The side facets of the rods are $\{11\bar{2}0\}_{\text{HEX}}/\{1\bar{1}0\}_{\text{BCR}}$ and the tip facets mostly consist of $\{10\bar{1}1\}_{\text{HEX}}/\{110\}_{\text{BCR}}$. Note that $\{1\bar{1}0\}_{\text{BCR}}$ and $\{110\}_{\text{BCR}}$ are equivalent in cubic symmetry but the rhombohedral distortion of Al_8Mn_5 splits them into two different families with six members each (three in each hemisphere). The three $\{10\bar{1}1\}_{\text{HEX}}/\{110\}_{\text{BCR}}$ tip facets on the experimental and simulated crystals in Figure 4(f) reflect this trigonal symmetry. The tip facets also sometimes included $\{3\bar{1}\bar{2}1\}_{\text{HEX}}/\{1\bar{2}1\}_{\text{BCR}}$ and $\{2\bar{2}01\}_{\text{HEX}}/\{100\}_{\text{BCR}}$ facets, which are consistent with the minor $\{100\}$ and $\{112\}$ facets on the equiaxed particles in Figure 3(e). It was further found in rare cases that the side facet can switch to $\{10\bar{1}0\}_{\text{HEX}}/\{11\bar{2}\}_{\text{BCR}}$, as in the rod in Figure 4(d).

Many of the Al_8Mn_5 rods had hollow cores such as those in Figure 4 (a), (c) and (e). Hollow rods are common during the faceted growth of many non-cubic intermetallics including rhombohedral Al_8Mn_5 here, hexagonal Cu_6Sn_5 [32,33], orthorhombic $\text{Al}_{11}\text{RE}_3$ (RE = rare earth element) [34,35], and orthorhombic Al_6Mn [36]. Frank et al. [37] proposed that hollow-core rods form when a rod grows around an axial screw dislocation and the core remelts when the strain energy of the dislocation core exceeds the new surface energy required to create a hollow. Therefore, the observation of hollow Al_8Mn_5 rods may be indirect evidence of screw-

dislocation mediated growth of Al_8Mn_5 , but further work is required to confirm this, but further work is required to confirm this. There may be additional factors that promote hollow forms during faceted growth. One is that all examples listed earlier in this paragraph involve intermetallics growing in liquid of very different composition to the crystal, and the accumulation of rejected solute (mostly Mg here) is a barrier to growth that inhibits the growth of faces more than edges and vertices and, therefore, promotes hollowing. A recent phase field study on hopper crystals [38], which can be considered a special form of hollow in cubic crystals, discusses this in more detail.

The growth crystallography of Al_8Mn_5 plates is overviewed in Figure 4(g)-(i). In Figure 4(g), most of the Al_8Mn_5 plates share an interface with $\text{Mg}_{17}\text{Al}_{12}$ phase. After deep etching, the plates in Figure 4(g) mostly had triangular plate shape and, the same as rods, were usually attached to an equiaxed Al_8Mn_5 particle. The EBSD IPF map on the main facet of the plate in Figure 4(h) shows there are two orientations in a plate with the grain boundary at the centre of the plate. These two orientations are twinned in the same manner as the cyclic twins. Arrows are drawn in the $[0001]_{\text{HEX}}/[111]_{\text{BCR}}$ pole figure and replicated in the micrograph, showing that the sides of the plate are along $[0001]_{\text{HEX}}/[111]_{\text{BCR}}$ of each orientation, which is the same as the growth direction of the rods. The two orientations share one common $\{11\bar{2}0\}_{\text{HEX}}/\{1\bar{1}0\}_{\text{BCR}}$, as highlighted by the black circle around an overlapping spot in the pole figure, and this common $\{11\bar{2}0\}_{\text{HEX}}/\{1\bar{1}0\}_{\text{BCR}}$ plane is the main facet of the plate. The two orientations share three common $\{2\bar{2}01\}_{\text{HEX}}/\{100\}_{\text{BCR}}$, i.e. there are two overlapping orientations at each spot in the pole figure. One of these common planes is highlighted by the black circle in the $\{2\bar{2}01\}_{\text{HEX}}/\{100\}_{\text{BCR}}$ pole figure and is plotted as the red plane in the unit cell wireframes based on the measured Euler angles in Figure 4(h). This red plane is consistent with the twin boundary in the micrograph. Figure 4(i) are EBSD results from the cross section of a deep-etched plate in slow cooled AZ91-0.2Mn and shows the same story as the plate in Figure 4(h). 15 plate twin boundaries from AZ31-0.5Mn (red dots) and 5 plate boundaries from AZ91-0.2Mn (red circles) are plotted in Figure 3(b). They confirm the twin boundaries in plates are $\{2\bar{2}01\}_{\text{HEX}}/\{100\}_{\text{BCR}}$, similar to the boundaries in equiaxed particles. By considering the facts that (i) the plates are attached to equiaxed particles; (ii) the plates have two twinned orientations and the side of the plates are the same as the growth direction of the rods and (iii) the main facet of the plate is the same as the side facet of the rods, it can be deduced that the triangular plates developed from two neighbouring rods growing out from a cyclic twinned particle in the slow cooled samples. This can be further confirmed from the deep etched AZ31-0.5Mn

example in Figure 4(g) where two rods are growing from an equiaxed particle and the region between the two rods is only partially filled as a plate.

