

Eutectic intermetallic formation during solidification of a Mg-Sn-Al-Zn-Mn alloy

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Abstract:

Multiple primary and eutectic intermetallic compounds (IMCs) often form during the solidification of multicomponent magnesium alloys. Here, we comprehensively explore eutectic intermetallic formation in Mg-4Sn-3Al-1.5Zn-0.6Mn (wt.%) as-cast alloy, in comparison with Mg-3Al-1Zn-0.3Mn, to better understand Mg₂Sn formation during complex multiphase solidification and how it affects the formation of other IMCs. Various IMCs formed at different stages of solidification: τ -AlMn and Al₈Mn₅ early during solidification and Mg₂Sn, β -Mg₁₇Al₁₂, and τ -MgAlZn as late forming eutectic phases. Most Mg₂Sn phase shared a faceted interface with β -Mg₁₇Al₁₂ and τ -MgAlZn grains, forming a fully divorced eutectic particle containing multiple phases. EBSD-based trace analysis in combination with XCT and TEM results revealed that β -Mg₁₇Al₁₂ and τ -MgAlZn phase grew adjacent to the {100} growth facets of Mg₂Sn. Within multi-phase particles, seven types of reproducible orientation relationships (ORs) were measured between each intermetallic. The ORs between Mg₂Sn and τ -MgAlZn were found to have the best lattice match among the observed phase pairs. For the defined ORs, Mg₂Sn can be correlated with the icosahedral coordination in τ -MgAlZn.

Keywords: Magnesium alloy, Eutectic intermetallic, EBSD, Orientation relationship.

1. Introduction

Mg-Al-based alloys are the most widely used Mg alloys because of their good castability and relatively low cost. After casting, the $\text{Mg}_{17}\text{Al}_{12}$ intermetallic compound (IMC) is located at α -Mg grain boundaries and between dendrite arms. While this can provide strengthening, $\text{Mg}_{17}\text{Al}_{12}$ results in the limitation of forming properties and gives poor high-temperature resistance [1]. Mg-RE alloys have excellent mechanical properties and high-temperature resistance compared with other Mg-based alloys. However, RE-containing Mg alloys are not cost-effective and significantly reduce castability, hindering the wide application of Mg-RE alloys in the auto industry, etc. Therefore, it is rational to further design affordable Mg alloys with improved properties. Mg-Sn-based alloys have attracted attention due to their age hardening ability [2,3]. Mg_2Sn intermetallic compounds nucleate and grow during both the solidification and aging processes due to the rapid change of solid solubility of Sn with temperature [4]. The formation of the Mg_2Sn phase with high thermal stability gives Mg-Sn-based alloys good elevated temperature resistance and deformation ability [2,5,6].

For the Mg-Sn alloy system, Al and Zn elements are often added to improve castability and age hardening ability, thus improving the overall mechanical properties of the alloys. Mg-Sn-Zn-Al wrought alloys, typically with extrusion and heat treatment process, were widely studied in recent years [6-10]. The new Mg-6.6Sn-5.9Zn-2.0Al-0.2Mn (TZAM6620) (wt.%) alloy developed by Sasaki et al. [10], was reported with superior yield strength over 370 MPa. It can be seen that past works on Mg-Sn-based wrought alloys mainly focused on the correlation between microstructure evolution (primarily Mg grains) and strengthening mechanism, during the casting and deformation process [8,11-17].

It is well known that $\text{Mg}_{17}\text{Al}_{12}$ binary phase and Mg-Al-Zn ternary phases can form with Al and Zn additions. There are two main ternary phases in Mg-Al-Zn-based alloys: τ phase ($\text{Mg}_{32}(\text{Al}, \text{Zn})_{49}$), and Φ phase ($\text{Mg}_{21}(\text{Al}, \text{Zn})_{17}$). These have been identified in previous studies of as-cast Mg-Al-Zn-based alloys [18-22] with a wide range of compositions and various Al/Zn ratios. Nave et al. [23] reported that eutectic morphology in multicomponent Mg-Al-Zn system became less divorced with Al content increasing, but more divorced with increasing either zinc

content or cooling rate [24,25]. During solidification of low Al and Zn containing alloys, α -Mg nucleates and grows dendritically as the primary phase, and rejected solute (Sn, Al, Zn, etc.) forms in eutectic reactions in the last stages of solidification. With α -Mg dendrite coarsening, eutectic phases nucleate/grow from the undercooled liquid, and form into eutectic colonies locally within interdendritic regions.

In previous studies of Mg-Sn-Al-Zn-based alloys, eutectic intermetallics frequently co-existed, forming uncoupled multi-phase particles with straight-line interfaces in the cross-sectioned as-cast microstructures [16,26-29]. However, few studies have discussed the detailed mechanisms of microstructure evolution during various reactions and phase transformations in Mg-Sn-Al-Zn-Mn alloys. For instance, influences of Sn alloying on the uncoupled eutectic growth morphology in Mg-Al-Zn-Sn alloys need to be understood further, especially the interaction between eutectic intermetallic phases within these multi-phase particles. These features play important roles in determining the formability [6,7], mechanical properties [9,10,16,29,30], and corrosion resistance [31-33] of Mg-Sn-Al-Zn alloys.

The Mg_2Sn microstructure formed during casting, including multiphase particles containing Mg_2Sn , is important for (i) the performance of components used in the as-cast condition, and (ii) the dissolution and precipitation kinetics of Mg_2Sn in heat treated components. However, relatively little is known about Mg_2Sn solidification in multicomponent Mg-Sn-Al-Zn-Mn alloys.

Therefore, this paper explores how the Mg_2Sn phase forms and interacts with other IMCs during the solidification sequence. Intermetallic formation during the solidification of Mg-4Sn-3Al-1Zn-0.6Mn (wt.%) alloy was investigated, combining thermodynamic calculation, analytical scanning electron microscopy, and transmission electron microscopy as well as micro computed tomography. First, we identified the intermetallic phases that existed in as-cast Mg-4Sn-3Al-1Zn-0.6Mn alloy. Then we analyzed Mg-Sn/Mg-Al/Mg-Al-Zn eutectic intermetallics in comparison to Mg-3Al-1Zn-0.3Mn alloy with a focus on growth morphology, crystallography, and interactions between the various eutectic intermetallics.

2. Experimental

Mg-4Sn-3Al-1Zn-0.6Mn and Mg-3Al-1Zn-0.3Mn (AZ31) alloys (wt.%) were prepared from pure Mg, Al, Zn, Sn (>99.9 wt.%), and Mg-1.83Mn (wt.%) master alloy, by melting in an electric resistance furnace at 700 °C under the protection of cover gas with 99.5% CO₂ and 0.5% SF₆ mixture. The alloy melt was held at 700 °C for 30 min to homogenize, followed by cooling down to 680 °C and then casting into the permanent mold which had been coated and preheated to 250 °C. Ingots with the dimensions of $\varnothing 100 \times 500$ mm were obtained. Alloy compositions, as shown in Table 1, were measured by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, SPECTRO BLUE SOP, Germany).

For microstructural analysis, samples were cut into sizes of $10 \times 8 \times 6$ mm and $4 \times 3 \times 1$ mm. The as-solidified microstructure was characterized by a scanning electron microscope (SEM, TESCAN MIRA3, Czech) equipped with energy dispersive spectroscopy (EDS, Oxford Instrument Ultim Max, UK) and electron backscatter diffraction (EBSD, Oxford Instrument C-Nano, UK) detectors, at an acceleration voltage of 20 kV. Electron probe microanalysis (EPMA, JEOL JXA-8530F, Japan) was further employed to quantitatively measure the compositions of various intermetallic compounds (IMCs) with 15 kV acceleration voltage. High-angle annular dark-field (HAADF-STEM) images and selected area electron diffraction (SAED) patterns were obtained using a transmission electron microscope (TEM, FEI Titan G2 60-300, Thermo Fisher Scientific, USA).

Samples for both SEM and EPMA were mechanically ground and polished. The final step of polishing was carried out with 0.05 μm colloidal silica suspension, followed by etching in 4 vol.% nital solution for some SEM characterization. Site-specific membranes for TEM observation were prepared with a standard lift-out method using focused ion beam (FIB) milling (FEI Helios NanoLab 600 dual beam system, USA) [34]. EBSD datasets were processed using AZtecCrystal 1.1 software (Oxford Instruments, UK) and MATLABTM 9.5 (Mathworks, USA) with MTEX 5.7 toolbox [35]. To reveal the three-dimensional (3D) morphologies of IMCs, α -Mg was selectively dissolved from SEM observation samples by etching in 10 vol.% nital solution for 10 min. 3D X-ray Microscopy (XRM) (ZEISS Xradia 620 Versa, Carl Zeiss X-ray

Microscopy Inc., USA) was performed on $\varnothing 3 \times 12$ mm samples of both alloys. The samples were imaged at 80 kV with a resolution of $0.7 \mu\text{m}\cdot\text{voxel}^{-1}$ and an exposure time of 3.5 s per projection. A total of 2400 projections were collected per each tomography scan. 3D reconstructions were performed using the reconstruction software (XMReconstructor, Carl Zeiss X-ray Microscopy Inc., USA), which is based on the filtered back-projection-based algorithm. Reconstructed datasets were segmented and quantitatively analyzed using ImageJ (US NIH, USA) and Avizo 9.2(Thermo Fisher Scientific, USA).

Table 1 Alloy compositions determined by inductively coupled plasma emission spectrometer (ICP-OES).

Alloys	Compositions (wt.%) [*]					
	Mg	Sn	Al	Zn	Mn	Si
Mg-4Sn-3Al-1Zn-0.6Mn	Bal.	3.920	2.860	1.320	0.590	0.008
Mg-3Al-1Zn-0.3Mn	Bal.	/	2.700	1.310	0.290	0.009

^{*}Fe, Cu, and Ni were 0.005 wt.% or lower

3. Results

3.1. As-solidified microstructure

As shown in Fig. 1, we explored the equilibrium and Scheil model solidification paths of Mg-4Sn-3Al-1Zn-0.6Mn and Mg-3Al-1Zn-0.3Mn based on thermodynamic calculation, using PANDATTM [36] software with the PanMg2020 database. There were various reactions involved at different stages of solidification. Each reaction and their corresponding temperature range are listed in Fig. 1. The final mass percentages of IMCs in the two alloys are given in Table 2.

Under the equilibrium solidification path, there were only two reactions with the formation of Al_8Mn_5 and α -Mg phase in both alloys. Normally in gravity casting of magnesium alloys, the solidification is more close to the Scheil mode than the equilibrium solidification path [37]. As shown in Fig. 1, various Al-Mn IMCs formed throughout the Scheil solidification range in both alloys, with Al_8Mn_5 being the majority Al-Mn phase (mass percentages of intermetallic

were shown in Table 2). In Mg-3Al-1Zn-0.3Mn alloy (Fig. 1b), β -Mg₁₇Al₁₂ phase would form below the temperature of 401 °C. With 4 wt.% Sn addition (Fig. 1a), the Mg₂Sn phase was calculated to form at 472 °C in Mg-4Sn-3Al-1Zn-0.6Mn alloy, and then formed with α -Mg and β -Mg₁₇Al₁₂ below 401 °C. The ternary Mg-Al-Zn phases (Φ and τ) would form subsequently at the last stages of solidification in both alloys. As predicated from the calculation, the formation temperature of τ -MgAlZn is only a couple of degrees lower than the reaction temperature range of $L \rightarrow \alpha\text{-Mg} + \text{Mg}_2\text{Sn} + \text{Al}_4\text{Mn} + \Phi\text{-MgAlZn}$ (Fig. 1a). It can be seen in Table 2 that the amount of ternary Mg-Al-Zn IMCs is relatively high because the Zn content is towards the upper end of the AZ31-based alloy composition range (~1.3 wt.% Zn in both alloys in Table 1).

