Crystallographic Orientation Relationship between Discontinuous Precipitates and Matrix in Commercial AZ91 Mg Alloy

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Discontinuous precipitates (DPs) have a random distribution at grain boundaries in commercial AZ91 Mg alloy, whereas continuous precipitates exist in the matrix. Previous studies have mainly focused on continuous precipitates and their orientation relationship with the matrix. In this study, thin cross sections of DPs in commercial AZ91 magnesium alloy aged at 489 K were prepared by focused ion beam milling. Their morphologies and the orientation relationship between the DPs and the matrix were investigated by transmission electron microscopy. The results reveal that the DPs have the shape of platelets. Selected-area electron diffraction patterns of the DPs allowed them to be identified as $\beta$-Mg$_{17}$Al$_{12}$. The DPs were found to have the same orientation relationship (i.e., Burgers, Potter or Crawley) as the continuous precipitates in the matrix. However, their longitudinal directions were not fixed, but were distributed about their (111) zone axis.

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1. Introduction

AZ91 Mg alloy is one of the most widely used commercial Mg alloys due to its superior castability, mechanical strength, and ductility. According to its phase diagram, the intermetallic compound $\beta$-Mg$_{17}$Al$_{12}$ is the only precipitate formed in AZ91 Mg alloy during aging after solution heat treatment. Discontinuous precipitates (DPs) are formed at grain boundaries in this alloy whereas continuous precipitates occur in the $\alpha$-Mg matrix. Table 1 summarizes the results of studies on the crystallographic orientation relationship (OR) between continuous precipitates and the matrix. In the present paper, the four major ORs are referred to as Burgers, Crawley, Gjones and Ostmoe (GO), and Porter ORs. The habit plane of $\beta$-phase DPs at grain boundaries are also summarized in Table 1. The Potter ORs have additional habit planes according to Duly et al. Figure 1 shows a schematic illustration of the habit planes of both the continuous precipitates and DPs.

Figures 1(a) and (b) show projections of plate-shaped $\beta$-phase ($\beta$-plates) parallel to the [0001] and [2110] zone axes of the Mg matrix. The $\beta$-plates labeled 1 to 4 in Fig. 1 correspond to plates with Burgers (or GO), Crawley, Porter, and Potter ORs, respectively. The $\beta$-plates with a Burgers OR can be classified with DPs with a Crawley OR in terms of their morphology (see Fig. 1), because the $\beta$-plates are perpendicular to each other. However, DPs with a GO OR cannot be classified with the $\beta$-plates with a Burgers OR because the $\beta$-plates are parallel to each other in the [0001] matrix. Duly et al. found that DPs in pure Mg–Al alloys consist of long parallel lamellae and bush-like structures. The bush-like precipitates have various habit planes, which correspond to low-index planes in the matrix, and in which the precipitate has a high atomic density. The relationship between the OR and the DP morphology in commercial AZ91 alloys has not yet been determined.

The present study investigates the microstructure of DPs in commercial AZ91 Mg alloy by electron back-scattered diffraction (EBSD) and transmission electron microscopy (TEM). It was hoped that such a study would lead to a better understanding of the DPs, their ORs, and the relationship between DPs and the matrix. Specimens for TEM were prepared by focused ion beam (FIB) milling, which is a useful technique for producing samples from important regions that contain DPs.

2. Experimental Procedure

An alloy with the same chemical composition as commercial AZ91E Mg alloy (i.e., 9.1 mass% Al, 0.68 mass% Zn, 0.21 mass% Mn, and 0.03 mass% Si) was prepared by conventional sand casting. Fe, Cu, and Ni impurities in this alloy were less than 0.002 mass%. Two types of samples were prepared in the present study: a cast alloy that was solution heat treated, quenched in water, and then aged, and a rolled alloy that was warm rolled until its thickness was about 50% less than that of the ingot and then solution heat treated. Both samples were solution heat treated in an Ar atmosphere at 686 K for 57.6 ks. Aging was performed in an oil bath at 489 K. The microstructure of the samples was observed by scanning electron microscopy (SEM; Hitachi, S-3500H), EBSD (Oxford, Opal) and by TEM (Topcon, EM-002B, 120 keV) in conjunction with energy-dispersive X-ray spectroscopy (EDS). Thin TEM specimens were prepared using a FIB system (Hitachi, Dual Beam FB-2100).