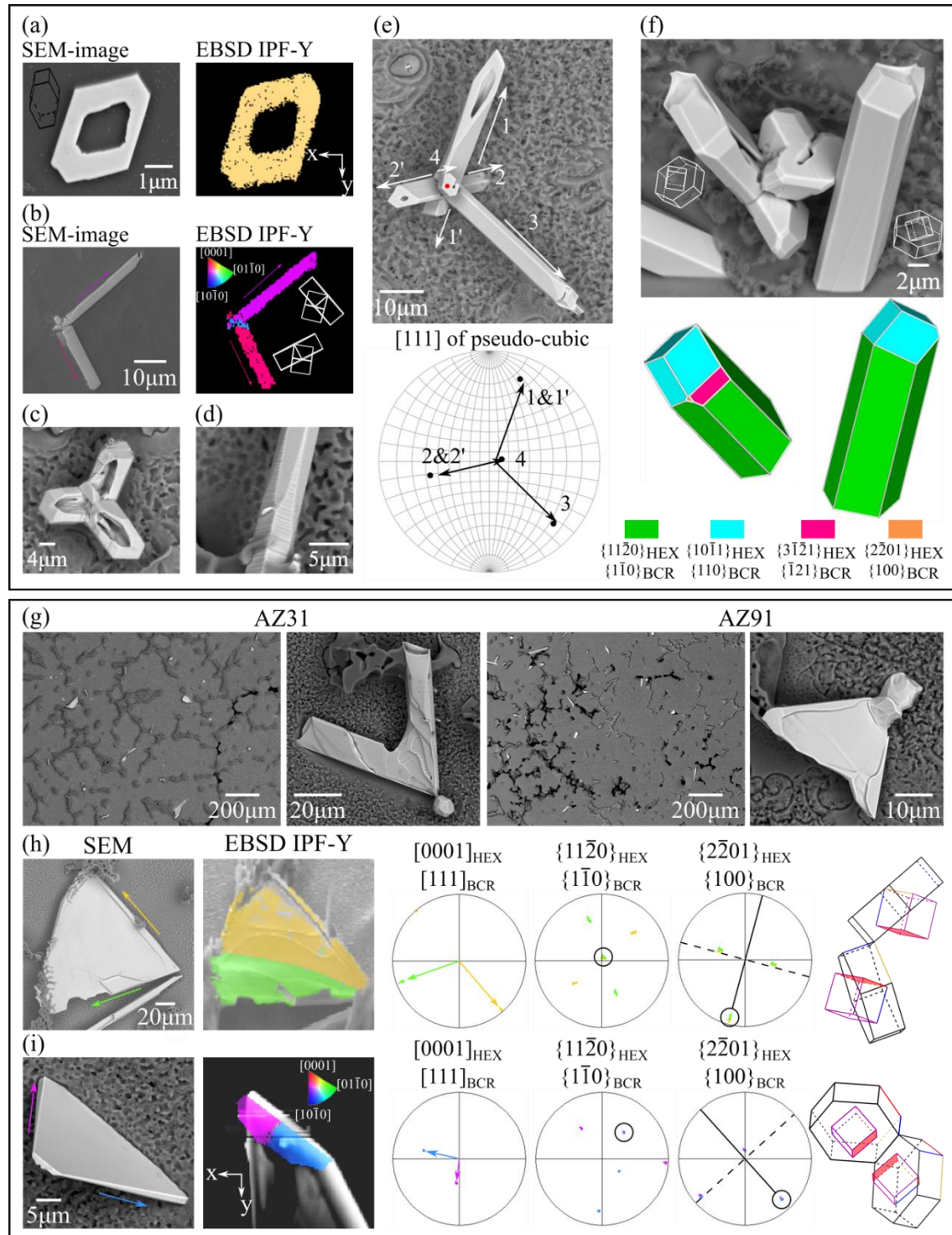


Figure 4 Growth crystallography of (a)-(f) rods from moderately cooled AZ31-0.5Mn and (g)-(i) plates from slow cooled AZ31-0.5Mn and AZ91-0.2Mn. (a) SEM-BSE and EBSD IPF-Y map of a transverse cross section of a rod. (b) SEM-BSE and EBSD IPF-Y map of a longitudinal cross section of a rod. (c) and (d) Deep-etched 3D microstructure of rods. (e) 3D microstructure of multiple rods growing off the central equiaxed particle and [111] pole figure in pseudo-cubic symmetry. (f) Crystallographic facet models of rods. (g) SEM-BSE images of deep-etched slow cooled AZ31-0.5Mn and AZ91-0.2Mn and microstructure of plates. (h) and (i) SEM, EBSD IPF-Y map, pole figures and unit cell frames of Al₈Mn₅ plates from slow cooled AZ31-0.5Mn and AZ91-0.2Mn. In the pole figures common planes are highlighted by black circles.

It can be concluded that the growth morphology of Al_8Mn_5 depends strongly on growth twinning: (i) In the early stages of growth, Al_8Mn_5 grew as equiaxed particles containing four cyclic twinned orientations. The equiaxed faceted growth morphology has combined cubic pseudosymmetry, growing as a four-orientation particle with an overall shape consistent with a cubic point group. (ii) Single crystal Al_8Mn_5 rods grew off the equiaxed particles along the $\langle 0001 \rangle_{\text{HEX}} / \langle 111 \rangle_{\text{BCR}}$ directions of the four Al_8Mn_5 orientations in the equiaxed particle. There can be up to eight rods growing off one equiaxed particle. The single crystal faceted growth morphology is consistent with a trigonal point group symmetry as expected of a rhombohedral crystal. (iii) Plates contained two twinned orientations and developed from two adjacent single crystal rods growing off a cyclic twinned equiaxed particle.

3.2 Effects of cooling rate and alloy composition on Al_8Mn_5 morphologies

The occurrence of the different Al_8Mn_5 morphologies depended on the cooling rate and alloy composition. The number density (number per mm^2) of Al_8Mn_5 particles with equiaxed or rod/plate morphology was measured in at least ten micrographs of the deep-etched microstructures in each condition and is summarised in Figure 5. Here, rods and plates are considered together because plates develop from rods during growth and both are not desired morphologies due to their large size and interface area with $\alpha\text{-Mg}$. ~~Examples of the deep-etched microstructures that were quantified for Figure 5 are shown in Figure SI.3.~~

The effect of cooling rate is overviewed in Figure 5(a), using AZ31-0.5Mn as an example. Faster cooling rate promotes the nucleation of Al_8Mn_5 – the number density of Al_8Mn_5 particles in the gravity casting is 3 and 7 times more than in moderate and slow cooled samples. The cooling rate also had a significant effect on the fraction of the morphologies. The higher cooling rate in gravity casting resulted in the majority of Al_8Mn_5 being complex branched particles with a morphology similar to the flower-like Al_8Mn_5 in high pressure die casting [21], twin roll casting [19] and rapid solidification [18]. This complex branched Al_8Mn_5 morphology is related to faceted dendrite growth and is not considered further in this work. In moderately cooled AZ31-0.5Mn, the majority of Al_8Mn_5 were equiaxed particles. In slow cooled AZ31-0.5Mn, the morphology changed significantly and the majority of Al_8Mn_5 were rods/plates

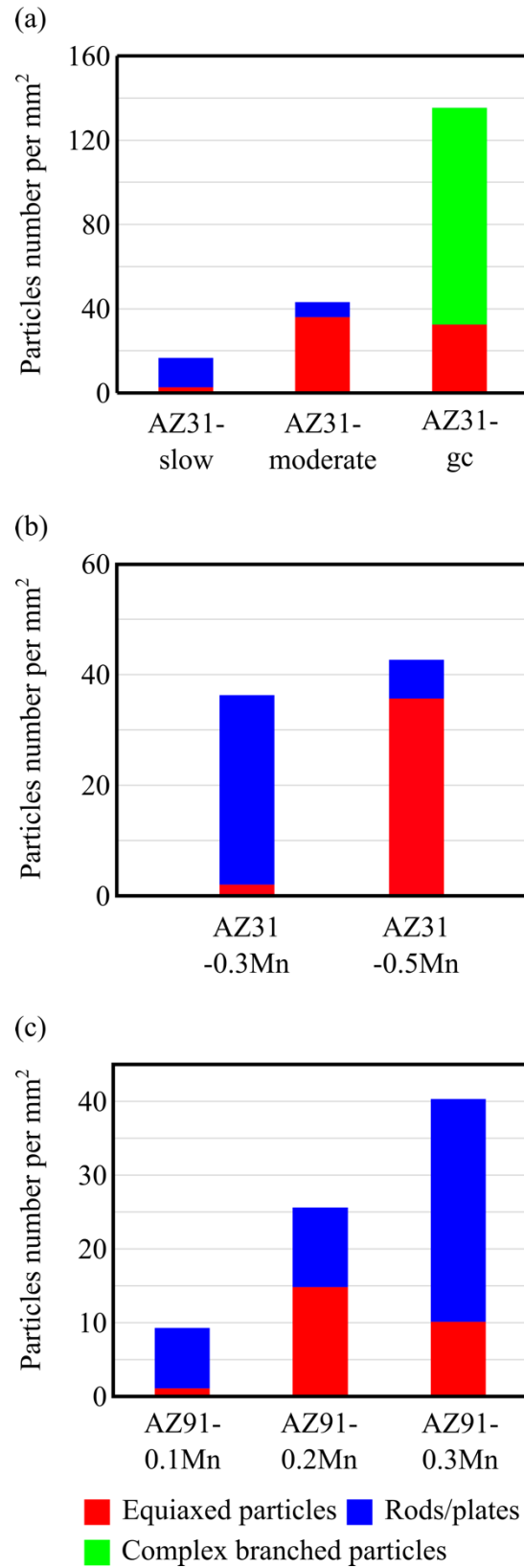


Figure 5 Effects of cooling rate and alloy composition on the number density of Al_8Mn_5 particles and the fraction of Al_8Mn_5 growth morphologies. (a) Number density of Al_8Mn_5 per mm^2 in AZ31-0.5Mn with three cooling rates. Number density of Al_8Mn_5 per mm^2 in (b) AZ31 and (c) AZ91 with different Mn content. All samples in (b) and (c) are from the moderate cooling condition. gc = gravity cast.

The effects of Mn content on Al_8Mn_5 morphologies are shown for AZ31 in Figure 5(b) and for AZ91 in Figure 5(c). All these samples were cooled with moderate cooling. In both AZ31 and AZ91, increasing the Mn content increased the final number density of Al_8Mn_5 . There was also a complex effect of Mn content on the Al_8Mn_5 morphology, where the lowest Mn concentrations resulted in a high fraction of rods/plates, and increasing the Mn content first increased the fraction of equiaxed particles and a further increase in Mn content decreased the fraction of equiaxed particles.

