The effect of Al$_8$Mn$_5$ intermetallic particles on grain size of as-cast Mg–Al–Zn AZ91D alloy

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ABSTRACT

Al$_8$Mn$_5$ intermetallic particles are usually present in most of commercial Mg–Al based alloys. In recent years, the ability for the Al$_8$Mn$_5$ particles to act as potent nucleation sites for the $\alpha$-Mg grains during the solidification of the Mg–Al alloys has been the subject of debate. In this work, the effect of Al$_8$Mn$_5$ particles on grain size of an Mg–9Al–1Zn (AZ91D) alloy was assessed. The experimental result from two AZ91D alloys with different Mn concentrations, i.e., 0.02 wt.% and 0.22 wt.% respectively, indicated that the grain size did not show any notable change. Further, high resolution transmission electron microscopy (HRTEM) was conducted on samples with concentrated Al$_8$Mn$_5$ particles collected by pressurised filtration of the AZ91D alloy melt. The extensive TEM examination on the Al$_8$Mn$_5$/\(\alpha\)-Mg interfaces revealed no crystallographic orientation relationship (OR) between the Al$_8$Mn$_5$ and \(\alpha\)-Mg crystals. It is therefore concluded that Al$_8$Mn$_5$ particles are unlikely to act as effective nucleation sites for the $\alpha$-Mg during solidification of Mg–Al based alloys.

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1. Introduction

A primary objective of solidification processing is to achieve a microstructure with a fine and uniform grain size, homogeneous chemistry and free from casting defects, such as gas pores, hot cracks and large inclusions. This is usually achieved by controlling the solidification conditions, and/or addition of grain refiners, i.e., grain refinement [1,2]. Compared with Al-alloys, grain refinement is more desirable for Mg-alloys for the following reasons. Firstly, magnesium has an HCP crystal structure and, therefore, it is difficult to achieve grain size reduction by thermo-mechanical processing due to the limited slip systems which restrict its ability to deform. Secondly, Mg-alloys usually have a much larger Hall–Petch coefficient compared with Al-alloys [3], indicating a higher efficiency for strengthening through grain refinement. However, effective and practical grain refiners are not commercially available for Mg–Al alloys, although zirconium has been identified as an effective grain refiner for other Mg-alloys [4].

The search for effective grain refiners applicable to Mg–Al based alloys has been a hot topic in solidification research over the last decade. Approaches used for grain refining Mg–Al alloys with varying success include carbon inoculation and superheating [5]. For carbon inoculation, using carbon-containing organic compounds, direct addition of carbon-containing particles and bubbling of carbonaceous gases through the melt have been considered for grain refinement [6,7]. In the superheating process, the Mg–Al alloy melt is heated to a temperature considerably higher than the alloy liquidus and then fast cooled to the pouring temperature before casting [5]. Although some success in grain refinement has been achieved with both carbon inoculation and superheating, such approaches are not always reliable, and further improvement is hindered by the unknown mechanisms of grain refinement provided by such approaches. Recently, Al–Mn–(Fe) [8–11], SiC [12–14], TiB$_2$ [15,16], TiC [16], TiN [17] and ZnO [18] were reported as potential nucleation sites during solidification of Mg-alloys. The relative potency of such compounds and other carbon-containing compounds (e.g., Al$_4$C$_3$ and AlCO$_2$) was critically accessed by Zhang and co-workers using a crystallographic approach [19–21].

Manganese is one of the common elements added to most commercial magnesium alloys, such as AZ91D, AM50A and AM60B, etc. The Mn addition is essential for enhancing the corrosion resistance by removing the detrimental effect of iron [22]. In the aluminium-containing magnesium alloys, manganese is usually found to exist in the form of equilibrium Al$_8$Mn$_5$ intermetallic inclusions or Al$_6$(Mn, Fe)$_3$ in which iron replaces some of the Mn atoms.

