Heterogeneous Nucleation of α-Al on naturally formed $MgAl_2O_4$ Particles during Solidification of Al-Mg-Si-Fe-Mn alloys

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Abstract

The nature of the native $MgAl_2O_4$ particles found in an Al-5Mg-2Si-0.7Mn-1.1Fe alloy was investigated with scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). An orientation relationship (OR) was identified to be: 8.5° $(-1\ 1\ -1)[-1\ 1\ 0]_{\alpha\text{-Al}}//(2\ -2\ 2)[-1\ 1\ 0]_{MgAl_2O_4}$. Different from the OR between the α-Al and the $MgAl_2O_4$ particles with a "clean" surface [1], a tilt angle (8.5°) was observed. The atomic templating layer during the nucleation process of α-Al on $MgAl_2O_4$ was investigated by considering the interfacial segregation. The contribution of native $MgAl_2O_4$ particles to the grain refinement was investigated.

Keywords: $MgAl_2O_4$, heterogeneous nucleation, tilt angle, interfacial segregation, Al-5Mg-2Si-0.7Mn-1.1Fe alloy

1. Introduction

Traditionally, grain refiners are added into liquid melts to refine the average grain size, consequently improving the mechanical properties of the alloys [2-5]. The mechanism of grain refinement with inoculants was understood as supplying of potent particles for heterogeneous nucleation and by alloying to control the surfaces of such refiners or reduce the rate of grain growth [5]. Some grain refiners, such as Al-5Ti-1B master alloy has been successfully developed to refine some Al based alloys [7]. The TiB_2 particles with "clean" surface are not potent for nucleation of α-Al due to the larger lattice misfit (-4.2%) with α-Al compared to others such as Al_3Ti and α-Al (0.09%). However, TiB_2 particles in commercial Al-5Ti-1B grain refiner which have an Al_3Ti templating layer [8] is very potent for nucleation of α-Al due to a very small lattice mismatch at the interface between the Al_3Ti layer and α-Al. However, the TiB_2 particles from the grain refiners are not suitable for all of Al alloys. For example, it was reported that, when alloy elements such as Si [9-10], Zr [3, 11] are present in Al alloys, the Al_3Ti layer is dissolved [11]. Therefore, the TiB_2 particles in Al-5Ti-1B master alloy become not potent, resulting in a coarse grain structure. These results indicate that the nucleation potency of a substrate can change significantly by changing the interface through interfacial segregation or other chemical interactions at the interface. Therefore, investigation on the interaction between melt including impurities and nucleation substrates including both external grain refiners and native inoculant particles in alloy melts are very important to enhance heterogeneous nucleation and achieve the final grain refinement.

Oxides particles are unavoidable in Al alloy melts during the casting process, which could act as substrates for heterogeneous nucleation. Some common oxides in Al-alloys are $MgAl_2O_4$ and α-Al_2O_3. The effect of Mg additions on the oxides in liquid Al alloys have been extensively investigated in the last decades and show that Mg addition favours the formation of $MgAl_2O_4$ [12-15]. In this study, the major oxide was identified as $MgAl_2O_4$ particles in an Al-5Mg-2Si-0.7Mn-1.1Fe alloy which contains Mg as high as 5wt.%. The lattice misfits between these in-situ oxides and the α-Al were calculated to be small [16], which means that these particles should be favourable to nucleate α-Al. However, these oxides normally agglomerate in oxide bi-films [17-18], which reduce their grain refinement efficiency. Recently, some studies have demonstrated that the in-situ oxide particles can be utilized to enhance the heterogeneous nucleation when were well-dispersed, and thus achieve grain refinement in Al- and Mg-alloys especially with the use of the intensive melt shearing technique [16, 19-20]. In particular, it has been shown that the native $MgAl_2O_4$ particles with {1 1 1} faceted surface nucleated α-Al in Mg-containing Al based alloys [16]. Li. et al investigated the heterogeneous nucleation of α-Al on $MgAl_2O_4$ particles in the pure Al. The surface of the naturally formed oxide particles can be modified due to interfacial segregation in the melt. The atomic templating on the substrate surface will therefore change during the modification process, and thus affects the lattice mismatching/ nucleation potency for nucleation [21].