This effect of Mn content in Figure 5(b) and (c) can be partially understood from the liquidus projection in Figure 1. There, increasing the Mn content in AZ31 or AZ91 changes the solidification reactions in which Al_8Mn_5 forms and the temperature range over which Al_8Mn_5 solidifies. For example, for the AZ31 and AZ91 alloys with the lowest Mn concentrations studied, solidification occurs with almost no primary Al_8Mn_5 , and Al_8Mn_5 mostly forms during solidification along the $L \rightarrow \alpha\text{-Mg} + \text{Al}_8\text{Mn}_5$ eutectic groove (Figure 1). Increasing the Mn content of the alloy results in some primary Al_8Mn_5 solidification and, further increasing the Mn content increases the fraction of primary Al_8Mn_5 formed and the Al_8Mn_5 freezing range. Combining this information with the results in Figure 5(b) and (c), the following correlations are implied – (i) solidification along the $L \rightarrow \alpha\text{-Mg} + \text{Al}_8\text{Mn}_5$ eutectic groove promotes the growth of rods and plates and, the corollary, primary Al_8Mn_5 growth promotes equiaxed Al_8Mn_5 particles; and (ii) increasing the volume fraction and/or freezing range of primary Al_8Mn_5 promotes the growth of rods and plates. To explain these correlations, we next turn to in-situ X-ray imaging.

3.3 In-situ imaging of Al_8Mn_5 during the solidification of AZ91

3.3.1 Nucleation and growth dynamics of Al_8Mn_5 particles

Synchrotron radiographs of AZ91-0.13Mn cooled at 5 K/min are shown in Figure 6. This composition lies in the Al_8Mn_5 primary phase field (Figure 1). In Figure 6, dark Al_8Mn_5 nucleated first and grew by the primary solidification reaction $L \rightarrow \text{Al}_8\text{Mn}_5$. Next, $\alpha\text{-Mg}$ dendrites nucleated in a narrow temperature range from 596 °C to 594 °C. Then $\alpha\text{-Mg}$ and Al_8Mn_5 grew simultaneously but without sharing interfaces by divorced eutectic solidification over a temperature range. Most Al_8Mn_5 nucleated before the nucleation of $\alpha\text{-Mg}$, and a smaller number of Al_8Mn_5 nucleated after the nucleation of $\alpha\text{-Mg}$ later during the divorced eutectic

reaction: $L \rightarrow \alpha\text{-Mg} + \text{Al}_8\text{Mn}_5$. Three examples of such late-nucleating Al_8Mn_5 are indicated by yellow arrows in Figure 6.

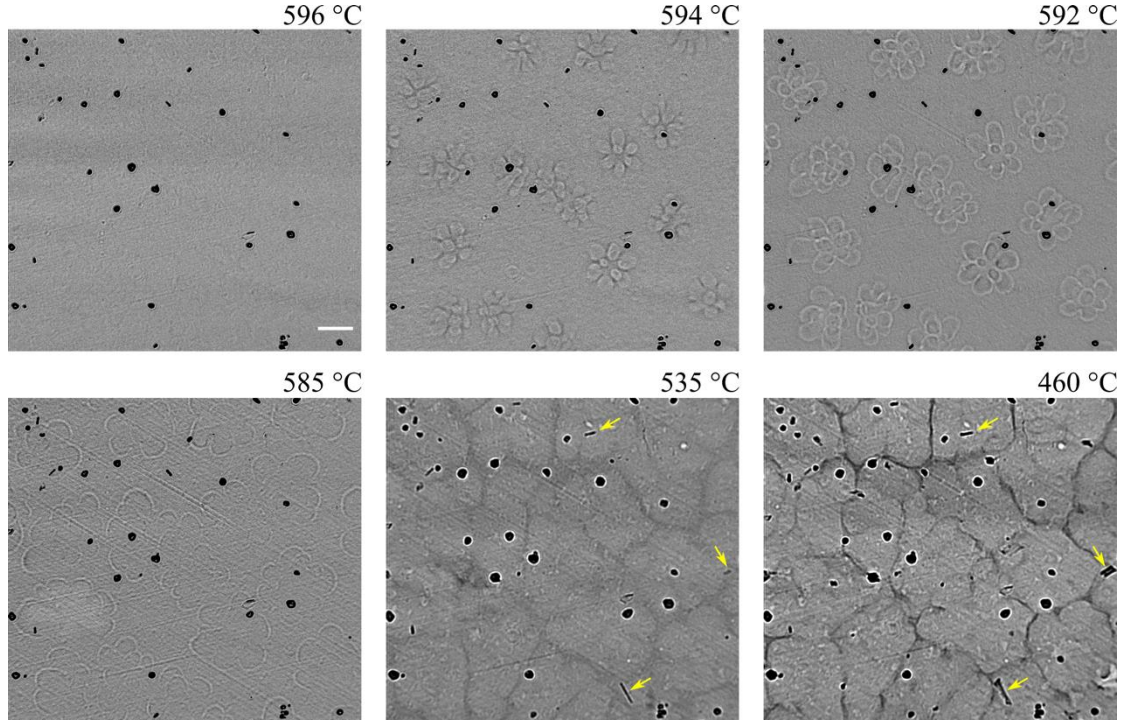


Figure 6 Synchrotron radiographs of AZ91-0.13Mn cooled at 5 K/min. Three Al_8Mn_5 nucleating after the nucleation of $\alpha\text{-Mg}$ are highlighted by yellow arrows. All radiographs have the same scale. The scale bar represents 100 μm .

The nucleation events of $\alpha\text{-Mg}$ dendrites and Al-Mn particles in AZ91-0.13Mn solidified at 5 K/min are quantified in Figure 7(a), in which the number density of $\alpha\text{-Mg}$ dendrites and Al-Mn particles are plotted as a function of temperature. The liquidus for $\alpha\text{-Mg}$ and $\text{Mg}_{17}\text{Al}_{12}$ are highlighted by vertical dashed grey lines. Nucleation and growth features are linked to the solidification path at the bottom of Figure 7. During solidification, $\alpha\text{-Mg}$ nucleated within a narrow temperature range of 2 K and no new $\alpha\text{-Mg}$ nucleated on further cooling. In contrast, Al_8Mn_5 nucleated throughout the freezing range. Figure 7(a) shows that Al_8Mn_5 nucleated continuously from ~ 630 °C as primary Al_8Mn_5 . Then, once $\alpha\text{-Mg}$ nucleated, there were few Al_8Mn_5 nucleation events until a second wave of Al_8Mn_5 nucleation events occurred from ~ 545 °C. These particles nucleating at ~ 545 °C are considered as Al_8Mn_5 and not LT- $\text{Al}_{11}\text{Mn}_4$ since this temperature is far above the calculated equilibrium onset formation temperature of 512 °C for LT- $\text{Al}_{11}\text{Mn}_4$ [1].