There is a continuing debate on whether Al$_8$Mn$_5$ intermetallic particles can act as potent nucleation sites, for the $\alpha$-Mg during the solidification of Mg–Al based alloys. Tamura et al. [8] reported that
Al–Mn–(Fe) particles were frequently observed when an AZ91E alloy melt was rapidly cooled from a superheating temperature to the pouring temperature of 700 °C. Therefore they suggested that the Al–Mn–(Fe) intermetallic particles were the potent sites for heterogeneous nucleation of the α-Mg grains in the superheating approach to grain refinement. Recently, during investigations of the slurry formation process of AZ91 alloys containing different Mn concentrations ranging from 0.23 wt.% to 0.45 wt.%, Byun et al. [9] observed Al5(Mn, Fe)2 particles at the centres of the α-Mg grains. This led to the belief that the Al5(Mn, Fe)2 particles acted as effective nucleation sites during solidification. In addition, Kim et al. [10] studied the effect of carbon addition on the grain refinement of AZ91D alloy, revealing that carbon addition modifies the formation mechanism and morphology of Al5(Mn, Fe)2 particles. They suggested that Al5(Mn, Fe)2 served as a nucleation site for α-Mg through a duplex nucleation mechanism, in which aluminium carbides enhance the nucleation of Al5(Mn, Fe)2 particles and, in turn, Al5(Mn, Fe)2 particles promote nucleation of the α-Mg phase. However, Cao et al. [11] found that when an Al–60 wt.%Mn master alloy (containing mainly Al5Mn3 and a small amount of high temperature ε-AlMn phase) was added to the AZ31 molten alloy, the grain size of as-cast ingots decreased for a short holding time, but increased for long holding time. Since Al5Mn3 is the only potential equilibrium phase at the pouring temperature, the grain coarsening may result from the transformation of the metastable ε-AlMn phase to the Al5Mn3 phase during the long period of isothermal holding. Therefore, they suggested that the high temperature ε-AlMn intermetallic phase, rather than Al5Mn3, is the effective grain refiner [11]. This conclusion from Cao et al. has found support from the theoretical prediction by Zhang and co-authors [19]. From a crystallographic view point, they analysed the actual atomic row matching across the interface between the Al5(Mn, Fe)2 intermetallic compound and the α-Mg matrix, concluding that the crystallographic matching at the interface was so poor that the Al5(Mn, Fe)2 phase could not provide an effective nucleation site for the α-Mg grains. However, there are still doubts about whether the grain refinement can be credited to the ε-AlMn phase. Qiu et al. [20] pointed out that the authors Cao et al. [11] incorrectly applied the crystallographic data of the ε-AlMn phase to estimate its crystallographic potency, and that there was no convincing evidence to show the presence of the high temperature ε-AlMn phase in the master alloy and its existence in the Mg–Al alloy at the low pouring temperature. Qiu et al. [20] suggested that, according to their crystallographic calculation, a metastable ε-AlMn phase was the most-likely candidate to act as an effective heterogeneous nucleation site for the grain refinement of α-Mg grains [20]. In contrast, Easton et al. [12] observed that Mn addition to Mg–Al alloys resulted in an increase in grain size when Al concentration was above 2.0 wt.%. It is generally accepted that a necessary condition for a solid particle to be a potent heterogeneous nucleation site is the formation of a low energy interface between the solid nucleating particle and the nucleated phase, i.e., a coherent or at least a semi-coherent interface with small lattice misfit along the interface. From a crystallographic view point, this means the existence of a specific crystalline orientation relationship (OR) between the potent nucleating particle and the nucleated solid phase. Therefore, direct evidence for a potent nucleating particle is the existence of a well-defined OR between the nucleating particles and the nucleated solid phase. On the basis of assessment of the effect of different Mn concentrations on the grain size of an Mg–Al–Zn AZ91D alloy, the present work focuses on examination of the Al5Mn3 intermetallic particles and their interface with the α-Mg grain by high resolution transmission electron microscopy (HRTEM), aiming to settle this argument in the literature.