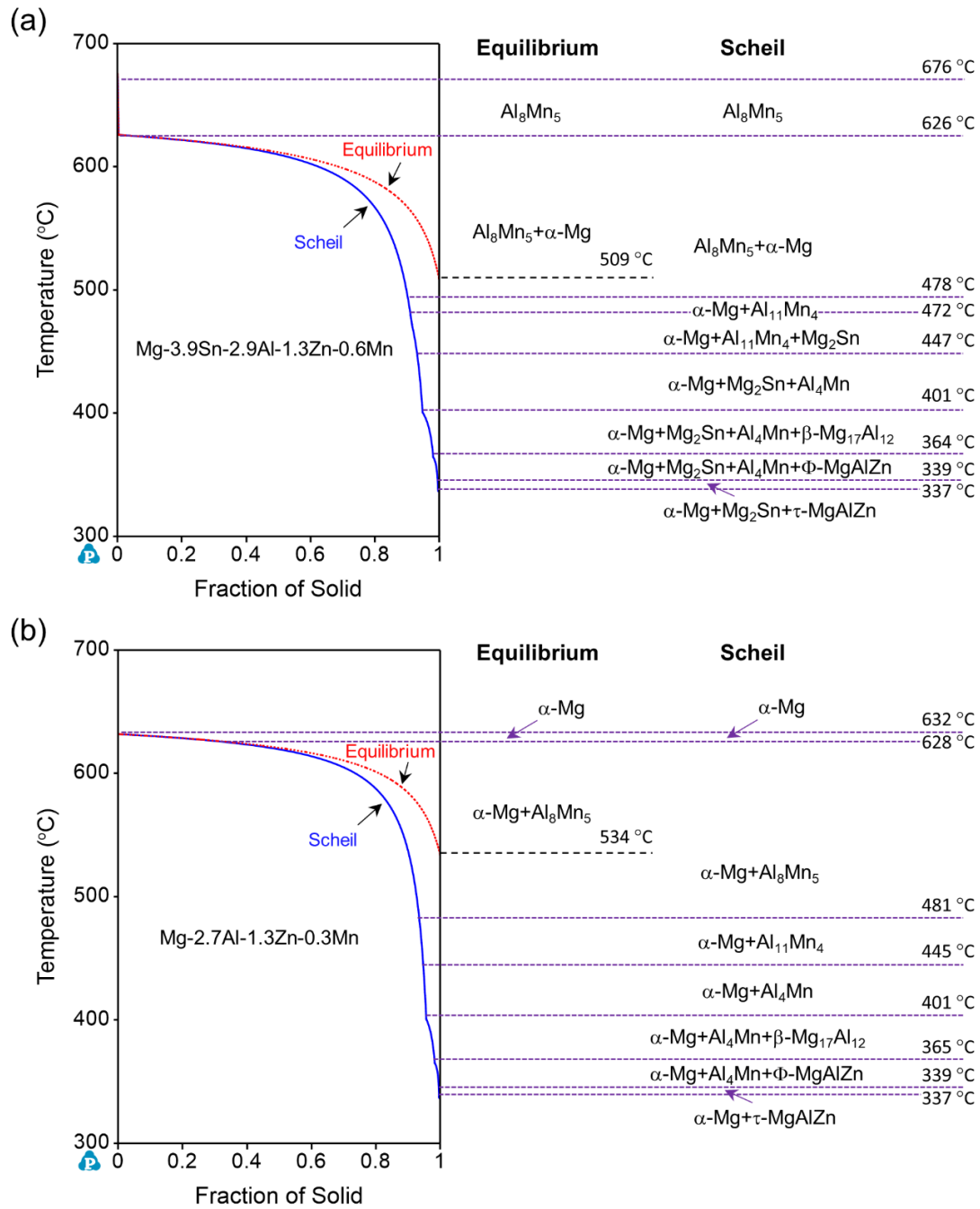


Fig. 1 Calculated equilibrium and Scheil solidification paths for (a) Mg-4Sn-3Al-1Zn-0.6Mn alloy and (b) Mg-3Al-1Zn-0.3Mn alloy, using PANDATTM software with PanMg2020 database.

Table 2 Final mass percentages of intermetallic calculated with the Scheil model using the PanMg2020 database.

	Al_8Mn_5	$\text{Al}_{11}\text{Mn}_4$	Al_4Mn	$\text{Mg}_{17}\text{Al}_{12}$	$\Phi\text{-MgAlZn}$	$\tau\text{-MgAlZn}$	Mg_2Sn
Mg-4Sn-3Al-1Zn-0.6Mn	0.69	1.65×10^{-5}	7.35×10^{-6}	2.33	1.19	0.12	1.37
Mg-3Al-1Zn-0.3Mn	0.19	1.39×10^{-5}	5.98×10^{-6}	1.97	1.16	0.08	/

Fig. 2 displays as-cast microstructures for both Mg-4Sn-3Al-1Zn-0.6Mn and Mg-3Al-1Zn-0.3Mn. Backscatter electron (BSE) images captured by SEM are shown in Fig. 2a and g. The microstructure consisted of equiaxed α -Mg dendrites with a variety of IMC particles within interdendritic areas. It is consistent with the previous studies on Mg-Sn-Al-Zn and Mg-Al-Zn cast alloys with slight variation in compositions [16,17,38]. EBSD orientation maps (IPF-Z) of the as-cast α -Mg grain morphology are presented in Fig. 2b and h. Dendrite envelopes were measured and quantified. Equiaxed α -Mg grains with random crystal orientation were present in as-cast microstructure, which is well documented [39]. The two batches had similar α -Mg grain size of $\sim 137\ \mu\text{m}$ versus $\sim 159\ \mu\text{m}$. This indicates that Sn solute was not effective in grain refinement under the casting condition of this study.

As seen from BSE micrographs in Fig. 2a and g, the darker region was α -Mg matrix and the interdendritic regions with brighter grayscale were various IMC phases, with a range of different morphologies. The typical IMCs in the two alloys are summarized in the bottom rows of Fig. 2. Rod-like and blocky particles were observed for both alloys in the BSE micrographs. IMCs with irregular morphology and multiple grayscale levels often co-existed, forming multi-phase particles (Fig. 2e-f and i).

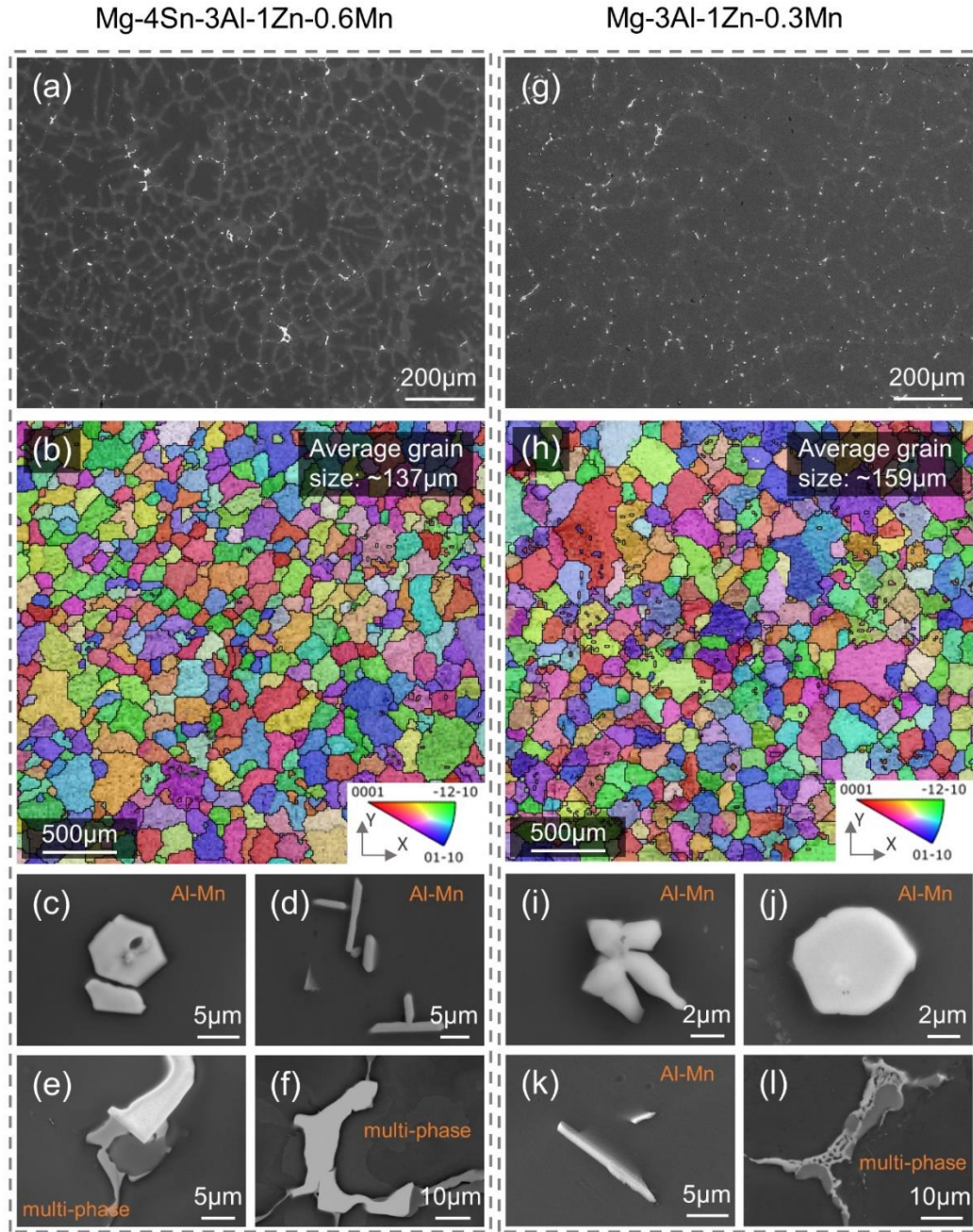


Fig. 2 Typical solidified microstructural features in Mg-4Sn-3Al-1Zn-0.6Mn alloy and Mg-3Al-1Zn-0.3Mn alloy. (a, g) Lower magnification BSE images of two cast alloys, (b, h) EBSD orientation map (IPF-Z) of α -Mg phase with average grain size shown in maps, intermetallic compounds (IMCs) in (c-f) Mg-4Sn-3Al-1Zn-0.6Mn alloy and (i-l) Mg-3Al-1Zn-0.3Mn alloy.

3.2. Phase identification

Phase identification of IMCs in Mg-4Sn-3Al-1Zn-0.6Mn alloy was performed with the combination of morphology, composition, and crystal structure, using thermodynamic calculations and analytical SEM (EPMA and EBSD), along with TEM methods.

Fig. 3 summarizes the morphology and composition of representative IMC phases present in the as-cast Mg-4Sn-3Al-1Zn-0.6Mn alloy from BSE micrographs with point EPMA measurements. EPMA results of corresponding IMC phases from Fig. 3a and b are displayed in Table 3. Experimental Kikuchi patterns for various intermetallics are shown in Fig. 4, as indexed by Hough transformations using AZtec 5.1 software. Crystal structures of possible IMCs present in the as-cast alloy are listed in Table 4 [20,40-44].

Combining the information of compositions and EBSD indexing, the majority of rod-like and some blocky Al-Mn particles with Al/Mn ratio ~ 0.88 were indexed as metastable τ -AlMn ($P4/mmm$) phase (Fig. 4d-f), which are the same metastable Al-Mn particles found in Refs.[45-48]. A small amount of polyhedral Al-Mn IMCs, with Al/Mn ratio close to $1.44 \sim 1.51$, as shown in Fig. 4a-c, was confirmed as Al_8Mn_5 (with space group $R3m$) phase with EBSD indexing, which is consistent with Ref.[49]. $\text{Al}_{11}\text{Mn}_4$ and Al_4Mn phases were not detected throughout this study due to their lower phase fraction.

Interdendritic regions contained abundant multi-phase particles, with mainly three levels of grayscale, as displayed in BSE micrographs (Fig. 3b-c). EDS mapping is shown in Fig. 3c-h for a typical multi-phase particle. To identify the correct crystal structure of the IMCs, EBSD measurements (point analysis in Fig. 4g-o and mapping in Fig. 6) were used to obtain Kikuchi patterns and compare them with the candidate phases expected from composition and thermodynamic calculations. Moreover, the HAADF-STEM image in Fig. 5a shows a typical multi-phase particle, prepared by the lift-out method using a focused ion beam (FIB). EDS-STEM mapping for this particle, displaying Mg, Sn, Al, Zn elements in Fig. 5c, appeared similar to the SEM-EDS mapping for the multi-phase particle in Fig. 3c, although with much higher spatial resolution.

EPMA and EBSD analysis (Table 3 and Fig. 4) shows that the brightest one among the three phases was Mg_2Sn ($Fm-3m$ space group) phase (Point C in Fig. 3b, and Fig. 4g). Two other phases were Mg-Al-Zn phases, with two distinct levels of Zn content. For Mg-Al-Zn particle with <10 at.% Zn content, it was $\beta\text{-Mg}_{17}\text{Al}_{12}$ ($I-43m$) (Point D in Fig. 3b, and Fig. 4j), with a certain amount of Zn solubility. The other Mg-Al-Zn particle (with >10 at.% Zn content)

was confirmed as τ -MgAlZn ($Im\bar{3}$, $Mg_{32}(Al, Zn)_{49}$) phase (Point E in Fig. 3b, and Fig. 4m) rather than Φ -MgAlZn ($Pbcm$, $Mg_{21}(Al, Zn)_{17}$) phase, which is easy to distinguish from EBSPs. In the current work, most of the ternary Mg-Al-Zn IMCs with higher Zn content (>10 at.%) in both alloys were found to be τ -MgAlZn phases throughout the indexing process of multiple particles.

