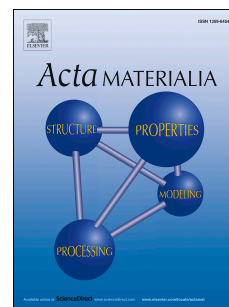


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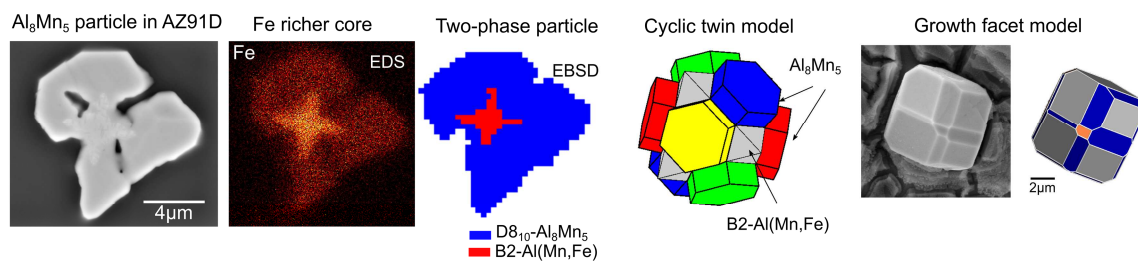
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Nucleation and growth crystallography of Al_8Mn_5 on B2-Al(Mn,Fe) in AZ91 magnesium alloys

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Abstract

Manganese is widely added to Mg-Al-based alloys to form Al-(Mn,Fe) intermetallics that combat impurity Fe. Here EBSD, deep etching and FIB-tomography are combined to study the nucleation and growth crystallography of Al-Mn-Fe particles in Mg-9Al-0.7Zn-0.15Mn-0.002Fe (wt%) solidified at $1\text{K}\cdot\text{s}^{-1}$. It is shown that Al_8Mn_5 nucleates on B2-Al(Mn,Fe) particles and an incomplete peritectic transformation results in a Fe-rich B2-Al(Mn,Fe) core enveloped by a low-Fe Al_8Mn_5 shell. A reproducible orientation relationship (OR) is measured, and the close lattice match and OR are discussed in terms of the group-subgroup relationship between these phases. It is found that most rhombohedral Al_8Mn_5 particles are twinned, consisting of four orientations related by $\sim 90^\circ$ rotations around three common $\langle 1\bar{1}02 \rangle$, which is discussed in terms of the pseudo-cubic $\langle 100 \rangle$ axes of the Al_8Mn_5 rhombohedral gamma brass. Al_8Mn_5 grew as equiaxed particles that are explained by polyhedron models based on $\{100\}$, $\{110\}$ and $\{112\}$ facets of the pseudo-cubic Al_8Mn_5 cell. The results indicate that, at low Fe:Mn ratio, most impurity Fe is dissolved in B2 particles that are encapsulated by low-Fe Al_8Mn_5 which may be important for corrosion resistance.

Keywords electron backscatter diffraction, intermetallics, crystal growth

1. Introduction

Manganese is added to most Mg-Al-based alloys to combat impurity iron. For AZ91 (Mg-9Al-0.7Zn in wt%), sufficient Mn is usually added to ensure that the Fe:Mn ratio is less than 0.032 which substantially improves the corrosion resistance [1, 2].

Both Mn and Fe are almost insoluble in α -Mg, do not form intermetallic compounds (IMCs) with Mg, and instead react with Al solute to form $\text{Al}_x(\text{Mn,Fe})_y$ IMCs [3]. A series of Mn-containing IMCs can form at different stages of AZ91 melt handling, solidification and heat treatment, where $\text{Al}(\text{Mn,Fe})$, $\text{Al}_8(\text{Mn,Fe})_5$, and $\text{Al}_{11}\text{Mn}_4$ have been identified in previous work [4-12].

At typical Mn and Fe levels, $\text{Al}_x(\text{Mn,Fe})_y$ IMCs begin to form above the α -Mg liquidus temperature and can be removed to some extent by gravitational sedimentation which gives some control of the Fe content of melts. However, $\text{Al}_x(\text{Mn,Fe})_y$ particle settling also creates sludge in die casting pots [13] and can block filters in the launders of direct chill (DC) casting units. For a given IMC density, the size and shape of the primary IMCs determines their settling behaviour as well as their packing and clumping behaviour. Therefore, it is important to understand and be able to control the size and shape of primary IMCs in Mg-Al-based alloys.

$\text{Al}_x(\text{Mn,Fe})_y$ IMCs also form during solidification both before α Mg nucleation as primary phases and, later, between α -Mg dendrite arms and between dendritic grains in higher order reactions. After solidification, this results in $\text{Al}_x(\text{Mn,Fe})_y$ particles distributed both inside α -Mg grains and at α -Mg grain boundaries [9, 14-16].

A large body of work has explored the role of $\text{Al}_x(\text{Mn,Fe})_y$ IMCs in two areas: (i) the grain refinement of α -Mg [5, 15, 17, 18] and (ii) the corrosion performance of Mg-Al-based alloys[1, 2, 19-22]. However, much less work has studied the nucleation and growth of

$\text{Al}_x(\text{Mn,Fe})_y$ IMCs during solidification and the factors affecting their size and morphology. For example, while there have been advances in the understanding Al_8Mn_5 formation [5, 16, 23, 24] and the morphologies that can develop [9], there remain many outstanding questions such as where Al_8Mn_5 particles nucleate, how they grow, and what role the IMC crystallography plays in heterogeneous nucleation and faceted growth mechanisms.

In recent years, there have been major developments on phase equilibria and phase diagrams associated with Al-Mn-Fe intermetallics [25, 26] and their incorporation into Mg-Al-(Zn)-containing systems [3, 27]. However, much less research has explored the kinetics and microstructure evolution of Al-Mn-Fe intermetallics in Mg alloys. This paper combines recent Mg-Al-Zn-Mn-Fe phase diagrams with analytical SEM studies of $\text{Al}_x(\text{Mn,Fe})_y$ IMC microstructures in AZ91 with three main aims: (i) to identify the natural heterogeneous nucleant for Al_8Mn_5 crystals in AZ91; (ii) to understand the growth crystallography of faceted Al_8Mn_5 primary particles; and (iii) to identify the location of impurity Fe in the microstructure to gain a deeper understanding of how Mn additions ameliorate against the negative effects of Fe.

2. Methods

90g of AZ91D with composition given in Table 1 (batch #1) was melted in boron nitride (BN) coated mild steel cylindrical cups using a mixture of 1.5 vol.% SF₆ and CO₂ as a cover gas. A K-type thermocouple (calibrated against 99.98 wt% Al) was placed in the centre of the melt and the alloy was held at 700°C (~100°C superheat) for 20 min before being removed from the furnace and solidified naturally in air. The cooling rate in the liquid prior to α -Mg nucleation was $\sim 1^{\circ}\text{C}\cdot\text{s}^{-1}$.

Samples for microstructural analysis were cut into slices of 10mm×10mm×1mm. Metallographic polishing was carried out down to 0.05 μm colloidal silica by standard preparation methods. For EBSD characterisation, the final step of preparation was Ar-ion milling for 40 minutes using a Gatan PECSII instrument. The 4 kV-accelerated beam hit the sample rotating at 2 rpm, at a grazing incidence angle of 4°. To reveal the 3-dimensional (3D) morphology of the Al-Mn-Fe intermetallics, α -Mg was selectively dissolved from some samples using a solution of 4% nitric acid in ethanol.

A Zeiss AURIGA field emission gun SEM (FEG-SEM) equipped with a focused ion beam (FIB), an Oxford Instruments INCA x-sight energy dispersive X-ray (EDX) detector and a BRUKER e-FlashHR EBSD detector was used. EDS measurement was performed at 10kV with 5mm working distance. EBSD measurement was performed at 20kV with 14.5-15.0mm working distance and 70° tilted stage. BRUKER ESPRIT 2.1 software was used to acquire and index EBSD patterns. For this instrument, the angle between the FIB and the SEM column was 54°. FIB serial sectioning was performed on deep etched Al₈Mn₅ particles without stage tilt, at 30 kV with working distance of 5mm. The slice distance was 90nm and the milling current was 600pA.

To determine the 3D growth crystallography of intermetallics, EBSD and FIB tomography were combined. Polished particles after EBSD measurements were serially-sliced using a FIB (FEI Helios NanoLab 600 dual beam system) and imaged in SE mode. Serial-sectioning was performed at 30kV, at 52° tilt angle. The slice distance was 100nm and the milling current was 2.8nA. EBSD datasets were analysed using MATLAB™ 9.2 (Mathworks, USA) with the MTEX 4.4 toolbox [28]. For FIB tomography, 2D slices were aligned, cropped, and processed by an anisotropic diffusion filter in ImageJ [29] (US NIH, USA). 3D reconstruction and crystallographic analysis was performed using Avizo (Visualization Science Group, France) and MATLAB 9.2™. Having measured the growth facets, the 3D growth habit of intermetallic particles was plotted using KrystalShaper 1.4 (JCrystalSoft).

3. Results and Discussion

3.1 Solidified microstructure of AZ91 and primary Al_8Mn_5 intermetallics

Fig. 1(a) shows the typical solidified microstructure of AZ91 cooled at $\sim 1^\circ\text{C}\cdot\text{s}^{-1}$, containing a α -Mg matrix, $\text{Mg}_{17}\text{Al}_{12}$, and Al-Mn-Fe intermetallics. The 3D morphologies of the Al-Mn-Fe intermetallics, revealed by deep-etching, are shown in Fig. 1(b) and (c). Two main morphologies were found: equiaxed-polyhedral (Fig. 1(c)) and elongated rods/plates (Fig. 1(b)). Recent in-situ observations of AZ91 solidification by synchrotron radiography [30] at similar cooling rate confirmed that the primary Al_8Mn_5 crystals that grow prior to α -Mg nucleation have equiaxed polygonal morphology. This can be further confirmed by noting in Fig. 1(a) that Al-Mn-Fe particles with equiaxed morphology settled to the bottom of the sample during solidification, indicating that they are primary particles that formed before α -Mg nucleation. The elongated Al_8Mn_5 in Fig. 1(b) formed in higher order reactions (eutectic etc.), and further examples with a complex faceted morphology ranging from rod, to sheet, and folded plate-like are given in reference [31]. As shown in Fig. 1(b), eutectic Al_8Mn_5 were often attached to primary Al_8Mn_5 particles, indicating that eutectic Al_8Mn_5 grew from primary Al_8Mn_5 particles. For batch #1 of AZ91D (Table 1) solidified at $1\text{K}\cdot\text{s}^{-1}$, the mean size (Feret diameter of particles in deep etched samples) of primary Al_8Mn_5 particles was $10 \pm 2\ \mu\text{m}$, as shown in the size distribution histogram from 59 particles in Fig. 1(d).

Fig. 1(e) shows the solidification path of AZ91 calculated for the composition $\text{Mg-8.97Al-0.74Zn-0.15Mn-0.02Fe}$ for both equilibrium and Scheil solidification, using PANDATTM with the PanMg2016 database [32].

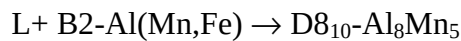
Fig. 1(e) predicts that several Mn-containing intermetallics form at different stages of solidification, although the total Al-Mn-Fe intermetallic fraction is low ($\sim 0.6\ \text{vol}\%$). B2-Al(Mn,Fe), Al_8Mn_5 and $\text{Al}_{11}\text{Mn}_4$ are predicted for equilibrium solidification, and B2-

Al(Mn,Fe), Al₈Mn₅, Al₁₁Mn₄ and Al₄Mn are predicted for Scheil solidification up to 99.8% solid. Note that impurity Fe dissolves into B2-Al(Mn,Fe) and Al₈(Mn,Fe)₅ by substituting onto Mn lattice sites [25, 26].