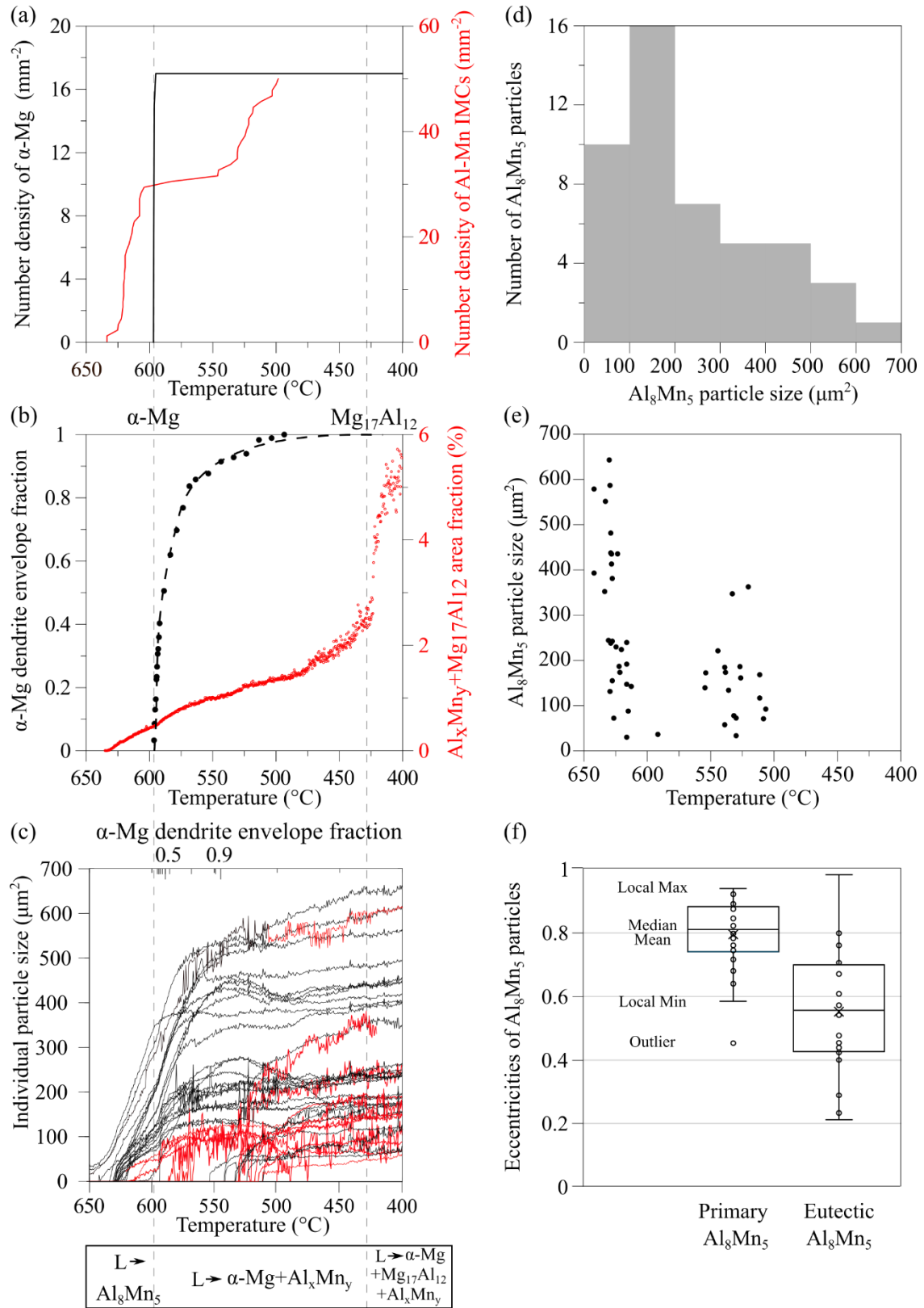


Figure 7 Quantification of the nucleation and growth of Al-Mn particles and α -Mg dendrite envelopes from X-ray imaging of AZ91-0.13Mn cooled at 5 K/min. (a) Number density of α -Mg dendrite and Al-Mn particle vs. temperature. (b) α -Mg envelope fraction curve and Al-Mn and $\text{Mg}_{17}\text{Al}_{12}$ area fraction vs. temperature. (c) Individual Al_8Mn_5 growth curves vs. temperature. For each curve, red indicates eccentricity smaller than 0.6 (rods/plates) while black indicates eccentricities larger than 0.6 (equiaxed). (d) Size distribution of Al_8Mn_5 particles. (e) Final Al_8Mn_5 particle size and their nucleation temperature. (f) Eccentricities (minor axis length divided by major axis length) of primary Al_8Mn_5 and eutectic Al_8Mn_5 .

The growth curves of α -Mg dendrites and Al-Mn+Mg₁₇Al₁₂ IMCs are plotted in Figure 7(b). The α -Mg envelope fraction was measured with respect to its final envelope size (averaged data from three magnesium dendrites) and Al-Mn+Mg₁₇Al₁₂ IMCs are considered together owing to their high contrast (both are dark in the radiographs) and their area fraction is plotted with respect to the whole field of view. Once α -Mg nucleated, the dendrite envelopes initially grew quickly and then gradually slowed. In the early stages of solidification, this deceleration is associated with the overlapping of solute fields between neighbouring dendrites (soft impingement) and, in the later stages, it is due to an increasing proportion of α -Mg solidification occurring by the filling-in of envelopes rather than the growth of envelopes. When averaging over the whole field of view, the fraction of Al-Mn+Mg₁₇Al₁₂ intermetallics increased steadily with small undulations, and there was then a substantial increase in the fraction at ~ 430 °C, corresponding to the onset of the final Mg₁₇Al₁₂-containing eutectic reaction. Note that the values in Figure 7(b) are area fractions measured from a 2D projection of a thin 3D sample, which will give a substantially higher value than the volume fraction. Specifically, the measured projected fraction of Al-Mn intermetallics is ~ 2 % in Figure 7(b) which is much higher than the volume fraction of ~ 0.1 vol% calculated using the Scheil model in ThermoCalc 2024b with the Mg-Alloys v7.0 database. Nonetheless, Figure 7(b) provides useful in-situ information on the development of phases during solidification.

Individual growth curves of Al₈Mn₅ particles are shown in Figure 7(c) with colours corresponding to their real-time projected eccentricities (minor axis length divided by major axis length). Particles with eccentricities smaller than 0.6 are considered as rods/plates and are coloured red while particles with eccentricities larger than 0.6 are considered as equiaxed particles and are coloured black. The coloured growth curves show rods/plates formed both before the nucleation of α -Mg as primary Al₈Mn₅ and after α -Mg as divorced eutectic Al₈Mn₅. Despite the post-mortem SEM observation that almost all rods/plates grew from a central equiaxed particle (Figure 2 and Figure 4), in the X-ray images most rods/plates appeared to grow directly in the liquid. However, due to their fast initial evolution and weaker contrast when particles are small, the initial equiaxed particles are likely to have been undetected before rods/plates grew out. An example where a rod/plate grew out from an existing equiaxed particle can be seen in Figure 7(c). Here, the rod/plate grew out from a large (~ 550 μm^2) equiaxed particle at ~ 520 °C causing the growth curve to change from black to red.

The distribution of Al₈Mn₅ particle size is given in Figure 7(d), showing that most Al₈Mn₅ particles had a size smaller than 200 μm^2 . Al₈Mn₅ particle size is plotted as a function of their

nucleation temperature in Figure 7(e), which shows there were two periods of Al_8Mn_5 nucleation during solidification, one between $650\text{ }^{\circ}\text{C} - 600\text{ }^{\circ}\text{C}$ before $\alpha\text{-Mg}$ nucleated and another below $550\text{ }^{\circ}\text{C}$ during divorced eutectic growth. The eccentricity of primary and eutectic Al_8Mn_5 particles at $510\text{ }^{\circ}\text{C}$ are given in Figure 7(f); the average eccentricity of primary Al_8Mn_5 is ~ 0.8 while the average eccentricity of eutectic Al_8Mn_5 is less than 0.6. Combining Figure 7(c) and (f) confirms there was a higher fraction of Al_8Mn_5 rods/plates in the eutectic Al_8Mn_5 compared to the primary Al_8Mn_5 . We note that using eccentricity values from 2D projections to distinguish between equiaxed particles and rods/plates leads to some uncertainty. For example, rods growing along the X-ray direction would appear as equiaxed particles in projection imaging. However, this will affect only a small minority of crystals since only a small deviation from this growth direction is required for a rod to have an eccentricity < 0.6 in projection imaging. Using eccentricity values is a reasonable method to measure the general differences in the growth morphology of primary vs. eutectic Al_8Mn_5 (Figure 7(f)), and to show that rods/plates formed both as primary Al_8Mn_5 and eutectic Al_8Mn_5 (Figure 7(c)).

It is next useful to consider how Al_8Mn_5 microstructure development is affected by cooling rate. Examples of synchrotron X-ray radiographs of AZ91-0.13Mn cooled at 2, 5 and 15 K/min are given in Figure 8. The corresponding videos of these time sequence radiographs are presented in Videos 1, 2, and 3, respectively. These are frames shortly after the nucleation of $\alpha\text{-Mg}$. The number density of Al_8Mn_5 particles increased with cooling rate from 14.1 mm^{-2} to 32.3 mm^{-2} to 63 mm^{-2} at 2, 5 and 15 K min^{-1} respectively, similar to the post-mortem results in Figure 5(a). The number density of $\alpha\text{-Mg}$ grains also increased with cooling rate from 7.6 mm^{-2} to 19.4 mm^{-2} to 39.9 mm^{-2} at 2, 5 and 15 K min^{-1} respectively. In both cases, this can be attributed to a deeper local undercooling being reached for higher cooling rates [39].

