Transmission Electron Microscopy for Precipitate Phases in Rapidly Solidified Mg-2 at% Ce-1 at% Zn and Mg-2 at% Ce Alloys

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Precipitate phases in Mg-2 at% Ce-1 at% Zn ($\text{Mg}_{97}\text{Ce}_2\text{Zn}_1$) and Mg-2 at% Ce ($\text{Mg}_{98}\text{Ce}_2$) alloys, prepared by a melt-quenching method, have been examined by high-resolution transmission electron microscopy (HRTEM) and high-angle annular detector dark-field scanning transmission electron microscopy (HAADF-STEM). A precipitate phase formed at grain boundaries has an ordered structure with a hexagonal unit cell of $\sqrt{3}a_0$ and c_0 , in which a_0 and c_0 are lattice parameters of an h.c.p. structure of the Mg-matrix. On the other hand, a precipitate phase embedded in Mg-matrix grains has a long-period modulated structure formed by the appearance of two-dimensional anti-phase boundaries with a hexagonal symmetry in the fundamental hexagonal structure with lattice constants of $\sqrt{3}a_0$ and c_0 . [doi:10.2320/matertrans.48.476]

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1. Introduction

In the last two decades, Mg alloys have been used in electronic, automotive and aviation industries where weight reduction is a necessary requirement.^{1,2)} In general, Mg alloys prepared by an ingot metallurgy (I/M) processing exhibit lower strength, ductility, creep resistance and corrosion resistance. The application of rapid solidification (RS) processing to Mg alloys results in the grain refinement, extended solid solubility, formation of novel metastable phases and improved chemical homogeneity with a consequent improvement of mechanical properties and corrosion resistance.³⁾ Recently, nanocrystalline Mg-Y-Zn alloys with high specific tensile strength, high temperature tensile strength and large elongation have been developed by rapidly solidified powder metallurgy (RS P/M) technology.⁴⁾ The addition of rare earth elements (RE) remarkably enhances the mechanical properties of RS Mg alloys due to solution hardening and precipitation hardening.⁵⁾ In the previous studies, it was found that the RS Mg-La-Zn and Mg-Ce-Zn alloys showed higher Vickers hardness than RS Mg-Y-Zn alloys⁶⁾ and higher corrosion resistance.⁷⁾ These alloys have attracted a great deal of attention, because they possess much better strengths as compared with conventional Mg I/M alloys.

In the course of the investigation of microstructures of RS Mg-Zn-RE alloys, a new phase, which has not been proposed in the Mg-Ce-Zn ternary phase diagram,⁸⁾ has been reported as an $\text{Mg}_{17}\text{Ce}_2$ compound in as-quenched state of the RS $\text{Mg}_{97}\text{Ce}_2\text{Zn}_1$ alloy.⁹⁾ However, its structure is not known in detail. In the previous study, one-dimensional anti-phase structures based on a stable Mg_{12}Ce structure¹⁰⁾ in an $\text{Mg}_{91}\text{Ce}_6\text{Zn}_3$ cast alloy has been successfully determined by using high-resolution transmission electron microscopy (HRTEM) and high-angle annular detector dark-field scanning transmission electron microscopy (HAADF-STEM).¹¹⁾ The combination of HRTEM and HAADF-STEM is a powerful technique for determining the crystal structures in compounds consisted of Mg and RE elements. The aim of this study is to determine the crystal structures of the

metastable phases in RS $\text{Mg}_{97}\text{Ce}_2\text{Zn}_1$ and $\text{Mg}_{98}\text{Ce}_2$ alloys by HRTEM and HAADF-STEM.

2. Experimental Procedures

$\text{Mg}_{97}\text{Ce}_2\text{Zn}_1$ and $\text{Mg}_{98}\text{Ce}_2$ alloys were prepared by a single roller melt-spinning method and then annealed at various temperatures from 200°C to 400°C. Samples for transmission electron microscopy (TEM) were prepared by an ion-milling method. HRTEM images were taken using a 400 kV electron microscope (JEM-4000EX) with a resolution power of 0.17 nm, and HAADF-STEM images were taken using a 300 kV electron microscope (JEM-3000F) equipped with a scanning transmission model. A beam probe with a half width of about 0.2 nm was scanned on the sample, and intensity of transmission high-angle scattering beam is recorded with an annular detector.

