Effect of Amount of Gd and Y Contents on Precipitation in Mg–Gd–Y Alloys Aged at 473 K

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Precipitation in Mg–Gd–Y (Gd:Y = 3:1) alloys without Zr were investigated by HRTEM and SAED technique, and calculation of HRTEM images and electron density using DV-Xα technique. The diffuse scattering was obtained in as-quenched samples in each alloy by SAED and the mono-layer zones have been discovered before the β-phase in the aged sample. HRTEM images obtained for these precipitates were compared with calculated HRTEM images. The contrast of atomic columns of the matrix in HRTEM image was calculated simplified model of cluster based on the Mg-matrix including one or some atomic columns of RE. This is also corresponded the distribution of electron density of the cluster. [doi:10.2320/matertrans.L-M2012829]

(Received April 11, 2012; Accepted November 2, 2012; Published January 19, 2013)

Keywords: magnesium alloys, gadolinium, yttrium, precipitation, transmission electron microscope

1. Introduction

Mg–RE alloys have been investigated for their typical age-hardening behavior which have higher amount of solubility for Mg matrix.1) Particularly, the Mg–Gd alloy shows the highest age-hardenability among those Mg alloys.2,3) Mg–RE alloys are classified for as two groups of Y- and Ce-groups which depend on their solubility at higher temperature. Gd belongs to the Y-group and it could be replaced as other element, for example Y, to obtain age-hardenability. Kamado et al.4) developed GY122K and GY84K series alloys and the morphology of precipitate in those alloys has been clarified by our previous works using an high-resolution transmission electron microscopy (HRTEM)5). The ratio of Gd/Y for GY122K and GY84K alloys are 3:1 and 1:1. In our previous study, the mono layered structure looks like GP zones has been discovered before β’-phase in the aged sample at 473 K, and the β’- and β-phases co-existed at the peak-aged condition. GY122K, however, includes Zr, and it is difficult to understand the effect of such minor element on precipitation. Also, its amount of solute elements of Gd and Y in GY122K alloy is 2.7 at%, not so high to obtain clear evidence for the precipitation at early stage of aging. Nishijima and Hiraga6) have reported about precipitates in binary Mg–5 at% Gd alloy which exceeds the solubility in Mg–Gd alloy using an high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM). They concluded that there is the short-range ordered Gd-enriched regions with an about 2 nm size, not β’-phase with D0₁₉ structure which reported by Gradwell7).

In this study, two kind of Mg–Gd–Y alloys, which are Mg–2.9 at%Gd–0.8 at% Y and Mg–2.1 at%Gd–0.6 at% Y alloys including the same ratio of Gd:Y = 3:1 without Zr, have been investigated to clarified the effect of the addition of Zr and total amount of solute atoms on age-hardening and precipitation using HRTEM and calculations of images and electron density.

2. Experimental

Mg–2.9 at% Gd–0.8 at% Y and Mg–2.1 at% Gd–0.6 at% Y alloys (Gd/Y = 3) were prepared by casting using 99.9% Mg, Gd and Y purity ingots. The obtained alloys were homogenized at 773 K for 43.2 ks, and then hot rolled at 773 K to 1 mm in thickness. The sample was capsulated into the pyrex glass tube with argon gas. Then, it was solution heat-treated at 773 K for 3.6 ks and quenched in hot water at 353 K, and aged in a silicon oil bath at 473 K. TEM specimens were cut from plate samples and thinned by the twin-jet electro polishing technique using an electrolyte of 10 percent perchloric acid-ethanol solution at about 243 K. HRTEM observations were performed by using a TOPCON EM-002B operated at 120 kV. The specimen thickness for TEM observation was estimated using by EELS, and it is usually less than 50 nm. The defocusing to obtain HRTEM image was about Δf = −30−50 nm. Calculated HRTEM images were obtained by the conventional multi-slice method using a rectangular cell of 1.92 nm × 2.22 nm × 0.52 nm including 96 atoms based on the hcp structure of Mg.

The HRTEM image was calculated using the multi-slice method and the electron density was calculated using the DV-Xα program.8)

3. Results and Discussion

Figure 1 shows the age-hardening curves of 2.9Gd–0.8Y and 2.1Gd–0.6Y alloys. Two curves are parallel to each other, and the level of curves depends on the total amount of solute
atoms. Figures 2 and 3 are TEM images obtained for alloys aged at 473 K for several aging time indicated by arrows in Fig. 1.

The diffuse scattering can be seen in the as-quenched sample of Fig. 2(a) marked by an arrow, and its intensity becomes stronger increasing with aging time of 7.2 ks in Fig. 2(b). The diffraction pattern for the $\beta'$-phase\(^9\) obviously appeared in the samples aged at 28.8 and 230.4 ks of Figs. 2(c) and 2(d). The morphology of $\beta'$-phase can not be seen in the bright field images of Figs. 2(e)–2(g), and the typical contrast of the platelet $\beta'$-phase has appeared in the peak-aged sample of Fig. 2(h).

