Characterization of Coherent Precipitates in Mg-RE(-Zn) (RE: Gd, Y) Alloys by the Combination of HRTEM and HAADF-STEM

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Introduction

Utilization of Mg-based alloys is spreading in automotive, aerospace and electronic industries, because of their low density and high recyclability. High strength of the Mg-based alloys is performed using precipitation hardening by aging of supersaturated solid solutions at low temperatures, and so it is important to elucidate microstructures of precipitates. We have studied structures of fine precipitates in Mg-Gd, Mg-Y and Mg-Gd-Zn alloys by the combination of HRTEM and HAADF-STEM, and obtained some valuable information, which can be achieved by only HRTEM or HAADF-STEM. In this paper, we review recent results about crystal structures and morphology of precipitates in the Mg-Gd, Mg-Y and Mg-Gd-Zn alloys.

Mg-based alloys containing rare earth elements have been paid much attention as industrial materials, because of their low density and high recyclability. These alloys show remarkable precipitation hardening by aging of supersaturated solid solutions at low temperatures, and so it is important to elucidate microstructures of precipitates. We have studied structures of fine precipitates in Mg-Gd, Mg-Y and Mg-Gd-Zn alloys by the combination of HRTEM and HAADF-STEM, and obtained some valuable information, which cannot be achieved by only HRTEM or HAADF-STEM. In this paper, we review recent results about crystal structures and morphology of precipitates in the Mg-Gd, Mg-Y and Mg-Gd-Zn alloys.

Experimental Procedure

Mg-RE(-Zn) alloys were prepared by melting construction metals by high frequency induction heating under an Ar gas in carbon crucibles. The alloys were homogenized at 520°C for 2 hrs and then quenched in water, and finally were aged at 200°C. TEM specimens were cut from the alloys, and thinned by mechanical polishing and finally by ion-milling. TEM and HRTEM observations were performed by a 400 kV electron microscope (JEOL JEM-4000EX) with a resolution of 0.17 nm, and HAADF-STEM images were taken by a 300 kV electron microscope (JEOL JEM-3000F) equipped with a field emission gun in the scanning transmission electron microscope mode. In HAADF-STEM observations, a beam probe with a half width of about 0.2 nm was scanned on samples.

Short-range ordering in the early stage of aging in Mg-Gd alloy

Diffuse reflections in electron diffraction patterns have been found in the early stage of aging for many Mg-RE alloys, as can be seen in Figure 1(a) that is an electron diffraction pattern of the Mg-5at%Gd alloy aged at 200°C for 5 hrs, taken with the incident beam parallel to the [001]m direction of the Mg-matrix. Diffuse reflections are observed at 1/2 0 0-typed positions between strong reflections of an Mg-hexagonal lattice. Since the 1/2 0 0-typed positions correspond to ones of superlattice reflections of the D0_19 (Mg,RE) structure, the diffuse reflections have been considered to result from fine precipitates of the Mg,RE.

Figures 1(b) and (c) show HRTEM and HAADF-STEM images, respectively, corresponding to the diffraction pattern of Fig. 1(a). Structural modulations producing the diffuse reflections in Fig. 1(a) are represented as weak and fine contrast modulations in lattice fringes of the Mg-matrix in the HAADF-STEM image of Fig. 1(b), but it is impossible to elucidate structural modulations from Fig. 1(b). On the other hand, the HAADF-STEM image of Fig. 1(c) can reproduce individual Gd atoms, projected along the incident beam, as bright dots without the disturbance of the Mg-matrix. Contrasts of the bright dots correspond to occupation probabilities of Gd atoms in atom columns along the incident beam, and arrangements of bright dots show those of Gd atoms projected along the incident beam. The arrangement of the bright dots in Fig. 1(c) indicates a short-range ordered state without the existence of fine precipitates with periodic arrangements in wide regions. The bright dots are mainly arranged with an interval of about 0.37 nm, which corresponds to a second nearest neighbor distance in a hexagonal close-packed (hcp) structure, and form characteristic local arrangements such as hexagonal arrangements indicated by arrows and zigzag lines with an interval of about 1.1 nm, indicated by arrowheads. The hexagonal arrangement of Gd atoms can be seen in the D0_19 structure, which is formed by ordering of Gd atoms located at second nearest neighbor positions in the hcp structure, as shown in Figure 2(c). In the D0_19 structure, the ordering
of Gd atoms forms a hexagonal arrangement with a side length of \((2a_0\sqrt{3})/3=0.37\) nm, where \(a_0\) is a lattice parameter of a Mg hexagonal lattice, as can be seen in Fig. 2(c). The zigzag lines with an interval of 1.1 nm correspond to those of Gd atoms with an interval of \(2a_0\sqrt{3}/3\) in the Mg-Gd structure of the \(\gamma\) phase, as shown in Figure 2(b). That is, nuclei of the Mg-Gd structure occur in the short-range ordered state by aging at 200 \(\degree C\) for 5 hrs.

