Long-Period Hexagonal Structures in Melt-Spun $\text{Mg}_{97}\text{Ln}_2\text{Zn}_1$ (Ln=Lanthanide Metal) Alloys

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Novel long-period hexagonal structures with six and fourteen layered atomic configurations were formed in melt-spun $\text{Mg}_{97}\text{Ln}_2\text{Zn}_1$ (Ln=Y, Gd and Sm) ternary alloys annealed at 573 K for 1.2–3.6 ks and in an as-spun $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ alloy, respectively. The Mg-based alloys containing La or Ce as the Ln element have a mixed structure of hcp Mg and compound phases and no long-period hexagonal structure is formed in the as-spun and annealed states. There is a clear formation tendency of the novel long-period structure to increase with a decrease in the precipitation tendency of the intermetallic compound, an increase in the atomic size ratio of Ln/Mg and an enhancement of the formation tendency of Mg-based reinforced solid solution. The formation of the novel long-period structure is interpreted to result from the necessity of relaxation of strains caused by the reinforced solid solution of Ln and Zn elements into the Mg phase. In addition, the enrichment of Y and Zn elements was observed at the misfit sites of the atomic array in the fourteen layered hexagonal structure of the as-spun $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ alloy. The atomic level segregation of Y and Zn elements is also thought to be the origin for the high stability of the long-period structure. The two types of long-period hexagonal structures found in the Mg–Ln–Zn alloys are important as a new mechanism for future development of high-strength Mg-based alloy.

(Received April 15, 2003; Accepted August 19, 2003)

Keywords: magnesium-based alloy, long-period hexagonal phase, fourteen-layered atomic array, six-layered atomic array, high-resolution transmission electron microscopy, high-angle annular detector dark-field

1. Introduction

There has been a strong demand to develop a high-strength material with light weight because its development is expected to bring about the savings of energy and natural resources and the reduction of pollution in the environment. Considering that Mg metal is the lightest metal among the conventional alloys and one of the abundant elements in addition to having a high recycling efficiency,¹⁾ it is important to develop a high-strength alloy using Mg-based alloy systems. In recent years, much effort has been devoted to fabricating high-strength Mg-based alloys by various production techniques as well as by various structural modification methods. Since 1988, our group has also performed a series of studies on the formation and mechanical properties of Mg-based alloys consisting of nonequilibrium phases such as glassy, supersaturated solid solution and nanoscale mixed phases by using the rapid solidification and casting techniques.^{2–4)} In 1990, we, for the first time, reported that bulk glassy alloys with a high tensile strength of 820 MPa are produced in Mg–Y–Cu and Mg–La–Ni systems,⁵⁾ though the high strength decreases significantly after room temperature aging for about six months because of the progress of structural relaxation. It has subsequently been reported that nanoscale mixed structures consisting of fine compounds of MgCa or MgAl embedded in the hcp-Mg matrix in Mg–Ca–Al and Mg–Al–Zn systems exhibit the high tensile strength of approximately 600 MPa.^{6,7)} However, the elongation of these nanoscale mixed phase alloys is less than 2% and the poor ductility has prevented their further development as a high strength material with light weight. Recently, based on the effectiveness of the three component rules leading to the formation of bulk glassy alloys as well as to the stabilization of supercooled liquid, *i.e.*, (1) a multi-

component of more than three elements, (2) significant atomic size mismatches above 12%, and (3) negative heats of mixing,^{8–11)} we have searched for a new nonequilibrium phase in the glassy and crystalline states of various alloy systems. Very recently, we have found that excellent mechanical properties, *i.e.*, 610 MPa for tensile yield strength and 6% for plastic elongation, are obtained in a $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ alloy produced by warm extrusion of atomized alloy powders at 573 K^{12,13)} and the high-strength alloy has a nanograin structure consisting of a long-period hexagonal atomic configuration.^{12,14)} It has subsequently been reported that the Y and Zn elements are enriched in the long-period region and the periodicity changes from six layers to fourteen layers with increasing cooling rate during sample preparation.¹⁵⁾ It is important to clarify the novel structure of the long-period hexagonal phase, in correlation with achieving good mechanical properties. However, there has been no data presented on the formation of such a novel long-period hexagonal structure in other Mg-based alloys except for Mg–Y–Zn alloys. In this paper, we intend to present the formation of similar novel long-period structures in melt-spun Mg–Ln–Zn (Ln=Y, Ce, Gd, Sm or La) alloys and to demonstrate that the formation of the novel structures is a universal phenomenon in the Mg-based alloys with the three component rules.