The diffuse scattering in the as-quenched sample of 2.9Gd–0.8Y alloy marked by an arrow has become stronger than that of 2.1Gd–0.6Y alloy as shown in Fig. 3(a). The
diffraction pattern for the $\beta'$-phase can be seen in the 2.9Gd–0.8Y alloy, even aged for 7.2 ks in Fig. 3(b), and its intensity was also stronger than 2.1Gd–0.6Y alloy. The contrast of the platelet $\beta'$-phase can be seen in the bright field image of Fig. 3(h).

Figure 4 shows HRTEM images obtained for as quenched samples of 2.1Gd–0.6Y (a) and 2.8Gd–0.8Y (b) alloys. There are some lines which have brighter (or darker) dots having spacing of 0.64 nm on the mono-layer of [1100] plane. This contrast exists just in the present alloys to compare with pure Mg sample of Fig. 4(c). The zigzag lines can not be in the as-quenched samples. Figure 5 shows HRTEM images obtained for the alloys aged at 473 K for 7.2 ks. There are some characteristic periodicities of the bright dots in there. The hexagonal networks can be seen in the 2.1Gd–0.6Y alloy of Fig. 5(a) and its spacing was 0.64 nm marked in the picture. The spacing of 0.64 nm was also confirmed in the 2.8Gd–0.8Y alloy of Fig. 5(b), many dark lattice fringes appeared and its periodicity was a rectangle, not a hexagon. These two characteristics can be classified as the $\beta''$ (D0$_{19}$) and $\beta'$ (BCO)-phases. This means that the alloy including higher content of RE is not clear the existence of the $\beta''$-phase. After prolonged aging, $\beta'$-phase was confirmed and it became predominant phase in each alloy as shown in Fig. 6.

Figure 6(b) shows a HRTEM image of the $\beta'$-phase consisted of darker zigzag lines having a spacing of 1.11 nm. The zigzag lines were not so clear in Fig. 6(a), although the $\beta''$-phase which has a hexagonal network of dark dots appeared between two large $\beta'$-phase in Fig. 6(a). According to this work, precipitates in Mg–Gd–Y alloys appear the same as those in a Mg–Gd–Y(–Zr) alloy, namely, Zr does not affect for the precipitation of $\beta''$ phase, and its phase is not predominant in the present aging condition. The ratio of Gd/Y is also not so effective for the existence of $\beta''$ phase rather than the total amount of RE elements. We need more research to understand this phenomenon.

Some bright/dark contrast can be seen in HRTEM images in this work, the effect of RE atom for the HRTEM image is discussed in this session. Figure 7 shows a series of simulated HRTEM images for the Mg-matrix including a single atomic column of Gd in the Mg matrix, simply. Just two atoms of Mg and Gd were used for the simulation of HRTEM images, because the atomic positions for Gd and Y in precipitates could not decide in this work. The atomic position of Gd and Y was not distinguished and only Gd was put in this unit. Figure 7(d) is a projected potential of the
crystal lattice parallel to the [0001] direction of the matrix and this is used for the HRTEM simulation. Open single circles and double circles indicate atomic columns of the matrix which has different position along to the c-axis. A hatched circle located at the center of this lattice is one Gd atomic column, and its position along to the c-axis is the same as the single open circles. Simulated condition was 50 nm in thickness and defocusing of ~40 nm. Bright dots correspond to the empty space of crystal lattice and atomic columns locate the black region in this simulation. Comparing to Figs. 7(a) and 7(b), or 7(c), there are 3 darker dots marked by dotted circle at the center in Figs. 7(b) and 7(c) than other bright dots, although brightness of dots in the just Mg atomic columns in Fig. 7(a) is the same as each other. The crystal lattice and the simulated HRTEM image were superimposed and compared in as Fig. 7(e). The atomic position just consisted of the RE or Mg columns show the black contrast, and the bright dots correspond to the space surrounding by the 6 Mg columns of hexagonal network with 0.18 nm. Darker dots like as 3 dots at the center, however, consist of 1 RE and 5 Mg columns of hexagonal network. Howe et al.¹¹ discussed about simulated HRTEM image of $\theta'$ phase in Al–Li–Cu alloy. In $\theta'$ structure, both Al and Cu atoms scatter electrons strongly, causing them to appear dark, while electrons travelling through relatively open regions in the $\theta'$ structure leads to asymmetric bright spots among the
Cu and Al atoms. The same effect is probably caused by the effect of RE atoms on strong scattering for electrons in Mg-matrix.