The present observations clearly verify that precipitates of a \(\beta'\) phase with a \(D0_{19}\) structure, proposed by many previous papers [6-9], do not exist in the early stage of aging, showing diffuse reflections in electron diffraction patterns, and that a short-range ordered state in Gd-enriched regions is formed and nuclei of the Mg-Gd structure occur in the short-range ordered region.

**Crystal structure of the \(\beta'\) phase**

The \(\beta'\) phase of an ordered structure with an orthorhombic unit precipitates in many Mg-RE alloys aged at a peak hardness condition. Figure 3 shows an HAADF-STEM image of the \(\beta'\) phase in the Mg-5at% Gd alloy aged at 200 \(\degree C\) for 100 hrs, taken with the incident beam parallel to the c-axis of the orthorhombic structure. The deformation of a unit cell indicated by white lines from a rectangle in Fig. 3 results from the sample drift during scanning of the incident beam. In the image of Fig. 3, zigzag arrays of bright dots along the a-axis are observed. From this image, a structure model of the \(\beta'\) phase can be directly derived as Fig. 2(b). In the model of Fig. 2(b), Gd atoms are arranged with face-centered symmetry in \(z=0\) and \(z=1/2\) planes in an orthorhombic unit cell of \(a=2a_0=0.64\) nm, \(b=4a_0\sqrt{3}=2.22\) nm and \(c=c_0=0.52\) nm, where \(a_0\) and \(c_0\) are lattice constants of a hexagonal unit of the Mg-matrix. In the atomic arrangement of Fig. 2(b) projected along the c-axis, zigzag arrays of Gd atoms, indicated by thick line, along the a-axis correspond to those of bright dots in Fig. 3.
Fig. 4 HAADF-STEM images of $\beta'$ precipitates in an Mg-5at%Gd alloy aged at 200 °C for 10 hrs (a) and Mg-2at%Y alloy aged at 200 °C for 150 hrs (b), taken with the incident beam parallel to the [001]$_h$ direction of the hexagonal Mg-matrix.

Fig. 5 HRTEM images of $\beta'$ precipitates in an Mg-5at%G alloy aged at 200 °C for 100 hrs (a) and Mg-2at%Y alloy aged at 200 °C for 150 hrs (b), taken with the incident beam parallel to the [001]$_h$ direction of the hexagonal Mg-matrix.

The structure model has an atomic ratio of Mg-Gd, which shows a good correspondence to a composition of the $\beta'$ phase (88 at%Mg and 12 at%Gd) evaluated by EDS. It should be noted here that the present structural model of the $\beta'$ phase is apparently different from a previous model (Figure 2(a)) proposed by HRTEM observations [14]. As for the atomic arrangement in the z=0 plane, both the models are the same, but the z=1/2 plane in the previous model is formed by only Mg atoms without any Gd atoms, and so a composition of the previous model becomes Mg$_{15}$Gd. Obviously, the previous model can not explain the zigzag arrays of bright dots in the HAADF-STEM image of Fig. 3 and also the evaluated composition of the $\beta'$ phase (88 at%Mg and 12 at%Gd). We have confirmed that the $\beta'$ phase in an Mg-Y alloy has the same structure as Fig. 2(b) [12].