2. Experimental

A commercial AZ91D Mg-alloy (supplied by MEL, Manchester, UK) with a composition of Mg–8.6 wt.%Al–0.67 wt.%Zn–0.22 wt.%Mn was used in this study. The AZ91D alloy ingots 10 kg were melted in a steel crucible at 675 °C under a protective atmosphere of N2 + 0.4 vol% SF6. The alloy melt was intensively sheared in an MCAST (Melt Conditioning by Advanced Shearing Technology) unit at 640 °C and 500 rpm for 45 s. The MCAST process is a special technique developed for conditioning the liquid metal prior to solidification processing [23]. In the MCAST process the liquid metal is subjected to intensive shearing under a high shear rate and high intensity of turbulence, thus offering well dispersed oxide particles and intermetallic particles with fine particle size and narrow size distribution. The detailed description of the MCAST process and its effects on solidification microstructures can be found elsewhere [23–25]. A pressurised melt filtration technique was used to collect the Al5Mn3 intermetallic particles from the AZ91D alloy melt, so that the intermetallic particles are concentrated locally enough to facilitate the TEM examination of large numbers of the Al5Mn3 particles. The AZ91D alloy melt (1.5 kg) containing 0.2 wt.% Mn produced by the MCAST unit was transferred into a pre-heated crucible positioned in the pressure chamber of the filtration unit. Argon was introduced to the pressure chamber to force the liquid metal to flow through a steel filter attached at the bottom of the crucible. A thermocouple fixed to the lid of the pressure chamber was used to detect the melt temperature during the filtration process. Solid inclusions, including Al5Mn3 intermetallic particles, were collected above the porous filter in the crucible together with the remaining melt, which were allowed to solidify in the crucible outside the pressure chamber under the same protective atmosphere for melting. The residue material close to the filter concentrated with the intermetallic particles was sectioned and prepared for microscopic examinations.

In order to assess the effect of different Mn addition levels on grain refinement, the Mn concentration in AZ91D alloy was deliberately lowered from 0.22 wt.% to 0.02 wt.% by mixing commercially pure Mg ingot with elemental Al and Zn. The Aluminium Association TP1 mould [26] offering a cooling rate of 3.5 K/s was used for casting the individual alloys, and samples for metallographic examination were taken from the middle part of a cross-section 38 mm from the bottom of the TP1 samples. Before cast into the TP1 mould, both alloys were melted and extensively sheared under the same conditions as described previously. Colour etching was used to reveal the grain structure.

The metallographic specimens for scanning electron microscopy (SEM) were prepared according to the standard metallography preparation procedure. SEM was carried out with an FEG Zeiss Supra 35 microscope, equipped with an energy dispersive spectroscopy (EDS) facility, at an accelerating voltage of 15 kV. To prepare thin foils for conventional TEM and HRTEM examinations, slices from the filtered residue materials were mechanically ground and cut to 3 mm diameter discs. They were then manually polished to a thickness of less than 80 μm and, finally, ion beam thinned on a Gatan precision ion polishing system (PIPS) at 5.0 kV and an incident angle of 4–6 °. Conventional TEM and HRTEM analyses were conducted on a Tecnai FEG F30 TEM instrument operated at an accelerating voltage of 300 kV.

3. Results

3.1. Morphology and chemistry of Mn-containing intermetallic particles

Fig. 1a and b shows the general view and detailed morphology of the collected Mn-containing intermetallic particles in the region...
immediately above the filter, which is indicated at the bottom of the micrograph. A large number of intermetallic particles were collected by the pressurised filtration of the intensively sheared A291D alloy melt. These particles exhibit two distinctive morphologies; the majority of the particles have a polygonal morphology and a few of them display a rod-like morphology. SEM energy dispersive spectroscopy (EDS) analysis on large number of the intermetallic particles indicated the consistence in their composition, with the representative results being given in Table 1. The measured average composition for the intermetallic particles is 59.32 ± 1.3 at. % Al, 39.66 ± 1.4 at. % Mn and 1.03 ± 0.25 at. % Fe, and the average Al/(Mn + Fe) ratio is 1.46 ± 0.08. This is in the composition range of Al8Mn5 phase, which is a non-stoichiometric phase (rhombohedral structure, a = 1.2645 nm and c = 1.5855 nm) [29]. In addition, extensive SEM/EDS analysis of the intermetallic particles with different morphologies indicated that there is no compositional difference between the equiaxed and rod-like intermetallic particles, suggesting that they are the same phase but may be formed under different conditions during solidification. It is possible that the rod-like Al8Mn5 particles were formed from the high temperature liquid before intensive shearing, while the equiaxed particles were formed under intensive melt shearing. The average size of the Al8Mn5 particles was 3–5 μm in diameter with a narrow distribution, which can be attributed to the effect of intensive melt shearing.

