Characterization of Precipitates in Mg-Sm Alloy Aged at 200°C, Studied by High-Resolution Transmission Electron Microscopy and High-Angle Annular Detector Dark-Field Scanning Transmission Electron Microscopy

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Precipitates in an Mg-0.99 at%Sm (Mg₀.₉₉Sm₀.₉₉) alloy aged at 200°C were studied by the combination of high-resolution transmission electron microscopy (HRTEM) and high-angle annular detector dark-field scanning transmission electron microscopy (HAADF-STEM). Fine precipitates of a meta-stable phase, which is called γ here, in the alloy aged at 200°C for 4 h have a thin lens-shape with a thickness of 2–5 nm and a diameter of 20–60 nm. The γ precipitate has an incommensurate structure with an orthorhombic unit cell of a = 2a₀ = 0.64 nm, b = 6a₀/√3 = 3.334 nm and c = c₀ = 0.52 nm, where a₀ and c₀ are lattice constants of a hexagonal unit of the Mg-matrix. In the early stage of aging at 200°C for 0.5 h, isolated structure units forming the γ structure are dispersed in an Mg hexagonal lattice. By annealing at 200°C for 100 h, coarse precipitates of a stable Mg₃Sm phase are formed along grain boundaries and inside grains of the Mg-matrix, and wide γ precipitate-free zones appear around them. [doi:10.2320/matertrans.M2009046]

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1. Introduction

Magnesium-based RE (RE: rare-earth metals) alloys are known to show remarkable precipitation hardening, because of their relatively wide solubility limits at high temperatures and narrow solubility at low temperatures.¹⁻³) By isothermal aging of supersaturated solid solutions at about 200°C, the hardness increases and finally reaches peak values, and then decreases. The variation in hardness has been considered by a precipitation process of β'' (D0₁₉ structure) → β' meta-stable phase (base-centered orthorhombic structure) → stable phases.³⁻⁵) However, electron diffraction and HRTEM used in previous studies are not sufficient tools to obtain detailed information about crystals structures and microstructures of fine precipitates. Recently, some of the authors have studied precipitates in Mg-Gd,⁶⁻⁷) Mg-Y,⁸) Mg-Cu-Y⁹) and Mg-Zn-Gd¹⁰) alloys by the combination of HRTEM and HAADF-STEM, and successfully obtained valuable information about crystal structures and microstructures of fine precipitates, which cannot be established by only HRTEM. In particular, atomic-scaled HAADF-STEM observations make possible to image directly arrangements of RE atoms in the Mg-matrix lattice. Also, HRTEM gives us information about crystallographic relations between precipitates and the Mg-matrix. As a result, the β'' phase considered to be fine precipitates with a D0₁₉ structure is established to be a short-range ordered state being related to the β' meta-stable phase,⁷) and a new model of Mg₁₋₂RE is proposed for the crystal structure of the β' phase.⁶⁻⁸) Also, the structure of planar GP-zones in an Mg-Zn-Gd alloy has been derived by direct observations of an arrangement of Zn/Y atoms on the GP-plane.¹⁰) The characterization of precipitation processes in the Mg-RE alloys is an important object for the development of mechanical properties for the alloys, and the combination of HRTEM and HAADF-STEM is expected to be a significant tool for the investigation of the object.

The purpose of the present paper is to characterize a precipitate process of an Mg-Sm alloy from the early stage of aging to over-aging at 200°C. The alloy shows a peak hardness by aging at 200°C for about 4 h, and several stages with successive formation of GP-zones and precipitate phases with different morphologies and structures were reported,¹¹) but the details of the structures of the precipitates have not been understood well in the previous paper. Therefore, the Mg-Sm alloy system is a good sample for the comparison with precipitate phases in other Mg-RE alloys examined in the previous papers.⁶⁻¹⁰) In the present paper, the morphologies and crystal structures of precipitates in the Mg-Sm alloy system will be revealed from HRTEM and HAADF-STEM observations.

2. Experimental

An alloy with a nominal composition of Mg-0.99 at%Sm was prepared by melting Mg (99.9%) and Sm (99.9%) metals by induction heating under 0.09 MPa argon gas in a carbon crucible. The alloy was quenched in water after annealing at 520°C for 2 h and then aged at 200°C for various times. Specimens for transmission electron microscopy were cut from the aged samples and thinned by mechanical polishing, and finally by ion-milling milling. HRTEM observations were performed in a 400 kV electron microscope (JEM-4000EX), having a resolution of 0.17 nm. HAADF-STEM images were taken by a 300 kV electron microscope (JEM-3000F) equipped with a field emission gun in the scanning transmission mode. In HAADF-STEM observations, a beam probe with a half width of about 0.2 nm was scanned on samples. Energy dispersive X-ray spectroscopy (EDS) was
also performed with the JEM-3000F microscope operated at 300 kV.