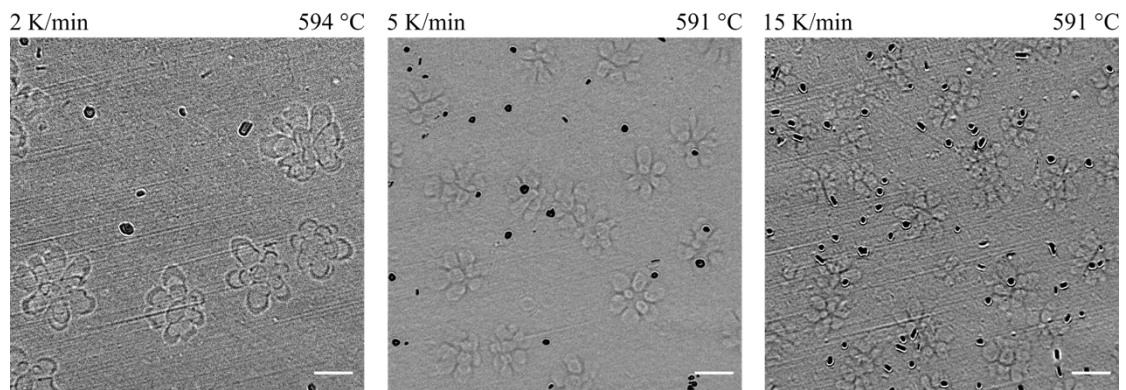


Figure 8 Synchrotron radiographs of AZ91-0.13Mn cooled at 2, 5 and 15 K/min, shortly after the nucleation of $\alpha\text{-Mg}$. Scale bars represent $100\text{ }\mu\text{m}$.

The features of Al_8Mn_5 at the three cooling rates are summarised in Table 3. At all three cooling rates, the major morphology was equiaxed particle for primary Al_8Mn_5 (all more than 70%), which confirms the implication (i) obtained from Figure 5. The 2-D projected size of Al_8Mn_5 particles in the 2 K/min sample varies significantly, which is because it has the highest fraction of Al_8Mn_5 rods/plates that looks much greater than equiaxed particles in the 2-D projection. Note that the fraction of rods/plates in synchrotron samples generally decreased with increasing cooling rate (although at 5 K/min and the 15 K/min samples essentially remained the same), which is consistent with the results shown in Figure 5(a) from laboratory samples, which involved a larger sample area.

Table 3 Summary of Al_8Mn_5 particles in the synchrotron imaging study.

Sample (K/min)	Number density of Al_8Mn_5 (per mm^2)	Average particle size (μm^2)	Number density of Al_8Mn_5 rods/plates (per mm^2)	Fraction of rods/plates over all Al_8Mn_5 (%)	Fraction of equiaxed particle in primary Al_8Mn_5	Fraction of equiaxed particle in eutectic Al_8Mn_5
2	30.2	377 ± 354	13.8	45.7	72.9%	36.3 %
5	51.2	294 ± 182	12.6	24.6	87.4%	53.6%
15	110.5	173 ± 79	34	25.2	72.8%	64.0%

The nucleation and growth profiles of Al-Mn in AZ91-0.13Mn with three cooling rates are shown in Figure 9, including the development of area fraction of Al-Mn IMCs during cooling (Figure 9(a)), the number density of Al-Mn particles (Figure 9(b)), the nucleation rate of Al_8Mn_5 (Figure 9(c)), and the Al-Mn area fraction as a function of Al-Mn particle number density (Figure 9(d)). Examination of panels (a)-(d) reveals that the nucleation and growth of Al_8Mn_5 can be split into the same three stages for all cooling rates. Stage 1: Primary Al_8Mn_5 solidification before α -Mg nucleates; Stage 2: Divorced eutectic solidification of Al_8Mn_5 shortly after α -Mg nucleates; and Stage 3: Divorced eutectic solidification of Al_8Mn_5 when there is a high fraction of α -Mg dendrite envelopes. In Figure 9, the behaviour in each stage is significantly affected by the cooling rate.

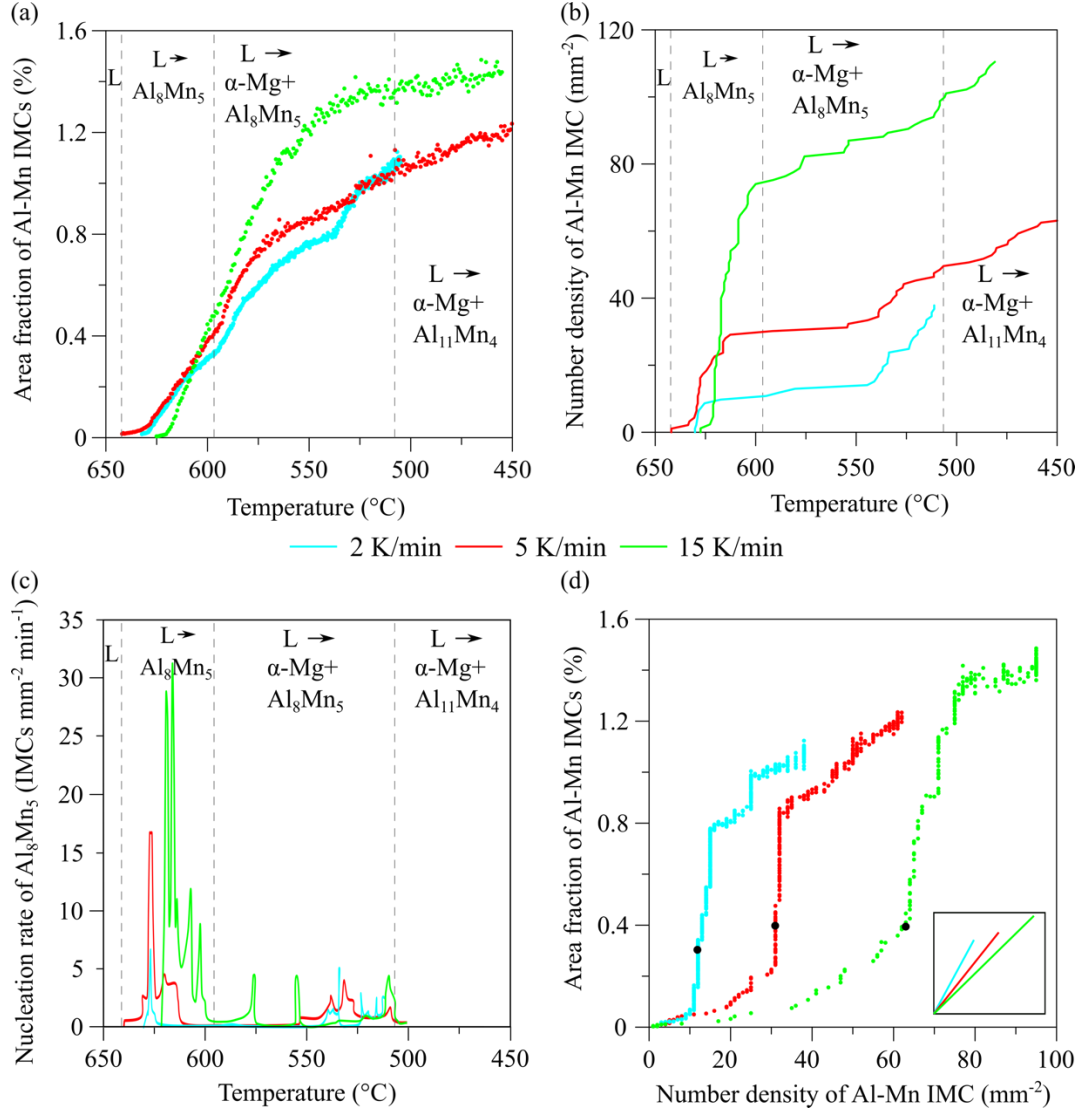


Figure 9 Nucleation and growth dynamics of Al-Mn IMCs in AZ91-0.13Mn cooled at 2, 5 and 15 K/min. (a) Al-Mn area fraction as a function of temperature. (b) Number density of Al-Mn particles as a function of temperature. (c) Nucleation rate of Al_8Mn_5 (IMCs mm⁻² min⁻¹). The nucleation rate curve for AZ91-0.13Mn cooled at 15 K/min is plotted in IMCs mm⁻² 15s⁻¹. (d) Al-Mn area fraction as a function of number density of Al-Mn particles. The average slope of Al-Mn area fraction vs. number density for each solidification condition is plotted in the bottom right corner of (d). Black dots are used to indicate where $\alpha-Mg$ started nucleating on each curve.