### Table 1

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<td>39.66±1.4</td>
<td>1.03±0.25</td>
<td>40.68±1.3</td>
<td>1.46±0.08</td>
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3.2. HRTEM examination of the interface between Al8Mn5 and α-Mg grain

Fig. 2a shows a high resolution TEM lattice image of the interface between an Al8Mn5 particle and the α-Mg matrix, where the thin foil specimen was tilted to align the incident beam parallel to the Mg [1 −1 0] orientation. From the right part of the micrograph, the measured d-spacing of the crystal planes Mg (0 0 0 2) and Mg (1 1 −2 0) was 0.267 nm and 0.159 nm, respectively. These values are comparable with the corresponding d-spacing of 0.26075 nm and 0.16046 nm calculated according to the reported lattice parameters, a = 0.32094 nm and c = 0.52112 nm, for the HCP structured pure Mg at 25 °C [30]. Selected area diffraction (SAD) patterns taken from the area including both the Al8Mn5 particle and the α-Mg grain are shown in Fig. 2b where, in addition to the diffraction spots from the α-Mg matrix at [1 −1 0] direction as indexed in Fig. 2c, the extra spots are from the intermetallic particle. Both the HRTEM micrograph and the SAD patterns show that, while the α-Mg matrix is in the [1 −1 0] zone axis orientation, the Al8Mn5 intermetallic compound is off any low index orientation. This indicates that there is no well-defined OR between these two crystals along the direction of Mg [1 −1 0].

Large number of the Al8Mn5 intermetallic particles and their interfaces with the α-Mg matrix were extensively examined with HRTEM by tilting the specimen to allow the incident beam to be parallel to various low index crystal directions of either the intermetallic particles or the α-Mg matrix. Such analysis along many interfaces failed to observe any well-defined ORs between the Al8Mn5 particles and the α-Mg matrix under the experimental conditions of the present work. Figs. 3a and 3b give two more such examples of the HRTEM examinations, where the thin foil specimen is observed along the direction of Mg [1 −2 1 0] and Al8Mn5 [−1 2 −3 1], respectively. When the incident beam was parallel to Mg [1 −2 1 0], the Al8Mn5 particle was found to be off any low index zone axis orientation, as shown in Fig. 3a. As shown on the right part of micrograph in Fig. 3b, the measured d-spacings for Al8Mn5 (0 2 −2 −2) and Al8Mn5 (3 0 −3 0) crystal planes were 0.448 nm and 0.365 nm respectively, compared to the corresponding values of 0.4533 nm and 0.3672 nm calculated according to the reported...
lattice parameters, \( a = 1.2645 \text{ nm} \) and \( c = 1.5855 \text{ nm} \), for the rhombohedral \( \text{Al}_8\text{Mn}_5 \) intermetallic [29]. It is seen from the HRTEM micrograph that, when the \( \text{Al}_8\text{Mn}_5 \) particle was observed along its \([1 1 2 0]\) direction, the \( \text{a-Mg} \) matrix was not orientated in a low index direction. Based on the extensive HRTEM analysis, it can be confidently concluded that there is no well-defined OR between the \( \text{Al}_8\text{Mn}_5 \) intermetallic particles and the \( \text{a-Mg} \) matrix, and therefore that \( \text{Al}_8\text{Mn}_5 \) particles are very unlikely to be potent heterogeneous nucleation sites for \( \text{a-Mg} \) during solidification of the \( \text{Mg-Al} \) alloy.