3. Results

Figures 1(a) and 1(b) show electron diffraction patterns of the Mg-0.99 at%Sm alloy aged at 200°C for 4 h around a peak-hardness condition, which includes \( \gamma \) precipitates formed along three equivalent directions of the hexagonal Mg lattice. (c) is an enlarged electron diffraction pattern taken from a region including some \( \gamma \) precipitates along one direction, and (d) is a schematic illustration showing a characteristic feature of a distribution of streak reflections. Indexes of reflections and reciprocal lattices indicated by thin lines in (d) are shown by the orthorhombic unit cell indicated by a rectangle in Fig. 4.

Fig. 1 (a) and (b) are electron diffraction patterns taken with the incident beam parallel to the [001]_m and [010]_m directions of the Mg-matrix, respectively, for the Mg-0.99 at%Sm alloy aged at 200°C for 4 h around a peak-hardness condition, which includes \( \gamma \) precipitates formed along three equivalent directions of the hexagonal Mg lattice. (c) is an enlarged electron diffraction pattern taken from a region including some \( \gamma \) precipitates along one direction, and (d) is a schematic illustration showing a characteristic feature of a distribution of streak reflections. Indexes of reflections and reciprocal lattices indicated by thin lines in (d) are shown by the orthorhombic unit cell indicated by a rectangle in Fig. 4.

Figure 2 shows HRTEM images of the Mg-0.99 at%Sm alloy aged at 200°C for 4 h, taken with the incident beam parallel to the [001]_m (the subscript “m” hereafter denotes the Mg-matrix) and [010]_m directions of the Mg-matrix, respectively. In the diffraction pattern of Fig. 1(a), one can see star-shaped streak reflections at \( 1/2 \ 0 \ \tau \)-typed positions being halfway between strong reflections of the hexagonal Mg-matrix. The star-shaped reflections result from \( \gamma \) precipitates formed along three equivalent directions of the hexagonal Mg lattice. An enlarged electron diffraction pattern taken from a region including some precipitates along one direction is shown in Fig. 1(c). In the figure, one can see relatively strong streak reflections (indicated by arrowheads) centered on \( 1/2 \ 0 \ \tau \)-type positions and weak streaks (indicated by arrows) around the positions divided into three between the stronger ones. From Fig. 1(c), a distribution feature of the strong and weak streak reflections is characterized, as shown in Fig. 1(d). In the figure, indexes of reflections and reciprocal lattices indicated by thin lines are described by a fundamental orthorhombic structure with a unit cell indicated by a rectangle in Fig. 4. The strong streak reflections are located exactly at reciprocal lattice points, whereas weak ones are slightly shifted in the directions indicated by arrows from reciprocal lattice points, as shown in Fig. 1(d). The schematic shifts of \( \delta \) for the weak reflections suggest an incommensurate structure of precipitates. The value of \( \delta \) is estimated as about 0.1 from the pattern of Fig. 1(c).

Figure 2 shows HRTEM images of the Mg-0.99 at%Sm alloy aged at 200°C for 4 h, taken with the incident beam parallel to the [001]_m (a) and [210]_m (b) directions. In Fig. 2(a), planar precipitates with 2–5 nm in thickness and 20–60 nm in length are observed along the three equivalent \( 210 \)_m-type directions indicated by three arrows. The thickness and length directions of the precipitates are parallel to a-axis and b-axis of the orthorhombic structure of the \( \gamma \) precipitates, respectively, as will be mentioned in Fig. 4. It is easily understood that the streak reflections elongated along the a*-direction in Fig. 1(c) result from the thin planar precipitates with 2–5 nm in thickness along the a-axis. In Fig. 2(b), precipitates with the b-axis being parallel to the incident beam and inclined with a 30 degree from the incident beam are observed at left and right sides, respectively. It can be seen that the \( \gamma \) precipitates have lengths of
about 20 nm along the c-axis, which is parallel to the c\textsubscript{m}-axis of the hexagonal Mg-matrix. The planar \gamma precipitates have edges thinned, as can be seen Fig. 2, and so they have a thin lens-shape to be exact.