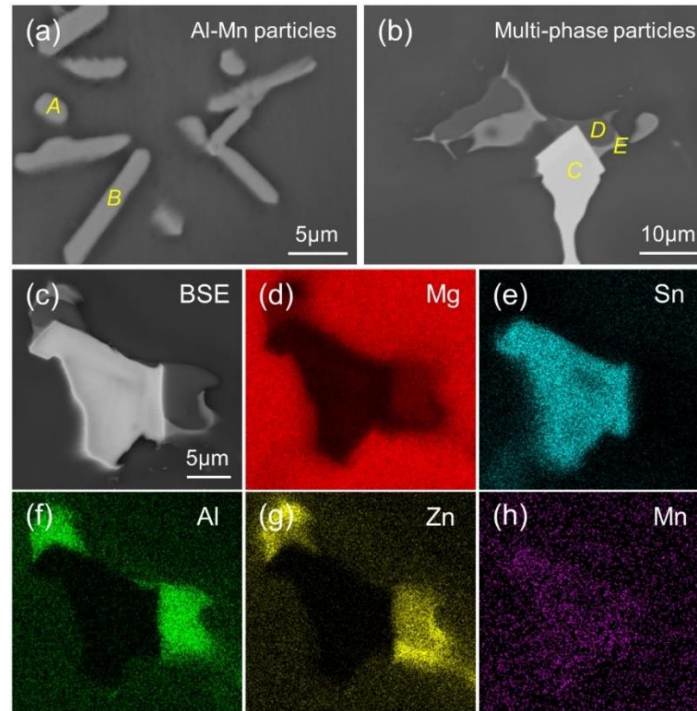


Fig. 3 Intermetallic compounds present in as-cast Mg-4Sn-3Al-1Zn-0.6Mn alloy. (a) BSE image of rod-like and blocky particles with point **A** and **B** indexed, (b) BSE image of one multi-phase particle with point **C**, **D**, and **E** indexed, (c) BSE image of another typical multi-phase particle, (d-h) EDS maps of Mg, Sn, Al, Zn, and Mn element for the particle in (c).

Table 3 Quantitative EPMA point analysis (at.%) marked in Fig. 3a and b.

	Mg	Sn	Al	Zn	Mn	Phases
Point A	2.23	0.02	45.86	0.09	51.80	τ -AlMn
Point B	4.99	0.07	44.25	0.10	50.59	τ -AlMn
Point C	66.33	33.24	0.20	0.22	0.01	Mg_2Sn
Point D	62.07	0.49	29.41	8.02	0.01	β - $Mg_{17}Al_{12}$
Point E	62.47	0.14	21.30	16.07	0.02	ternary MgAlZn

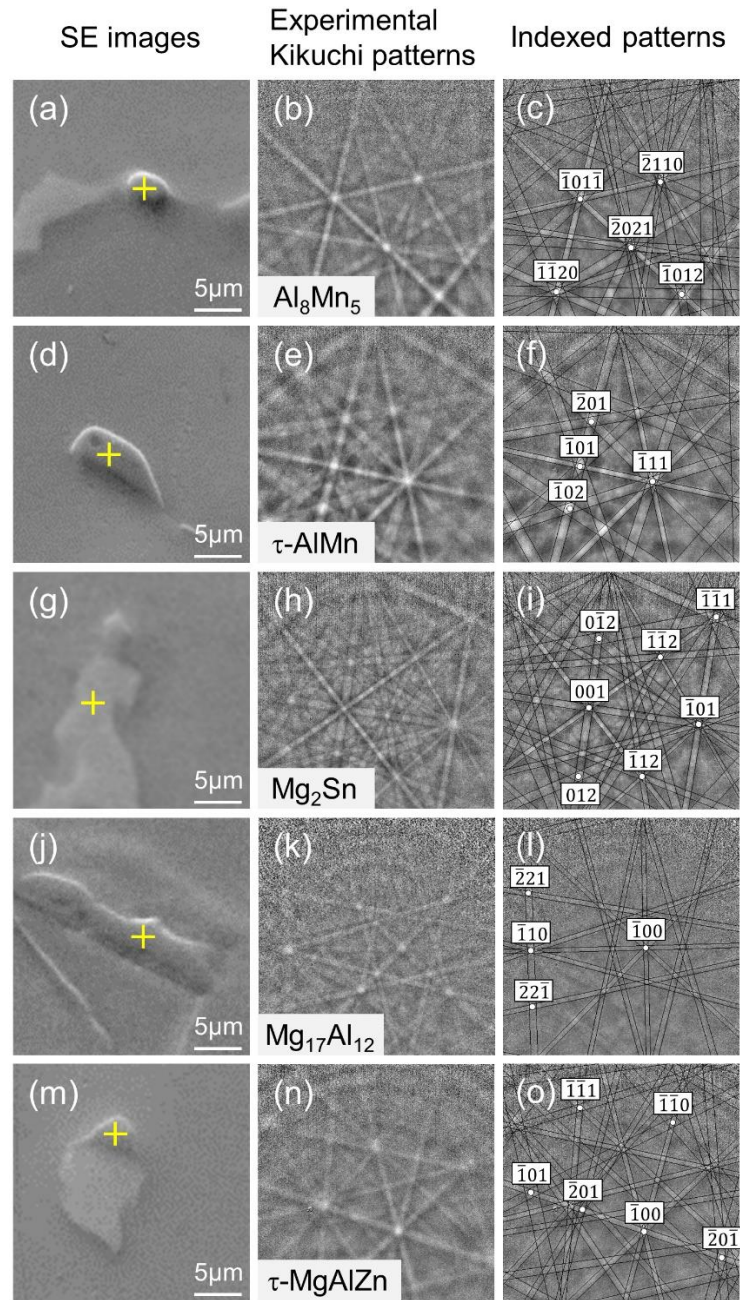


Fig. 4 Phase identification of various intermetallics using experimental Kikuchi patterns. (a-c) Al₈Mn₅ phase; (d-f) τ-AlMn phase; (g-i) Mg₂Sn phase; (j-l) Mg₁₇Al₁₂ phase; (m-o) τ-MgAlZn phase. The left column is SE image, and middle column is experimental pattern, and right column is indexed result on the same pattern.

Table 4 Crystal structures of possible intermetallic compounds.

Phase	Space group	Pearson symbol	Lattice parameter						ICSD
			a[Å]	b[Å]	c[Å]	α [°]	β [°]	γ [°]	
Al ₈ Mn ₅	<i>R3mH</i>	<i>hR26</i>	12.667	12.667	7.942	90	90	120	608465[40]
τ -AlMn	<i>P4/mmm</i>	<i>tP2</i>	2.770	2.770	3.540	90	90	90	57970[41]
Mg ₂ Sn	<i>Fm-3m</i>	<i>cF12</i>	6.765	6.765	6.765	90	90	90	104869[42]
β -Mg ₁₇ Al ₁₂	<i>I-43m</i>	<i>cI58</i>	10.549	10.549	10.549	90	90	90	158247[43]
τ -MgAlZn	<i>Im-3</i>	<i>cI162</i>	14.160	14.160	14.160	90	90	90	57968[20]
Φ -MgAlZn	<i>Pbcm</i>	<i>oP152</i>	8.937	16.812	19.586	90	90	90	424664[44]

Selected area electron diffraction (SAED) patterns using TEM for three phases within a multi-phase particle were also indexed in Fig. 5. The interphase boundaries were indicated by colored dashed lines in Fig. 5a, and three phases were marked as phase **A**, **B**, and **C**. Phase **A** was Mg₂Sn viewing along [110] zone axis. Note that the brighter speckles observed in Fig. 5a in Mg₂Sn phase are likely caused by surface damage as exposed to focused ion beam or chemical reagents, which frequently occurred during the sample preparation process. Phase **B** was mainly enriched with Mg and Al, and relatively lower Zn content. It was indexed as β -Mg₁₇Al₁₂ ([110] zone axis, N.B. sample is slightly tilted for each phase), which is consistent with the EDS/EPMA results shown in Fig. 3b and Table 3. Phase **C** with higher Zn content could be considered as ternary Mg-Al-Zn (τ -MgAlZn) phase similar to the particle in Fig. 3b and Fig. 4m with Zn content of more than 10 at.%. Note that the τ -MgAlZn phase has a complex body-centered cubic structure (162 atoms per unit cell) [20,50] with space group *Im-3*. It was identified by X-ray Diffraction (XRD) [18,19,21,28] and TEM [51] method in previous studies, with a wide range of compositions. Combining the EDS/EPMA results, EBSD indexing, and SAED indexing in this work, phase **C** was suggested to be τ -MgAlZn phase ([302] zone axis). These phase analyses from STEM are also in good agreement with our EBSD indexing, EBSD mapping, and phases in Mg-Sn-Al-Zn alloys which were individually reported in Refs.[26,51].

Elemental mapping under STEM in Fig. 5c indicates there was no obvious elemental segregation across each phase. The three phases contained within this particle could be clearly distinguished from the EDS mapping, especially the Sn and Zn maps. From 2D cross-section, there was a straight-line interface for **A** (Mg_2Sn) adjacent to both **B** ($\beta\text{-Mg}_{17}\text{Al}_{12}$) and **C** ($\tau\text{-MgAlZn}$) which is similar with the as-cast microstructure in Refs.[26,27,29,30,52]. Note that the interphase boundaries between **A** and **B/C** in this particle were slightly curved, as indicated by red arrows in Fig. 5a.

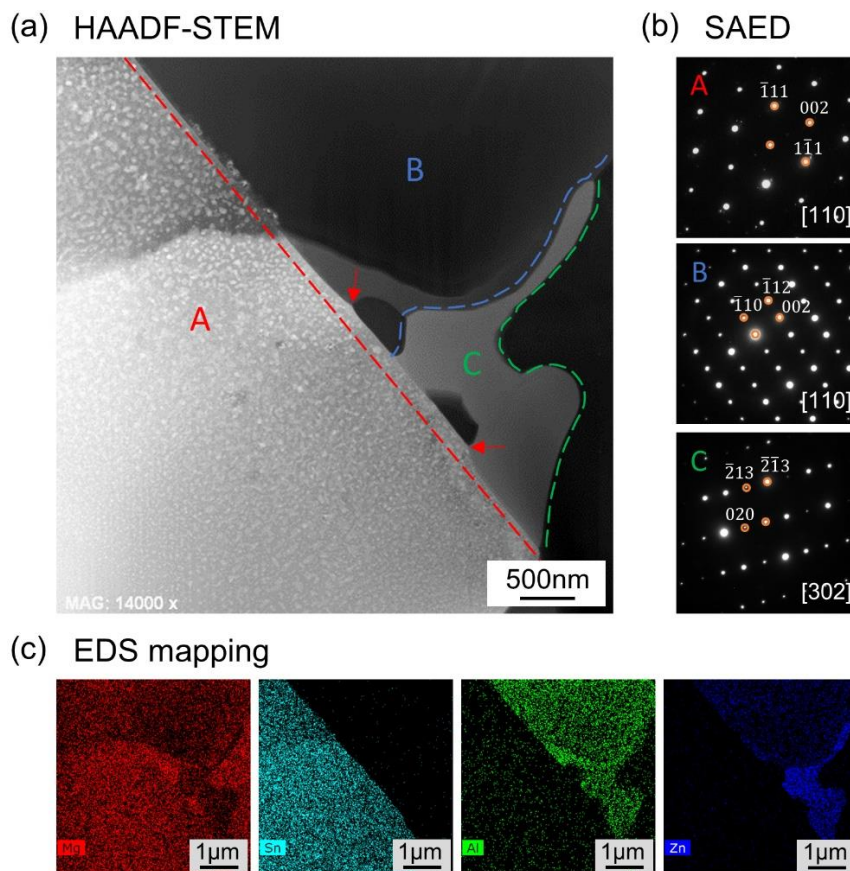


Fig. 5 TEM characterization of a typical eutectic multi-phase particle in Mg-4Sn-3Al-1Zn-0.6Mn alloy. (a) HAADF-STEM image of the particle with three phases (**A**, **B**, **C**) separated by the colored dashed line, (b) representative SAED patterns for **A** = Mg_2Sn , **B** = $\beta\text{-Mg}_{17}\text{Al}_{12}$, and **C** = $\tau\text{-MgAlZn}$ phase, (c) EDS-STEM maps of Mg, Sn, Al, Zn elements for the particle.

Fig. 6 shows EBSD mapping of a representative multi-phase eutectic particle in Mg-4Sn-3Al-1Zn-0.6Mn alloy. Eutectic phases were identified as Mg_2Sn (**A**), $\beta\text{-Mg}_{17}\text{Al}_{12}$ (**B**), and $\tau\text{-MgAlZn}$ (**C**) (Fig. 6b). From the IPF-Z map in Fig. 6c, it shows that each eutectic phase in this

particle was a single crystal. In the present study, this is the case for all the datasets/particles we measured. Unit cell geometric models plotted from Euler angles were superimposed in the IPF-Z map to illustrate the crystallographic orientation for each phase. Moreover, there were straight Mg_2Sn (A) phase boundaries adjacent to $\beta\text{-Mg}_{17}\text{Al}_{12}$ (B) / $\tau\text{-MgAlZn}$ (C) and Mg matrix.