2. Experimental Procedure

Ternary Mg-based alloy ingots with compositions of $\text{Mg}_{97}\text{Ln}_2\text{Zn}_1$ (Ln=Y, La, Ce, Gd or Sm) were prepared by induction melting the mixtures of pure metals in an argon atmosphere. The alloy compositions represent the nominal atomic percentages. Rapidly solidified alloy ribbons with a cross section of $0.02 \times 1.2 \text{ mm}^2$ were produced by a melt spinning method. Their structures in as-spun and annealed

states were examined by X-ray diffraction, conventional TEM, high-resolution TEM equipped with nanobeam diffraction pattern, EDS and HAADF instruments. Thin foils for TEM and STEM were prepared by electrical polishing, followed by ion beam etching. The TEM and HAADF observations were carried out with JEM-3000F and JEM-2010 microscopes. The simulation of high-resolution TEM and STEM contrasts was made by using MAC Tempus.

3. Results

Figure 1 shows high-resolution TEM image and nanobeam

Fig. 1 Bright-field TEM image and selected-area electron diffraction pattern of a melt-spun $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ alloy.

electron diffraction pattern of the melt-spun $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ alloy. The melt-spun structure consists of hcp grains with an average grain size of about $1.2\ \mu\text{m}$ and each grain contains a high density of faulted regions. The electron diffraction pattern taken from the faulted region reveals extra reflection spots at the positions of $N/7(0001)_{\text{hcp}}$ ($N = 1, 2, 3, \dots$), in addition to the ordinary hcp reflection spots. It is therefore clarified that the faulted region has a long-period hexagonal structure with a long periodicity which is seven times longer than that of the ordinary hcp structure. Considering that the atomic configuration of the ordinary hcp phase consists of a two layered atomic array as indicated by ABABAB,¹⁶⁾ the long-period hcp phase is concluded to have a fourteen layered atomic array. This periodicity is different from the six layered atomic array which has previously been observed in a $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ alloy produced by the warm extrusion of atomized alloy powers. This distinct difference indicates that the periodicity is dependent on the preparation condition of the alloy. In order to clarify the details of the new hcp atomic configuration with a fourteen layered structure, the high-resolution TEM and HAADF images of the melt-spun $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ alloy are shown in Fig. 2. The atomic configuration can be identified as ABABABACACACAC, indicating clearly the formation of the fourteen layered structure. In addition, the HAADF image indicates the enrichment of Y and Zn elements with larger atomic numbers to the two layered sites in the fourteen layered regions. The period segregation of Y and Zn elements is presumed to cause an increase in the stability of the novel long-period hcp structure.

The fourteen layered atomic array was found to change to a six layered atomic array structure under subsequent anneal-

Fig. 2 (a) High-resolution TEM image, (b) high-resolution HAADF image and (c) intensity profile of the HAADF image of a melt-spun $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ alloy.

Fig. 3 Bright-field TEM image and selected-area electron diffraction pattern of a melt-spun $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ alloy subjected to annealing at 573 K for 3.6 ks.

Fig. 5 Bright-field TEM image and selected-area electron diffraction pattern of a melt-spun $\text{Mg}_{97}\text{La}_2\text{Zn}_1$ alloy.