Figure 3 shows atomic-scaled HRTEM (a) and HAADF-STEM (b) images of \gamma precipitates embedded in the Mg-matrix, taken with the incident beam parallel to the [001]\textsubscript{m} direction. In the figures, one can see arrays of ring contrasts and zigzag lines, which are indicated by arrows and arrowheads, respectively. By close examination of HRTEM observations, the ring contrasts are hexagonal ones, and hexagonal and zigzag contrasts are coherently formed in the Mg-matrix lattice. The HAADF-STEM image of Fig. 3(b) shows that the hexagonal contrasts and zigzag lines of bright dots directly correspond to arrangements of Sm atoms located at hexagonal lattice points of the Mg-matrix. The HAADF-STEM image of Fig. 3(b) shows that the hexagonal contrasts and zigzag lines of bright dots directly correspond to arrangements of Sm atoms located at hexagonal lattice points of the Mg-matrix. From Fig. 3, a structure model of the \gamma precipitate can be directly derived, as shown in Fig. 4. In the model, a unit cell of a fundamental orthorhombic structure formed by only arrays of a hexagonal arrangement of Sm atoms is indicated by a rectangle. The orthorhombic structure has the space group of \textit{Cmc}_2\textsubscript{1} (No. 36) and produces a reflection condition of \( h + k = 2n \), which is consistent with that of observed reflections in the case of \( \delta = 0 \), as can be seen in Fig. 1(d).

The appearance of zigzag arrays of Sm atoms, which are indicated by an arrowhead in Fig. 4 and correspond to zigzag line contrasts in Fig. 3, in the fundamental structure produces an incommensurate structure resulting in shifts of the weak streak reflections from the condition of \( h + k = 2n \), as can be seen in Fig. 1(d). In order to confirm the schematic shifts of \( \delta \) for the weak reflections in Fig. 1(d), we perform a simulation of diffraction pattern for a model of Fig. 5(a), in which zigzag arrays are randomly introduced in hexagonal arrays of Sm atoms. In Fig. 5(b), which is a Fourier diffractogram obtained from the model of Fig. 5(a), weak peaks indicated by arrows show the schematic shifts, as can be seen in Fig. 1(d). An atomic ratio of the fundamental structure formed by only arrays of a hexagonal arrangement of Sm atoms in Fig. 4 is Mg:Sm, and the incommensurate structure including zigzag arrays of Sm atoms become to have an atomic ratio of Mg\textsubscript{5}\textsubscript{x}Sm. The observed diffraction patterns of the \gamma precipitates in the Mg-0.99 at%Sm alloy are obviously different from those of \beta phases precipitated in Mg-Gd and Mg-Y alloys aged at peak-hardness conditions.

Fig. 2 HRTEM images of the Mg-0.99 at%Sm alloy aged at 200°C for 4 h, taken with the incident beam parallel to the [001]\textsubscript{m} (a) and [210]\textsubscript{m} (b) directions. In images of precipitates in (a), one can see dotted contrasts of zigzag lines and hexagonal arrays, as shown in Fig. 3.

Fig. 3 Atomic-scaled HRTEM (a) and HAADF-STEM (b) images of \gamma precipitates in the Mg-0.99 at%Sm alloy aged at 200°C for 4 h, taken with the incident beam parallel to the [001]\textsubscript{m} direction. Arrowheads and arrows indicate contrasts of zigzag lines and hexagonal arrays, respectively.
However, it should be noted that the crystal structure of the \(\beta'\) precipitates in Mg-Gd and Mg-Y alloys is formed by zigzag arrays of RE atoms, which are the same as the zigzag arrays of Sm atoms in Fig. 4, and has an atomic ratio of \(\text{Mg}:\text{RE}\).\(^{6,8}\)

The hexagonal arrangement of RE atoms is found in a short-range ordered state, which is formed in the early stage of aging for an Mg-Gd alloy,\(^7\) and also is a basic one in an ordered \(\text{D}0_{19}\) structure.

Figure 6 shows HRTEM (a) and HAADF-STEM (b) images of the Mg-0.99 at\%Sm alloy aged at 200°C for 0.5 h, taken with the incident beam parallel to the \([001]\) direction. In the images, one can see some isolated hexagonal contrasts and short zigzag lines, which are indicated by arrows and an arrowhead, respectively. As indicated by pairs of small arrows in Fig. 6, the isolated hexagonal contrasts appear with a definite distance, which corresponds to that indicated by an arrow with arrowheads at both terminations in Fig. 4. The results show that the hexagonal arrangement of Sm atom is stably formed as nuclei in the early stage of the formation of precipitates and neighboring ones are arrayed so as to form the \(\gamma\) precipitates.