In this work, we aimed to investigate the efficiency of native $MgAl_2O_4$ particles for heterogeneous nucleation of α-Al in Al-alloys containing multiple alloying additions. The oxide films were reduced/eliminated via the intensive melt shearing technique, to investigate the nature and the efficiency of native $MgAl_2O_4$ for heterogeneous nucleation of α-Al. The effects of interfacial segregation (impurities or the other alloying elements) on the terminating planes of native $MgAl_2O_4$ particles on the nucleation efficiency were studied by investigating the orientation relationship changes between the α-Al and $MgAl_2O_4$.

2. Experimental

Al-5Mg-2Si-0.7Mn-1.1Fe alloy investigated in this work has a composition of 5.7%±0.5% Mg, 2.1%±0.2%Si, 0.65%±0.04%Mn and 1.12%±0.05% Fe (all compositions are in wt.%). The melting temperature of this alloy is 668.01°C calculated using the Pandat software using PanAl2018 database. The starting materials were commercially pure Al (>99.86wt.%), commercially pure Mg (>99.95wt.%), and Al-50Si, Al-20Mn and Al-38Fe master alloys. The Al-2Si-0.7Mn-1.1Fe alloy melt was prepared at 750°C in an electric resistance furnace followed with stirring and sufficiently long holding time to ensure melt homogeneity. The melt was isothermally held for 30 minutes after Mg addition. To disperse the native inoculant particles, the intensive melt shearing [22] was used on the alloy melt with shearing unit operated at 4000rpm for 5 minutes. The melt was cast into a TP 1 mould [23] at 720°C before and after intensive melt shearing. In order to facilitate direct examination of oxides particles, a pressurised melt filtration technique was used after intensive melt shearing to collect the oxide particles [24].

The TP-1 sample was sectioned at the cross section at 38mm height from the bottom of the casting which has a cooling rate of 3.5K/s. The filtration materials immediately above the filter were sectioned, where the oxide particles were concentrated. Scanning electron microscope (SEM) observation was carried out with a Zeiss Supera 35 SEM, at accelerating voltages between 5-20kV. The filtration sample was made into 3mm diameter discs for transmission electron microscopy (TEM) examinations. The discs were then manually ground to a thickness of less than 60μm, followed by ion-beam-thinning using a Gatan precision ion polishing system (PIPS) at energy between 2.0-5.0kV and incident angles of 3-6°. TEM examination was performed on a JEOL 2100F transmission electron microscope at an accelerating voltage of 200kV equipped with EDX spectroscopy facility operated.

3. Results

Different types of inoculant particles such as oxides ($MgAl_2O_4$), nitride (AlN) and carbide can be collected from the Al alloys melt, which are reported elsewhere [25-27]. The major type of inoculant particles in Al-5Mg-2Si-0.7Mn-1.1Fe alloy was identified as $MgAl_2O_4$ (spinel) using SEM-EDX, TEM-EDX and TEM analyses. Figs.1a-b show the 2- and 3-diemensional morphology of the native $MgAl_2O_4$ particles collected. The size of these $MgAl_2O_4$ particles ranges from 0.5 to 1μm. The agglomeration of these $MgAl_2O_4$ particles was rarely observed.

The TEM-EDX results from more than 20 $MgAl_2O_4$ particles indicated that they have a composition of O 39.8±0.5at.%, Mg 20.2±0.2at.% and Al 40.0±0.6at.%. The TEM examination results show that these $MgAl_2O_4$ particles have the face-centred cubic (fcc) crystal structure with a=8.08±0.005Å, and are {1 1 1} faceted. One such example is shown in Fig.1c. It shows that the $MgAl_2O_4$ particle is {1 1 1} faceted when viewed along its <1 1 0> zone direction, and the angles between two adjacent termination planes are measured to be 109.5 ± 0.4°or 70.5 ± 0.5°.