Under both equilibrium and Scheil conditions, B2-Al(Mn,Fe) is predicted to be the first solid phase to form, with a liquidus temperature of 711°C.



It is followed by a peritectic transformation;



B2-Al(Mn,Fe) and D8₁₀-Al₈Mn₅ are predicted to form prior to α-Mg (602°C), and further Al₈Mn₅, Al₁₁Mn₄ and Mg₁₇Al₁₂ (and Al₄Mn for sufficiently limited back diffusion) are predicted to form in polyphase reactions with α-Mg later during solidification. These Al-Mn phases have been experimentally reported in previous work [5, 6, 8, 9, 12, 23, 27, 33-37]. In this work, the primary particles were B2-Al(Mn,Fe) and D8₁₀-Al₈Mn₅ as discussed in the next section, and the main eutectic intermetallics observed were Al₈Mn₅ (e.g. Fig. 1(b)) and Mg₁₇Al₁₂. Only traces of Al₁₁Mn₄ and Al₄Mn were measured in the eutectic.

Fig. 1(f) is a plot of the Mg-Fe isopleth at 8.97Al-0.74Zn-0.1Mn from the PanMg2016 database in PANDAT™ [32]. It predicts that, when the Fe content in AZ91 is more than ~6ppm (0.0006wt.%), B2-Al(Mn, Fe) is the first solid phase to form on cooling. Fig. 1(f) also predicts that, for the Fe level in the AZ91 used (~20ppm, 0.002wt.% Fe in batch #1), the liquid was already saturated in Fe at the peak melting temperature (700 °C).

Cooling curve analysis was performed to compare with the predictions in Fig. 1(e) and (f). From the cooling curve and first derivative curve in Fig. 1(h), the onset of α-Mg and Mg₁₇Al₁₂ nucleation can be clearly identified but the formation of Al-Mn-(Fe) intermetallics cannot be reliably detected. This is due to the small latent heat release from Al-Mn-(Fe)

intermetallics as the phase fractions are very small (each is less than 0.2 mass % [32]). To compare the development of solid fraction on cooling with the calculations in Fig. 1(e), Newtonian cooling curve analysis was performed on the cooling curve data in Fig. 1(h) using the approach widely adopted in past work [38-40] and the data for the specific heat capacity and latent heat of α -Mg and $\text{Mg}_{17}\text{Al}_{12}$ from Ref.[40]. The result is shown in Fig. 1(g), where it can be seen that the experimental solidification path is intermediate between the equilibrium and Scheil predictions. Note that the experimental solidification path is not significantly affected by ignoring the Al-Mn-(Fe) intermetallics since they contribute so little to the latent heat flux. The cooling curve analysis result in Fig.1 (g)-(h) is consistent with past work [40-44] and highlights the need for detailed microstructural studies to investigate Al-Mn-Fe intermetallic formation in AZ91.

3.2 Two-phase B2-Al(Mn,Fe)/D8₁₀-Al₈Mn₅ particles

It was found that many primary Al-Mn-Fe particles were two phase particles with a core-shell structure. Fig. 2 shows typical images. Fig. 2(a-b) were imaged in BSE mode and show the core-shell structures on polished surfaces. Fig. 2(c) shows EDS analysis on a primary particle. It can be seen from both the EDS line-scan and EDS mapping that the core has substantially higher Fe content and is depleted in Al and Mn, compared to the shell region. EDS mapping also shows that Fe exists in the shell region, although the content is substantially lower than the core.

Since the core phase can be missed using random 2D cross-sectioned surfaces, FIB serial sectioning was performed on deep-etched samples. In Fig. 2(d-e), the α -Mg phase has been selectively etched away and the 3D morphology of Al-Mn-Fe particles was imaged in SE

mode. Video 1 in the Supplementary Information shows the process of serially sectioning through an intermetallic particle using a 90 nm slice spacing to search for a core particle. With this approach, a core particle such as those in Fig. 2(d-e) was confirmed in 18 out of 22 particles and the remaining 4 were inconclusive. From this it can be concluded that most, and maybe all, primary Al-Mn-Fe particles had a core phase near their centre. The morphology of the core phase varied from dendrites (e.g. Fig. 3) to cubes and was often associated with a pore near the centre (e.g. Fig. 2b, d-e).

A combination of EDS and EBSD was used for phase identification of these two-phase particles. Fig. 3 shows a typical example where EBSD patterns were taken from the locations marked with white crosses in the phase map. With the EDS data in Table 2 and indexing of these EBSD patterns via the Hough transform, the core phase was indexed as cubic B2-Al(Mn,Fe) (red region in the EBSD phase map of Fig. 3) and the shell was indexed as rhombohedral $D8_{10}$ - Al_8Mn_5 (blue in the phase map). For this particle, EDS point analysis (Table 2) gave an Fe content of 13.6 at.% in the core and 1.4 at.% in the shell regions. These primary IMC phases are consistent with the predictions in Fig. 1(e).

The relationship between these IMCs can be understood with reference to the centre of the binary Al-Mn phase diagram in Fig. 4(a) based on Refs [3, 26, 45, 46], which contains four intermetallic phases with crystallography summarised in Table 3 from Refs [46-49]. A2-AlMn and B2-AlMn are disordered and ordered BCC structures respectively (Fig. 4(b))[26]. $D8_2$ - Al_8Mn_5 is a body-centred cubic gamma brass with the Cu_5Zn_8 -structure, and $D8_{10}$ - Al_8Mn_5 is a rhombohedral gamma brass that is closely related to the $D8_2$ structure (Fig. 4(c))[46]. There are some fundamental similarities between these crystal structures as can be seen from the similarities in the B2 and $D8_{10}$ EBSD patterns in Fig. 3(b). One important factor is that there are maximal group/subgroup relations between the four space groups in Table 3: $Im\bar{3}m/Pm\bar{3}m \rightarrow I\bar{4}3m \rightarrow R3m$; and $Im\bar{3}m/Pm\bar{3}m \rightarrow R\bar{3}m \rightarrow R3m$ [47] where

arrows point to subgroups. These crystallographic similarities are important in understanding the nucleation and growth of B2-Al(Mn,Fe) and D8₁₀-Al₈Mn₅ core/shell particles and are discussed in more detail next.

For the rhombohedral crystal structure, there are two standard settings: a primitive rhombohedral lattice, R3mR, with $a=b=c$ and $\alpha=\beta=\gamma$; and a hexagonal lattice, R3mH, with $a=b \neq c$, $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$ [50]. For D8₁₀-Al₈Mn₅, there is a third non-standard setting which can be useful in crystallographic studies [48, 51] in which the hexagonal cell is transformed to a body-centred rhombohedral (BCR) cell with 52 atoms. The three different settings of the D8₁₀-Al₈Mn₅ structure are shown in Fig. 4(d) viewed along [0001] in the hexagonal setting, and [111] in the primitive rhombohedral and body centred rhombohedral settings. Note that the rhombohedral axes are pointing out of the page. Fig. 4(e) shows the same D8₁₀-Al₈Mn₅ structure as Fig. 4(d) rotated to show the 3D structure where the atoms have been removed for clarity. It can be seen that the cross-diagonal (i.e. [111]) of the BCR cell equals 2c_{Hex} hexagonal cells whereas the primitive rhombohedral cell has [111] equal to c_{Hex}. This gives the BCR cell twice the volume of the primitive rhombohedral cell. Note that the three unit cells are three different ways of describing the same crystal structure. The lattice transformation from/to the BCR cell is given by Eq.1, where primes refer to the hexagonal cell;

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} 2/3 & 1/3 & -2/3 \\ -1/3 & -2/3 & -2/3 \\ -1/3 & 1/3 & -2/3 \end{pmatrix} \begin{pmatrix} a' \\ b' \\ c' \end{pmatrix} \quad (\text{Eq. 1})$$

When considered with a BCR cell, D8₁₀-Al₈Mn₅ has an angle $\alpha = \beta = \gamma = 89.09^\circ$, which is very close to cubic (Fig. 4(e) and Table 3). The BCR cell is slightly rhombohedrally distorted from its supergroup cubic γ brass cell (D8₂, space group $I\bar{4}3m$) [48, 52] and can be considered to be a pseudo-cubic. Fig. 4(c) compares the high temperature cubic D8₂ gamma brass and the low temperature rhombohedral D8₁₀ gamma brass in the BCR setting, where

both are viewed along the (001) plane normal. When viewed in this way, the similarities between the $D8_2$ and $D8_{10}$ structures are clear. For clarity, in the remainder of this paper, $D8_{10}$ - Al_8Mn_5 will be represented using both the hexagonal and BCR settings in parallel and referred to simply as Al_8Mn_5 . For example, in Fig. 3(b) and (c), Al_8Mn_5 is indexed in both the hexagonal and BCR settings.

Fig. 5 shows stereographic projections to reveal the symmetry relationships among the cubic ($A2$, $B2$ or $D8_2$) and $D8_{10}$ rhombohedral γ brass structures (Fig. 5(a) versus Fig. 5(b-c)), as well as the lattice transformation from the hexagonal setting to BCR setting in Al_8Mn_5 (mappings from Fig. 5(b) to Fig. 5(c)). In the cubic crystals ($Im\bar{3}m$ - $A2$, $Pm\bar{3}m$ - $B2$ and $I\bar{4}3m$ - $D8_2$) of Fig. 5(a), poles of crystal planes are plotted with solid circle symbols. Each symmetrically equivalent pole is displayed with the same colour and symbol. When the body-centred cubic crystal is rhombohedrally distorted to a lower symmetry trigonal structure, symmetry-equivalent poles are divided into smaller groups. For instance, for the $\{112\}$ poles of cubic (labelled in blue) there are 24 symmetry-equivalent, which become three inequivalent groups in the lower symmetry trigonal cell, consisting of 6, 6 and 12 symmetry-equivalent poles. As the orientation of the three cells are plotted using the same convention, these stereographic projections directly show the miller index relationships between the three lattices: cubic $\leftrightarrow$ rhombohedral in hexagonal setting $\leftrightarrow$ rhombohedral in body-centred rhombohedral setting. For example, the Al_8Mn_5 planes in the EBSD patterns of Fig. 3 can be reindexed in the hexagonal or BCR settings by reading off Fig. 5.

3.3 Orientation relationship between B2 and Al₈Mn₅

In the EBSD patterns of Fig. 3(b) it is clear that there are multiple near-parallel planes and zone axes between the B2 core and Al₈Mn₅ shell. The OR can be written as either Eq. 2a or Eq. 2b where the misorientation from this OR is 4.7° based on the measured Euler angles:

$$\{111\}_{\text{B2-cubic}} \parallel \{0001\}_{\text{Al8Mn5-HEX}} \ \& \ \langle 1\bar{1}0 \rangle_{\text{B2-cubic}} \parallel \langle 11\bar{2}0 \rangle_{\text{Al8Mn5-HEX}} \quad \text{Eq. 2a}$$

$$\{111\}_{\text{B2-cubic}} \parallel \{111\}_{\text{Al8Mn5-BCR}} \ \& \ \langle 1\bar{1}0 \rangle_{\text{B2-cubic}} \parallel \langle 1\bar{1}0 \rangle_{\text{Al8Mn5-BCR}} \quad \text{Eq. 2b}$$

It can also be seen in Fig. 3(b) that the indexing of the cubic B2 core and the Al₈Mn₅ shell in the BCR setting are the same (accounting for symmetrically equivalent planes). Thus, the OR between B2 and D8₁₀ is also given by the stereographic projections in Fig. 5 and the OR can be equally written in terms of any of the parallelisms between the cubic and rhombohedral lattices in Fig. 5. Note that these stereographic projections are each centred on the three-fold rotation axis that is common to all of the space groups associated with the A2, B2, D8₂ and D8₁₀ phases.