Fig. 4 High-resolution TEM image and nanobeam electron diffraction pattern of a melt-spun $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ alloy subjected to annealing at 573 K for 3.6 ks.

ing. Figure 3 shows the high-resolution TEM image and selected-area electron diffraction pattern of the melt-spun $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ alloy subjected to annealing at 573 K for 3.6 ks. It is seen that the hcp grain includes faulted regions along the $(0001)_{\text{hcp}}$ plane and the diffraction pattern taken from the faulted region includes extra reflection spots at the positions of $N/3(0001)_{\text{hcp}}$. The atomic configuration in the faulted region consists of the ABACAB array mode, as shown in Fig. 4. This result is in agreement with that of the $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ alloy produced by warm extrusion of atomized alloy powders. The decrease in the periodicity from the fourteen layered array to the six layered array is thought to result from the annealing-induced decrease in solid solution strain generated by the reinforced solid solution of Y and Zn elements into the Mg phase.

Fig. 6 Bright-field TEM image and selected-area electron diffraction pattern of a melt-spun $\text{Mg}_{97}\text{Ce}_2\text{Zn}_1$ alloy.

We further examined whether or not the formation of the novel hcp structure is a universal phenomenon for $\text{Mg}_{97}\text{Ln}_2\text{Zn}_1$ ternary alloys including the $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ alloy. It has previously been pointed out that the generation of the novel long-period hcp structure is attributed to one of the methods leading to the relaxation of strains generated by the reinforced solid solution of Y and Zn with significantly different atomic size ratios into the Mg phase. On the basis of this concept, the $\text{Mg}_{97}\text{Ln}_2\text{Zn}_1$ alloys containing La, Ce, Sm and Gd were chosen because the atomic size ratio of Ln/Mg leading to the generation of the solid solution strain changes from 1.12 to 1.17. Figures 5 and 6 show bright-field TEM images and selected-area electron diffraction patterns of the melt-spun $\text{Mg}_{97}\text{La}_2\text{Zn}_1$ and $\text{Mg}_{97}\text{Ce}_2\text{Zn}_1$ alloys with larger atomic size ratios of 1.17 and 1.15 for Ln/Mg, respectively. The structure of the two alloys consists of two phases, *i.e.*, hcp-Mg and either the $\text{Mg}_{17}\text{La}_2$ or $\text{Mg}_{17}\text{Ce}_2$ compound. No appreciable plane fault is seen in the Mg phase of the former alloy, while the Mg phase of the latter alloy includes some plane faults. However, no extra reflection spots due to the formation of a long-period hcp phase are seen in the Mg phase of the Mg-Ce-Zn alloy. Furthermore, the precipitation

Fig. 7 Bright-field TEM image and selected-area electron diffraction pattern of a melt-spun Mg₉₇Gd₂Zn₁ alloy.

of the Mg₁₇La₂ compound is thought to reflect the difficulty of the reinforced solid solution of La into Mg phase because of the largest atomic size ratio. The features of the microstructure consisting of hcp-Mg and compound phases remain almost unchanged even after annealing at 573 K for 1.2 ks, though the precipitation amount of their compound phases appears to increase, accompanying the increase in the particle size.

Figure 7 shows the bright-field TEM image and selected-area electron diffraction pattern of the melt-spun Mg₉₇Gd₂Zn₁ alloy. The structure also consists of hcp-Mg and compound phases and no appreciable plane faulted region is seen. The features are similar to those for the Mg₉₇La₂Zn₁ and Mg₉₇Ce₂Zn₁ alloys in as-spun and annealed states. However, the microstructure of the hcp-Mg phase in the Mg-Gd-Zn alloy was found to change significantly with subsequent annealing treatment. Figure 8 shows the bright-field TEM image and selected-area electron diffraction pattern of the melt-spun Mg₉₇Gd₂Zn₁ alloy subjected to

Fig. 8 Bright-field TEM image and selected-area electron diffraction pattern of a melt-spun Mg₉₇Gd₂Zn₁ alloy subjected to annealing at 573 K for 1.2 ks.