Most of the $MgAl_2O_4$ particles are distributed in the oxides films and have no specific in-plane orientation relationship with α-Al. However, those naturally formed $MgAl_2O_4$ particles observed to be embedded in α-Al grains, have specific OR with α-Al, Fig.2. The HRTEM observation on the α-Al/$MgAl_2O_4$ interface is shown in Fig.2a. The indexed fast fourier transform (FFT) patterns from α-Al and $MgAl_2O_4$ were shown in Fig.2b and c, respectively. The incident electron beam is parallel to <1 1 0> of α-Al and <1 1 0> of $MgAl_2O_4$. This reveals an orientation relationship (OR) as: $8.5°(1\ -1\ 1)_{\alpha\text{-Al}}//(2\ -2\ 2)_{MgAl_2O_4}$ and $[-1\ 1\ 0]_{\alpha\text{-Al}}//[-1\ 1\ 0]_{MgAl_2O_4}$. $(1\ -1\ 1)_{\alpha\text{-Al}}$ and $(2\ -2\ 2)_{MgAl_2O_4}$. It has an angle of 8.5° between the two planes. This observation of the OR provides evidence that the in-situ $MgAl_2O_4$ particles do nucleate α-Al in Al-5Mg-2Si-0.7Mn-1.1Fe alloy. However, the orientation relationship between $\{1\ 1\ 1\}_{\alpha\text{-Al}}$ and $\{1\ 1\ 1\}_{MgAl2O4}$ has a 8.5° deviation from the reported OR [1] observed on the "clean" $MgAl_2O_4$ surface.

In-situ oxide particles in Al alloys always form and contained in the double oxide films therefore difficult to achieve the effective grain refinement [28-29]. With intensive melt shearing, these oxide films can be dispersed uniformly allowing them to be more effective inoculant particles to grain refine the alloys [16, 19-20]. In this study, $MgAl_2O_4$ particles formed as the major native oxides and was confirmed to be the potent nucleation substrates for α-Al (Fig.2). Therefore, the nucleation efficiency of the in-situ $MgAl_2O_4$ particles needs to be investigated. The microstructure of Al-5Mg-2Si-0.7Mn-1.1Fe alloy applied without and with intensive melt shearing is shown in Fig. 3. Quantitative measurement of the grain size is given in Table 2. It shows that the average α-Al grain size was reduced from 423±47µm in the un-sheared sample to 151±22µm in the sheared. The α-Al gains were refined by the dispersing naturally formed inoculant particles. Our previous research reported that although the equilibrium primary phase of Al-5Mg-2Si-0.7Mn-1.1Fe alloy was calculated to be α-$Al_{15}(Fe,Mn)_3Si_2$ (α-AlFeSi), the primary α-AlFeSi phase was suppressed when cast at 720°C with a cooling rate of 3.5K/s [30]. Therefore, the effect of the formation of α-AlFeSi phase on the grain refinement of α-Al can be excluded.

4. Discussion

In this study, the native $MgAl_2O_4$ particles were generated in Al-alloys containing multiple additives including Si, Fe and Mn. Those alloying elements were found segregate on TiB_2 particles [21]. Therefore, it is possible for these elements to segregate on the $MgAl_2O_4$ particles as well. The angle (8.5°) between the $\{1\ 1\ 1\}_{\alpha\text{-Al}}$ and $\{1\ 1\ 1\}_{MgAl_2O_4}$ suggests that the {1 1 1} planes of $MgAl_2O_4$ in this alloy may be modified. In this case, the structure of $MgAl_2O_4$ particles at the nucleation interface is determined by the newly templated atomic layer(s) caused by interfacial segregation or chemical interaction rather than the {1 1 1} planes of $MgAl_2O_4$. From another point of view, the α-Al at the interface with the $MgAl_2O_4$ are not {1 1 1} planes but the $\left\{\frac{1}{x}\ \frac{1}{x}\ 1\right\}_{\alpha\text{-Al}}$ after accounting for the tilt angle (θ). (where x is an integer value greater than 1). Due to the limited information on the modified {1 1 1} planes of $MgAl_2O_4$, we focus on the nucleating planes of α-Al. Consequently, the OR between α-Al and the native $MgAl_2O_4$ particles could be considered as $\left\{\frac{1}{x}\ \frac{1}{x}\ 1\right\}_{\alpha\text{-Al}}//\{1\ 1\ 1\}_{MgAl_2O_4}$.