To explore the origins of the B2-D8₁₀ OR, we note from Table 3 that the B2 unit cell dimensions are almost 3x3x3 times the BCR cell of Al₈Mn₅ (with <2% misfit). Fig. 3(d) are projection views along the common $\langle 111 \rangle_{\text{cubic}}$ and $\langle 111 \rangle_{\text{BCR}} / [0001]_{\text{HEX}}$ three-fold rotation axis showing 3x3x3 B2 unit cells and one Al₈Mn₅ BCR unit cell.

The planar lattice match for $(111)_{\text{cubic}} // (111)_{\text{BCR}}$ is shown in Fig. 3(d). Note that the $(111)_{\text{BCR}}$ is a slightly corrugated plane and all atoms close to the plane have been included. It can be seen that the atomic matching is very good for most atoms. The mean planar disregistry is ~2.5% using Bramfitt's method [53]. A similarly good planar match also exists on the $\{100\}_{\text{cubic}} // \{100\}_{\text{BCR}}$ planes which is ultimately due to the group-subgroup relations combined with the similar cell dimensions (Table 3).

Comparing the two phase particles (Fig. 2 and Fig. 3) with the predicted solidification path in Fig. 1(e), it can be inferred that the core-shell structure is the result of a $L + B2\text{-Al(Mn,Fe)} \rightarrow \text{Al}_8\text{Mn}_5$ peritectic reaction whereby $B2\text{-Al(Mn,Fe)}$ formed first from the liquid and then Al_8Mn_5 enveloped the $B2\text{-Al(Mn,Fe)}$. The remaining $B2$ core is consistent with an incomplete peritectic reaction due to limited diffusion through the solid Al_8Mn_5 shell. The close lattice match in Fig. 3(d) is likely to cause Al_8Mn_5 to require only a small nucleation undercooling to nucleate on $B2$.

3.4 Growth crystallography of Al_8Mn_5

It was found that most primary Al_8Mn_5 particles were polycrystals. Fig. 6(a) shows a typical EBSD orientation analysis of a $B2\text{-Al(Mn,Fe)}$ and Al_8Mn_5 core-shell particle. Raw EBSD data has been post-processed using Matlab with the MTEX toolbox. Grains were reconstructed with 10° as the threshold misorientation angle, and a smoothing spline filter with 5 iterations was used. From the IPF-Y map, it is clear that the $B2\text{-Al(Mn,Fe)}$ core is a single crystal (coloured in light grey), whilst Al_8Mn_5 is a polycrystal and has four dominant orientations. To confirm the presence of four Al_8Mn_5 orientations, a quantitative pattern matching approach based on simulations using the dynamical theory of electron diffraction using BRUKER DynamicS[54] was applied, as shown SI Fig. 1. The simulated patterns were pre-aligned to the experimental patterns indexed using a standard Hough-transform based indexing of the Kikuchi diffraction patterns. Subsequently the orientation was refined by best-fit pattern matching based on the normalized cross-correlation coefficient r ($0 < |r| < 1$, where $r = 1$ means the greatest similarity) [55]. SI Fig. 1 confirms the presence of four

orientations of Al_8Mn_5 using the pattern matching method, showing that the four orientations are not an artefact of pseudosymmetry [56].

There are various choices of colour key to show orientations in rhombohedral crystals [57]. In Supplementary Figs. 2-8 we show the orientations in multiple Al_8Mn_5 particles using three different colour keys with respect to three directions (IPF-X, Y and Z) to ensure that all inequivalent directions are distinguished. In Supplementary Figs. 2-8 it can be seen that, in all Al_8Mn_5 particles, there are only four orientations, and all are related by $\sim 90^\circ$ misorientations. Since there are only up to four main orientations in each Al_8Mn_5 particle, we use a simple Red-Green-Blue-Yellow (RGBY) colour scheme. As shown in Fig. 6(d) and Table 4, all orientations cluster around four points in Euler angle space with less than 1.5° deviation in each Euler angle which corresponds to $<5^\circ$ overall misorientation. Thus, an R, G, B, Y colour was assigned to each cluster.

In the pole figures of Fig. 6 the following features can be seen: (i) The B2-Al(Mn,Fe) core has all three of its $\{100\}$ poles coinciding with the $\{2\bar{2}01\}_{\text{HEX}} / \{100\}_{\text{BCR}}$ poles of Al_8Mn_5 , and all four Al_8Mn_5 grains have all three $\{2\bar{2}01\}_{\text{HEX}} / \{100\}_{\text{BCR}}$ poles overlapped (i.e. all four RGBY overlap at each of the three $\{2\bar{2}01\}_{\text{HEX}} / \{100\}_{\text{BCR}}$ spots); (ii) The $\{110\}$ planes of B2-Al(Mn,Fe) align with the $\{11\bar{2}0\}_{\text{HEX}} / \{110\}_{\text{BCR}}$ poles of Al_8Mn_5 , and each Al_8Mn_5 orientation shares a $\{11\bar{2}0\}_{\text{HEX}} / \{110\}_{\text{BCR}}$ plane with each of the other three Al_8Mn_5 orientations (i.e. there are two RGBY colours at each $\{2\bar{2}01\}_{\text{HEX}} / \{100\}_{\text{BCR}}$ spot); And (iii) the $\{0001\}_{\text{HEX}} / \{111\}_{\text{BCR}}$ plane of each Al_8Mn_5 crystal aligns with each one of the four $\{111\}$ equivalents in B2-Al(Mn,Fe). The mean misorientation between these near-parallelisms was calculated from the measured Euler angles to be $2.5 \pm 0.8^\circ$.

Based on poles figures such as those in Fig. 6(b), geometrical models were created to represent the orientation relationship between B2-Al(Mn, Fe) and the four Al_8Mn_5

orientations as shown in Fig. 6(c). Each grain orientation is plotted using its mean Euler angles from EBSD measurements. For the B2-Al(Mn,Fe) single crystal core, the eight $\{111\}$ planes have been constructed to form an octahedron. The four Al_8Mn_5 grains are plotted as hexagonal unit cells. These eight (four pairs of) hexagonal prisms have been translated (retaining the orientations) onto the surfaces of the octahedron which causes the $\{0001\}_{\text{HEX}}$ of the four Al_8Mn_5 orientations to align with the eight $\{111\}$ of B2-Al(Mn,Fe). The adjacent Al_8Mn_5 orientations share a common $\langle 11\bar{2}0 \rangle_{\text{HEX}}$ direction (a axis) which results in edge-sharing hexagons. Note that this geometrical model is to scale where the octahedron represents $7 \times 7 \times 7$ unit cells of B2-Al(Mn,Fe) and the hexagonal prisms each represent one hexagonal unit cell of Al_8Mn_5 . This geometrical representation of the OR is further illustrated in Video 2.

In the BCR setting, the equivalent geometrical model is a simple stacking of eight rhombohedrons that are each nearly a cube since $\{100\}_{\text{BCR}}$ are common planes and $\langle 001 \rangle_{\text{BCR}}$ are common axes for the four Al_8Mn_5 orientations (Fig. 6(b-c)). With the BCR geometrical model, it is clear that each Al_8Mn_5 orientation is almost 90° rotated from its neighbour.

From the pole figures in Fig. 6(b), the OR between B2 and Al_8Mn_5 in Eq. 2a and Eq. 2b can be clearly seen. The geometrical models in Fig. 6(c) also show that there are four variants of this OR, since there is one $\{0001\}_{\text{HEX}}$ and four $\{111\}_{\text{cubic}}$ in each hemisphere, and that each Al_8Mn_5 orientation has one variant of the OR with the B2-Al(Mn,Fe) core phase.

Fig. 7 explores the internal interfaces within Al_8Mn_5 particles. Fig. 7(a) are three typical Al_8Mn_5 particle cross-sections, Fig. 7(b) and (c) are EBSD orientation maps of these particles in the IPF-Y and RGBY colour scheme, respectively. The pole figures in Fig. 7(d) show that the Al_8Mn_5 orientation relationships are the same as in Fig. 6.

In Fig. 7 (b) and (c), it can be seen that the four orientations have simple near-linear Al_8Mn_5 internal interfaces in cross-sections. Geometrical models plotted using the measured Euler angles are shown for the four orientations in each Al_8Mn_5 particle in Fig. 7(e) for the hexagonal setting and in Fig. 7(f) for the BCR setting. By digitally sectioning through the BCR geometrical models (video 3), the internal interfaces were commonly found to be consistent with $\{100\}$ planes of the BCR cell. For example, Fig. 7(g) shows images of the digitally sectioned BCR geometrical models where the digital sectioning has been stopped at a depth that best matches the measured interfaces in Fig. 7(c). It can be seen that the measured interfaces (Fig. 7(c)) and the digitally sectioned BCR geometrical model based on $\{100\}$ interfaces (Fig. 7(g)) are in good agreement.

The Al_8Mn_5 results in Fig. 7 are a form of cyclic twinning. Specifically, the $\{2\bar{2}01\}_{\text{HEX}}/\{100\}_{\text{BCR}}$ interfaces between Al_8Mn_5 grains in Fig. 7 and the $\{0001\}_{\text{HEX}}/\{111\}_{\text{BCR}}$ and $\langle 1\bar{1}02 \rangle_{\text{HEX}}/\langle 100 \rangle_{\text{BCR}}$ pole figures in Fig. 6(b) and Fig. 7(c) are consistent with fourfold cyclic twinning, where the composition/habit planes are $\{2\bar{2}01\}_{\text{HEX}}/\{100\}_{\text{BCR}}$, and the Al_8Mn_5 unit cells are rotated $\sim 90^\circ$ around three common $\langle 1\bar{1}02 \rangle_{\text{HEX}}/\langle 001 \rangle_{\text{BCR}}$ twinning axes. Fig. 8 illustrates the four-fold cyclic twinning of Al_8Mn_5 . It can be understood as twinning operations of four-fold $\sim 90^\circ$ rotations around three common $\langle 1\bar{1}02 \rangle_{\text{HEX}}/\langle 001 \rangle_{\text{BCR}}$ axes or mirrored by $\{2\bar{2}01\}_{\text{HEX}}/\{100\}_{\text{BCR}}$ planes. These twin elements are also pseudosymmetry elements (cubic) for the lattice of the individual (rhombohedral). The twin obliquity is $\omega = 0.9$.

3.5 Growth facets of Al_8Mn_5

To determine the 3D growth habit of Al_8Mn_5 particles, EBSD and FIB serial sectioning were combined. The procedures are summarised in Fig. 9 and a step-by-step guide is given in SI-Figs. 9-13. First, the orientation of a Al_8Mn_5 particle was measured on a 2D (x-y) sectioned surface by EBSD (Fig. 9(a)). At this step the Al_8Mn_5 was indexed as the D8_2 cubic supergroup to remove the complexity of D8_{10} rhombohedral twinning (this was possible due to the similarities between the D8_2 and D8_{10} structures shown in Fig. 4(c)). Thus, a single pseudo-cubic orientation was considered for the first step of facet indexing. The Al_8Mn_5 particle was then serially-sectioned using a FIB as shown in Fig. 9(b), and the 3D morphology was reconstructed from >100 FIB x-z slices with 100 nm slice thickness occupying a volume of $\sim 13 \times 12 \times 11 \mu\text{m}$ as shown in Fig. 9(c) and Videos 4 and 5. With knowledge of the crystal coordinate system (a,b,c) relative to the FIB coordinate system (x,y,z), directions and plane normals from the crystal and particle could be plotted in pole figures using a single Cartesian coordinate system. To do this for facet plane normals, we manually picked points on each facet surface and found the best fit plane equation to each facet. Then the plane-normal direction was calculated for each facet, as illustrated in Fig. 9(d). Considering Al_8Mn_5 in its pseudo-cubic form, indexing of facets was performed by super-imposing facet plane normals (calculated from the reconstructed 3D volume) and crystal plane normals (measured from EBSD) within pole figures (Fig. 9(e)). As displayed in Fig. 9 (e), all facets could be indexed to one of $\{100\}$, $\{110\}$ and $\{112\}$ (in pseudo-cubic). This indexing procedure was performed in multiple datasets and 25 facets were investigated in total. The mean misalignment of indexing as $\{100\}$, $\{110\}$ and $\{112\}$ in pseudo-cubic was $5.1 \pm 2.0^\circ$. The $< 7^\circ$ uncertainty due to misalignment was small enough to uniquely identify facets if we consider only low index planes.