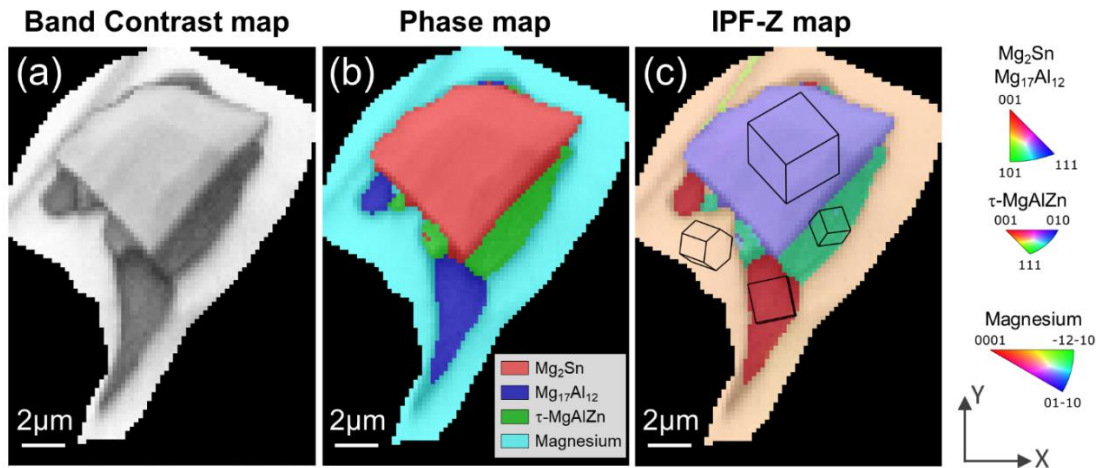


Fig. 6 EBSD mapping for a representative divorced eutectic particle in Mg-4Sn-3Al-1Zn-0.6Mn alloy. (a) Band contrast map, (b) Phase map, (c) IPF-Z map.

3.3. Growth morphology and crystallography of multi-phase particle

The overall 3D morphology of eutectic IMCs was observed using micro-X-ray computed tomography (XCT) and deep-etched SEM micrographs [53,54]. Rendered eutectic particles are shown in Fig. 7a (Mg-4Sn-3Al-1Zn-0.6Mn alloy) and Fig. 7d (Mg-3Al-1Zn-0.3Mn alloy) based on the 3D reconstruction of XCT images. $\beta\text{-Mg}_{17}\text{Al}_{12}$ and $\tau\text{-MgAlZn}$ particles (in blue) were distributed in the form of discontinuous colonies in both alloys. IMCs in the multi-phase particles could be distinguished by Z-contrast in BSE images. Fig. 7b-c and e-f show 2D cross-section and 3D deep-etched images of representative multi-phase eutectic particles in BSE mode. In Mg-4Sn-3Al-1Zn-0.6Mn alloy (Fig. 7b-c), Mg_2Sn (the brightest one, A) and $\beta\text{-Mg}_{17}\text{Al}_{12}$ (B) / $\tau\text{-MgAlZn}$ (C) were co-existing, frequently forming fully divorced eutectic. For Mg-3Al-1Zn-0.3Mn alloy, the eutectic intermetallics (Fig. 7e-f) consisted of $\beta\text{-Mg}_{17}\text{Al}_{12}$ (B) and $\tau\text{-MgAlZn}$ (C), and the coupled region were found to be of $\tau\text{-MgAlZn}$ (C) / $\alpha\text{-Mg}$ phases.

Straight interphase boundaries between Mg_2Sn and other phases were observed in 2D, while flat facets of Mg_2Sn were revealed in 3D by deep etching. The growth morphology of Mg_2Sn was also observed from rendered particles in reconstructed XCT, as displayed in Fig. 8a. The 3D morphology for the majority of Mg_2Sn was a mixture of non-faceted and faceted faces, and pairs of growth facets of Mg_2Sn were revealed. Importantly, facets of Mg_2Sn were also found to be attached to $\alpha\text{-Mg}$ (Fig. 7c and Fig. 8c). It indicates that the straight common interphase boundaries within multi-phase particles observed in the 2D cross-section (Fig. 7b and Fig. 8b) were essentially the growth facets of Mg_2Sn to the liquid (Fig. 7c and Fig. 8c). After selective dissolution of $\alpha\text{-Mg}$, the 3D morphology of eutectic phases was revealed with BSE imaging in the SEM. Growth facets of Mg_2Sn marked in dashed lines could be clearly seen in Fig. 8c. It also shows that $\beta\text{-Mg}_{17}\text{Al}_{12}$ and/or $\tau\text{-MgAlZn}$ phase in $\text{Mg-4Sn-3Al-1Zn-0.6Mn}$ alloy mostly co-exist and grow adjacent to the facets of Mg_2Sn , forming multi-phase eutectic particles.

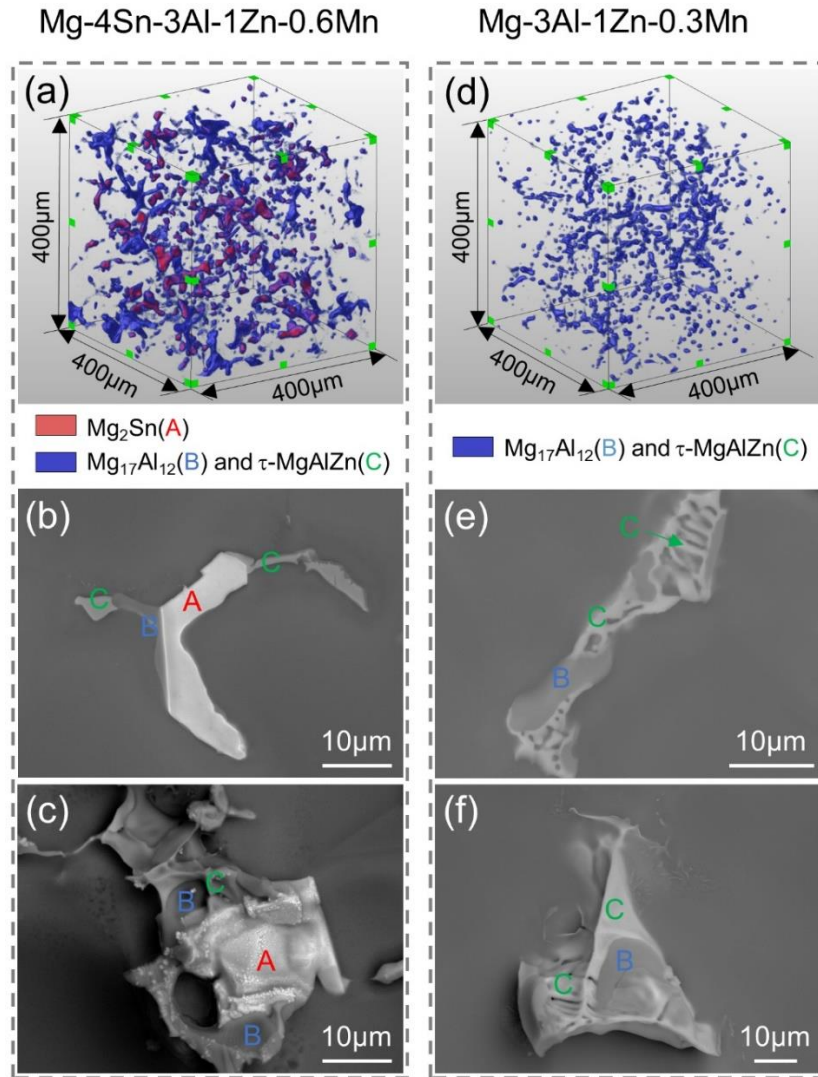


Fig. 7 Typical multi-phase eutectic particles in Mg-4Sn-3Al-1Zn-0.6Mn alloy and Mg-3Al-1Zn-0.3Mn alloy. (a, d) Three-dimension (3D) reconstruction of XCT images; (b, e) 2D cross-section BSE images; (c, f) deep-etched micrograph of eutectics. A = Mg₂Sn, B = β-Mg₁₇Al₁₂, and C = τ-MgAlZn phase.

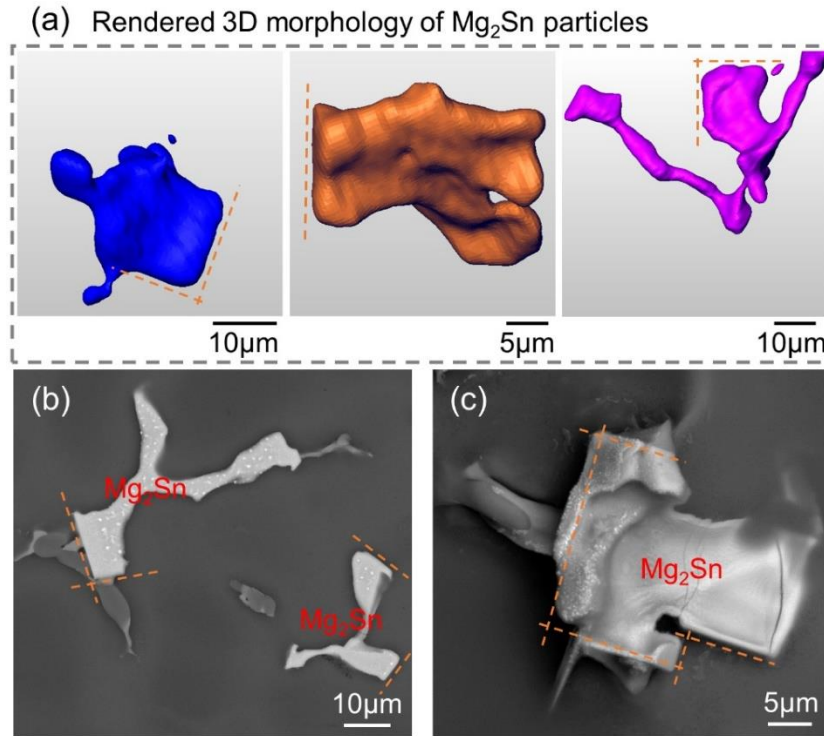


Fig. 8 Facets of Mg_2Sn phase revealed by XCT and deep etching methods. (a) Rendered Mg_2Sn phase from datasets in Fig. 7a; (b) Facets of Mg_2Sn between $\beta\text{-Mg}_{17}\text{Al}_{12}$, $\tau\text{-MgAlZn}$, and $\alpha\text{-Mg}$ phase in 2D cross-section; (c) 3D morphology of eutectic phases after selectively dissolving of $\alpha\text{-Mg}$. The facets of Mg_2Sn are marked with orange dashed lines.

Based on the multi-phase particles we measured by EBSD, the facets of Mg_2Sn were indexed by 2D plane traces analysis. Fig. 9a-c shows band contrast maps of multi-phase particles superimposed by Mg_2Sn phase. The 3D shape of Mg_2Sn phase was bounded by a combination of faceted and non-faceted growth morphology (Fig. 8a). These appeared to be straight or curved interphase boundaries in 2D cross-section (Fig. 9d-f), respectively. Since the Euler angles of the particles (shown in Fig. 9a-c) were measured on a 2D (X-Y plane) cross-section by EBSD, intersection traces between the symmetry equivalent crystal planes to the X-Y sample reference plane were calculated using MATLAB with MTEX toolbox. Crystallographic plane traces of the chosen plane families of the Mg_2Sn (cubic symmetry) were plotted on the X-Y plane as the black line marked in Fig. 9a-c. 2D straight interphase boundaries were presented with orange dashed lines in Fig. 9d-f. These straight boundaries in BSE images belonged to one or several $\{100\}$ plane traces of Mg_2Sn phase (Fig. 9a-c). In the present study, 41 out of

44 facets were consistent with $\{100\}$ planes of Mg_2Sn .

The growth facets of Mg_2Sn were further analyzed in STEM, with the membrane prepared by FIB lift-out. Fig. 10a shows one typical multi-phase particle used for FIB sectioning (the same particle in Fig. 5). A TEM membrane was sectioned through the particle perpendicular to the major facet (as indicated by the orange dashed line in Fig. 10a) after deposition of a Pt layer. The cross-sectioned microstructure of this particle was seen from the thinning process SEM images (Fig. 10b-c), where the Mg_2Sn particle clearly showed a facet. The bright-field TEM image showed the Mg_2Sn facet (dashed line in orange, Fig. 10d) view along $[110]_{\text{Mg}_2\text{Sn}}$ zone axis, with SAED pattern inserted in Fig. 10e. As marked by the red dashed line with arrow, the normal direction of the growth facet of Mg_2Sn was near-parallel to the reciprocal lattice vector of the $(002)_{\text{Mg}_2\text{Sn}}$ plane, which further supports the trace analysis of EBSD in Fig. 9.

Therefore, Mg_2Sn showed $\{100\}$ faceting mixed with non-faceted morphology during solidification of the $\text{Mg-4Sn-3Al-1.3Zn-0.6Mn}$ alloy. It is noted that $\beta\text{-Mg}_{17}\text{Al}_{12}$ and $\tau\text{-MgAlZn}$ phases often grew from a common $\{100\}$ facet of Mg_2Sn , forming a multi-phase particle. It is emphasized that, the actual atomic interface between Mg_2Sn and $\beta\text{-Mg}_{17}\text{Al}_{12}$ / $\tau\text{-MgAlZn}$ might not be $\{100\}$ planes, as stepped and curved interfaces were observed from cross-sectioned micrographs of a multi-phase particle using TEM (Fig. 5a and Fig. 10d).