In order to verify the above conclusion, a different approach was taken to examine the effect of Mn level on the final solidified grain size of the \( \text{Mg-Al} \) alloy. Direct measurement of the grain sizes was conducted on two AZ91D alloys containing different Mn levels, i.e. 0.22 wt.% Mn and 0.02 wt.% Mn, with one order of magnitude difference in the Mn concentration. Both alloys were processed under the same shearing and casting conditions, being melted at 675 \(^\circ\text{C}\), sheared intensively at 640 \(^\circ\text{C}\) and 500 rpm for 45 s, and solidified in the same TP1 mould. The resultant microstructures of the two alloys are presented in Fig. 4. The measured average grain sizes were 188 \( \pm 20 \) \( \mu \text{m} \) and 180 \( \pm 18 \) \( \mu \text{m} \) for 0.22 wt.% and 0.02 wt. % Mn alloys respectively, showing no notable difference in grain size for the two alloys. This further reinforced the previous conclusion that \( \text{Al}_8\text{Mn}_5 \) particles are unlikely to be potent nucleation sites and do not affect the \( \text{a-Mg} \) grain size of the as-cast AZ91D alloy.

**Fig. 2.** (a) High resolution transmission electron micrograph of the interface between \( \text{Al}_8\text{Mn}_5 \) intermetallic particle and \( \text{a-Mg} \) matrix. The incident beam is parallel to \( \text{Mg [1 1 0]} \), but the \( \text{Al}_8\text{Mn}_5 \) intermetallic is off any low index crystal orientation; (b) selected area diffraction pattern taken from both \( \text{a-Mg} \) matrix and the \( \text{Al}_8\text{Mn}_5 \) particle; and (c) schematic diagram of (b) SAD pattern indexed according to \( \text{Mg [1 1 0]} \) zone direction.

**Fig. 3.** High resolution transmission electron micrographs of other interfaces between \( \text{Al}_8\text{Mn}_5 \) intermetallic particles and \( \text{a-Mg} \) grains. (a) The \( \text{a-Mg} \) is in \([1 2 1 0]\) zone axis orientation and (b) the \( \text{Al}_8\text{Mn}_5 \) is in \([1 2 1 3]\) zone axis orientation, respectively. However, the \( \text{Al}_8\text{Mn}_5 \) intermetallic in (a) and the \( \text{a-Mg} \) matrix in (b) are off any low index orientations.

### 4. Discussion

Although the search for effective grain refiners has been continued for over one-half a century [1,2,5], to date, there are no simple rules to follow for their selection, due to the complexity of heterogeneous nucleation phenomenon. Much research in this area has been based on a trial and error approach. However, some empirical or semi-empirical rules are commonly accepted by the community for the selection of effective grain refiners, including:

- They have to be stable crystalline solid particles at temperatures above the alloy liquidus.
- Such solid particles have to be wetted by the liquid alloy.
- They should ideally have sufficient population densities, favourable particle size and a narrow size distribution.
- They should have a crystalline structure which matches closely that of the solid phase to be nucleated, i.e., the crystallographic disregistry should be small.
- From a practical consideration, their potency should be insensitive to the processing conditions.
Based on the above empirical rules, the possibility of Al₈Mn₅ intermetallic particles acting as effective nucleation sites for Mg–Al based alloys is now considered.

During equilibrium solidification of the commercial AZ91D alloy (usually containing 0.2 wt.% Mn), Al₈Mn₅ particles form at 642 °C and HCP α-Mg forms at 600 °C and solidification finishes at 431 °C through a binary eutectic reaction between the β-Mg₁₇Al₁₂ and α-Mg phases [31]. This solidification sequence confirms that Al₈Mn₅ intermetallic is a stable solid phase over the temperature range of 598–642 °C. In addition, Al₈Mn₅ particles are formed in situ from the alloy melt and, therefore, will be completely wetted by the alloy melt. This means that Al₈Mn₅ particles have the potential to be effective nucleation sites during solidification of Mg–Al based alloys.