The 3D growth morphology of polyhedral Al_8Mn_5 particles was plotted using combinations of $\{100\}$, $\{110\}$ and $\{112\}$ facets and a pseudo-cubic cell. To recreate particles

observed in SEM, planes were plotted at set distances from the centre and the inner envelope was taken to give the crystal form, as shown in Fig. 10. Since the particles are not regular polyhedra, the distances to the centre were manually tuned to match SEM images of each deep etched Al_8Mn_5 particle. It can be seen that, overall, the mathematical recreation of polyhedral Al_8Mn_5 particles matches closely to the SEM observations. The main feature in Fig. 10 is that the wide range of complex polyhedral forms of primary Al_8Mn_5 can be understood as simple combinations of $\{100\}$, $\{110\}$ and $\{112\}$ facets using a pseudo-cubic cell.

In Fig.9 and Fig.10, Al_8Mn_5 is approximated as pseudo-cubic which ignores the presence of four twinned orientations in each particle. Fig. 11 is a deeper analysis of the facets where direct EBSD measurements on the facets show that there were commonly multiple orientations on a single Al_8Mn_5 facet. This can be understood from Fig. 6(b) where four Al_8Mn_5 share each $\{100\}_{\text{BCR}}$ spot and two Al_8Mn_5 share each $\{110\}_{\text{BCR}}$ spot. Thus, theoretically, there can be up to four Al_8Mn_5 orientations on a single $\{100\}_{\text{BCR}}$ facet and up to two Al_8Mn_5 orientations on a $\{110\}_{\text{BCR}}$ facet. In Fig. 11, examples of two orientations on $\{110\}_{\text{BCR}}$ and $\{100\}_{\text{BCR}}$ facets are shown. The left-hand sides show SE images without tilt which correspond to the orientation of the geometrical models; whereas the other SE image, the orientation map, and band contrast map are all at the tilt angles annotated on the figures. The tilted EBSD orientation maps have been undistorted to the 0° tilt condition and superimposed on the relevant facet in the 0° tilt SE images. It can be seen that the twin boundaries on the 0° tilt SE images are generally consistent with the $\{100\}_{\text{BCR}}$ twin boundaries in a section of each BCR geometrical model. That is to say, the multiple orientations on a single facet are due to $\{100\}_{\text{BCR}}$ twin boundaries intersecting the facet surfaces with the same twinning operation as in Fig. 8. Fig. 11(c) also shows a $\{112\}_{\text{BCR}}$ facet

with a single Al_8Mn_5 orientation which is consistent with most $\{112\}_{\text{BCR}}$ spots being not shared for the twinned Al_8Mn_5 OR.

It was also common for facets to have near-linear ledges and grooves in SE imaging that corresponded to twin boundaries in EBSD mapping. For example, in Fig 11 (a), the ledges in the 70° tilted SE image match to part of the boundaries between the green/red orientations in the EBSD orientation map.

This paper has focussed in detail on one batch of AZ91 (batch #1 in Table 1) solidified under one cooling condition. To test for the generality of the findings, we also investigated Al_8Mn_5 particles in an ingot of AZ91D with higher Mn and Fe content (batch #2 in Table 1), and AZ91E with lower Fe content (batch #3 in Table 1). Typical results are shown in SI-Fig. 7 and SI Fig. 8 from each batch. It can be seen that Al_8Mn_5 has grown in a similar 4-fold cyclic twinned manner with clear $\{100\}_{\text{BCR}}$ twin planes. Additionally, some Al_8Mn_5 particles contained a B2-Al(Mn,Fe) core phase in the centre of the cross-section. Thus, it seems that the nucleation and growth mechanisms deduced here are general features of Al_8Mn_5 solidification in AZ91 Mg alloys.

4. Conclusions

EBSD, FIB and selective etching techniques have been combined with thermodynamic calculations and polyhedral models to extract new insights into the nucleation and 3D growth crystallography of Al_8Mn_5 in AZ91D/E. The following conclusions can be drawn:

- 1) Many Al_8Mn_5 particles contained a B2-Al(Mn,Fe) particle near their centre due to Al_8Mn_5 nucleation on B2 followed by an incomplete peritectic transformation.
- 2) Most Fe was in the B2 core phase ($\sim 13\text{at\%}$ Fe) which was encapsulated by a lower-Fe Al_8Mn_5 shell ($\sim 1\text{at\%}$ Fe). This prevented the Fe-rich phase from contacting the αMg matrix and may be important in corrosion resistance.
- 3) It has been found that most rhombohedral Al_8Mn_5 particles are polycrystals consisting of four twinned orientations, each related by $\sim 90^\circ$ rotations around three common $\langle 1\bar{1}02 \rangle_{\text{HEX}} (\langle 100 \rangle_{\text{BCR}})$ axes with $\{2\bar{2}01\}_{\text{HEX}} (\{100\}_{\text{BCR}})$ twin habit planes. This growth form is a consequence of the small rhombohedral distortion of the Al_8Mn_5 gamma brass.
- 4) The four twinned orientations are the four variants of the orientation relationship with the central cubic B2 particle:

$$\{111\} \parallel \{0001\} \text{ and } \langle 1\bar{1}0 \rangle \parallel \langle 11\bar{2}0 \rangle$$
- 5) When Al_8Mn_5 grew as polyhedral particles, the growth facets were the $\{2\bar{2}01\}$, $\{10\bar{1}1\}$, $\{11\bar{2}0\}$, $\{1\bar{1}02\}$, $\{1\bar{2}31\}$ and $\{1\bar{1}00\}$ in the hexagonal setting, which correspond to $\{100\}$, $\{110\}$ and $\{112\}$ when considering Al_8Mn_5 as a pseudo-cubic cell. Many of the polyhedral forms were recreated by polyhedron models using the $\{100\}$, $\{110\}$ and $\{112\}$ facets of the pseudo-cubic Al_8Mn_5 cell.
- 6) It was common for the twin planes to intersect the facet surfaces in a manner consistent with the measured twinning habit planes, leading to up to four orientations on a single facet whose interfaces were often associated with small re-entrant angles or steps.

7) Examination of Al_8Mn_5 particles in different AZ91D and AZ91E ingots revealed that the Al_8Mn_5 particles in these cases also had four twinned orientations, and sometimes contained a central B2-Al(Mn,Fe) core phase in the cross-section, showing that the findings and measurements made here are generally valid for different batches of commercial purity AZ91D/E.

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References

- [1] G.L. Song, A. Atrens, Corrosion mechanisms of magnesium alloys, *Adv. Eng. Mater.* 1(1) (1999) 11-33.
- [2] M. Liu, P.J. Uggowitzer, A.V. Nagasekhar, P. Schmutz, M. Easton, G.-L. Song, A. Atrens, Calculated phase diagrams and the corrosion of die-cast Mg–Al alloys, *Corros. Sci.* 51(3) (2009) 602-619.
- [3] Y. Du, J. Wang, J. Zhao, J.C. Schuster, F. Weitzer, R. Schmid-Fetzer, M. Ohno, H. Xu, Z.-k. Liu, S. Shang, Reassessment of the Al-Mn system and a thermodynamic description of the Al-Mg-Mn system, *Int. J. Mater. Res.* 98(9) (2007) 855-871.
- [4] B. Oberlander, C. Simensen, J. Svalestuen, A. Thorvaldsen, Phase diagram of liquid magnesium-aluminium-manganese alloys, *Magnesium Technology*, 1986, pp. 133-137.
- [5] Y. Wang, M. Xia, Z. Fan, X. Zhou, G.E. Thompson, The effect of Al_8Mn_5 intermetallic particles on grain size of as-cast Mg–Al–Zn AZ91D alloy, *Intermetallics* 18(8) (2010) 1683-1689.
- [6] C.J. Simensen, B.C. Oberlander, J. Svalestuen, A. Thorvaldsen, Determination of the equilibrium phases in molten Mg-4 wt.% Al-Mn alloys, *Z. Metallkd.* 79(8) (1988) 537-540.
- [7] C.J. Simensen, B.C. Oberlander, J. Svalestuen, A. Thorvaldsen, The effect of iron on Mg-4 wt.% Al-Mn Alloys, *Z. Metallkd.* 80 (1989) 101-103.
- [8] C.J. Simensen, B.C. Oberlander, J. Svalestuen, A. Thorvaldsen, Phase diagram for magnesium-aluminium-manganese above 650 °C, *Z. Metallkd.* 79 (1988) 696-699.
- [9] S. Lun Sin, D. Dubé, R. Tremblay, Characterization of Al–Mn particles in AZ91D investment castings, *Mater. Charact.* 58(10) (2007) 989-996.
- [10] F. Pan, Z. Feng, X. Zhang, A. Tang, The types and distribution characterization of Al-Mn phases in the AZ61 magnesium alloy, *Procedia Engineering* 27 (2012) 833-839.
- [11] A. Kaya, P. Uzan, D. Eliezer, E. Aghion, Electron microscopical investigation of as cast AZ91D alloy, *Mater. Sci. Technol.* 16(9) (2000) 1001-1006.