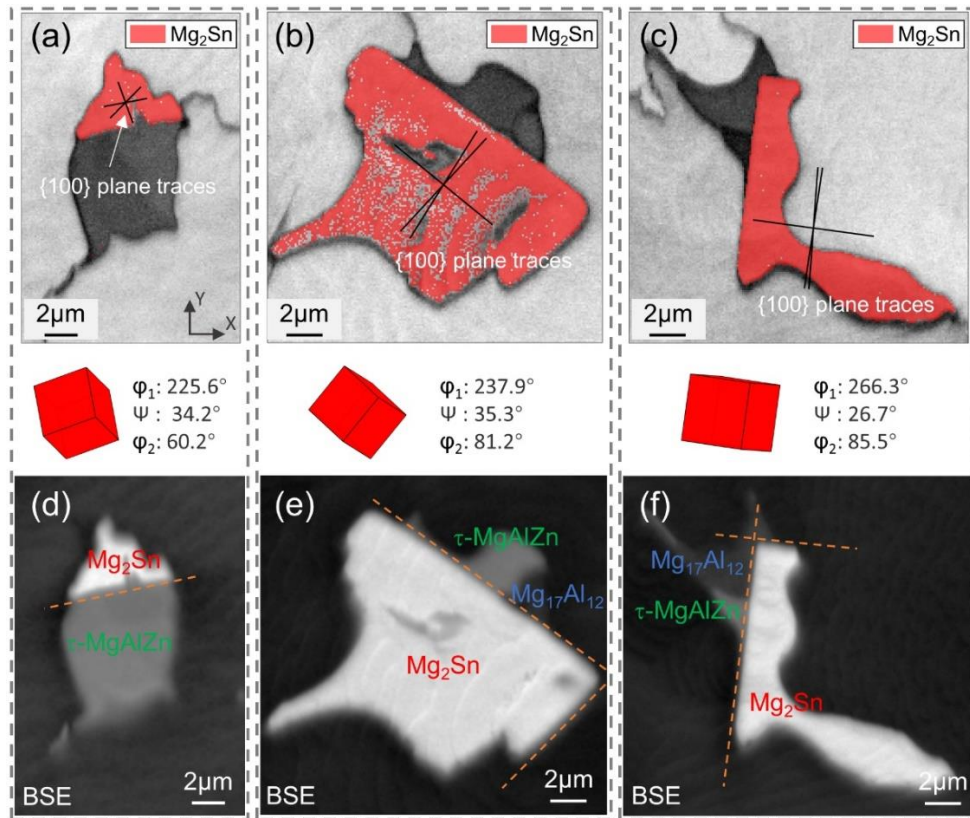


Fig. 9 Two-dimension (2D) facet analyses for three typical multi-phase particles in Mg-4Sn-3Al-1Zn-0.6Mn alloy. (a-c) Phase map with $\{100\}$ crystallographic plane traces and Euler angle of Mg_2Sn in three particles; (d-f) BSE images of three particles, and 2D straight interphase boundaries were presented with orange dashed line.

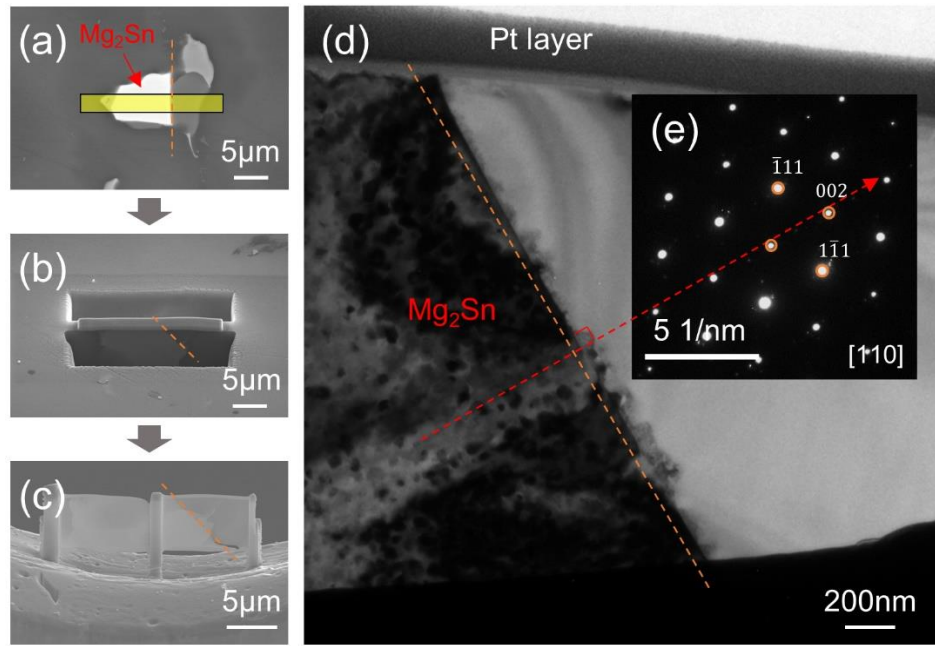


Fig. 10 A typical site-specific multi-phase particle was analyzed, combining FIB sectioning and TEM. (a) one typical multi-phase particles with faceted Mg_2Sn and other two phases ($\beta\text{-Mg}_{17}\text{Al}_{12}$, and $\tau\text{-MgAlZn}$); (b-c) SEM images of cross-section profile during FIB sectioning process; (d) bright-field TEM image view along $[110]_{\text{Mg}_2\text{Sn}}$ zone axis, with (e) the diffraction pattern of Mg_2Sn inserted. The orange dashed lines represent growth facets of Mg_2Sn , while the red dashed line with an arrow represents the normal direction to facet.

4. Discussion

4.1. Orientation relationships between IMCs within eutectic multi-phase particles

In $\text{Mg-4Sn-3Al-1Zn-0.6Mn}$ alloy, three phases (Mg_2Sn (A), $\beta\text{-Mg}_{17}\text{Al}_{12}$ (B), and $\tau\text{-MgAlZn}$ (C)) within multi-phase eutectic particles usually had reproducible ORs among each other. A reproducible misorientation angle (MOA) between two phases is considered as a critical prerequisite for a reproducible OR. MOA was defined as the smallest angle between all possible pairs of symmetrically equivalent orientations from two phases. The advantages of EBSD based OR analysis over TEM techniques were mainly that numerous particles could be efficiently measured, and statistical information about ORs was accessible for multiple particles. Our analysis approach is similar to Refs.[55-60].

Fig. 11 summarized the determined ORs between three phases (Mg_2Sn (A, in red), $\beta\text{-Mg}_{17}\text{Al}_{12}$ (B, in blue), and $\tau\text{-MgAlZn}$ (C, in green)). From now on we use this color code to show the identity of these three phases. The left column in Fig. 11 displays EBSD phase maps of several multi-phase particles for (a-b) Mg_2Sn and $\beta\text{-Mg}_{17}\text{Al}_{12}$, (c-d) Mg_2Sn and $\tau\text{-MgAlZn}$,

and (e-g) β -Mg₁₇Al₁₂ and τ -MgAlZn. The middle two columns present pole figures to reveal the planes and directions in parallel, with marked circles showing the coincidence of poles between phases. Unit cell models were also plotted here using Euler angles of each grain as inputs, to geometrically describe the ORs between phases. Note that equal size cubes were used for better visual comparisons, regardless of the lattice parameters of each phase. The right column is the MOA distribution histogram of the corresponding two phases within one particle, and calculated from uncorrelated misorientation between pixels of each phase. The reproducibility of each OR described here was confirmed with the coincidence of crystallographic planes/directions in pole figures, and arrangement of cubic geometrical models, as well as similar values of uncorrelated MOA, as shown in Fig. 11. All the determined ORs are summarized in Table 5, including corresponding crystallographic parallelism, MOA value, and the determined frequency of each OR. Note that in Table 5, theoretical MOAs were also calculated after the defined ORs and found to fall within the range of the measured MOAs ($\pm$ std), suggesting good agreements between measured and defined ORs.

As an example, Fig. 11a shows a particle that contains Mg₂Sn (**A**) and β -Mg₁₇Al₁₂ (**B**). The MOA between the two phases was $45.8 \pm 2.6^\circ$. A reproducible OR named **OR-AB1** was presented in the pole figure with one of the $\{012\}_A$ poles overlapping with one of the $\{1\bar{1}1\}_B$, and further, one $\langle 22\bar{1} \rangle_A$ pole overlapping with one $\langle 110 \rangle_B$. The OR between Mg₂Sn (**A**) and β -Mg₁₇Al₁₂ (**B**) in another multi-phase particle in Fig. 11b was defined as **OR-AB2**. The coincidence of $\{1\bar{1}1\}_A$ and $\{2\bar{3}3\}_B$ poles, and $\langle 1\bar{1}0 \rangle_A$ pole overlapping with $\langle 30\bar{2} \rangle_B$ were observed. MOA of **OR-AB2** in this particle was calculated to be $52.6 \pm 1.0^\circ$. Among 26 particles containing Mg₂Sn (**A**) and β -Mg₁₇Al₁₂ (**B**), 11 particles were pertinent to the **OR-AB1**, while 5 **OR-AB2** were measured. Note that standard angle deviation in MOA for each OR was calculated from reproducible MOA value in datasets, and the smaller the deviation indicates the better reproducibility. Thus, the **OR-ABs** between Mg₂Sn (**A**) and β -Mg₁₇Al₁₂ (**B**) could be summarized as follows:

$$\{012\}_A \parallel \{1\bar{1}1\}_B \ \& \ \langle 22\bar{1} \rangle_A \parallel \langle 110 \rangle_B \text{ with MOA } 45.8 \pm 2.6^\circ \quad (\text{OR-AB1})$$

$$\{1\bar{1}1\}_A \parallel \{2\bar{3}3\}_B \ \& \ \langle 1\bar{1}0 \rangle_A \parallel \langle 30\bar{2} \rangle_B \text{ with MOA } 52.6 \pm 1.0^\circ \quad (\text{OR-AB2})$$

With the same method, the determined ORs between Mg_2Sn (A) and $\tau\text{-MgAlZn}$ (C) are shown in Fig. 11c-d and Table 5. The **OR-AC1** was identified in the pole figures as shown in Fig. 11c, where one pole of the $\{1\bar{1}1\}_A$ and three poles of the $\langle 110 \rangle_A$ coincided with $\{1\bar{1}1\}_C$ and $\langle 53\bar{2} \rangle_C$ poles, respectively. **OR-AC2** was also identified as presented in Fig. 11d. As listed in Table 5, 18 out of 33 particles have the **OR-AC1** and 10 are consistent with the **OR-AC2**, indicating reproducibility and validity of the ORs. Hence, the **OR-ACs** between Mg_2Sn (A) and $\tau\text{-MgAlZn}$ (C) could be written as follows:

$$\{1\bar{1}1\}_A \parallel \{1\bar{1}1\}_C \ \& \ \langle 110 \rangle_A \parallel \langle 53\bar{2} \rangle_C \text{ with MOA } 23.1 \pm 0.8^\circ \quad (\text{OR-AC1})$$

$$\{1\bar{1}\bar{1}\}_A \parallel \{0\bar{1}0\}_C \ \& \ \langle 110 \rangle_A \parallel \langle 00\bar{1} \rangle_C \text{ with MOA } 54.8 \pm 1.1^\circ \quad (\text{OR-AC2})$$

As shown in section 3.3, $\beta\text{-Mg}_{17}\text{Al}_{12}$ (B) and $\tau\text{-MgAlZn}$ (C) phases existed in the form of fully divorced eutectic in $\text{Mg-4Sn-3Al-1Zn-0.6Mn}$ alloy. Fig. 11e-g show **OR-BCs** parallelisms within three multi-phase particles in $\text{Mg-4Sn-3Al-1Zn-0.6Mn}$ alloy, with MOA 35.6 ± 1.0 , 40.9 ± 1.4 , 56.0 ± 1.3 degrees for **OR-BC1,2,3**, respectively. Therefore, **OR-BCs** could be written as follows:

$$\{\bar{1}10\}_B \parallel \{\bar{1}\bar{1}\bar{1}\}_C \ \& \ \langle 001 \rangle_B \parallel \langle \bar{3}\bar{2}5 \rangle_C \text{ with MOA } 35.6 \pm 1.0^\circ \quad (\text{OR-BC1})$$

$$\{0\bar{1}1\}_B \parallel \{\bar{3}35\}_C \ \& \ \langle 566 \rangle_B \parallel \langle \bar{1}\bar{1}0 \rangle_C \text{ with MOA } 40.9 \pm 1.4^\circ \quad (\text{OR-BC2})$$

$$\{1\bar{1}\bar{1}\}_B \parallel \{00\bar{1}\}_C \ \& \ \langle 110 \rangle_B \parallel \langle 100 \rangle_C \text{ with MOA } 56.0 \pm 1.3^\circ \quad (\text{OR-BC3})$$

The same **OR-BCs** were also found in partially divorced $\beta\text{-Mg}_{17}\text{Al}_{12}$ (B) / $\tau\text{-MgAlZn}$ (C) eutectic particles in Mg-3Al-1Zn-0.3Mn alloy, as shown in Fig. 12. Table 5 summarizes the consistency of three types of **OR-BCs** in Mg-3Al-1Zn-0.3Mn with $\text{Mg-4Sn-3Al-1Zn-0.6Mn}$ alloy, indicating these three types of reproducible ORs between $\beta\text{-Mg}_{17}\text{Al}_{12}$ (B) and $\tau\text{-MgAlZn}$ (C) all existed in both alloys.