Based on this discussion, we assumed different $\left\{\frac{1}{x}\ \frac{1}{x}\ 1\right\}$ planes viewed along the <1 1 0> zone direction of α-Al which have different tilt angle (0~10°) with $\{1\ 1\ 1\}_{\alpha\text{-Al}}$. The lattice misfits between these $\left\{\frac{1}{x}\ \frac{1}{x}\ 1\right\}$ planes of α-Al and the fixed nucleation substrate ($(2\ \text{-}2\ 2)_{MgAl_2O_4}$) were calculated. The results were shown in Table 1. The lattice parameters of α-Al and $MgAl_2O_4$ used are calculated at 660°C taking into account the thermal expansion of both structures [31-32]. With the increased θ, the $d\left\{\frac{1}{x}\ \frac{1}{x}\ 1\right\}_{\alpha\text{-Al}}$ increases. The very small changes in $\left\{\frac{1}{x}\ \frac{1}{x}\ 1\right\}_{\alpha\text{-Al}}$ indicates the large atomic distances at the interface. If the $d\left\{\frac{1}{x}\ \frac{1}{x}\ 1\right\}_{\alpha\text{-Al}}$ is analysed using the coincidence site lattice (CSL) for the mismatch between the solid α-Al and the substrates {1 1 1} of $MgAl_2O_4$, then the match due to CSL increases with the increased θ (0~10°). When the tilt angle is 8.5°, same angle as the experimental results, the OR is $(7\ \text{-}7\ 5)_{\alpha\text{-Al}}//(2\ \text{-}2\ 2)_{MgAl2O4}$. Therefore, the actual heterogeneous nucleation interface was calculated to be $(7\ \text{-}7\ 5)_{\alpha\text{-Al}}$ and modified $(2\ \text{-}2\ 2)_{MgAl2O4}$ rather than that of $(1\ \text{-}1\ 1)_{\alpha\text{-Al}}//(2\ \text{-}2\ 2)_{MgAl_2O_4}$. However, it shows that the misfit between the $(7\ \text{-}7\ 5)_{\alpha\text{-Al}}$ and the $(2\ \text{-}2\ 2)_{MgAl_2O_4}$ is 5.53% which is much bigger than that the misfit (1.36%) between (1 -1 1)$_{\alpha\text{-Al}}$ and (2 -2 2)$_{\mathrm{MgAl_2O_4}}$. The heterogeneous nucleation occur at an interface with a larger misfit rather than that with a smaller misfit, indicating some surface modification on MgAl$_2$O$_4$. Therefore, the lattice mismatch between the $\left\{\frac{1}{x}\ \frac{1}{x}\ 1\right\}_{\alpha\text{-Al}}$ and modified (2 -2 2)$_{\mathrm{MgAl2O4}}$ need to be reconsidered. The calculation in Table 1 is not suitable for the modified surface. Other factors that affect the interface structure such as surface roughness, interfacial segregation need to be considered.

The grain refinement shown in Fig.3 indicated that these native MgAl$_2$O$_4$ particles were potent to refine the α-Al grains after intensive melt shearing. This indicates that the native MgAl$_2$O$_4$ particles with modified surface are potent for the nucleation of α-Al, i.e. the mismatch between the (7 -7 5)$_{\alpha\text{-Al}}$ and modified (2 -2 2)$_{\mathrm{MgAl_2O_4}}$ did not affect the potency of the particles significantly. The comparison of interfacial atomic match between the (1 -1 1)$_{\alpha\text{-Al}}$ on the (2 -2 2)$_{\mathrm{MgAl_2O_4}}$ with and without the tilt angle was simulated with Crystal Maker software, Figs.4a-b, and using schematics illustrate the interface atomic matching with the crystal lattice parameters. The MgAl$_2$O$_4$ particles were reported to have multiple of possibilities on surface planes and surface atomic arrangements [33-34]. In this simulation, the surface atoms on the (2 -2 2) surface planes of MgAl$_2$O$_4$ particles which formed in Al melts were set to be Al. Fig.4 a shows that the clean {1 1 1} $_{\mathrm{MgAl_2O_4}}$ has perfect matching with the {1 1 1}$_{\alpha\text{-Al}}$. However, the surface of the MgAl$_2$O$_4$ particles in Al-5Mg-2Si-0.7Mn-1.1Fe was modified by a 8.5° tilt angle as observed during the heterogeneous nucleation of α-Al (Fig.2). Fig.4b shows that when the interface between α-Al was tilted, the parallel plane of α-Al with the (2 -2 2) plane of MgAl$_2$O$_4$ changes from close-packed (1 -1 1) to (7 -7 5) which lower atomic density.