- [12] Y. Tamura, J. Yagi, T. Haitani, T. Motegi, N. Kono, H. Tamehiro, H. Saito, Observation of manganese-bearing particles in molten AZ91 magnesium alloy by rapid solidification, *Mater. Trans., JIM* 44(4) (2003) 552-557.
- [13] C. Corby, N. Ricketts, M. Qian, R. Bailey, Investigation of intermetallics in magnesium die-casting sludge, *Magnesium Technology*, 2004, pp. 14-18.
- [14] L.Y. Wei, H. Westengen, T.K. Aune, D. Albright, Characterisation of manganese-containing intermetallic particles and corrosion behaviour of die cast Mg-Al-based alloys, *Magnesium Technology*, 2000, pp. 153-160.
- [15] T. Laser, M.R. Nürnberg, A. Janz, C. Hartig, D. Letzig, R. Schmid-Fetzer, R. Bormann, The influence of manganese on the microstructure and mechanical properties of AZ31 gravity die cast alloys, *Acta Mater.* 54(11) (2006) 3033-3041.
- [16] V.Y. Gertsman, J. Li, S. Xu, J.P. Thomson, M. Sahoo, Microstructure and second-phase particles in low- and high-pressure die-cast magnesium alloy AM50, *Metall. Mater. Trans. A* 36(8) (2005) 1989-1997.
- [17] D. Qiu, M.X. Zhang, J.A. Taylor, H.M. Fu, P.M. Kelly, A novel approach to the mechanism for the grain refining effect of melt superheating of Mg-Al alloys, *Acta Mater.* 55(6) (2007) 1863-1871.
- [18] G.W. Qin, Y. Ren, W. Huang, S. Li, W. Pei, Grain refining mechanism of Al-containing Mg alloys with the addition of Mn-Al alloys, *J. Alloys Compd.* 507(2) (2010) 410-413.
- [19] K. Gusieva, C.H.J. Davies, J.R. Scully, N. Birbilis, Corrosion of magnesium alloys: the role of alloying, *Int. Mater. Rev.* 60(3) (2015) 169-194.
- [20] C. Blawert, E. Morales, W. Dietzel, K.U. Kainer, C. Scharf, A. Ditzel, Influence of the copper content on microstructure and corrosion resistance of AZ91 based secondary magnesium Alloys, *SAE International*, 2006.
- [21] R. Arrabal, E. Matykina, F. Viejo, P. Skeldon, G.E. Thompson, Corrosion resistance of WE43 and AZ91D magnesium alloys with phosphate PEO coatings, *Corros. Sci.* 50(6) (2008) 1744-1752.
- [22] S. Pawar, X. Zhou, G. Thompson, G. Scamans, Z. Fan, The role of intermetallics on the corrosion initiation of twin roll cast AZ31 Mg alloy, *J. Electrochem. Soc.* 162(9) (2015) C442-C448.
- [23] G. Han, X. Liu, Phase control and formation mechanism of Al-Mn(-Fe) intermetallic particles in Mg-Al-based alloys with FeCl₃ addition or melt superheating, *Acta Mater.* 114 (2016) 54-66.
- [24] S. Pawar, X. Zhou, T. Hashimoto, G.E. Thompson, G. Scamans, Z. Fan, Investigation of the microstructure and the influence of iron on the formation of Al₈Mn₅ particles in twin roll cast AZ31 magnesium alloy, *J. Alloys Compd.* 628 (2015) 195-198.
- [25] B.B. Lindahl, B.P. Burton, M. Selleby, Ordering in ternary BCC alloys applied to the Al-Fe-Mn system, *Calphad* 51 (2015) 211-219.
- [26] B.B. Lindahl, M. Selleby, The Al-Fe-Mn system revisited-An updated thermodynamic description using the most recent binaries, *Calphad* 43 (2013) 86-93.
- [27] M. Ohno, D. Mirkovic, R. Schmid-Fetzer, Phase equilibria and solidification of Mg-rich Mg-Al-Zn alloys, *Mater. Sci. Eng., A* 421(1-2) (2006) 328-337.
- [28] F. Bachmann, R. Hielscher, H. Schaeben, Texture analysis with MTEX-free and open source software toolbox, *Solid State Phenomena, Trans Tech Publ*, 2010, pp. 63-68.
- [29] J. Schindelin, I. Arganda-Carreras, E. Frise, V. Kaynig, M. Longair, T. Pietzsch, S. Preibisch, C. Rueden, S. Saalfeld, B. Schmid, Fiji: an open-source platform for biological-image analysis, *Nature Methods* 9(7) (2012) 676-682.
- [30] G. Zeng, K. Nogita, S. Belyakov, J.W. Xian, S.D. McDonald, K.V. Yang, H. Yasuda, C.M. Gourelay, Real-Time Observation of AZ91 Solidification by Synchrotron Radiography, *Magnesium Technology* 2017, pp. 597-603.
- [31] G. Zeng, J.W. Xian, C.M. Gourelay, Growth of Al₈Mn₅ Intermetallic in AZ91, *Magnesium Technology*, 2017, pp. 85-92.
- [32] PANDAT PanMag2016 Database 2016.
- [33] M. Ohno, D. Mirkovic, R. Schmidfetzer, Liquidus and solidus temperatures of Mg-rich Mg-Al-Mn-Zn alloys, *Acta Mater.* 54(15) (2006) 3883-3891.
- [34] C.J. Simensen, N. Hansen, The effect of silicon upon alloys of Mg-2. 2 wt.% Al-Mn, *Z. Metallkd.* 79 (1988) 541-543.
- [35] C.P. Corby, M. Qian, N. Ricketts, J.A. Taylor, Intermetallic morphology development in AM60 alloy, *Magnesium Technology*, 2005, pp. 451-456.

- [36] P. Bakke, D.O. Karlsen, Inclusion assessment in magnesium and magnesium base alloys, SAE Technical Paper, 1997.
- [37] C.P. Liu, F.S. Pan, W.Q. Wang, Phase Analysis of Al-Mn Compounds in the AZ Magnesium Alloys, *Mater. Sci. Forum*, Trans Tech Publ, 2007, pp. 395-398.
- [38] J. Tamminen, Thermal analysis for investigation of solidification mechanisms in metals and alloys, University of Stockholm Sweden, 1988.
- [39] A. Dahle, L. Arnberg, Development of strength in solidifying aluminium alloys, *Acta Mater.* 45(2) (1997) 547-559.
- [40] Y. Riddle, M. Makhlof, Characterizing solidification by non-equilibrium thermal analysis, *Magnesium Technology*, 2003, pp. 101-106.
- [41] C.M. Gourlay, B. Meylan, A.K. Dahle, Shear mechanisms at 0–50% solid during equiaxed dendritic solidification of an AZ91 magnesium alloy, *Acta Mater.* 56(14) (2008) 3403-3413.
- [42] X. Liu, Y. Osawa, S. Takamori, T. Mukai, Grain refinement of AZ91 alloy by introducing ultrasonic vibration during solidification, *Mater. Lett.* 62(17-18) (2008) 2872-2875.
- [43] H. Men, Z. Fan, Effects of solute content on grain refinement in an isothermal melt, *Acta Mater.* 59(7) (2011) 2704-2712.
- [44] B. Pourbahari, M. Emamy, H. Mirzadeh, Synergistic effect of Al and Gd on enhancement of mechanical properties of magnesium alloys, *Progress in Natural Science: Materials International* 27(2) (2017) 228-235.
- [45] X.J. Liu, I. Ohnuma, R. Kainuma, K. Ishida, Thermodynamic assessment of the Aluminum-Manganese (Al-Mn) binary phase diagram, *J. Phase Equilib.* 20(1) (1999) 45-56.
- [46] M. Ellner, The structure of the high-temperature phase MnAl(h) and the displacive transformation from MnAl(h) into Mn₅Al₈, *Metall. Trans. A* 21 (1990) 1669-1672.
- [47] S. Balanetsky, D. Pavlyuchkov, T. Velikanova, B. Grushko, The Al-rich region of the Al–Fe–Mn alloy system, *J. Alloys Compd.* 619 (2015) 211-220.
- [48] S. Balanetsky, G. Meisterernst, M. Heggen, M. Feuerbacher, Reinvestigation of the Al–Mn–Pd alloy system in the vicinity of the T- and R-phases, *Intermetallics* 16(1) (2008) 71-87.
- [49] B. Grushko, G.R. Stafford, A CsCl-type phase in electrodeposited AlMn alloys, *Scripta Metallurgica et Materiala* 31 (1994) 1711-1716.
- [50] T. Hahn, *International Tables for Crystallography Volume A: Space Group Symmetry*, Springer, New York, 2005.
- [51] A. Kelly, K.M. Knowles, *Crystallography and crystal defects*, John Wiley & Sons 2012.
- [52] J.K. Brandon, W.B. Pearson, P.W. Riley, C. Chieh, R. Stokhuyzen, γ -Brasses with R cells, *Acta Crystallogr. Sect. B: Struct. Sci.* 33(4) (1977) 1088-1095.
- [53] B.L. Bramfitt, The effect of carbide and nitride additions on the heterogeneous nucleation behavior of liquid iron, *Metallurgical Transactions* 1(7) (1970) 1987-1995.
- [54] A. Winkelmann, Principles of depth-resolved Kikuchi pattern simulation for electron backscatter diffraction, *J Microsc* 239(1) (2010) 32-45.
- [55] A. Winkelmann, G. Nolze, Point-group sensitive orientation mapping of non-centrosymmetric crystals, *Appl. Phys. Lett.* 106(7) (2015) 072101.
- [56] G. Nolze, A. Winkelmann, A.P. Boyle, Pattern matching approach to pseudosymmetry problems in electron backscatter diffraction, *Ultramicroscopy* 160 (2016) 146-154.
- [57] G. Nolze, R. Hielscher, Orientations - perfectly colored, *J. Appl. Crystallogr.* 49(5) (2016) 1786-1802.

Figure Captions

Fig. 1 (a) Typical microstructure of AZ91D solidified at $1\text{K}\cdot\text{s}^{-1}$ (b) primary Al_8Mn_5 and eutectic Al_8Mn_5 , (c) equiaxed faceted primary Al_8Mn_5 , (d) histogram of mean Feret diameter of 59 primary Al_8Mn_5 particles, (e) calculated Scheil and equilibrium solidification paths of AZ91D (batch #1), and (f) Mg-8.97Al-0.74Zn-0.15Mn-xFe isopleth, (g) Newtonian cooling curve analysis of AZ91D (batch #1), comparing with the predictions in (e), and (h) cooling curve and its first derivative curve. (e)-(f) calculated using PANDAT with PanMg2016.

Fig. 2 Core/shell structure found in Al-Mn-(Fe) particles by (a-b) BSE imaging, (c) EDS analysis, and (d-e) serial sectioning of deep-etched particles using FIB.

Fig. 3 Phase identification and orientation relationship of core/shell particle. (a-b) EDS and EBSD indexing of two-phase particle. Fe-rich core (red in EBSD phase map) is cubic B2-Al(Mn,Fe) and the shell (blue in phase map) is rhombohedral $\text{D}_{8_{10}}\text{-Al}_8\text{Mn}_5$. (c) unit cell orientations plotted from Euler angles: $\text{D}_{8_{10}}\text{-Al}_8\text{Mn}_5$ is plotted as both a hexagonal cell and Body Centred Rhombohedral (BCR) cell. (d) projected view along the (111) plane normal in B2-AlMn and $\text{D}_{8_{10}}\text{-Al}_8\text{Mn}_5$ (BCR setting), and planar atomic lattice match.

Fig.4 (a) Intermetallics in the centre of the Al-Mn binary phase diagram based on refs [3,26,39,40], (b) atomic models of A2-AlMn and B2-AlMn; (c) projection views of $\text{D}_{8_{10}}\text{-Al}_8\text{Mn}_5$ and $\text{D}_{8_{10}}\text{-Al}_8\text{Mn}_5$ (BCR setting) along the {100} plane normal; (d) The three different settings of rhombohedral $\text{D}_{8_{10}}\text{-Al}_8\text{Mn}_5$ viewed along the c axis in the hexagonal setting, and [111] in the primitive rhombohedral and BCR settings; and (e) 3D unit cell wireframes showing the relationships between the three settings of rhombohedral $\text{D}_{8_{10}}\text{-Al}_8\text{Mn}_5$. Further details are given in Table 3.

Fig.5 Stereographic projections of plane normal directions in (a) cubic (A2 or B2 or D82), (b) rhombohedral $\text{D}_{8_{10}}$ in hexagonal setting, and (c) $\text{D}_{8_{10}}$ in the BCR setting.

Fig.6 Growth crystallography of B2-AlMn and Al_8Mn_5 . Reproducible OR between B2-AlMn and four orientations of Al_8Mn_5 represented by (a) orientation maps in both IPF-Y and RGBY colour scheme and, (b) pole figures, (c) geometrical models, and (d) orientations of all

points plotted ($D8_{10}$ - Al_8Mn_5 in hexagonal setting) in Euler angle space. an R, G, B, Y colour was assigned to each cluster. Further detail is in Table 4.

Fig.7 Three typical examples of cyclic growth twinning of Al_8Mn_5 particles (a) SEM images, (b) IPF-Y map, (c) orientation map in RGBY colour scheme, (d) corresponding pole figures, (e-f) geometrical models in (e) hexagonal setting and (f) BCR setting; (g) identification of internal $\{100\}$ BCR twin composition planes by digital sectioning of the models in (f).

Fig.8. Four-fold cyclic twinning of Al_8Mn_5 by rotating 90° around $[1\bar{1}02]_{HEX}/[100]_{BCR}$

Fig.9 Indexing of growth facets of Al_8Mn_5 by combined FIB serial sectioning and EBSD.