**Morphology of $\beta'$ precipitates in Mg-Gd and Mg-Y alloys**

Figure 4 is HAADF-STEM images of $\beta'$ precipitates in Mg-5at%Gd (a) and Mg-2at%Y alloys (b), taken with the incident beam parallel to the [001]$_h$ direction of the Mg-matrix. Bright lattice fringes in Fig. 4 correspond to zigzag arrays of bright dots in Fig. 3 viz., zigzag arrays of Gd or Y atoms along the a-axis in the $\beta'$ structure in Fig. 2(b). In Fig. 4, one can see three variants of $\beta'$ precipitates with different directions of a- and b-axes, which are equivalent directions in the Mg-hexagonal lattice, and also can notice that morphologies of the $\beta'$ precipitates in Fig. 4(a) and 4(b) are extremely different. In Fig. 4(a), the precipitates with an oval shape, which corresponds to the section of rod-shaped precipitates with a rod-axis along the c-axis, with a long radius along the b-axis and short one along the a-axis are joined along the b-axis. Successive joining of rod-shaped precipitates are performed along the b-axis, and consequently produces planar-shaped precipitates extended over an about 100 nm length along...
Fig. 8 HAADF-STEM images of GP-zones in the Mg-2at%Gd-1at%Zn alloy aged at 200 °C for 150 hrs, taken with the incident beam parallel to the $[00\bar{1}]_m$ (a) and $[0\bar{1}1]$ (b) directions of the hexagonal Mg-matrix. Dumbbells of two bright dots are periodically arranged along GP-zones in (a), and weak bright dots in (b) are arranged with a hexagonal lattice. The bright dots correspond to Gd and/or Zn atoms projected along the $[1-10]_m$ (a) and $[001]$ (b) directions.

Fig. 7 TEM (a) and HRTEM (b) images of the Mg-2at%Gd-1at%Zn alloy aged at 200 °C for 150 hrs, taken with the incident beam parallel to the $[1-10]_m$ direction of the hexagonal Mg-matrix. Line contrasts perpendicular to the c-axis in (a) are GP-zones. The HRTEM image of two GP-zones embedded in the Mg-matrix in (b) shows an ordered arrangement of bright and dark dots, with intervals of 2$d_{002}$ and 3$d_{110}$ spacings of a hexagonal lattice of the Mg-matrix, in the GP-zones.

[110]$_m$-typed directions of the Mg-matrix, as can be seen Fig. 4(a). Remains of junctions of the rod-shaped precipitates can be seen as concaves and dark fringes in Fig. 4(a). On the other hand, precipitates in the Mg-2at%Y alloy has no definite shape, being due to independent growth of Y-enriched atomic planes. Surfaces normal to the b-axis in the precipitates have definite facets parallel to the (010) plane, but those normal to the a-axis have no definite facets and the independent growth of Y-enriched atomic planes are observed.

The difference in morphologies of the $\beta'$ precipitates in Mg-Gd and Mg-Y alloys can be understood by values of lattice misfits between the $\beta'$ phases and the Mg-matrix. That is, it is considered to result from the difference between lattice parameters of a and b for the Mg-Gd and Mg-Y structures. Lattice parameters of the orthorhombic $\beta'$ phase in the Mg-5at%Gd alloy aged at 250 °C for 100 hrs were estimated as $a=0.650$ nm, $b=2.272$ nm and $c=0.521$ nm [12], which are remarkable differences from $2a_0=0.6418$ nm, $4a_0\sqrt{3}=2.2232$ nm and $c_0=0.5210$ nm. On the other hand, lattice parameters of the orthorhombic $\beta'$ phase in the Mg-2at%Y alloy are nearly $a=2a_0=0.6418$ nm and $b=4a_0\sqrt{3}=2.2232$ nm. Figure 5 shows HRTEM images of $\beta'$ precipitates embedded in the Mg-matrix in Mg-5at%Gd (a) and Mg-2at%Y (b) alloys. Lattice fringes in the $\beta'$ precipitates and Mg-matrix are continuously bound up without any interface dislocations. That is, the $\beta'$ phases precipitates with being fully coherent to the Mg-matrix. However, a relatively large lattice misfit between the $\beta'$ phase and Mg-matrix in the Mg-Gd alloy (Fig. 5(a)) produces lattice distortions in the both crystals. Consequently, the lattice distortions due to the lattice misfit are relaxed by the appearance of dislocations in the $\beta'$ precipitates, as indicated by an arrow in Fig. 5(a). On the other hand, a small lattice misfit between the $\beta'$ phase of the Mg-Y alloy and Mg-matrix produces no lattice distortions at interfaces between the $\beta'$ precipitates and Mg-matrix, and permits individual growth of Y-enriched atomic planes along the a-axis, as
can be seen in Fig. 5(b).