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3. Results and Discussion

Figure 2 shows age-hardening curves of the cast and rolled alloys aged at 489 K. The rolled alloy had a higher hardness than the cast alloy and the time taken to reach its peak hardness was shorter than that for the cast alloy. These differences are most likely due to the different distributions of solute atoms and different amounts of segregation in the cast and rolled alloys. Figure 3 shows optical micrographs and SEM images of the cast and rolled alloys. DPs appear as dark regions in the optical micrographs in Figs. 3(a) and (e). The SEM images in Figs. 3(b) and (f) reveal that the DPs in under-aged alloys (aged for 1.8 ks) have a lamellar structure. The DPs in the peak-aged cast alloy have a dendritic structure (Fig. 3(c)), whereas a dendritic structure is not observed in the peak-aged rolled alloy (Fig. 3(g)). This implies that warm

<table>
<thead>
<tr>
<th>Type</th>
<th>Alloy</th>
<th>OR</th>
<th>Morphology</th>
<th>Ref.#</th>
</tr>
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<tbody>
<tr>
<td>Burgers OR</td>
<td>Mg-9%Al</td>
<td>(111)<em>{p}//[2110]</em>{a}</td>
<td>Laths lie in the basal plane (0001)</td>
<td>4</td>
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<tr>
<td></td>
<td></td>
<td>(011)<em>{p}//(0001)</em>{a}</td>
<td></td>
<td></td>
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<tr>
<td>Crawley OR</td>
<td>AZ91</td>
<td>(211)<em>{p}//[2110]</em>{a}</td>
<td>Laths lie in the prismatic plane (0110)</td>
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<tr>
<td></td>
<td></td>
<td>(111)<em>{p}//(0001)</em>{a}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gjoness &amp; Ostmoe (GO) OR</td>
<td>Mg-9%Al</td>
<td>(211)<em>{p}//[1120]</em>{a}</td>
<td>Lens shaped precipitates lie in the prismatic plane (0110)</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(011)<em>{p}//(0001)</em>{a}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porter OR</td>
<td>Mg-9%Al</td>
<td>(011)<em>{p}//[1100]</em>{a}</td>
<td>Lens shaped precipitates lie in the prismatic plane (0110)</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(011)<em>{p}//[121]</em>{a}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potter OR</td>
<td>Mg-7.7, 10, 18%Al</td>
<td>(111)<em>{p}//[2110]</em>{a}</td>
<td>Lamellae</td>
<td>6</td>
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<tr>
<td></td>
<td></td>
<td>(101)<em>{p}//(0111)</em>{a}</td>
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</table>
rolling prior to solution heat treatment is effective for enhancing the segregation of solute atoms produced by solidification; the peak hardness results in Fig. 2 also support this conclusion. No distinct border between the DPs and matrix precipitates can be seen in Figs. 3(d) and (h) due to the large number of precipitates present. Figure 4 shows the distribution of grain boundary (GB) misorientations in the cast and rolled alloys. The white bars in Fig. 4 indicate all GBs and the gray bars represent GBs with DPs. The GBs with DPs in the cast alloys have a wider misorientation distribution (20–80°) than those in the rolled alloy (20–40°). The white bars have the same distribution as the gray bars, although they have different absolute values. This indicates that rolling prior to solution heat treatment has no effect on nucleation of DPs, which probably depends more on the initial misorientation distribution of GBs.