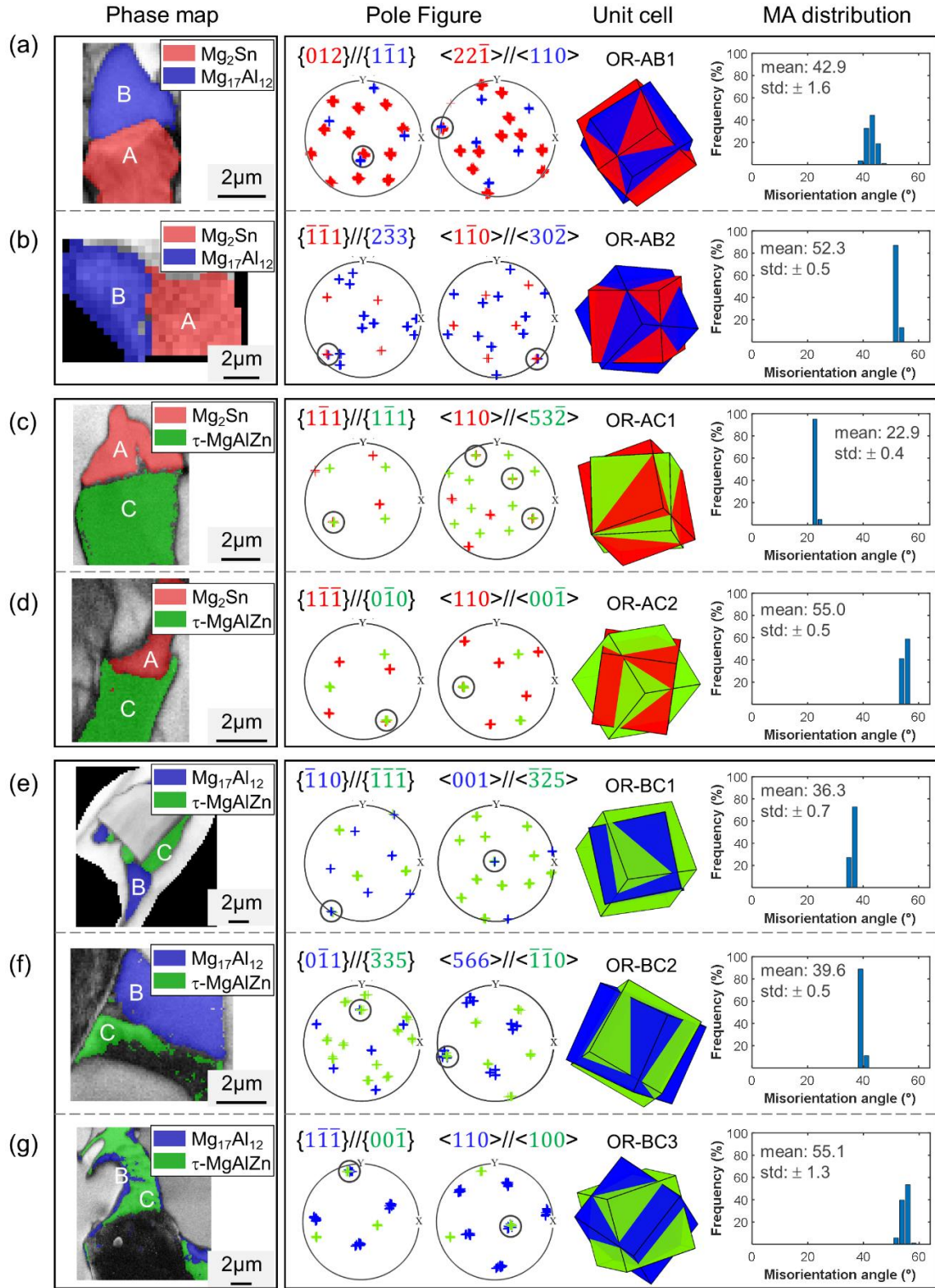


Fig. 11 Summary of the determined ORs within typical multi-phase particle pairs in Mg-4Sn-3Al-1Zn-0.6Mn alloy. (a-b) Mg₂Sn (A) and β-Mg₁₇Al₁₂ (B), (c-d) Mg₂Sn (A) and τ-MgAlZn (C), (e-g) β-Mg₁₇Al₁₂ (B) and τ-MgAlZn (C).

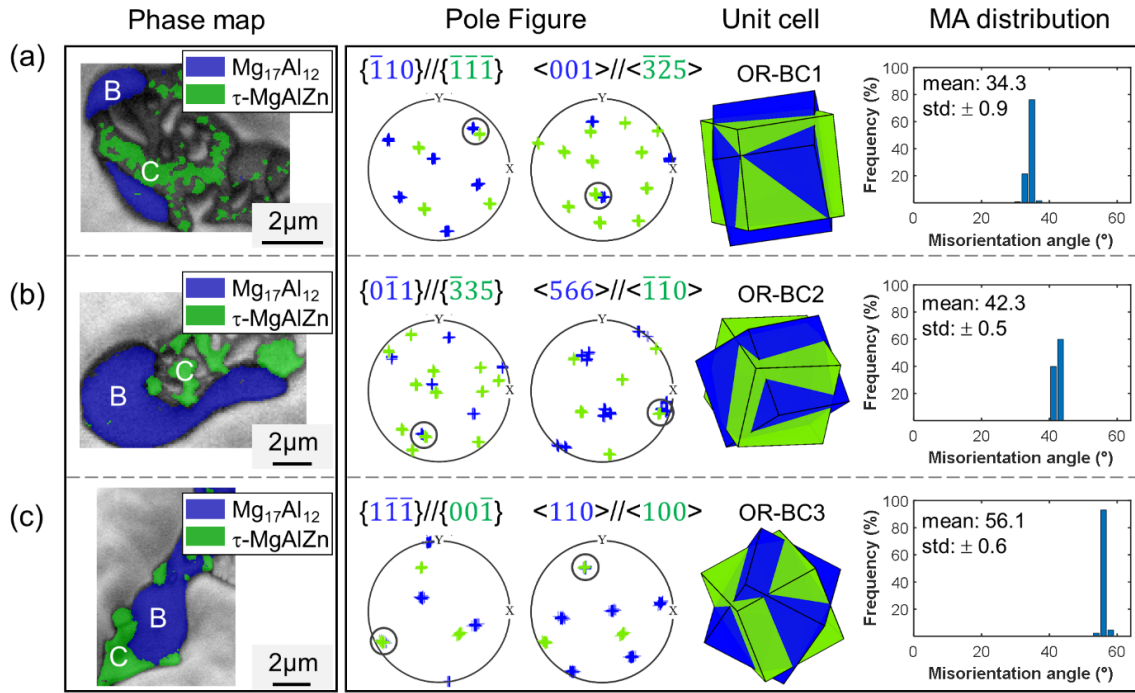


Fig. 12 Determined ORs within partially eutectic multi-phase particles in Mg-3Al-1Zn-0.3Mn alloy. (a-c) β-Mg₁₇Al₁₂ (B) and τ-MgAlZn (C) phase.

Table 5 A summary of orientation relationships (ORs) within multi-phase particles.

Alloy	Phase	OR	Parallelism	Misorientation	Theoretical	Determined
				Angle [°]	MOA [°]	Frequency
Mg-4Sn-3Al-1Zn-0.6Mn	Mg ₂ Sn / β-Mg ₁₇ Al ₁₂	AB1	{012} _A //{111} _B , <221> _A //<110> _B	45.8 ± 2.6	45.8	11 / 26
		AB2	{111} _A //{233} _B , <110> _A //<302> _B	52.6 ± 1.0	54.0	5 / 26
	Mg ₂ Sn / τ-MgAlZn	AC1	{111} _A //{111} _C , <110> _A //<532> _C	23.1 ± 0.8	22.7	18 / 33
		AC2	{111} _A //{010} _C , <110> _A //<001> _C	54.8 ± 1.1	56.6	10 / 33
	β-Mg ₁₇ Al ₁₂ / τ-MgAlZn	BC1	{110} _B //{111} _C , <001> _B //<325> _C	35.6 ± 1.0	35.9	5 / 24
		BC2	{011} _B //{335} _C , <566> _B //<110> _C	40.9 ± 1.4	39.5	4 / 24
		BC3	{111} _B //{001} _C , <110> _B //<100> _C	56.0 ± 1.3	56.6	6 / 24
	B / C					
Mg-3Al-1Zn-0.3Mn	β-Mg ₁₇ Al ₁₂ / τ-MgAlZn	BC1	{110} _B //{111} _C , <001> _B //<325> _C	35.9 ± 1.3	35.9	3 / 14
		BC2	{011} _B //{335} _C , <566> _B //<110> _C	41.2 ± 1.6	39.5	3 / 14
		BC3	{111} _B //{001} _C , <110> _B //<100> _C	55.6 ± 1.5	56.6	5 / 14

Fig. 13 shows EBSD mapping of three phases, Mg_2Sn (A), $\beta\text{-Mg}_{17}\text{Al}_{12}$ (B), and $\tau\text{-MgAlZn}$ (C), for three typical multi-phase particles in Mg-4Sn-3Al-1Zn-0.6Mn alloy. For each particle, the unit cell geometric models for various ORs were attached to the bottom and labeled, showing the interrelationship between the three phases. It shows that there were different combinations of ORs when three phases were simultaneously present in one particle.

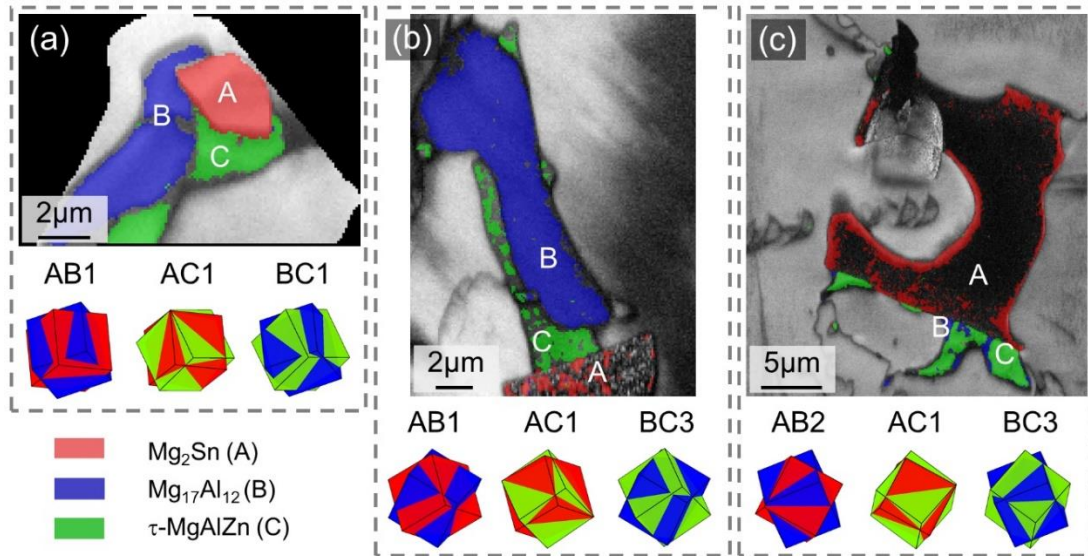


Fig. 13 EBSD mapping for three phases, Mg_2Sn (A, in red), $\beta\text{-Mg}_{17}\text{Al}_{12}$ (B, in blue), and $\tau\text{-MgAlZn}$ (C, in green), within three typical multi-phase particles in Mg-4Sn-3Al-1Zn-0.6Mn alloy. ORs between phase pairs are illustrated by unit cell geometric models with OR type labeled.