As discussed above, the most likely reason for the interfacial modification of {1 1 1} $_{\mathrm{MgAl_2O_4}}$ is the interfacial segregation. The interfacial segregation changes atomic arrangement above the MgAl$_2$O$_4$ particles in the melt by allowing Fe, Si or Mn or other impurity elements to segregate on the surface or chemically interact with the surface atoms of MgAl$_2$O$_4$. The atomic radii among the possible segregation elements such as Fe, Mn, Si and Al are different, and some vacancies might be generated which can cause the faceted {1 1 1} $_{\mathrm{MgAl_2O_4}}$ become rougher. The interfacial segregation and subsequent roughening on the nucleation substrates changes the atomic templating. As discussed before, the tilt angle corresponds to a higher indexed planes of the substrates, which means larger CSL and a rough surface on the modified MgAl$_2$O$_4$. Due to limited understanding of heterogeneous nucleation on the rough surfaces, our initial hypothesis was schematically presented in Fig.4c-d to describe this heterogeneous nucleation process.

Fig.4d shows the case that different elements segregate on the surface of native MgAl$_2$O$_4$ particles. The number, type and positions of the adsorbed atoms depending on the melt composition can be different, and Fig.4d only shows one of the possibilities. The atomic arrangement at the interface is predicted to affect the nucleation, which needs further investigation. In this case, the higher indexed planes ((7 -7 5) $_{\alpha\text{-Al}}$) as the first templating layer to accommodate the roughness of the surface due to segregation generated larger coincidence site lattice (CSL). After a few atomic layer templating, the nucleated solid grows into the crystal to minimise the interfacial energy.

Grain refinement not only requires potent nucleation substrates, but also requires suitable particle size and size distribution. More importantly, it requires an adequate number density (N_0). In this study, the number density was calculated in non-sheared and sheared cases with the assumption that each grain has a $MgAl_2O_4$ as a nucleus(Table 2). According to the grain size, the number of effective nucleated particles N_v can be calculated according to the equation:

$$Nv = \frac{0.5}{d^3}$$ [35].

The nucleation efficiency was assumed to be 0.5% in both non-sheared and sheared cases. Therefore, the particles number densities in these two cases were calculated as $1.3 \times 10^{12} m^{-3}$and $3.0 \times 10^{13} m^{-3}$, respectively. As reported [36], the number density of TiB_2 particles in 1000 ppm Al-5Ti-1B grain refiner addition is $7.3 \times 10^{12} m^{-3}$. The number density of native oxide particles therefore is adequate to cause grain refinement in Al-alloys.

5. Conclusions

The main results are summarized as:

(1) The major naturally formed oxides in Al-5Mg-2Si-0.7Mn-1.1Fe alloy were identified as $MgAl_2O_4$. These $MgAl_2O_4$ particles were {1 1 1} faceted, and have size rage from 0.5 to 1μm.

(2) A well-defined orientation relationship between α-Al and $MgAl_2O_4$ was observed and identified to be: 8.5° $(-1\ 1\ -1)_{\alpha\text{-}Al}$ // $(2\ -2\ 2)_{MgAl_2O_4}$, and $[-1\ 1\ 0]_{\alpha\text{-}Al}$// $[-1\ 1\ 0]_{MgAl_2O_4}$.

(3) The number density of native $MgAl_2O_4$ particles is sufficient to enhance the heterogeneous nucleation of α-Al in Al-alloys and lead to grain refinement.

Acknowledgement

The EPSRC is gratefully acknowledged for providing financial support under Grant EP/N007638/1.

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