During primary Al_8Mn_5 solidification (Stage 1), Figure 9(a) shows that the increasing area fraction of primary Al_8Mn_5 slows during continued cooling at all three rates. In Figure 9(a), the 2 K/min curve (cyan) exhibits a significant slowing before the nucleation of $\alpha-Mg$. This is less pronounced at 5 K/min and more subtle at 15 K/min. There is also a reduction in the primary Al_8Mn_5 nucleation rate during continued cooling at all rates. For example, in Figure 9(b) and (c), at 2 K/min, Al_8Mn_5 nucleation events stop (or slow dramatically with few new nucleation events) well before the nucleation of $\alpha-Mg$. At 5 K/min, nucleation events stop at lower temperature whereas, at 15 K/min, Al_8Mn_5 keeps nucleating, albeit at decreasing rate, almost

up to the point where α -Mg nucleates. These features in Figure 9(a), (b) and (c) all show that, during primary solidification $L \rightarrow \text{Al}_8\text{Mn}_5$, a higher cooling rate generates the conditions for continued Al_8Mn_5 nucleation and, the corollary, a lower cooling rate results in the Al_8Mn_5 nucleation rate slowing significantly and stopping. This behaviour is similar to past work on the nucleation and growth of equiaxed dendrites in alloys [40–43]. Increasing the cooling rate in near-isothermal solidification increases the interface velocity, steepens the concentration profile in the liquid in front of Al_8Mn_5 particles and leads to larger constitutional supercooling at a given distance ahead of the interface where new nucleation events can occur.

Stage 2 starts with the nucleation of α -Mg, which is indicated by a vertical dashed line at $\sim 598^\circ\text{C}$ in Figure 9(a)-(c) and initiates divorced eutectic solidification. In Figure 9(a), the nucleation of α -Mg is followed almost immediately by an increase in Al_8Mn_5 phase formation rate (i.e. steepening of the curves). However, in the early stages of α -Mg growth, there is no significant increase in the Al_8Mn_5 nucleation rate (Figure 9(b) and (c)). This indicates that the initial growth of α -Mg provides the conditions to increase the growth rate of existing Al_8Mn_5 but is not sufficient to nucleate new Al_8Mn_5 . This can be understood from the mechanism of divorced eutectic growth; as α -Mg starts to grow, it rejects Mn and Al solute into the liquid which diffuses towards Al_8Mn_5 , causing solute mixing, reducing the solute boundary layer ahead of Al_8Mn_5 and enabling the Al_8Mn_5 to accelerate forwards. i.e. here, divorced eutectic growth involves solute mixing by diffusion through the liquid between two phases that do not share an interface. In the early stages of α -Mg growth, the rejection of Mn and Al solute into the liquid does not generate sufficient constitutional supercooling to trigger new Al_8Mn_5 nucleation events.

Stage 3 occurs when $L \rightarrow \alpha\text{-Mg} + \text{Al}_8\text{Mn}_5$ divorced eutectic solidification has generated a high fraction of α -Mg dendrite envelopes. Since divorced eutectic growth occurs over a wide temperature range in these multicomponent alloys ($\sim 92^\circ\text{C}$ for AZ91-0.13Mn, Figure 1), this requires a relatively long time at the low cooling rates studied. Figure 9(b)-(c) show that, after an initial period of divorced eutectic growth with negligible Al_8Mn_5 nucleation events in Stage 2, there are then a series of bursts of Al_8Mn_5 nucleation in Stage 3. The first burst occurs earlier (and at higher temperature) at 15 K/min, than at 5 K/min and latest (and at lowest temperature) at 2 K/min. These bursts continue until the end of Al_8Mn_5 solidification. This indicates that, at higher cooling rate, the conditions for new Al_8Mn_5 nucleation events during divorced eutectic growth are generated in a smaller drop in temperature than at lower cooling rate. This is explored further in the final section.

Considering all stages together, the increase of total Al_8Mn_5 area fraction can be attributed to both the growth of existing Al_8Mn_5 and the nucleation of new Al_8Mn_5 particles. To illustrate which mechanism dominates at different temperatures during cooling, the Al-Mn area fraction is plotted as a function of Al-Mn particle number density in Figure 9(d). At the beginning of solidification of all three cooling rates, the slopes were shallow, indicating that Al_8Mn_5 nucleation was the dominant mechanism. Then they all transferred to a steep slope representing the growth of existing Al_8Mn_5 particles with almost no nucleation. After a period dominated by growth, new nucleation events led to a shallow gradient again where both new nucleation events and continued growth increase the Al-Mn area fraction. The average slope of the Al-Mn area fraction vs. number density of Al-Mn IMC for each solidification condition is plotted as an inset in the bottom right of Figure 9(d), which confirms that, with increasing cooling rate, nucleation events contributed more to the increase of Al-Mn area fraction.

3.3.2 Interplay between nucleation and growth in divorced eutectic solidification

When the α -Mg dendrite envelopes grew to fill most of the volume (Stage 3), there were new bursts of Al_8Mn_5 nucleation and, with higher cooling rate, a smaller temperature drop was required during divorced eutectic growth to initiate these bursts (Figure 9). To understand this, consider the small region from the X-ray experiments in Figure 10(a), which is idealised in Figure 10(b). Here, there is a narrow liquid channel between two advancing α -Mg dendrite arms. In the channel, there is one Al_8Mn_5 particle growing on the right side and no Al_8Mn_5 on the left side but one Al_8Mn_5 is going to nucleate soon at the position indicated by the dashed square. During solidification, the growing α -Mg rejects Al, Mn and Zn solute into the surrounding liquid, and the growing Al_8Mn_5 takes Al and Mn solute from the liquid. In Figure 10(b), on the right side of the domain, the Mn solute rejected by the growing α -Mg diffuses a short distance in the liquid and is consumed by the growing Al_8Mn_5 . In contrast, on the left side of the domain where there is no Al_8Mn_5 particle, the Mn solute accumulates in the liquid. The schematic Mn distribution in the liquid is sketched in Figure 10(c). On the left side, large local constitutional supercooling develops in the liquid with respect to the Al_8Mn_5 liquidus and not the α -Mg liquidus because of the asymmetry of the phase diagram. This can be understood with Figure 10(d), which is a vertical section at $(81.03-x)\text{Mg}-17.65\text{Al}-x\text{Mn}$ (wt.%) showing only liquidus lines and extended liquidus lines (dashed) where the red circle is a point on the eutectic groove at 547.7°C (cf. the liquidus projection in Figure 1), indicating the liquid composition

when AZ91-0.13Mn is cooled to such temperature. The Mg-rich region of the Mg-Al-Mn phase diagram is highly asymmetric both in terms of the steepness of the α -Mg and Al_8Mn_5 liquidus slopes and in terms of the volume fraction of phases forming (in the $L \rightarrow \alpha\text{-Mg} + \text{Al}_8\text{Mn}_5$ eutectic, the ratio of the volume fraction of α -Mg to Al_8Mn_5 is $>1000:1$). The α -Mg liquidus is very shallow compared with the steep Al_8Mn_5 liquidus such that accumulation of Mn in the liquid (moving to the right as indicated by the red arrow in the phase diagram in Figure 10(d)) would have little effect on the α -Mg liquidus temperature but a strong effect on the Al_8Mn_5 liquidus temperature. Thus, a large local constitutional supercooling develops in the liquid with respect to the Al_8Mn_5 liquidus and not the α -Mg liquidus. This asymmetry is ultimately responsible for the divorced eutectic growth with α -Mg dendrites and the continued nucleation of Al_8Mn_5 particles throughout the freezing range.

For near-isothermal solidification, increasing the cooling rate increases the interface velocity. In Figure 10(c), the Mn solute distribution in the liquid is sketched at two growth velocities, where $V_2 > V_1$. At higher velocity, the diffusion profile is both (i) steeper due to the reduced time for diffusion ahead of the Al_8Mn_5 particle and (ii) has a higher maximum Mn concentration because the Mn continuously rejected by the advancing α -Mg has less time to diffuse to the right and more Mn accumulates at the left side. Thus, for a given growth distance, a higher growth velocity generates larger constitutional supercooling with respect to the Al_8Mn_5 liquidus in the liquid channel between α -Mg dendrite arms so, with higher cooling rate, a smaller temperature drop is required during divorced eutectic growth to initiate new Al_8Mn_5 nucleation events (as occurs in Figure 9). A further important feature of divorced eutectic growth in this system is that the two uncoupled eutectic phases have solute fluxes that are directed predominantly normal to the solid-liquid interfaces (see Fig. 10b) in contrast to conventional coupled eutectic growth where solute diffusion occurs laterally at the eutectic growth front providing effective solute mixing. There is also some similarity with irregular eutectic solidification, when a leading faceted phase grows substantially ahead of the majority non-faceted phase and growth can become decoupled [44,45].