3. Experimental Results

Figure 1 shows bright-field TEM (a) and HAADF-STEM (b) images of an as-quenched $\text{Mg}_{97}\text{Ce}_2\text{Zn}_1$ alloy. In Fig. 1(a), secondary phases with an about 50 nm thickness are observed as gray contrast along boundaries of matrix grains with an average size of 1 μm . On the other hand, another secondary phase with fine contrast can be seen around centers of crystal grains surrounded by bright contrast regions. The secondary phases along grain boundaries and inside of grains are observed as bright contrast in the Z-contrast image of Fig. 1(b) taken with HAADF-STEM, and consequently these phases have Ce- and/or Zn-rich compositions compared with the composition of the Mg-matrix. The secondary phase observed in the inside of the matrix grain in Fig. 1(b) is classified into two types, *i.e.*, platelet precipitates, indicated by the arrows, and polygonal precipitates with an about 50 nm size. The platelet precipitates show brighter contrast, compared with the other precipitates formed in the grain and at the grain boundary. Similar morphology of precipitates has been observed in an as-quenched $\text{Mg}_{98}\text{Ce}_2$ alloy. In the $\text{Mg}_{98}\text{Ce}_2$ alloy, compositions of platelet

Fig. 1 Bright-field TEM (a) and HAADF-STEM (b) images of the as-quenched MgCe_2Zn_1 alloy. The HAADF-STEM image (b) was taken with the incident beam parallel to the $[001]_m$ direction of the Mg-matrix. An arrowhead indicates a precipitate at a grain boundary, and arrows show platelet precipitates.

Fig. 2 Electron diffraction patterns of the as-quenched $\text{Mg}_{97}\text{Ce}_2\text{Zn}_1$ alloy, taken with the incident beam parallel to the $[001]_m$ (a) and $[110]_m$ (b) directions of the Mg-matrix. Diffraction spots are indexed by an h.c.p. Mg structure.

precipitates and the other precipitates are estimated as 80 at%Mg and 20 at%Ce, and 92 at%Mg and 8 at%Ce, respectively. This result shows that the platelet precipitates are a different phase from those of the other precipitates. In this paper, the platelet precipitates has not been investigated in detail.

Figure 2 shows electron diffraction patterns for Mg-matrix grains including precipitates, taken along matrix direction of $[001]_m$: (a) and $[110]_m$: (b). Strong spots due to the Mg-matrix and precipitates, and fine spots of precipitates appear around $1/3 \ 1/3 \ 0$ - and $1/3 \ 1/3 \ 1$ -typed positions of the h.c.p. Mg structure. These patterns show that the precipitates are fully coherent with the matrix. The distribution of the fine spots around $1/3 \ 1/3 \ 0$ - and $1/3 \ 1/3 \ 1$ -typed positions can be clearly seen in an enlarged diffraction pattern shown in Fig. 3(a) and a schematic illustration (Fig. 3(b)) showing a characteristic feature of the distribution of the fine spots. A distance between the fine spots is estimated as $1/4.5 \text{ nm}^{-1}$ and consequently the existence of a structural modulation with a period of $(2/\sqrt{3}) \times 4.5 \text{ nm} = 5.2 \text{ nm}$ is suggested. Positions of the fine spots along the line through 000 to 110_m spots are schematically drawn in Fig. 3(c). That is, the spots are located at positions shifted with $\delta/3$ and $2\delta/3$ from the $1/3 \ 1/3 \ 0$ and $2/3 \ 2/3 \ 0$ positions, where δ is an interval between fine spots along the line through 000 to 110_m spots.

In order to understand the appearance of the fine spots, we observed HRTEM images. Figure 4 shows HRTEM images of precipitates embedded in a matrix grain (a) and at a grain boundary (b). Hexagonal lattice fringes with a lattice

parameter of 0.57 nm are observed in a precipitate of Fig. 4(b), whereas a modulation of lattice fringes accompanied with bright and dark contrast can be seen in precipitates of Fig. 4(a). The lattice modulation in Fig. 4(a) has approximately hexagonal symmetry and an averaged distance of about 5 nm , which is consistent with a modulation period of 5.2 nm estimated from an interval of fine spots in the diffraction pattern of Fig. 3(a).

Figure 5 shows an enlarged HRTEM image of a precipitate embedded in the Mg-matrix. A small rhombus indicated by m and large one indicated by s are unit cells of the h.c.p. Mg structure and superlattice structure of the precipitate, respectively. The hexagonal unit of the precipitate structure has a lattice parameter of $\sqrt{3}a_0 = 0.571 \text{ nm}$, where a_0 is a lattice parameter of the Mg structure. By obliquely viewing along the vertical direction of Fig. 5, one can see that the precipitate is exactly coherent with the Mg-matrix and that there are several anti-phase boundaries, as can be seen as steps of lattice fringes indicated by white lines. That is, it can be concluded that the lattice modulation in Fig. 4(a) arises from the appearance of anti-phase boundaries. Also, it can be said that the polygonal shapes of the precipitates inside matrix grains, as can be seen in Fig. 1(b), are mainly formed by facets of (110) -typed planes.