Fig.10 SE-SEM images of six Al_8Mn_5 faceted particles and models based on $\{100\}$, $\{110\}$, $\{112\}$ facets using a pseudo-cubic cell.

Fig.11 Multiple orientations on $\{100\}_{BCR}$ and $\{110\}_{BCR}$ Al_8Mn_5 facets. $\{100\}_{BCR}$ twin planes intersect the facet surfaces.

Multimedia

Video 1 Serial-sectioning of a deep-etched Al-Mn-Fe particle using FIB to reveal a core particle inside an Al_8Mn_5 shell.

Video 2 Geometrical model to represent the OR between B2-AlMn and $D8_{10}$ - Al_8Mn_5 (in hexagonal setting). The OR between the four Al_8Mn_5 orientations is also shown.

Video 3 Digital sectioning through the polyhedral model of $D8_{10}$ - Al_8Mn_5 (BCR setting).

Video 4 FIB serial sectioning video of the Al_8Mn_5 particle as displayed in Fig.9

Video 5 3D reconstruction of Al_8Mn_5 from 2D slices processed from FIB serial-sectioning.

Table 1 Alloy composition as determined by ICP-AES

Batch No.	Alloy	Composition (wt.%)							
		Mg	Al	Zn	Mn	Fe	Cu	Si	Ni
1	AZ91D	Bal.	8.97	0.74	0.15	0.002	0.002	0.01	0.003
2	AZ91D	Bal.	9.30	0.63	0.32	0.003	0.021	0.05	0.001
3	AZ91E	Bal.	8.95	0.72	0.19	<0.001	0.001	0.04	<0.001

Table 2 EDS analysis of the two phases in the particle in Fig.3 (at.%).

	Al	Mn	Fe	Mg	Si
D8 ₁₀ -Al ₈ Mn ₅	64 ± 1	31 ± 1	1.4 ± 0.1	2 ± 1	0.8 ± 0.1
B2-Al(Mn,Fe)	57 ± 1	27 ± 1	14 ± 1	2 ± 1	\

Table 3 Crystal structures and settings of phases as shown in Fig.4.

Other Names	Crystal system	Strukturbericht designation	Pearson Symbol	Space Group	Setting	Lattice parameters				Ref.	
						a (Å)	b (Å)	c (Å)	α, β, γ		
D8 ₁₀ -Al ₈ Mn ₅	γ_2 Al ₈ Mn ₅ (LT)	Rhombohedral	D8 ₁₀	hR26	R3m	Hexagonal	12.667	12.667	7.942	$\alpha= \beta=90^\circ,$ $\gamma=120^\circ$	[40]
						Primitive Rhombohedral	7.778	7.778	7.778	$\alpha= \beta= \gamma= 109.04^\circ$	
						Body Centred Rhombohedral	9.029	9.029	9.029	$\alpha= \beta= \gamma= 89.09^\circ$	
D8 ₂ -Al ₈ Mn ₅	γ_1 Al ₈ Mn ₅ (HT)	Cubic	D8 ₂	cI52	I $\bar{4}$ 3m	\	8.890	8.890	8.890	$\alpha= \beta= \gamma= 90^\circ$	[42]
A2-AlMn	γ	Cubic	A2	cI2	Im $\bar{3}$ m	\	3.063	3.063	3.063	$\alpha= \beta= \gamma= 90^\circ$	[40]
B2-AlMn	γ	Cubic	B2	cP2	Pm $\bar{3}$ m	\	3.083	3.083	3.083	$\alpha= \beta= \gamma= 90^\circ$	[43]

Table 4: Summary of Euler angles for all Al_8Mn_5 EBSD points in Fig. 6 (indexed in the hexagonal setting). All points cluster around four orientations with $<1.5^\circ$ deviation in each Euler angle. Each cluster is assigned a different RGBY colour.

	$\phi_1 (^\circ)$	$\Phi (^\circ)$	$\phi_2 (^\circ)$	Number of points	Colour in RGBY
Orientation 1	76.9 ± 0.4	85.6 ± 0.6	318.0 ± 0.4	2846	R
Orientation 2	188.7 ± 1.4	73.9 ± 0.6	229.6 ± 0.7	3049	G
Orientation 3	318.7 ± 0.7	52.3 ± 0.2	80.8 ± 0.4	1335	B
Orientation 4	112.3 ± 1.3	19.5 ± 0.3	231.8 ± 1.3	613	Y

Figures

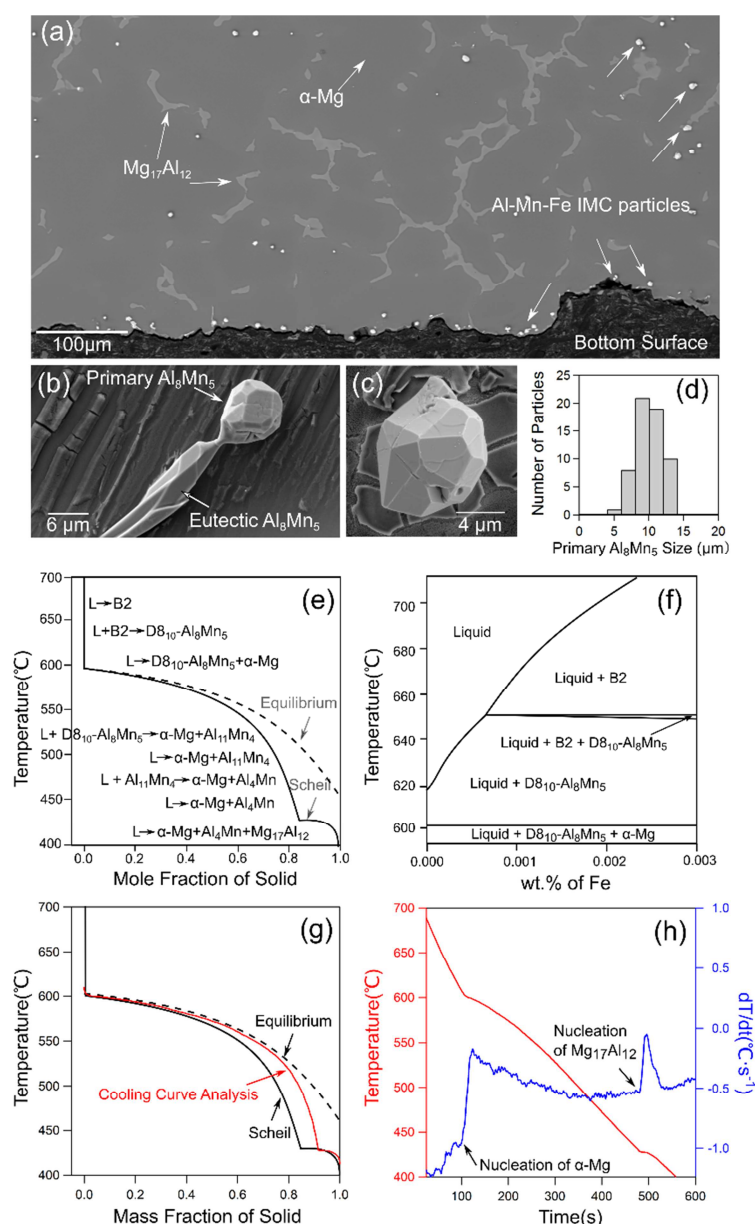


Fig. 1 (a) Typical microstructure of AZ91D solidified at $1\text{K}\cdot\text{s}^{-1}$ (b) primary Al_8Mn_5 and eutectic Al_8Mn_5 , (c) equiaxed faceted primary Al_8Mn_5 , (d) histogram of mean feret diameter of 59 primary Al_8Mn_5 particles, (e) calculated Scheil and equilibrium solidification paths of AZ91D (batch #1), and (f) Mg-8.97Al-0.74Zn-0.15Mn-xFe isopleth, (g) Newtonian cooling curve analysis of AZ91D (batch #1), comparing with the predictions in (e), and (h) cooling curve and its first derivative curve. (e)-(f) calculated using PANDATTM with PanMg2016.

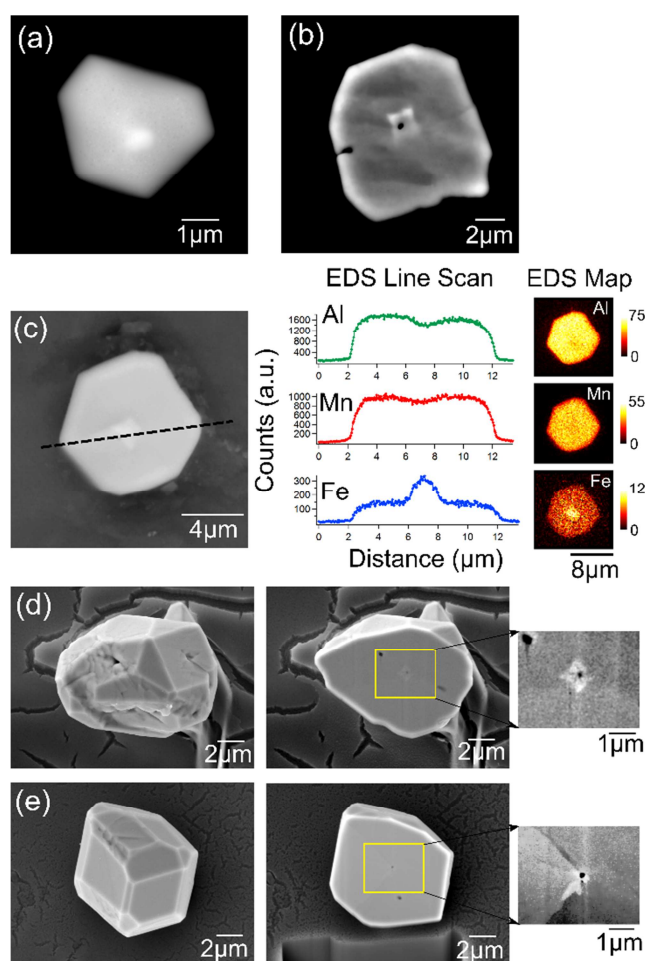
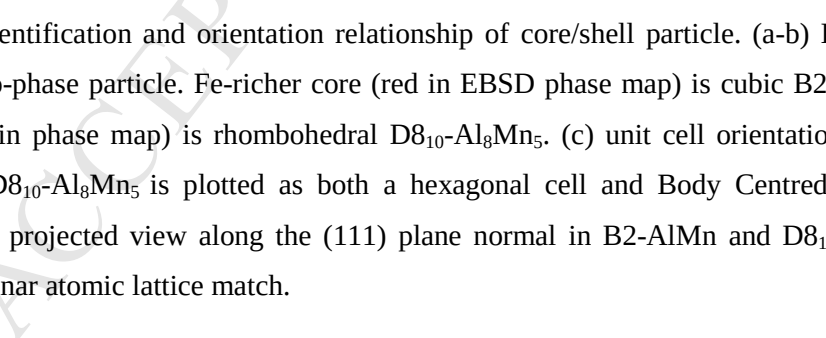


Fig. 2 Core/shell structure found in Al-Mn-(Fe) particles by (a-b) BSE imaging, (c) EDS analysis, and (d-e) serial sectioning of deep-etched particles using FIB.