**Guinier-Preston zone in Mg-Gd-Zn alloy**

Figures 6(a) and (b) are electron diffraction patterns of the Mg-2at%Gd-1at%Zn aged at 200 °C for 150 hrs, taken with the incident beam parallel to the [001]m and [110]m directions of the hexagonal Mg-matrix, respectively. In the diffraction patterns, 1/3 1/3 0-typed extra spots indicated by arrows in Fig. 6(a) and streak reflections indicated by arrows in Fig. 6(b) are observed in addition to superlattice reflections of β' precipitates between strong reflections of a hexagonal lattice of the Mg-matrix. From the comparison between Fig. 6(a) and Fig. 6(b), it can be concluded that the 1/3 1/3 0-typed extra spots in Fig. 6(a) correspond to sections of the streak reflections in Fig. 6(b), and that the streak reflections in Fig. 6(b) have a rod-shape.

In HRTEM images taken with the incident beam parallel to the [001]m direction of the hexagonal Mg-matrix, the β' precipitates are observed, but precipitates showing the 1/3 1/3 0-typed extra reflections in Fig. 6(a) cannot be recognized.

Figures 7(a) and (b) show a TEM and an HRTEM images of the Mg-2at%Gd-1at%Zn alloy, respectively, taken with the incident beam parallel to the [001]m direction of the hexagonal Mg-matrix. Planar faults producing the streak reflections in Fig. 6(b) are observed as line contrasts perpendicular to the c-axis in Fig. 7(a). The line contrasts are GP-zones formed by two close-packed planes with an ordered arrangement of Gd and/or Zn atoms, as will be shown later. On the other hand, the β' precipitates are observed as blurred bright and dark contrasts in Fig. 7(a). The HRTEM image of Fig. 7(b) shows that the GP-zones precipitate coherently in the Mg-matrix, and bright and dark dots in the GP-zones show an ordered arrangement with intervals of 2d_{002} and 3d_{110} spacings of a hexagonal lattice of the Mg-matrix.

Figures 8(a) and (b) show HAADF-STEM images of the GP-zones, taken with the incident beams parallel to [110]m and [001]m directions of the Mg-matrix, respectively. In Fig. 8(a), dumbbells of bright dots with an interval of about 0.5 nm are periodically arranged with an interval of about 0.5 nm along the GP-zones. It is reasonably considered that these intervals correspond to those of 2d_{002}=0.52 nm and 3d_{110}=3a_{0}/2=0.48 nm, respectively, as shown in Fig. 7(b), and that the bright dots represent Gd and/or Zn atoms projected along the [110]m direction. On the other hand, the image of Fig. 8(b) shows a hexagonal arrangement of weak bright dots, with an interval of about 0.6 nm. The weak contrast in Fig. 8(b) is due to only two layers of Gd and/or Zn atoms of the GP-zone embedded in about 100 atomic layers of the Mg-matrix. That is, the result demonstrates that HAADF-STEM makes it possible to observe an image contrast of two layers of Gd and/or Zn atoms embedded in the Mg-matrix with a few tens of nm in thickness. Although many GP-zones embedded in the Mg-matrix produce the 1/3 1/3 0-typed extra spots in Fig. 6(a), it is impossible to form the image contrast of the GP-zone in the HRTEM observation.

From the images of Fig. 7(b), 8(a) and 8(b), we can directly derive a structural model of the GP-zone, as shown in Figure 9. In the model, Gd and/or Zn atoms occupy at ordered positions in two close-packed planes sandwiching a close-packed plane of Mg-atoms. The bright dots in Figs. 8(a) and 8(b) represent Gd and/or Zn atoms projected along the incident beam parallel to the [110]m and [001]m directions, respectively. The atomic arrangement of the GP-zone is similar to that of plate-like precipitates found in Mg-2.4wt%RE-0.4wt%Zn-0.6wt%Zr alloys [15], and also can be seen in the crystal structure of a precipitate phase in rapidly solidified Mg-2at%Ce-1at%Zn and Mg-2at%Ce alloys [16].

**Conclusion**

We have reviewed recent results for microstructures of coherent precipitates in Mg-based alloys containing rare earth elements, studied by the combination of HRTEM and HAADF-STEM. Direct observations of individual rare earth atoms projected along the incident beam by HAADF-STEM enable us to determine directly arrangements of rare earth atoms in a hexagonal Mg-lattice. On the other hand, HRTEM images show crystallographic relationships between lattices of precipitates and the Mg-matrix. Therefore, it can be concluded that the combination of HRTEM and HAADF-STEM is the most powerful tool for characterization of fine precipitates being coherent with the matrix crystals.

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