Recently, Zhang et al. [19] examined the crystallographic matching between the rombohedral Al₈Mn₅ intermetallic phase and HCP α-Mg using an edge-to-edge model. This model was then refined by Yang et al. to provide a more precise prediction of possible ORs between crystals [32]. According to the model [33], there is only one pair of directions, Mg [1 0 – 1 0]//Al₈Mn₅ [1 0 – 1 1], along which the interatomic spacing misfit is 7.4%, less than 10%, the critical value for a well-defined OR to be established. However, the two plane pairs, Mg [0 0 0 2]//Al₈Mn₅ [3 0 – 3 3] and Mg [0 0 0 2]//Al₈Mn₅ [3 3 – 6 0], involved in this direction pair have very large d-value mismatches, 17.8% and 19.5% respectively. Both the two d-value mismatches are much larger than 6%, the critical value for the edge-to-edge model to require the involved crystal planes to have in order to establish a defined OR. A large angle rotation (4.5°) of the possible matching planes would be also needed if a potentially possible OR between Mg and Al₈Mn₅ is to be predicted:

\[
\langle 1\ 0\ -1\ 0 \rangle_{\text{Mg}} // \langle 1\ 0\ -1\ 1 \rangle_{\text{Al₈Mn₅}}, \\
\langle 0\ 0\ 0\ 2 \rangle_{\text{Mg}} \sim 4.5^\circ \text{ from } \langle 3\ 0\ -3\ 3 \rangle_{\text{Al₈Mn₅}}
\]

The analysis indicates a very poor crystallographic match between the two crystalline phases and thus there is hardly well-defined OR between the two phases. Based on the theoretical analysis, they conclude that Al₈Mn₅ intermetallic particle is unlikely to be a potent grain refiner for Mg–Al alloys.

With the Al₈Mn₅ intermetallic particles being locally concentrated by the melt filtration, TEM and HRTEM examinations of up to a hundred (a few of thin foils) of such intermetallic particles as well as their interfaces with α-Mg shows that the Al₈Mn₅/α-Mg interface is incoherent without well-defined OR. For the first time, the present work provides the firm experimental evidence in support of the above theoretical prediction. In fact, the researchers who believe that Al₈Mn₅ can be effective nucleation sites for α-Mg did not provide convincing evidence to support their opinions [8–10], whilst authors who doubt this opinion provided only theoretical prediction according to the crystallographic match between Al₈Mn₅ and α-Mg [19–21].

Careful assessment on grain size of the AZ91D Mg-alloys with two different Mn concentrations by TP1 casting (fixed cooling rate) also provides firm evidence to verify the theoretical analysis and the findings by the TEM work. By altering the Mn concentration in the AZ91D alloy, the number of the Al₈Mn₅ particles would be changed because Mn does not form other intermetallics in the concentration range used in this work. Therefore, an increased Al₈Mn₅ particles would have expectedly generated more sites for α-Mg grains to nucleate heterogeneously on them if they were effective nucleation sites, and would have resulted in a higher nucleation rate and a smaller grain size. However, the present work reveals no such reduction in grain size of the as-cast alloys when the Mn concentration increases by an order of magnitude, i.e., from 0.02 wt.% to 0.22 wt.%, indicating that other particles other than Al₈Mn₅ are more effective and responsible for the heterogeneous nucleation of α-Mg. Based on all of the theoretical analysis, the extensive TEM work and the assessment of grain size of the as-cast alloy, it is concluded that Al₈Mn₅ is unlikely the effective heterogeneous nucleation sites for α-Mg during the solidification of Mg–Al alloy.