3

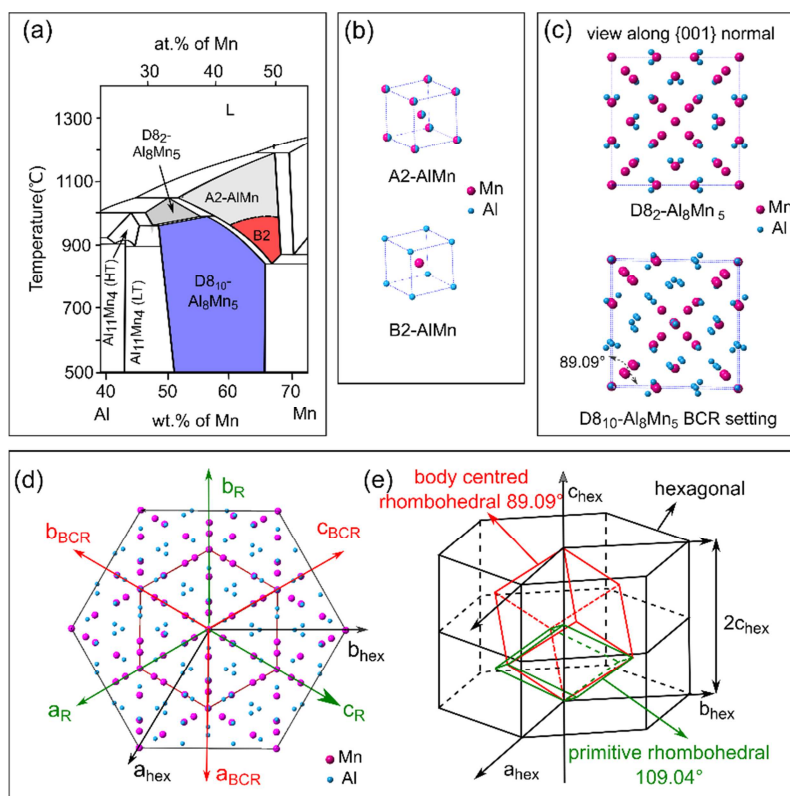


Fig.4 (a) Intermetallics in the centre of the Al-Mn binary phase diagram based on refs [3,26,39,40], (b) atomic models of A2-AlMn and B2-AlMn; (c) projection views of D8₂-Al₈Mn₅ and D8₁₀-Al₈Mn₅ (BCR setting) along the {100} plane normal; (d) The three different settings of rhombohedral D8₁₀-Al₈Mn₅ viewed along the c axis in the hexagonal setting, and [111] in the primitive rhombohedral and BCR settings; and (e) 3D unit cell wireframes showing the relationships between the three settings of rhombohedral Al₈Mn₅. Further details are given in Table 3.

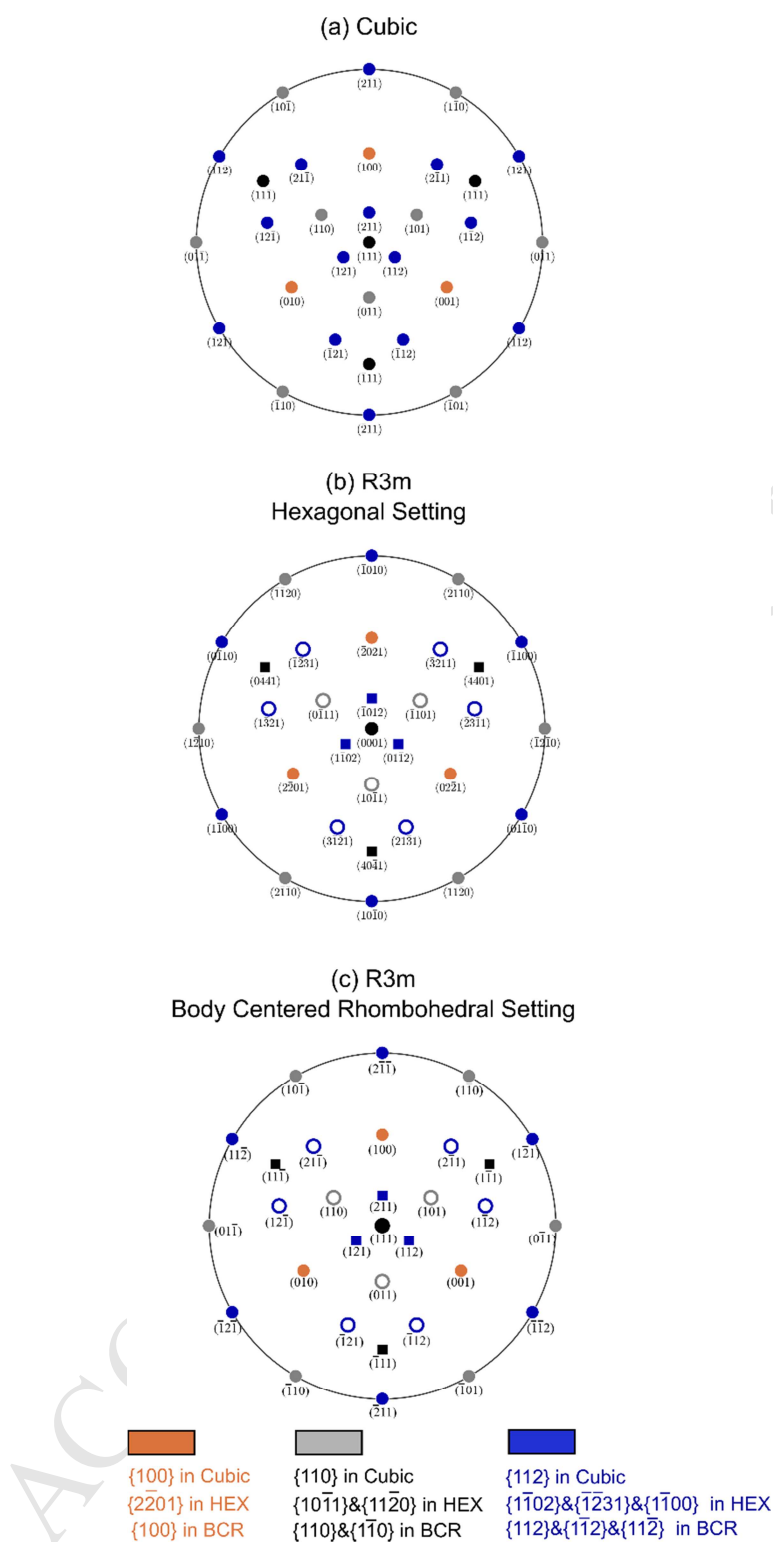


Fig.5 Stereographic projections of plane normal directions in (a) cubic (A_2 or B_2 or D_{8_2}), (b) rhombohedral $D_{8_{10}}$ in hexagonal setting, and (c) $D_{8_{10}}$ in the BCR setting.

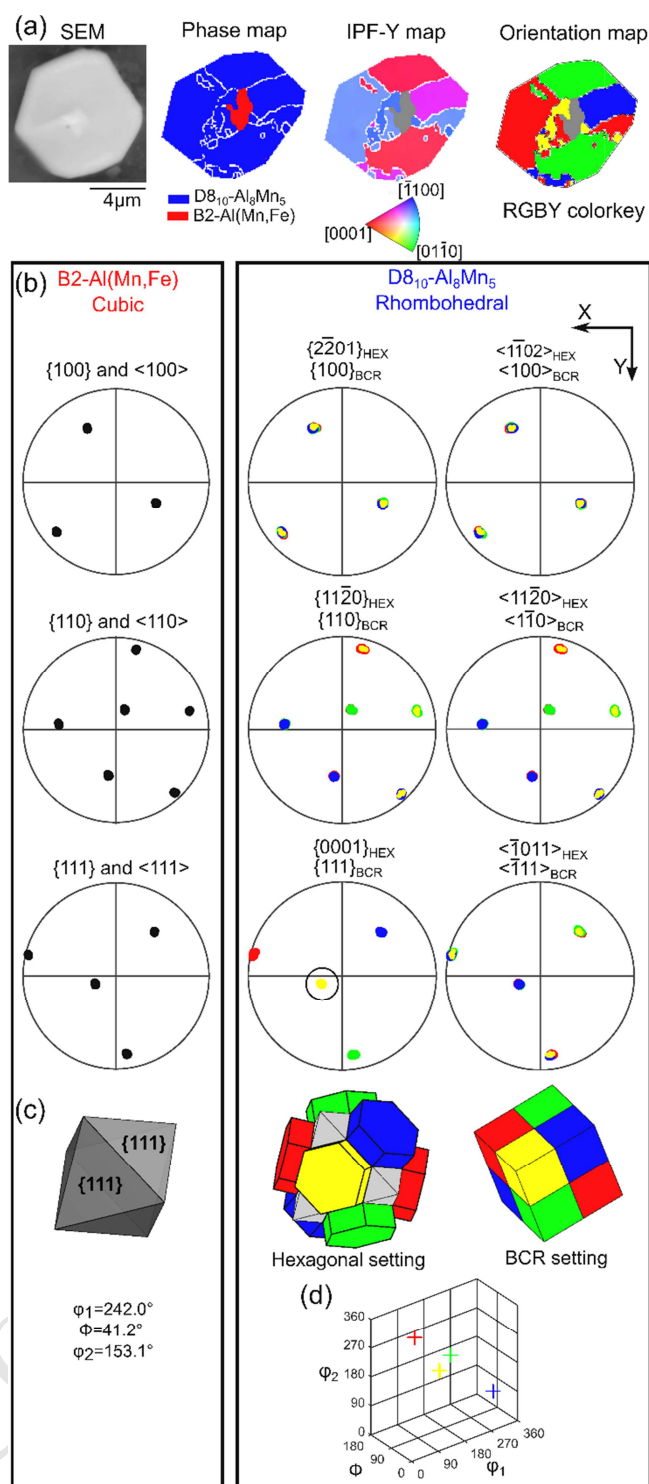


Fig.6 Growth crystallography of B2-AlMn and Al_8Mn_5 . Reproducible OR between B2-AlMn and four orientations of Al_8Mn_5 represented by (a) orientation maps in both IPF-Y and RGBY colour scheme and, (b) pole figures, (c) geometrical models, and (d) orientations of all points ($\text{D8}_{10}\text{-Al}_8\text{Mn}_5$ in hexagonal setting) plotted in Euler angle space. an R, G, B, Y colour was assigned to each cluster. Further detail is in Table 4.