The \(\gamma\) precipitates are meta-stable and disappear by the formation of stable precipitates in the alloy over-aged. Figures 7(a) and 7(b) are HAADF-STEM images of the stable precipitates appearing along a grain boundary and inside an Mg-matrix grain, respectively, taken from the Mg-0.99 at\%Sm alloy aged at 200°C for 100 h. In Fig. 7(a), one can see large precipitates with sizes of about 0.1 \(\mu\)m along a grain boundary and the \(\gamma\) precipitates, which are observed.

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**Fig. 4** Structure model of the \(\gamma\) phase. Arrows and an arrowhead indicate hexagonal arrays and a zigzag line of Sm atoms, respectively.

**Fig. 5** Typical structure model (a) consisting of zigzag arrays and hexagonal arrays of Sm atoms, and a Fourier diffractogram (b) obtained from the model of (a).

**Fig. 6** Atomic-scaled HRTEM (a) and HAADF-STEM (b) images of the Mg-0.99 at\%Sm alloy aged at 200°C for 0.5 h, taken with the incident beam parallel to the \([001]\) direction. Arrows and an arrowhead indicate hexagonal contrasts and a zigzag line, respectively. Distances of two neighboring hexagonal contrasts, indicated by pairs of small arrows, correspond to a distance of an arrow with arrowheads at both terminations in Fig. 4.
with fine bright contrasts in the upper and bottom sides, disappear in areas of 0.3μm in width at both sides of the grain boundary. On the other hand, in Fig. 7(b), one can see plane-shaped precipitates formed along three equivalent directions of the hexagonal Mg-matrix. A composition of the planar precipitates is evaluated as 76 at%Mg-24 at%Sm by STEM-EDS analysis. The precipitates, which are observed in the left and right edges of Fig. 7(b), also disappear in a wide region of 1μm in width around the stable precipitates. The appearances of wide γ precipitate-free zones around stable precipitates are considered to result in the remarkable decrease of mechanical strength.

The stable precipitates along the three equivalent directions of the hexagonal Mg-matrix are often formed with a special manner of a honeycomb shape, as shown in Fig. 8(a). An HRTEM lattice image of a planar precipitate embedded the Mg-matrix in Fig. 8(b) shows that the precipitate is an Mg2Sm cubic phase,12) which is called as a β1 phase in Mg-RE alloys,13) with a lattice parameter of a = 0.73 nm. This result is confirmed by the composition of 76 at%Mg-24 at%Sm estimated by STEM-EDS. The β1 phase precipitates with facets of a (112)p (the subscript “p” denotes precipitate) plane, indicated by arrows in Fig. 8(b), which is parallel to a (100)m plane of the hexagonal Mg-matrix, and with crystallographic relations of [001]m // [110]p and [110]m // [111]p to the Mg-matrix. The crystallographic relations can be understood by nearly perfect coincidence between lattice spacings of 3d111p = 1.278 nm and 8d110m = 1.280 nm.

4. Conclusion

Precipitates in an Mg-0.99 at%Sm alloy aged at 200°C for various times from 0.5 h to 100 h were studied by the combination of HRTEM and HAADF-STEM. Fine precipitates of a γ meta-stable phase in the alloy aged at 200°C for 4 h have a thin lens-shape with a thickness of 2-5 nm and a diameter of 20-60 nm. The γ phase has an incommensurate structure with an orthorhombic unit cell of a = 2a0 = 0.64 nm, b = 6a0√3 = 3.334 nm and c = c0 = 0.52 nm. In

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Fig. 7 HAADF-STEM images showing coarse precipitates along a grain boundary (a) and planar ones inside an Mg-matrix grain in the Mg-0.99 at%Sm alloy aged at 200°C for 100 h. Note γ precipitates with fine contrasts and wide γ precipitate-free zones around the grain boundary and planar precipitates.

Fig. 8 TEM image (a) and HRTEM image (b) of precipitates in the Mg-0.99 at%Sm alloy aged at 200°C for 100 h, taken with the incident beam parallel to the [001]m direction. In (a), one can see planar-shaped precipitates formed with a honeycomb arrangement. Weak and fine contrasts at the left-bottom side in (a) correspond to the γ precipitates. In (b), the β1 precipitate has facets of the (112)p plane, indicated by arrows.
the early stage of aging at 200°C for 0.5 h, isolated structure units forming the γ structure are dispersed in a hexagonal lattice of the Mg-matrix. By annealing at 200°C for 100 h, coarse precipitates of a stable Mg₃Sm phase are formed along grain boundaries and inside grains of the Mg-matrix, and wide γ precipitate-free zones appear around them.

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