Figure 5(a) shows a SEM image of a rolled alloy aged for 1.8 ks. An area of the alloy was FIB sputtered to enable a 3D image of the DPs to be obtained. The misorientation between grains A and B was 25°. The sample was then inserted in the FIB equipment and a region labeled “T” in Fig. 5(b) was deposited with tungsten to protect against the Ga⁺ ion beam. Two square holes were then formed by the FIB for use as markers when superimposing secondary ion images to obtain a 3D image. Finally, FIB sectioning was performed in the region labeled “S” in Fig. 5(b). Each sputtering step removed a 100-nm-thick layer. The sample was tilted to obtain a secondary ion image of the section and then sectioning was continued. The sectioned images were reconstructed by image processing after sectioning was completed. Figure 6(a) shows a 3D reconstruction of a DP superimposed on a secondary ion image of the cross section. Figures 6(b), (c), (d), and (e) respectively show top, bottom, left, and right views of the 3D DP image. The DP appears to be a fairly flat platelet with no branches or extreme curvature. Figure 7 shows TEM images and a selected area electron diffraction (SAED) pattern obtained from the same area as that in Fig. 5. The zone axis of the matrix was [1100]b. Indexing of the SAED pattern allowed the DP to be identified as β-Mg17Al12. In addition, the OR was determined to be a Burgers OR due to the relationships (0001)b//(011)b and [2110]b//[111]b. A previous study found that the plane of platelet precipitates with Burgers ORs was parallel to the basal plane of the matrix. As these precipitates are cross sections of β-platelets, their longitudinal axes shown in Fig. 7(c) are perpendicular to the basal plane of the matrix. This is consistent with the geometry depicted in Fig. 1. Precipitates in the same colony exhibit very similar SAED patterns and ORs between the precipitate and the matrix, even when they have different longitudinal orientations. Figure 8 shows the results obtained for DPs in a cast alloy that was aged for 1.8 ks. The zone axis of the matrix was [0001]. A TEM sample was obtained from the region indicated by the arrow in Fig. 8(b), and the TEM image is shown in Fig. 8(a). The SAED pattern shown in Fig. 8(d) was obtained from the region marked by a white square in Fig. 8(a). Small weak spots close to the main spot were indexed as the β-phase for an incident beam direction of [111]b. The white arrow shown in Fig. 8(d) indicates the
directions \([2110]_\alpha\) and \([2\bar{1}1]\beta\), which corresponds to a Crawley OR together with \(\langle 0001\rangle_\alpha//\langle 111\rangle_\beta\). The white broken arrow indicates the longitudinal direction of the \(\beta\)-phase, which makes an angle of about 12° with \([2110]_\alpha//\ [2\bar{1}1]\beta\) of the Crawley OR. An EDS analysis was also performed on the DP shown in Fig. 8(c). The average ratio of Mg to Al was found to be approximately 17/12. The TEM images show that the DPs marked by the black broken arrows in Figs. 8(a) and (c) are almost parallel to the white broken arrow in Fig. 8(d). It is also parallel to the matrix precipitates. Some DPs have different longitudinal orientations (see small white arrows in Fig. 8(a)); however, even these precipitates have a Burgers OR. Figure 9 shows the angular distribution of the longitudinal axes of the precipitates in the \([011]\) direction of the \(\beta\)-phase. Figure 9(a) shows the results for 102 \(\beta\)-plates with Crawley ORs in five colonies. Most have an orientation centered on a direction shifted about 10° from \([2110]_\alpha\) and \([2\bar{1}1]\beta\). Figure 9(b) shows the situation for 156 DPs with Burgers ORs in six colonies. Although most are
Fig. 9 Angular distribution of longitudinal axes of precipitates in the [011] direction of the $\beta$ phase. (a) DPs with Crawley ORs in a cast alloy aged for 1.8 ks; (b) DPs with Burgers ORs in a rolled alloy aged for 1.8 ks; (c) DPs with Potter ORs in a rolled alloy aged for 14.4 ks.

Fig. 10 Summary of longitudinal directions of $\beta$-Mg$_2$Al$_{12}$. (a) Standard stereographic projection triangle and (b) schematic illustration showing rotation relationship of the $\beta$-phase about the common axis of $[11\bar{1}]_{\beta}$.

aligned along a direction close to $[01\bar{1}]_\alpha$ and $[21\bar{1}]_\beta$, the angular distribution is wider than that seen in Fig. 9(a). Figure 9(c) shows the distribution for 65 DPs with Potter ORs in two colonies, which is seen to be much narrower, in agreement with the results of Duly et al. Figure 10(a) shows these longitudinal directions plotted on a standard stereographic projection for $\beta$-Mg$_2$Al$_{12}$. All orientations were plotted in the $[11\bar{1}]_\beta$ zone and the common zone axis is $[11\bar{1}]_\beta$. Figure 10(b) schematically depicts the relationship between the habit planes of $\beta$-plates and the ORs. The $\beta$-plates of the DPs labeled (1), (2) and (4) correspond to plates with Burgers (or GO), Crawley and Potter ORs, respectively. They have the rotation axes $(11\bar{1})_\beta$ and $(1\bar{2}0)_\alpha$ as their common zone axes and they can grow in several directions in the matrix. The lattice misfit for each OR in the present study did not reveal any preferential growth directions or predominant ORs for the DPs. A more detailed study of the preferential directions and nucleation mechanism of DPs is needed.

4. Conclusions

A microstructural and orientation analysis was carried out on DPs in aged AZ91 Mg alloy. The following findings were obtained:

(1) DPs in the aged alloy had a platelet morphology and corresponded to the $\beta$-Mg$_2$Al$_{12}$ phase.

(2) The DPs exhibited the same types of ORs as the continuous precipitates in the matrix. DPs in the same colony had the same OR.

(3) The longitudinal axes of DPs were distributed about the $(11\bar{1})$ zone axis of the precipitate.

(4) The relationship between the morphology and longitudinal direction of DPs was the same as that for precipitates in the $\alpha$-Mg matrix.

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