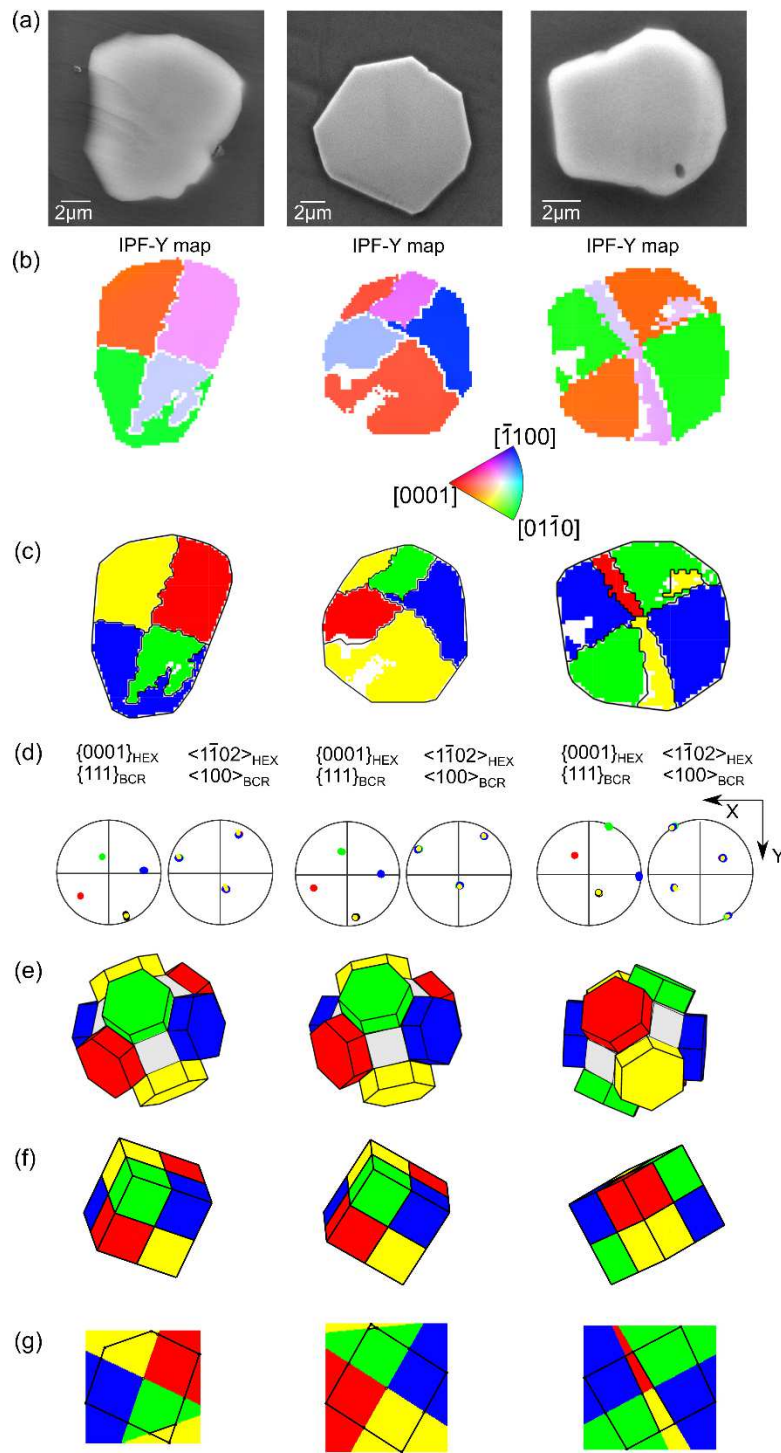


Fig.7 Three typical examples of cyclic growth twinning of Al_8Mn_5 particles (a) SEM images, (b) IPF-Y map, (c) orientation map in RGBY colour scheme, (d) corresponding pole figures, (e-f) geometrical models in (e) hexagonal setting and (f) BCR setting; (g) identification of internal $\{100\}_{\text{BCR}}$ twin composition planes by digital sectioning of the models in (f).

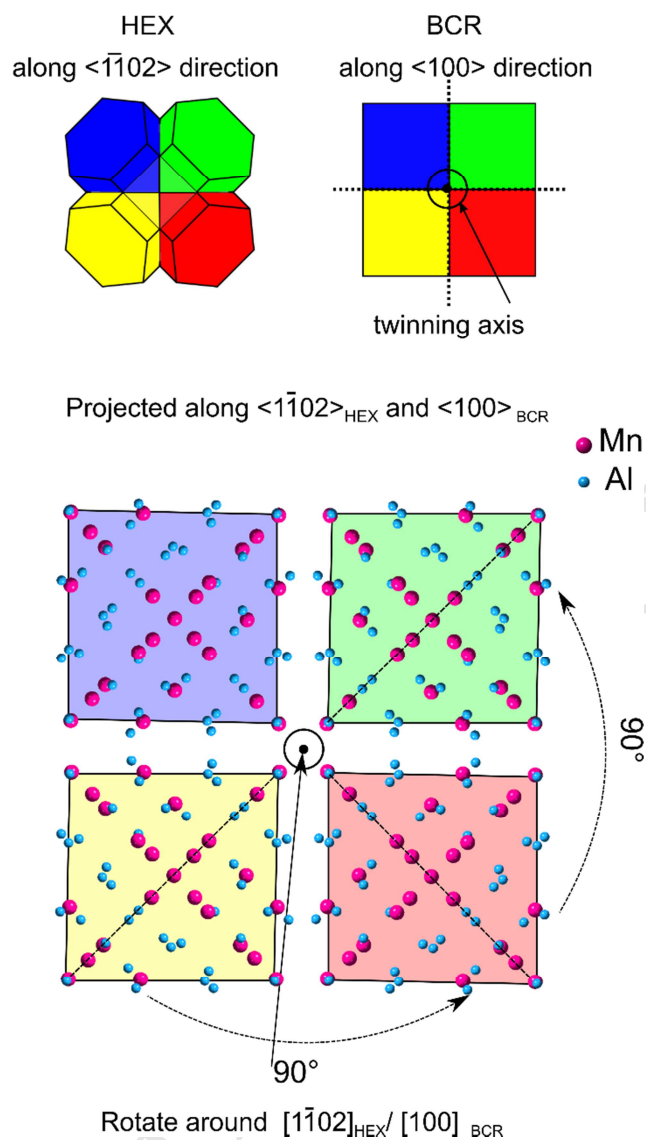


Fig.8. Four-fold cyclic twinning of Al_8Mn_5 by rotating $\sim 90^\circ$ around $[\bar{1}102]_{\text{HEX}} / [100]_{\text{BCR}}$

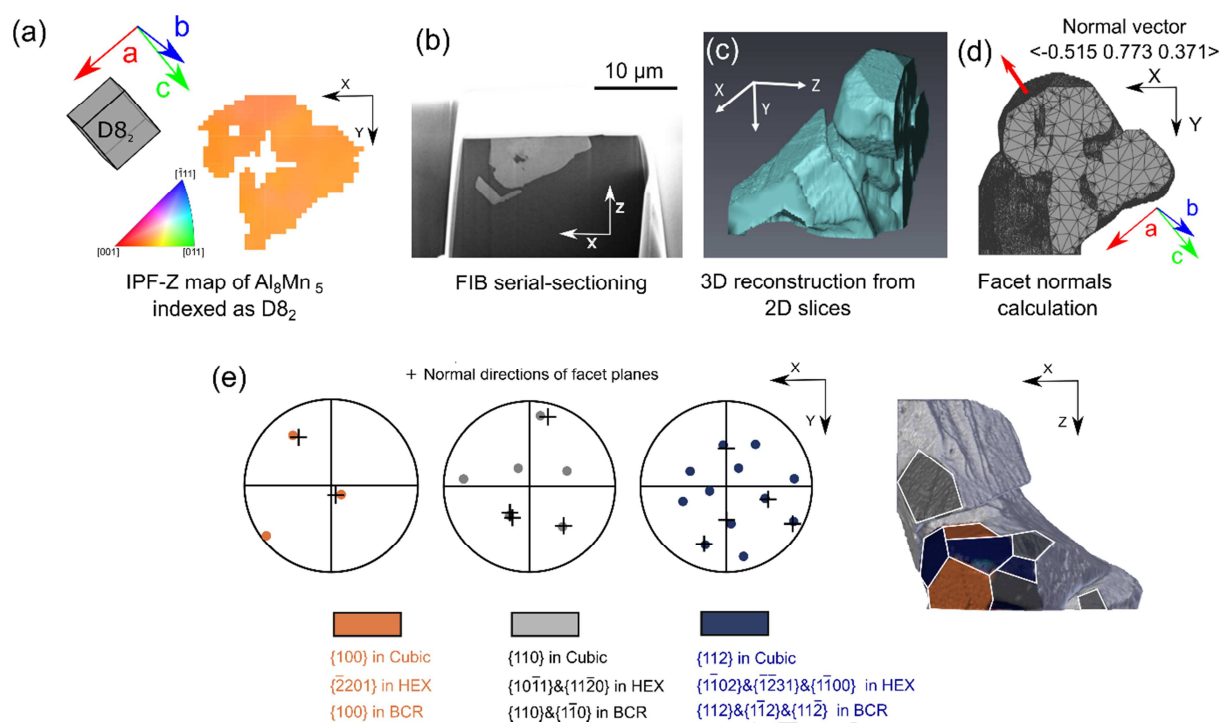


Fig.9 Indexing of growth facets of Al_8Mn_5 by combined FIB serial sectioning and EBSD.

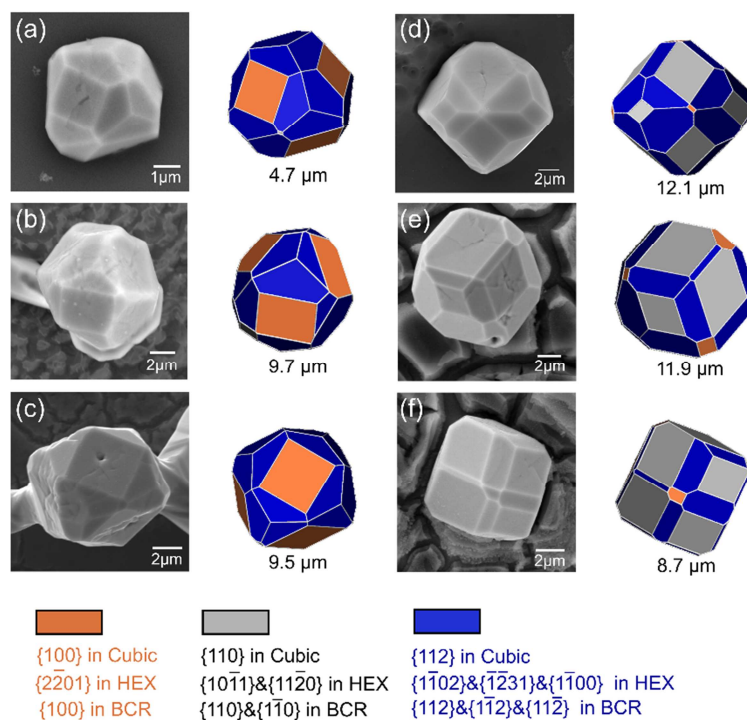


Fig.10 SE-SEM images of six Al_8Mn_5 faceted particles and models based on {100}, {110}, {112} facets using a pseudo-cubic cell.

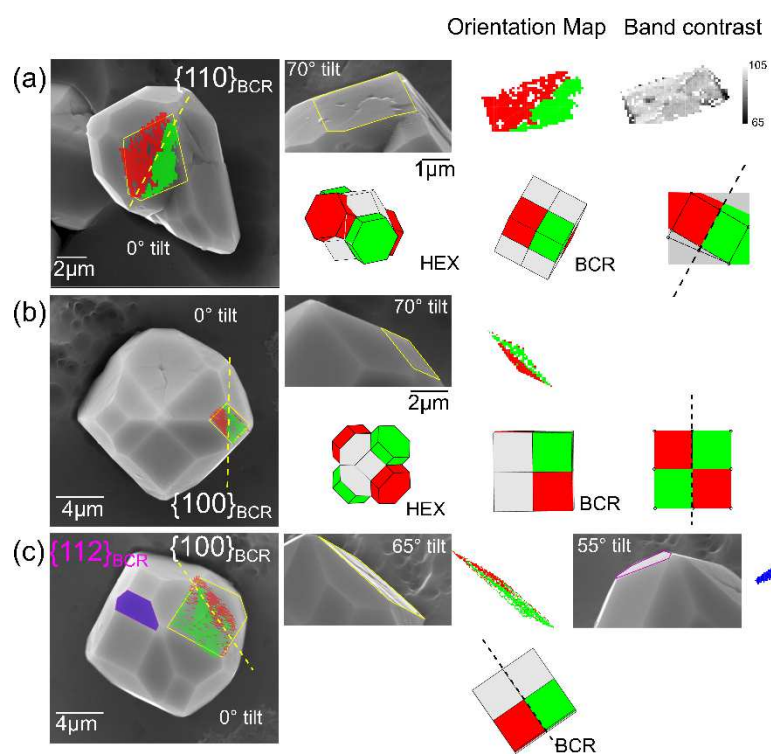


Fig.11 Multiple orientations on $\{100\}_{\text{BCR}}$ and $\{110\}_{\text{BCR}}$ Al_8Mn_5 facets. $\{100\}_{\text{BCR}}$ twin planes intersect the facet surfaces.