Heterogeneous nucleation is a complex phenomenon. Theoretically, any stable crystalline particles wetted by the liquid melt may act as potential heterogeneous nucleation sites if there are no other more effective particles present in the melt since they have a lower nucleation barrier compared with that for homogeneous nucleation. However, they may not be treated as effective nucleation sites. In classical nucleation theory [34,35], heterogeneous nucleation is treated by a spherical cap model, where the balance of the relevant interfacial energies is described by the well-known Young’s equation. In general, the contact angle plays determining roles in the efficiency of heterogeneous nucleation. However, studies by Cantor and co-workers [36,37] showed that the nucleation by “weak” (less-effective) particles can be described by the classical spherical cap heterogeneous nucleation model, but the theory breaks down for potent (more effective) nucleation particles with small contact angles and small undercoolings. The interfacial
energy between an effective solid particle and the nucleated solid phase is usually very small due to the coherent or semi-coherent interface, so that only a small undercooling is needed for the heterogeneous nucleation to occur. For instance, as small undercooling as 0.01–0.5 K has been measured for nucleation of commercially pure Al by Al–Ti–B inoculation [reviewed in (38)]. With such effective nucleation sites, the classical spherical cap model for heterogeneous nucleation appears to break down [38]. Instead, it has been suggested that an adsorption model may be appropriate, indicating that a thin adsorbed layer of the nucleated phase on the effective nucleating particle is thermodynamically favourable [39]. Although nucleation particles may not have a well-defined OR with the nucleated phase, a well-defined OR is a crucial condition for effective nucleating particles. In terms of crystallographic criterion, a coherent or semi-coherent interface between the nucleation particle and the nucleated solid is necessary to have a small interfacial energy. In this way the nucleation has a small energy barrier and thus the solid particle is effective for the heterogeneous nucleation. However, the Al9Mn3/Al12Mn2 interface is apparently incoherent and therefore the Al8Mn5 is unlikely effective for heterogeneous nucleation.

Usually, more than one type of solid particles may exist in the alloy melt [40]. For instance, there are numerous intermetallic compounds which could be present in Mg-alloys depending on the complexity of the melt. For instance, there are numerous intermetallic compounds usually were shown to have high melting points and would be stable as Mg-melt alloy [41]. These binary and ternary compounds usually were shown to have high melting points and would be stable in Mg-melt alloys [41], so that they could be the potential heterogeneous nucleation sites for Mg-Mg grains. When there are two or more types of the potential nucleation sites, the competition depends on their relative potency of the particles in the solidifying alloy system. The most effective particles would win over the other less-effective ones, and only the most effective particles with sufficient numbers and suitable particle size distribution can actually contribute to the heterogeneous nucleation during solidification.

During solidification, if the number of nuclei is sufficient, the initial growth of the nuclei will release sufficient latent heat to cause rescaling, preventing further heterogeneous nucleation by the less-effective particles which require larger undercooling for nucleation. Thus, the observation of stable crystalline particles in the melt and grain refinement in the solidified alloy sample cannot be taken as a sufficient evidence that the observed stable crystalline particles are responsible for the grain refinement. In addition, neither can observation of crystalline particles inside grains be reliable evidence of heterogeneous nucleation. It is well understood that solid particles situated at the solid/liquid interface can be either engulfed inside a growing crystal or pushed along the solidification front, eventually being located at the grain boundaries after solidification. For instance, Schaffer et al. [42] found that 28% of the TiB2 particles contained within Al–Al grains did not show any well-defined OR between the particles and the Al–Al matrix. Based on this argument, it is clear that research in favour of Al9Mn3 particles acting as potent nucleation sites [8–10] did not provide convincing evidence for their conclusions.

5. Conclusions

Al9Mn3 intermetallic particles were collected from a commercially pure Mg—9Al—1Zn AZ91D alloy melt by a pressurised filtration technique. The Al9Mn3 particles and their interfaces with Mg–Mg grains were extensively examined using high resolution transmission electron microscopy (HRTEM). Under the experimental conditions employed in the present work, no well-defined orientation relationship was observed between the Al9Mn3 intermetallic and Mg-Mg phase. Further, the assessment on the grain size did not show any notable variation in the Mg-Mg grain size for the as-cast AZ91D alloys with two different Mn concentrations, i.e., 0.02 wt.% and 0.22 wt.%. Based on such experimental evidences, it is therefore concluded that Al9Mn3 intermetallic particles are unlikely to be effective for heterogeneous nucleation of Mg–Mg grain during solidification of Mg–Al based alloys.

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