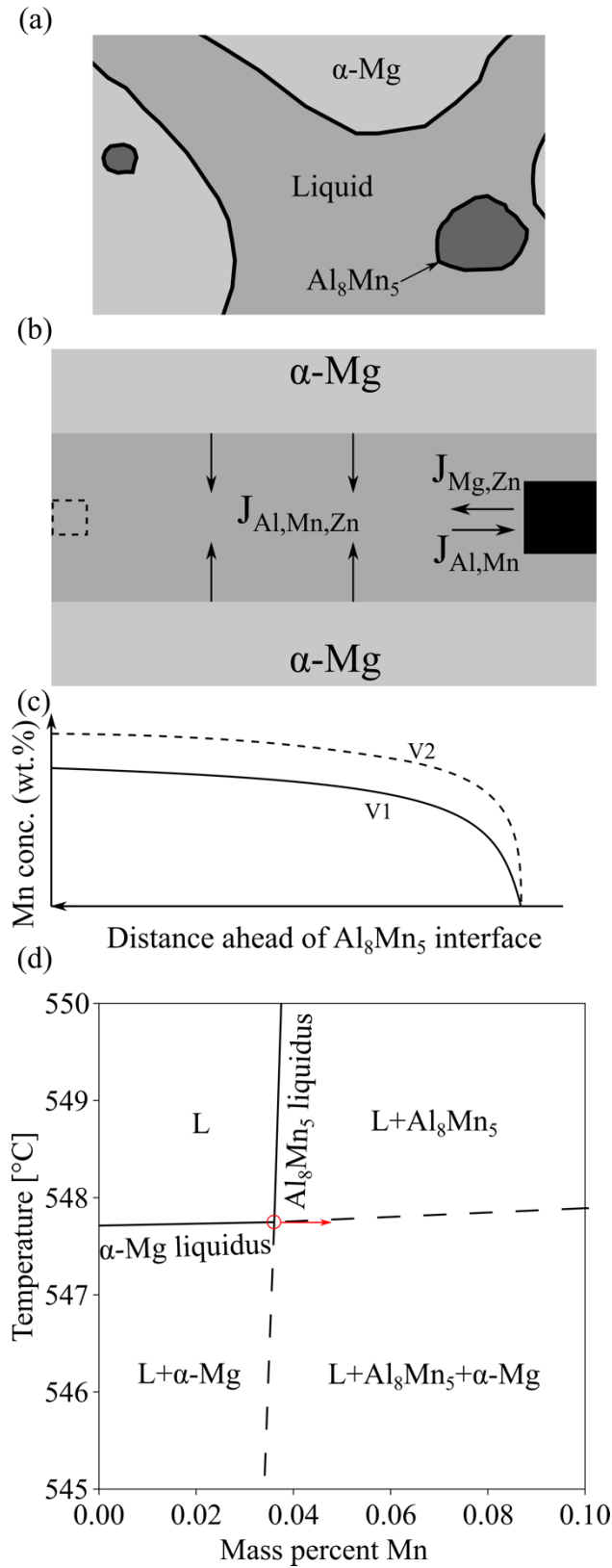


Figure 10 Constitutional supercooling of Al_8Mn_5 caused by $\alpha\text{-Mg}$. (a) Actual scenario involving projection imaging from AZ91-0.13Mn cooled at 2 K/min at 545 °C. This is the region highlighted by the dashed rectangle in Figure 11(b). (b) Idealised 2-D scenario. (c) Mn solute profile in the liquid corresponding to the case in (b); the interface velocity $V_2 > V_1$. (d) Isopleth of $(81.03-x)\text{Mg}-17.65\text{Al}-x\text{Mn}$ (wt.%) showing only equilibrium and extended liquidus lines from the Thermo-Calc TCMG6 database. The red circle indicates a point on the eutectic groove at 547.7 °C

A range of different local interactions were measured between individual Al_8Mn_5 particles late during divorced eutectic growth, all consistent with the mechanism overviewed in Figure 10. For example, Figure 11(a) and (b) are radiographs and corresponding schematic diagrams of a subregion, along with the growth curves of the three Al_8Mn_5 particles indicated by arrows in Figure 11(b). The growth curves show that, at the beginning of solidification in this region, two Al_8Mn_5 nucleated prior to the nucleation of α -Mg and then grew into an equiaxed particle (blue) and a rod/plate (red). At $\sim 540^\circ\text{C}$, a new Al_8Mn_5 nucleated in the liquid between α -Mg dendrite arms (pink arrow) and grew into a rod/plate at a relatively fast and near-constant rate. At the same time as the nucleation of the new plate, the two existing Al_8Mn_5 started to shrink remarkably. The shrinking of some Al_8Mn_5 particles during cooling was unexpected. It indicates competitive growth between the Al_8Mn_5 , for instance, by an Ostwald ripening-like mechanism-

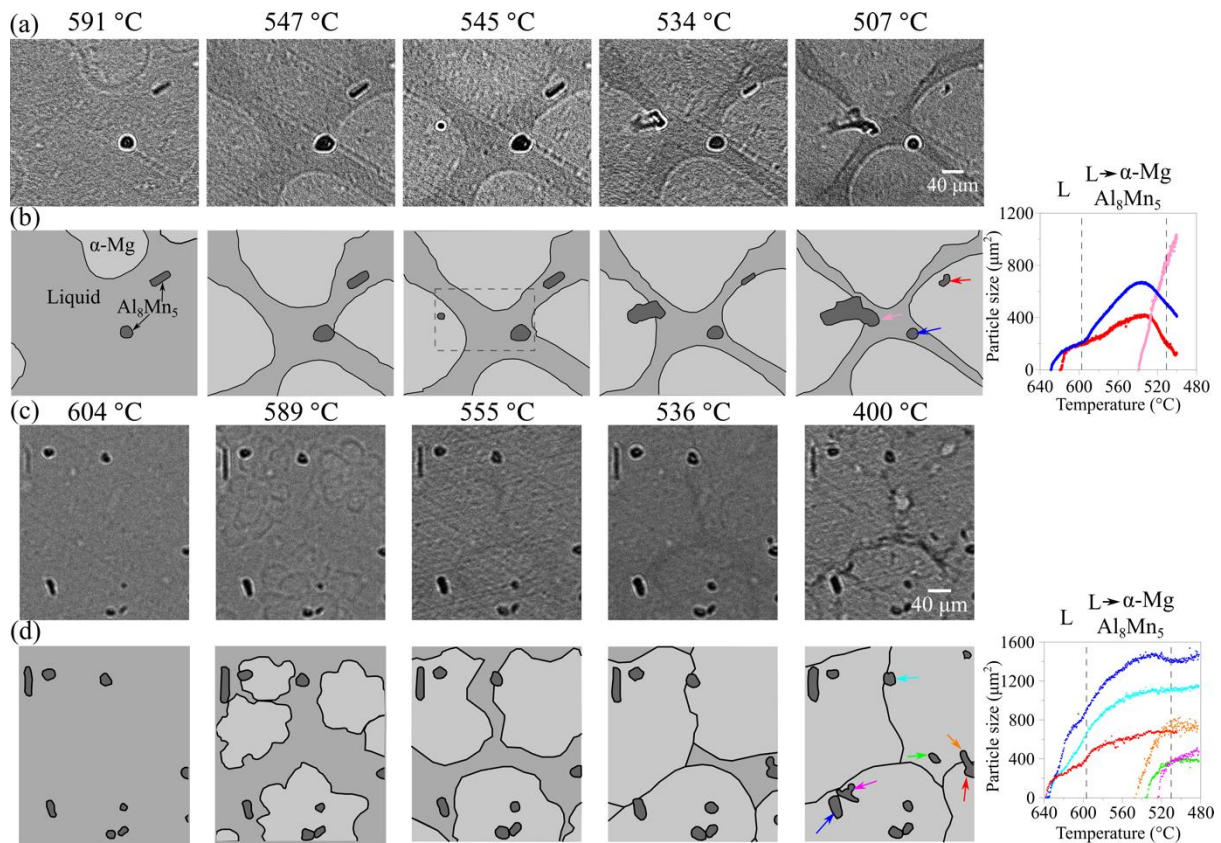


Figure 11 Examples of Al_8Mn_5 nucleation and growth late during divorced eutectic growth. (a) Radiograph sequence of a new Al_8Mn_5 nucleating at $\sim 540^\circ\text{C}$ and growing as a rod/plate and existing Al_8Mn_5 particles shrinking from AZ91-0.13Mn cooled at 2 K/min. (b) Corresponding schematic diagrams and particle growth curves. Colour links the growth curves and arrows. (c) and (d) are similar as (a) and (b) but from AZ91-0.13Mn cooled at 15 K/min.