Figure 6 is a HAADF-STEM image of a precipitate embedded in the Mg-matrix. A hexagonal arrangement of bright dots representing Ce/Zn atom columns is observed. From the image, a structure model of the fundamental superlattice structure of the precipitate can be directly

Fig. 3 (a): an enlarged diffraction pattern of Fig. 2(a), (b): a schematic illustration showing a two-dimensional distribution of fine spots, and (c): a distribution of fine spots on the line through 000 and 110_m spots. Pairs of small arrows in (c) indicate $1/3 \ 1/3 \ 0$ and $2/3 \ 2/3 \ 0$ positions.

derived, as shown in Fig. 7. The superlattice structure with an ordered arrangement of Ce/Zn atoms has a hexagonal structure with a lattice parameters of $a = \sqrt{3}a_0 = 0.571 \text{ nm}$

and $c = c_0 = 0.521 \text{ nm}$, the space group of $P\bar{6}2m$ (No. 189), and an atom ratio of $\text{Mg}_5(\text{Ce}, \text{Zn})$. The composition of $\text{Mg}_5(\text{Ce}, \text{Zn})$ is remarkably different from that of 92 at% Mg and 8 at% Ce, which was estimated from precipitates in an as-quenched $\text{Mg}_{98}\text{Ce}_2$ alloy. Probably, Ce and Zn atoms are located with an occupation probability of about 50%.

Diffraction patterns calculated from the structure model of Fig. 7 are shown in Fig. 8, in which 030, 002 and 110 spots correspond to 110_m, 002_m and 010_m ones in Fig. 2, respectively. It is suggested that diffraction patterns in Fig. 2 are understood by a structural modulation based on the fundamental structure of Fig. 7.

In order to understand a characteristic distribution of fine spots in the electron diffraction patterns of Figs. 2 and 3, we calculated diffraction patterns for two structural models of anti-phase boundaries with different displacement vectors in Fig. 9. The calculated patterns from the two models are shown in Fig. 10. The pattern of Fig. 10(b) reproduces the characteristic feature of Fig. 3(c) well. That is, it can be concluded that the structural modulation is formed by the appearance of anti-phase boundaries shown in Fig. 9(b).

The same modulated structure in precipitates inside the Mg-matrix has been found in $\text{Mg}_{97}\text{Zn}_1\text{Ce}_2$ and $\text{Mg}_{98}\text{Ce}_2$ alloys annealed at 300°C, and it transforms to a stable phase of $\text{Mg}_{12}\text{Ce}^{(10)}$ by annealing at 400°C.

4. Conclusion

Metastable phases are precipitated inside Mg-matrix grains and at grain boundaries in $\text{Mg}_{97}\text{Ce}_2\text{Zn}_1$ and $\text{Mg}_{98}\text{Ce}_2$ alloys prepared by the melt-quenching method. The precipitate phase at grain boundaries has a hexagonal structure with lattice parameters of $\sqrt{3}a_0$ and c_0 , where a_0 and c_0 are lattice parameters of the h.c.p. Mg structure, and the space group of $P\bar{6}2m$ (No. 189). The hexagonal structure is formed by an ordered arrangement of Ce/Zn atoms in a hexagonal lattice of the Mg structure. On other hand, two-types of precipitates with about 50 nm sizes appear inside Mg-matrix grains, and

Fig. 4 HRTEM images of precipitates embedded in the Mg-matrix (a) and at a grain boundary (b) in the as-quenched MgCe_2Zn_1 alloy. They were taken with the incident beam parallel to the $[001]_m$ direction of the Mg-matrix. The large arrow in (b) indicates a precipitate. Note that contrast modulation can be seen in only precipitates embedded in the Mg-matrix.

Fig. 5 A HRTEM image of a precipitate embedded in the Mg-matrix in the as-quenched MgCe_2Zn_1 alloy, taken with the incident beam parallel to the $[001]_m$ direction of the Mg-matrix. Rhombuses indicated by m and s are unit cells of the Mg-hexagonal lattice and a fundamental superlattice of the precipitate. Arrows show facets of (110) -typed planes of the fundamental superlattice of the precipitate. White lines indicate steps of lattice fringes across anti-phase boundaries.

Fig. 6 A HAADF-STEM image of a precipitate embedded in the Mg-matrix in the as-quenched MgCe_2Zn_1 alloy, taken with the incident beam parallel to the $[001]_m$ direction of the Mg-matrix. Note that bright dots representing Ce/Zn atom columns form a hexagonal lattice with a lattice parameter of 0.57 nm. White lines indicate a step of arrays of bright dots across an anti-phase boundary.

Fig. 7 A structure model of the fundamental superlattice structure of the precipitate phase.

Fig. 8 Diffraction patterns calculated from the structural model of Fig. 7, taken with the $[001]$ (a) and $[100]$ (b) directions.

Fig. 9 Two models of anti-phase boundaries with different displacement vectors.

Fig. 10 (a) and (b) are diffraction patterns calculated from two models of anti-phase boundaries in Figs. 9(a) and 9(b), respectively. Note that the pattern of (b) reproduces the characteristic of Fig. 3(c) well.

the major precipitate phase has a modulated structure based on the hexagonal structure with lattice parameters of $\sqrt{3}a_0$ and c_0 . The structural modulation is formed by the appearance of two-dimensional anti-phase boundaries with a hexagonal symmetry. The metastable phases still exist in alloys annealed at 300°C, but it transforms to a stable phase of Mg_{12}Ce by annealing at 400°C.

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