4.2. Orientation relationships between $\alpha\text{-Mg}$ matrix and IMCs

$\beta\text{-Mg}_{17}\text{Al}_{12}$ or Mg_2Sn have a variety of orientation relationships with the $\alpha\text{-Mg}$ matrix during solid-state phase transformations [61,62], as precipitating during the heat treatment process of Mg-(Sn)-Al-Zn alloys. The relationships between the $\alpha\text{-Mg}$ matrix and the eutectic IMCs were verified for as-cast microstructure in the present study. $\alpha\text{-Mg}$ has a hexagonal close-packed (HCP) crystal structure, while $\beta\text{-Mg}_{17}\text{Al}_{12}$ and Mg_2Sn are cubic structures; therefore we used the misfit angle between the $\{0001\}_{\text{hcp}}$ and the $\{100\}_{\text{cubic}}$ to discriminate the existence of ORs in our datasets. Once there is a reproducible OR, the angle between pre-defined axes of crystals remains constant [59,60]. Fig. 14a and b show a representative $\beta\text{-Mg}_{17}\text{Al}_{12}$ particle in Mg-3Al-1Zn-0.3Mn alloy and a Mg_2Sn particle in Mg-4Sn-3Al-1Zn-0.6Mn alloy, respectively. They were divorced eutectic particles located at the grain boundary with two $\alpha\text{-Mg}$

Mg grains 1 and 2. The geometric unit cell models plotted from Euler angles were superimposed on IPF maps. The unit cells and corresponding $\{0001\}_{\alpha\text{-Mg}}$ and $\{100\}_{\text{cubic}}$ pole figures were shown at the bottom of Fig. 14a and b. The misfit angle here, the minimum angle between $\{0001\}_{\alpha\text{-Mg}}$ and $\{100\}_{\text{cubic}}$, was calculated for two $\alpha\text{-Mg}$ grains and two eutectic IMCs, as displayed in the pole figure of $\{100\}_{\text{cubic}}$ superimposed by $\{0001\}$ of $\alpha\text{-Mg}$.

For $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase, seven ORs with $\alpha\text{-Mg}$ matrix have been determined in Refs.[63-65]. The large misfit angles ($>10^\circ$) between the pairs of parallelism for these possible ORs were calculated, indicating that the reported ORs do not exist between the eutectic $\beta\text{-Mg}_{17}\text{Al}_{12}$ and $\alpha\text{-Mg}$ matrix in the present study. Moreover, the misfit angle between $\{0001\}_{\alpha\text{-Mg}}$ and $\{100\}_{\beta\text{-Mg}_{17}\text{Al}_{12}}$, calculated from 47 pairs of our datasets, also exhibited a nearly random distribution, as shown in Fig. 14c. The statistical results prove that no specific ORs existed between the eutectic $\beta\text{-Mg}_{17}\text{Al}_{12}$ and $\alpha\text{-Mg}$ matrix, which is consistent with $\beta\text{-Mg}_{17}\text{Al}_{12}$ in Ref.[66]. For Mg_2Sn phase, the misfit angles for $\{100\}_{\text{Mg}_2\text{Sn}}$ and $\{0001\}_{\alpha\text{-Mg}}$, calculated from 49 pairs, were presented in Fig. 14d. There was an approximately random distribution of misfit angles within $15\text{-}45^\circ$. Furthermore, the misfit angles between $\{10\bar{1}0\}_{\alpha\text{-Mg}}$ and $\{100\}_{\text{Mg}_2\text{Sn}}$ were calculated for 15 pairs in $25\text{-}33^\circ$ range (gray frame in Fig. 14d). As shown in Fig. 14e, a discrete distribution ranged from 10° to 30° , and it confirms no reproducible OR between the eutectic Mg_2Sn and $\alpha\text{-Mg}$ matrix as well.

Hence, there are no reproducible ORs formed between $\alpha\text{-Mg}$ phase and multiple eutectic reaction products. Such a weak relationship suggests non-interactive nucleation of the eutectic intermetallics on the $\alpha\text{-Mg}$ phase in both Mg-Sn-Al-Zn-Mn and Mg-Al-Zn-Mn alloy. In contrast, there were frequently reproducible ORs among the various eutectic intermetallics within a multi-phase/dual phase particle in the two alloys, as discussed in section 4.1.

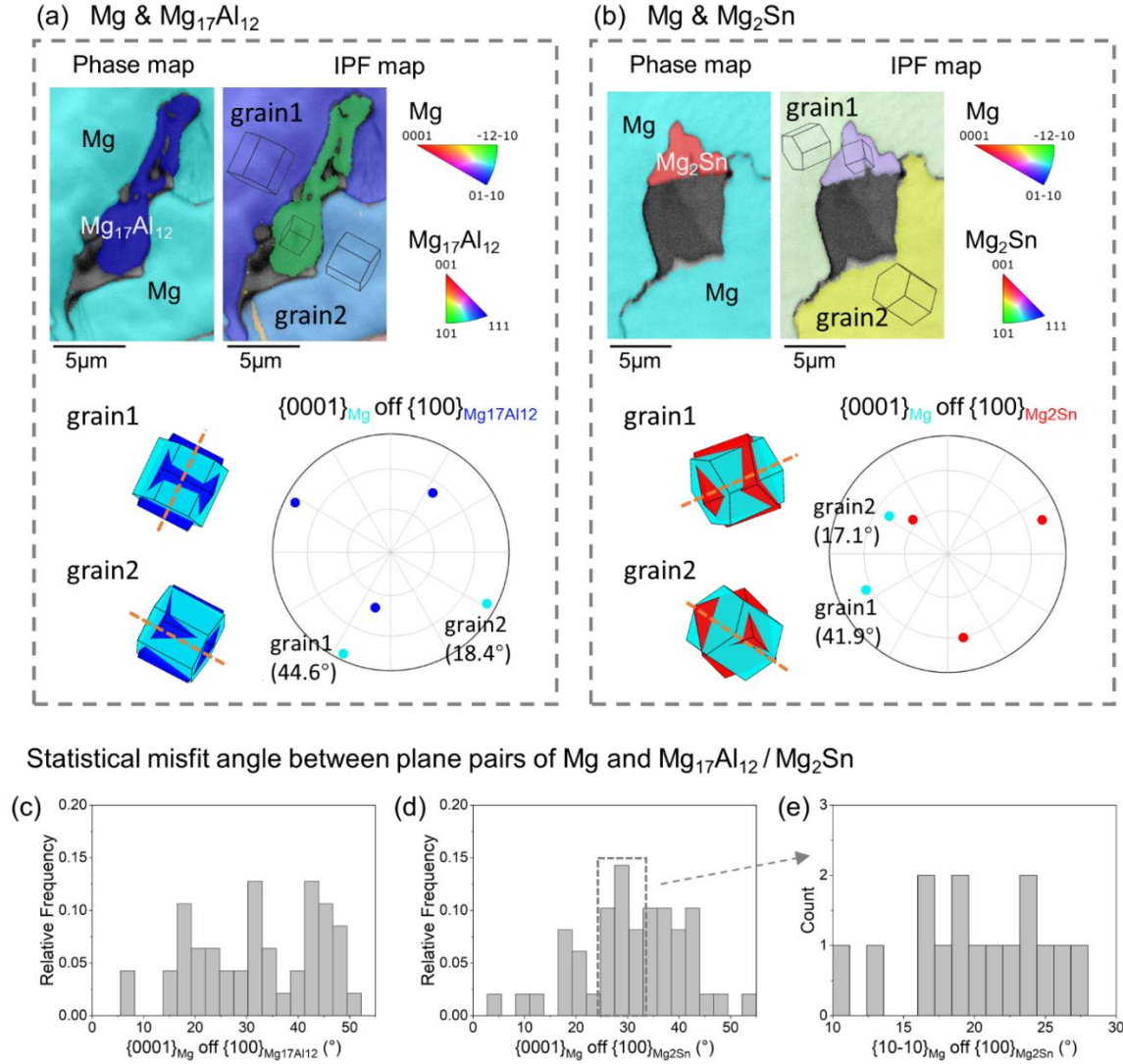


Fig. 14 EBSD datasets for (a) β -Mg₁₇Al₁₂ grain embedded in α -Mg matrix (Mg-3Al-1Zn-0.3Mn), and (b) Mg₂Sn particle surrounded by two α -Mg grains (Mg-4Sn-3Al-1Zn-0.6Mn). Unit cell models and pole figures of {0001} _{α -Mg} superimposed by {100} _{β -Mg₁₇Al₁₂} / {100}_{Mg₂Sn} were plotted here for each grain to illustrate the misfit angles. Misfit angle distribution was calculated between (c) {0001} _{α -Mg} / {100} _{β -Mg₁₇Al₁₂} (47 pairs), (d) {0001} _{α -Mg} / {100}_{Mg₂Sn} (49 pairs), and (e) {10 $\bar{1}$ 0} _{α -Mg} / {100}_{Mg₂Sn} (15 pairs).

4.3. OR correlations with τ -MgAlZn icosahedral approximant and lattice match

Among the ORs measured in Section 4.1, the two **OR-ACs** between Mg₂Sn (A) and τ -MgAlZn (C) had the best lattice match and can be linked to the orientation of the icosahedral clusters in the τ -MgAlZn (Mg₃₂(Al,Zn)₄₉) phase, a body-centered cubic crystalline approximant of a quasicrystalline phase [20]. This can be understood in Fig. 15, where the Mg₃-centred icosahedral coordination polyhedron (Fig. 15b and c) remains unchanged in the two ORs with

respect to a ‘fixed’ Mg_2Sn orientation. Note that the green polyhedron shown here is the innermost shell of icosahedral coordination and there are in total four similarly oriented shells with the same icosahedral symmetry in $\tau\text{-MgAlZn}$ [67,68]. It is also worth noting that not all the icosahedral variants were measured, and experimentally only two such variants were repeatedly measured, in the case of $\tau\text{-MgAlZn}$ nucleated on Mg_2Sn with reproducible **OR-ACs**.

These two preferred ORs were found to form a reasonable lattice match between the two phases. As shown in Fig. 15a, the origin ‘O’ of the planar lattice match is aligned with the Mg1 site of $(1\bar{1}1)_{\text{Mg}_2\text{Sn}}$ and the Mg3 site of $(1\bar{1}1)_{\tau\text{-MgAlZn}}$, from where hexagonal rings of atoms of each phase are well aligned despite a few vacancies. For **OR-AC1**, the common planes of **A-C** phases are of the same cubic $\{1\bar{1}1\}$ family, consequently they (i.e. plane normals) coincide with the rotation axis producing the MOA of $\sim 23.1 \pm 0.8^\circ$. This MOA of $\sim 23^\circ$ could be visually seen in Fig. 15a as a rotation around the common $\{1\bar{1}1\}$ planes. Fig. 15c shows the lattice match of **OR-AC2** originating at the Mg1 site of $(1\bar{1}\bar{1})_{\text{Mg}_2\text{Sn}}$ and the Mg4 site of $(0\bar{1}0)_{\tau\text{-MgAlZn}}$. Apart from the good lattice matching in rings of atoms around the origin ‘O’, there are additionally excellent linear atomic match vertically along $[\bar{1}12]_{\text{Mg}_2\text{Sn}} \parallel [100]_{\tau\text{-MgAlZn}}$. Note that two pairs of common directions are marked in Fig. 15c, which can occur at the same time crystallographically and we chose to define **OR-AC2** with the lower-index directions, $[110]_{\text{Mg}_2\text{Sn}} \parallel [00\bar{1}]_{\tau\text{-MgAlZn}}$.

The good lattice match between **OR-ACs** suggest the actual nucleation interface (i.e. common planes in defined ORs) on Mg_2Sn is likely to be $\{111\}_{\text{Mg}_2\text{Sn}}$ rather than the growth facets of $\{100\}_{\text{Mg}_2\text{Sn}}$ (see the curved interface in Fig. 5a), and the Mg_2Sn particles could serve as potent nuclei for $\tau\text{-MgAlZn}$. The lattice match of **OR-ABs** (Fig. S1) and **OR-BCs** (Fig. S2) can be found in supplementary information. They are not as good as those of **OR-ACs** probably due to the more complicated Kasper polyhedron (CN16 around the Al1 site) in $\text{Mg}_{17}\text{Al}_{12}$. However, the measured/defined ORs, which are highly reproducible, all contain parallelisms between the closely-packed planes in each phase, as summarized in Table 5.

In this study, the eutectic IMCs formed in a fully/partially divorced morphology, with no reproducible OR to the $\alpha\text{-Mg}$ but with multiple reproducible ORs among the eutectic IMCs

(Table 5). The measured ORs and relevant good lattice match, which involves parallel lattice directions in addition to parallel closed packed planes between the IMCs, imply Mg_2Sn being the potential nuclei in the ORs. This multicomponent divorced eutectic growth occurred over a wide temperature range ($>100\text{K}$, Fig. 1), where $\alpha\text{-Mg}$ started forming first, Mg_2Sn formed next and $\beta\text{-Mg}_{17}\text{Al}_{12}$ and $\tau\text{-MgAlZn}$ formed in the last stages of solidification. Therefore, these are not ORs due to coupled growth of phases growing together but are due to $\beta\text{-Mg}_{17}\text{Al}_{12}$ and $\tau\text{-MgAlZn}$ nucleating on pre-existing Mg_2Sn in the remaining liquid between $\alpha\text{-Mg}$ dendrites, in the last stages of divorced eutectic growth. This is due to both (i) Al and Zn solute being rejected and accumulating in the liquid ahead of both $\alpha\text{-Mg}$ and Mg_2Sn , and then (ii) Mg_2Sn offering the most favourable nucleation site for $\beta\text{-Mg}_{17}\text{Al}_{12}$ and $\tau\text{-MgAlZn}$ in the last remaining liquid.