In Figure 11(c) and (d), after primary Al_8Mn_5 growth, there were no Al_8Mn_5 nucleation events in this small area until $\sim 540^\circ\text{C}$. Then the orange, green and magenta Al_8Mn_5 nucleated and

grew faster than the existing Al_8Mn_5 . In this case, after the new Al_8Mn_5 nucleates, the cyan and red existing particles continue growing at a slow rate, whereas the blue existing particle shrinks slightly before growing at a slow rate. This shows the variability of the behaviour of individual Al_8Mn_5 particles once new particles nucleate, with some existing particles shrinking (red and blue in Figure 11(a) and (b)), some continuing to grow (cyan and red in Figure 11(c) and (d)) and some shrinking then growing again (Figure 11(c) and (d)). This is thought to be due to the locally different solute field in the liquid at each location, and the initial growth advantages of new particles once they nucleate in supercooled liquid. It should be noted that, at the length scale used for imaging, nucleation cannot be directly observed, and it is possible, in at least some cases, that an apparent nucleation event is the accelerated growth of a particle that nucleated earlier and had initially remained small. Such a scenario is still the response to the development of local constitutional supercooling for Al_8Mn_5 .

Overall, it can be concluded that constitutional supercooling led to the continuous nucleation of Al_8Mn_5 throughout the freezing range. The effects of continuous nucleation on the fraction of morphologies in the large samples in Figure 5 can be deduced as follows. The decreasing fraction of rods/plates with increasing cooling rate (Figure 5(a) and Table 3) is probably because, at higher cooling rate, the nucleation of new Al_8Mn_5 is promoted while the formation of rods/plates being suppressed.

The increasing number density of Al_8Mn_5 particles with higher Mn content at fixed cooling rate (Figure 5(b) and (c)) mainly occurs because increasing the Mn content increases the Al_8Mn_5 freezing range (Figure 1) and Al_8Mn_5 nucleation occurred continuously during cooling in the primary solidification stage, $L \rightarrow \text{Al}_8\text{Mn}_5$, (see Figure 9(b), noting that 15K/min is slower than moderate cooling in Figure 5(b) and (c)).

In Figure 5(b) and (c), the high fraction of rods/plates in AZ31-0.3Mn and AZ91-0.1Mn is because these compositions start on/near the eutectic groove and a higher proportion of rods/plates form during divorced eutectic solidification. Similarly, the higher proportion of equiaxed particles in AZ31-0.5Mn and AZ91-0.2Mn is due to their higher fraction of primary Al_8Mn_5 .

Some synchrotron samples solidified at 5K/min were analysed post-mortem which revealed that the Al_8Mn_5 particles were attached to the sample surface, as shown in Figure 12. This explains why the Al_8Mn_5 particles did not settle under gravity in our experiments which was useful for enabling this synchrotron study. This also highlights where some caution is required

in the interpretation of individual Al_8Mn_5 particle behaviour. For example, if two Al_8Mn_5 particles are on opposite surfaces of the sample, they may appear as close neighbours in projection imaging but would be relatively far apart ($\sim 150\text{ }\mu\text{m}$) in 3D.

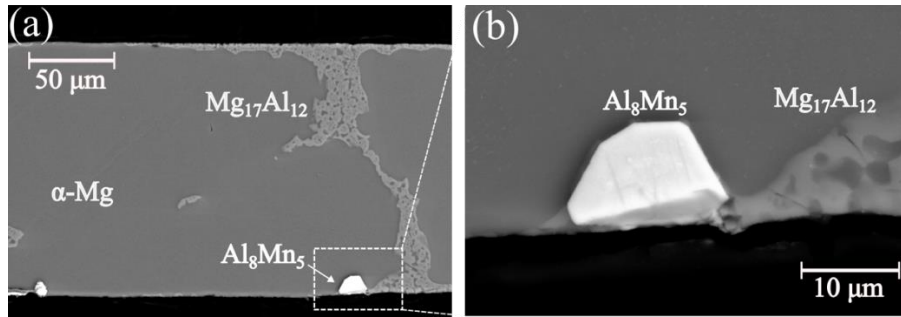


Figure 12 BSE-SEM micrographs of cross-sectioned samples Post-mortem from in-situ synchrotron experiments

The in-situ experiments also provide new insights into puzzling features of the Al_8Mn_5 morphology when studied after solidification. Looking back at Figure 3(e), we see significant variability in the detailed faceted shape of Al_8Mn_5 crystals. It is likely that this variability is at least partially due to the continuous nucleation throughout the long solidification sequence. For example, even for close neighbours after solidification, in-situ imaging showed that each Al_8Mn_5 particle nucleated at a different temperature in liquid of different composition and, in some cases, at different local constitutional supercooling. The first two factors affect the thermodynamics of the S-L interface, and the third factor affects the kinetics of atomic attachment, all of which may affect the slowest growing facets. The divorced eutectic growth mechanism observed here and the continuous Al_8Mn_5 nucleation also explain why it is often difficult to distinguish between primary and eutectic Al_8Mn_5 particles after solidification.

4 Conclusions

The formation of the complex intermetallic Al_8Mn_5 has been studied in the solidification of AZ31 and AZ91 magnesium alloys by combining electron microscopy measurements of the growth crystallography with in-situ synchrotron X-ray imaging of Al_8Mn_5 nucleation and growth and its interactions with the growing α -Mg phase. The following new insights have been revealed:

- Al_8Mn_5 solidified with three growth morphologies – equiaxed particle, rod and plate. Rods and plates were commonly found to grow from equiaxed particles. All three morphologies are related to the growth twinning of rhombohedral Al_8Mn_5 arising from its pseudo-cubic crystal structure.
- Equiaxed particles were always cyclic twinned with four orientations. Rods and plates usually grew from equiaxed particles. Rods were single crystals with up to eight rods growing along the eight $\langle 111 \rangle$ directions of the central equiaxed particle when considered in pseudo-cubic symmetry. Plates contained two twinned orientations that developed from two neighbouring rods.
- In-situ X-ray imaging revealed that Al_8Mn_5 nucleates and grows throughout the solidification sequence, in both the $\text{L} \rightarrow \text{Al}_8\text{Mn}_5$ and $\text{L} \rightarrow \alpha\text{-Mg} + \text{Al}_8\text{Mn}_5$ reactions, and rods/plates formed preferentially in the eutectic reaction. Increasing the Mn content increases the fraction of primary Al_8Mn_5 , and thereby increases the fraction of equiaxed particles. A further increase of Mn content increases the possibility of existing equiaxed particles to develop rod/plate morphology.
- In these multicomponent alloys, the reaction $\text{L} \rightarrow \alpha\text{-Mg} + \text{Al}_8\text{Mn}_5$ occurred by divorced eutectic growth involving equiaxed $\alpha\text{-Mg}$ dendrite growth plus the growth and continued nucleation of Al_8Mn_5 in the liquid between $\alpha\text{-Mg}$ dendrites and their arms. This occurred because Mn solute in the liquid has an insignificant effect on the $\alpha\text{-Mg}$ liquidus but strongly affects the Al_8Mn_5 liquidus, leading to large constitutional supercooling with respect to the Al_8Mn_5 phase only.
- Continued Al_8Mn_5 nucleation occurred during divorced eutectic growth due to the continued build-up of constitutional supercooling by the dual effects of Mn accumulation ahead of growing $\alpha\text{-Mg}$ and Mn depletion ahead of growing Al_8Mn_5 . By this mechanism, increasing the cooling rate resulted in more Al_8Mn_5 nucleation events occurring earlier during divorced eutectic growth and suppressed the formation of rods/plates.
- These findings explain the large variation in Al_8Mn_5 growth morphology after solidification and the new understanding can be used to develop approaches to minimise the formation of large, deleterious Al_8Mn_5 rods and plates.

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