The electron density around RE in the Mg matrix was calculated for the cluster which includes RE atom as a central atom as shown in Fig. 8. This cluster is the same as a unit cell of Mg, and 1 Mg atom in it is replaced to 1 RE atom. This is not the solute cluster for nucleation. Two basal planes consisted of 6 Mg atoms are triangles with 0.32 nm, and a half plane of hexagon with 0.32 nm consists of 6 Mg and 1 RE (or Mg) atoms. DV-Xα molecular Orbital method was performed for calculation of electron density using this cluster. Figure 9 shows the result for the calculation, and (a)–(c) show the cross-sections of contour maps of electron density for Mg, Gd atom on the [1210] plane of the Mg-matrix in Fig. 8. The distribution of electron density for each central atom which is parallel to [0001] direction marked by an arrow of A and B in Fig. 9(c) was calculated, and plotted in Fig. 9(d). The Intensity of electron density for Mg atom is lowest among Mg, Gd and Y atoms in Fig. 9(d). This means that the empty space of the hexagonal column surrounding by 5 Mg atomic columns with 1 RE atomic column has higher electron density than that consisted of just 6 Mg atoms, and electron scattering by hexagonal column including Gd or Y is stronger than the hexagonal columns consisted of just 6 Mg atomic column. This is the reason why the darker dots appear at the center of Figs. 1(b) and 1(c).

The simulation for HRTEM image of the mono-layer in the sample aged for short time after as quenching in Figs. 4(a) and 4(b) has been also performed and its result showed in Fig. 10. The model of the single atomic column of RE in Fig. 7(d) has been extended for the mono-layer zone in the present work. The atomic columns of RE atoms are parallel to the [0001] direction and these columns lies along to the \[\frac{1}{2}[1\overline{2}10]\] direction of the matrix which has a spacing of 0.64 nm as shown in Fig. 10(c). The simulated HRTEM image using this model was obtained in Fig. 10(b). Simulated condition was 50 nm in thickness and defocusing of \[\pm 40 \text{ nm}\]. It shows the periodicity of the bright dots having spacing of 0.64 nm along to the [1210] direction of the matrix, and it is in agreement with the processed HRTEM image of Fig. 10(a). Comparing between the crystal model and the simulated HRTEM image as Fig. 10(d), the atomic positions consisted of the RE or Mg columns show the black contrast, and the brightest and darker positions corresponds to the space surrounding by the 6 Mg columns or (1 RE + 5 Mg) columns.
of hexagonal network with 0.18 nm, respectively. This is also in good agreement with simulated images of Fig. 7(b) or 7(c).

Figure 11(a) shows an enlarged HRTEM image of β′-phase in Fig. 5(a) marked by a hexagonal net work. Figure 11(c) is the projected potential of the crystal structure of the β′-phase with D0_{19} structure. The atomic position of Gd and Y was not distinguished and only Gd was put in this unit. The simulated image was shown in Fig. 11(b) which was obtained for the condition of 50 nm in thickness and -40 nm for defocusing. The hexagonal network of bright dots with 0.64 nm can be seen in the simulated HRTEM image as the same as the original HRTEM image. According to the comparison between the crystal model and the simulated HRTEM image as Fig. 11(d), the atomic positions consisted of the RE or Mg columns also show the black contrast, and the brightest and brighter positions corresponds to the space surrounding by the 6 Mg columns or 1 RE and 5 Mg columns of hexagonal network with 0.18 nm, respectively. This is in good agreement with the result of the mono-layer zone in Fig. 10(d). Remarkable differences between them could not be obtained in the present work, although the atomic position of Gd and Y in the mono-layer zone or β′-phase was fixed periodically and calculated HRTEM images. This means that RE atoms of Gd and Y probably can be replaced to each other in each phase, not have any periodicity in there.

4. Conclusions

Precipitation in Mg–Gd–Y (Gd : Y = 3 : 1) alloys without Zr which have the different total amount of RE were investigated by HRTEM and SAED technique, and calculation of HRTEM images and electron density using DV-Xα to understand the relationship between precipitation in these alloys and HRTEM images.

(1) Two alloys of 2.9Gd–0.8Y and 2.1Gd–0.6Y appeared two step hardening in their age-hardening curves which belong to a typical Y-group, though these alloys did not include Zr. And 2.9Gd–0.8Y alloy showed higher hardness than that of 2.1Gd–0.6Y alloy.

(2) The diffuse scattering was obtained in as-quenched samples in each alloy by SAED and the mono-layer zones have been confirmed by HRTEM observation.

(3) The β-phase was confirmed in the 2.9Gd–0.8Y alloy by HRTEM, although the β-phase was confirmed in the 2.1Gd–0.6Y alloy before the β′-phase. The addition of Zr did not affect for the precipitation of β′-phase, but the existence of β′-phase probably depends on the amount of RE.

(4) The β-phase became predominant after prolonged aging. Zigzag lines were observed at the same time when the β-phase appeared in the sample.

(5) The contrast of atomic columns of the matrix in HRTEM image was calculated simplified model of cluster based on the Mg-matrix including one atomic column of RE. HRTEM images of monolayer zone and the β′-phase can be also explained using the same way as the one atomic column of RE atom in the Mg matrix.

REFERENCES


Fig. 11 (a) The practical and (b) simulated HRTEM images for the β′-phase in Fig. 5(a). (c) The projected potential of atoms along to [0001] direction and (d) the superimposed image of (b) and (c).