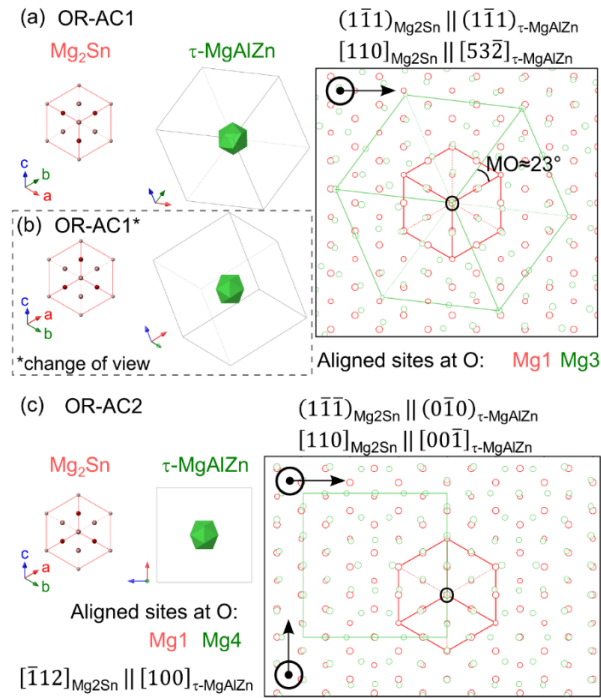


Fig. 15 Lattice match of OR-ACs and their correlations with the icosahedral coordination in $\tau\text{-MgAlZn}$ (C). (a) Unit cells aligned following OR-AC1 and projected lattice match of parallel planes only (with common directions pointing east). (b) A different view of OR-AC1, with parent Mg_2Sn wireframe reoriented equivalent to (c). (c) Unit cells aligned following OR-AC2 and projected lattice match of parallel planes only (with two pairs of common directions marked on).

5. Conclusions

Eutectic intermetallic compound (IMC) formation has been investigated during the solidification of a Mg-4Sn-3Al-1Zn-0.6Mn and Mg-3Al-2Zn-0.3Mn alloy by analytical SEM, EBSD, FIB-TEM, and XCT techniques, combined with thermodynamic calculations. Phase identification, 3D growth morphology, and crystallographic relationships for these intermetallics were explored. The following conclusions can be drawn from this study:

1. The as-cast microstructure consists of equiaxed α -Mg dendrites with various IMCs distributed in interdendritic areas: τ -AlMn, Al_8Mn_5 , Mg_2Sn , $\beta\text{-Mg}_{17}\text{Al}_{12}$, and $\tau\text{-MgAlZn}$ (also known as $\text{Mg}_{32}(\text{Al,Zn})_{49}$). The latter three IMCs formed in eutectic reactions late during solidification.
2. In Mg-Sn-Al-Zn-Mn alloy, the majority of multi-phase particles consisted of Mg_2Sn , $\beta\text{-Mg}_{17}\text{Al}_{12}$, and $\tau\text{-MgAlZn}$. Mg_2Sn eutectic phase formed in the temperature range of 472 °C to 337 °C (Fig. 1). Most Mg_2Sn phases shared an interphase boundary with $\beta\text{-Mg}_{17}\text{Al}_{12}$ and $\tau\text{-MgAlZn}$ grains, to form fully divorced eutectic multi-phase particles. $\beta\text{-Mg}_{17}\text{Al}_{12}$ and $\tau\text{-MgAlZn}$ phases in the Mg-Al-Zn-Mn alloy tended to form partially divorced eutectic morphology.
3. The 3D shape of Mg_2Sn exhibited $\{100\}$ faceting mixed with non-faceted morphology during solidification of the Mg-4Sn-3Al-1.3Zn-0.6Mn alloy. $\beta\text{-Mg}_{17}\text{Al}_{12}$ and $\tau\text{-MgAlZn}$ grains often simultaneously grew on a $\{100\}$ facet of Mg_2Sn .
4. Within multi-phase particles, reproducible orientation relationships (ORs) were found among the eutectic intermetallics of Mg_2Sn (**A**), $\beta\text{-Mg}_{17}\text{Al}_{12}$ (**B**) and $\tau\text{-MgAlZn}$ (**C**). Seven ORs (**OR-AB1,2**, **OR-AC1,2**, **OR-BC1,2,3**) have been determined. In contrast, no reproducible ORs existed between primary α -Mg matrix and the eutectic intermetallics during solidification.
5. The ORs between Mg_2Sn (**A**) and $\tau\text{-MgAlZn}$ (**C**) were found to have the best lattice match among the observed ORs. Both **OR-ACs** between two these phases, have the same OR between Mg_2Sn and the icosahedral building block in the $\tau\text{-MgAlZn}$ phase.

CRediT authorship contribution statement

Yangchao Deng: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Software, Writing - original draft. **Guang Zeng:** Conceptualization, Software, Writing - review & editing, Supervision, Funding acquisition. **Jingwei Xian:** Methodology, Writing - review & editing. **Hongyi Zhan:** Methodology. **Chuming Liu:** Supervision. **Christopher M. Gourlay:** Writing - review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could influence this work.

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Data Availability

The raw/processed data required to obtain these results can be shared upon reasonable request to the corresponding author.

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List of Figure captions:

Fig. 1 Calculated equilibrium and Scheil solidification paths for (a) Mg-4Sn-3Al-1Zn-0.6Mn alloy and (b) Mg-3Al-1Zn-0.3Mn alloy, using PANDATTM software with PanMg2020 database.

Fig. 2 Typical solidified microstructural features in Mg-4Sn-3Al-1Zn-0.6Mn alloy and Mg-3Al-1Zn-0.3Mn alloy. (a, g) Lower magnification BSE images of two cast alloys, (b, h) EBSD orientation map (IPF-Z) of α -Mg phase with average grain size shown in maps, intermetallic compounds (IMCs) in (c-f) Mg-4Sn-3Al-1Zn-0.6Mn alloy and (i-l) Mg-3Al-1Zn-0.3Mn alloy.

Fig. 3 Intermetallic compounds present in as-cast Mg-4Sn-3Al-1Zn-0.6Mn alloy. (a) BSE image of rod-like and blocky particles with point **A** and **B** indexed, (b) BSE image of one multi-phase particle with point **C**, **D**, and **E** indexed, (c) BSE image of another typical multi-phase particle, (d-h) EDS maps of Mg, Sn, Al, Zn, and Mn element for the particle in (c).

Fig. 4 Phase identification of various intermetallics using experimental Kikuchi patterns. (a-c) Al_8Mn_5 phase; (d-f) τ -AlMn phase; (g-i) Mg_2Sn phase; (j-l) $\text{Mg}_{17}\text{Al}_{12}$ phase; (m-o) τ -MgAlZn phase. The left column is SE image, and middle column is experimental pattern, and right column is indexed result on the same pattern.

Fig. 5 TEM characterization of a typical eutectic multi-phase particle in Mg-4Sn-3Al-1Zn-0.6Mn alloy. (a) HADDF-STEM image of the particle with three phases (**A**, **B**, **C**) separated by the colored dashed line, (b) representative SAED patterns for **A** = Mg_2Sn , **B** = β - $\text{Mg}_{17}\text{Al}_{12}$, and **C** = τ -MgAlZn phase, (c) EDS-STEM maps of Mg, Sn, Al, Zn elements for the particle.

Fig. 6 EBSD mapping for a representative divorced eutectic particle in Mg-4Sn-3Al-1Zn-0.6Mn alloy. (a) Band contrast map, (b) Phase map, (c) IPF-Z map.

Fig. 7 Typical multi-phase eutectic particles in Mg-4Sn-3Al-1Zn-0.6Mn alloy and Mg-3Al-1Zn-0.3Mn alloy. (a, d) Three-dimension (3D) reconstruction of XCT images; (b, e) 2D cross-section BSE images; (c, f) deep-etched micrograph of eutectics. **A** = Mg_2Sn , **B** = β - $\text{Mg}_{17}\text{Al}_{12}$, and **C** = τ -MgAlZn phase.

Fig. 8 Facets of Mg_2Sn phase revealed by XCT and deep etching methods. (a) Rendered Mg_2Sn phase from datasets in Fig. 7a; (b) Facets of Mg_2Sn between β - $\text{Mg}_{17}\text{Al}_{12}$, τ -MgAlZn, and α -Mg phase in 2D cross-section; (c) 3D morphology of eutectic phases after selectively dissolving of α -Mg. The facets of Mg_2Sn are marked with orange dashed lines.

Fig. 9 Two-dimension (2D) facet analyses for three typical multi-phase particles in Mg-4Sn-3Al-1Zn-0.6Mn alloy. (a-c) Phase map with $\{100\}$ crystallographic plane traces and Euler angle of Mg_2Sn in three particles; (d-f) BSE images of three particles, and 2D straight

interphase boundaries were presented with orange dashed line.

Fig. 10 A typical site-specific multi-phase particle was analyzed, combining FIB sectioning and TEM. (a) one typical multi-phase particles with faceted Mg_2Sn and other two phases ($\beta\text{-Mg}_{17}\text{Al}_{12}$, and $\tau\text{-MgAlZn}$); (b-c) SEM images of cross-section profile during FIB sectioning process; (d) bright-field TEM image view along $[110]_{\text{Mg}_2\text{Sn}}$ zone axis, with (e) the diffraction pattern of Mg_2Sn inserted. The orange dashed lines represent growth facets of Mg_2Sn , while the red dashed line with an arrow represents the normal direction to facet.

Fig. 11 Summary of the determined ORs within typical multi-phase particle pairs in $\text{Mg-4Sn-3Al-1Zn-0.6Mn}$ alloy. (a-b) Mg_2Sn (A) and $\beta\text{-Mg}_{17}\text{Al}_{12}$ (B), (c-d) Mg_2Sn (A) and $\tau\text{-MgAlZn}$ (C), (e-g) $\beta\text{-Mg}_{17}\text{Al}_{12}$ (B) and $\tau\text{-MgAlZn}$ (C).

Fig. 12 Determined ORs within partially eutectic multi-phase particles in Mg-3Al-1Zn-0.3Mn alloy. (a-c) $\beta\text{-Mg}_{17}\text{Al}_{12}$ (B) and $\tau\text{-MgAlZn}$ (C) phase.

Fig. 13 EBSD mapping for three phases, Mg_2Sn (A, in red), $\beta\text{-Mg}_{17}\text{Al}_{12}$ (B, in blue), and $\tau\text{-MgAlZn}$ (C, in green), within three typical multi-phase particles in $\text{Mg-4Sn-3Al-1Zn-0.6Mn}$ alloy. ORs between phase pairs are illustrated by unit cell geometric models with OR type labeled.

Fig. 14 EBSD datasets for (a) $\beta\text{-Mg}_{17}\text{Al}_{12}$ grain embedded in $\alpha\text{-Mg}$ matrix (Mg-3Al-1Zn-0.3Mn), and (b) Mg_2Sn particle surrounded by two $\alpha\text{-Mg}$ grains ($\text{Mg-4Sn-3Al-1Zn-0.6Mn}$). Unit cell models and pole figures of $\{0001\}_{\alpha\text{-Mg}}$ superimposed by $\{100\}_{\beta\text{-Mg}_{17}\text{Al}_{12}}$ / $\{100\}_{\text{Mg}_2\text{Sn}}$ were plotted here for each grain to illustrate the misfit angles. Misfit angle distribution was calculated between (c) $\{0001\}_{\alpha\text{-Mg}}$ / $\{100\}_{\beta\text{-Mg}_{17}\text{Al}_{12}}$ (47 pairs), (d) $\{0001\}_{\alpha\text{-Mg}}$ / $\{100\}_{\text{Mg}_2\text{Sn}}$ (49 pairs), and (e) $\{10\bar{1}0\}_{\alpha\text{-Mg}}$ / $\{100\}_{\text{Mg}_2\text{Sn}}$ (15 pairs).

Fig. 15 Lattice match of OR-ACs and their correlations with the icosahedral coordination in $\tau\text{-MgAlZn}$ (C). (a) Unit cells aligned following OR-AC1 and projected lattice match of parallel planes only (with common directions pointing east). (b) A different view of OR-AC1, with parent Mg_2Sn wireframe reoriented equivalent to (c). (c) Unit cells aligned following OR-AC2 and projected lattice match of parallel planes only (with two pairs of common directions marked on).

List of Table captions:

Table 1 Alloy compositions determined by inductively coupled plasma emission spectrometer (ICP-OES).

Table 2 Final mass percentages of intermetallic calculated with the Scheil model using the PanMg2020 database.

Table 3 Quantitative EPMA point analysis (at.%) marked in Fig. 3a and b.

Table 4 Crystal structures of possible intermetallic compounds.

Table 5 A summary of orientation relationships (ORs) within multi-phase particles.