Fig. 9 High-resolution TEM image and nanobeam electron diffraction pattern of a melt-spun Mg₉₇Gd₂Zn₁ alloy subjected to annealing at 573 K for 1.2 ks.

annealing at 573 K for 1.2 ks. Distinct plane faulted regions are seen in the TEM image and the selected-area electron diffraction pattern of the region indicates clearly the appearance of extra reflection spots at the positions of $N/3(0001)_{\text{hcp}}$, indicating the formation of the long-period hcp phase with a long periodicity which is three times longer than that for the ordinary hcp phase. The high-resolution TEM image of the long-period region in the annealed Mg-Gd-Zn alloy is shown in Fig. 9. It is seen that the faulted region has a six layered atomic configuration as identified as the ABACAB array. The layered atomic configuration is in agreement with that for the Mg-Y-Zn alloy produced by warm extrusion of atomized alloy powders. A similar six layered atomic configuration is also observed for the melt-spun Mg₉₇Sm₂Zn₁ alloy subjected to annealing at 573 K for 1.2 ks, as shown in Fig. 10. The bright-field TEM image reveals the formation of faulted regions and the selected-area electron diffraction pattern of the faulted region includes

Fig. 10 High-resolution TEM image and nanobeam electron diffraction pattern of a melt-spun Mg₉₇Sm₂Zn₁ alloy subjected to annealing at 573 K for 1.2 ks.

Table 1 Structural features of melt-spun $\text{Mg}_{97}\text{Ln}_2\text{Zn}_1$ (Ln=Y, La, Ce, Gd or Sm) ternary alloys in as-spun and annealed states. Some data taken from the equilibrium phase diagrams in Mg-Ln binary alloys are also shown for reference.

Ln	As-spun state	Annealed state	Equilibrium phase
Y	Ordinary hcp + 14 layered structure	Ordinary hcp + 6 layered structure	Ordinary hcp + Cubic(Mg_{24}Y_5)
La	Ordinary hcp + Hexagonal($\text{Mg}_{17}\text{La}_2$)	Ordinary hcp + Tetragonal(Mg_{12}La)	Ordinary hcp + Tetragonal(Mg_{12}La)
Ce	Ordinary hcp + Hexagonal($\text{Mg}_{17}\text{Ce}_2$)	Ordinary hcp + Tetragonal(Mg_{12}Ce)	Ordinary hcp + Tetragonal(Mg_{12}Ce)
Sm	Ordinary hcp	Ordinary hcp + 6 layered structure	Ordinary hcp + Tetragonal($\text{Mg}_{41}\text{Sm}_5$)
Gd	Ordinary hcp	Ordinary hcp + 6 layers structure	Ordinary hcp + Cubic(Mg_5Gd)

extra reflection spots of $N/3(0001)_{\text{hcp}}$, indicating the formation of the six layered faulted region.

4. Discussion

On the basis of the above-described experimental data, the features of the structures in as-spun and annealed states for the $\text{Mg}_{97}\text{Ln}_2\text{Zn}_1$ (Ln=Y, La, Ce, Gd and Sm) ternary alloys are summarized in Table 1, together with the data of the equilibrium phase diagrams in Mg-Ln binary alloys.¹⁷⁾ The structural features can be classified into the following three types; (1) absence of a long-period layered structure in the as-spun and annealed states of the La- and Ce-containing alloys, (2) absence of a long-period layered structure in the as-spun states and formation of the six layered hcp structure in the annealed states of Gd- and Sm-containing alloys, and (3) formation of the fourteen layered hcp structure only in the as-spun Y-containing alloy and the six layered hcp structure in the annealed state. It is thus said that the formation tendency of the novel long-period layered structure is opposite to the precipitation tendency for their compounds. This opposite tendency indicates that the formation of the layered structure is attributed to the dissolution of Ln and Zn elements. The absence of the compounds also implies that the generation of solid solution strains caused by the reinforced solid solution of their solute elements into the Mg phase plays an important role in the formation for the layered structure. Based on the good correspondence of the formation tendencies among the layered structures, intermetallic compounds and solid solution, we can propose the following formation criteria for the long layered hcp structures; (1) large atomic size ratios against Mg above 1.10, (2) high formation tendency of Mg-based reinforced solid solution, (3) low precipitation tendency of Mg-rich intermetallic compounds, and (4) the existence of atomic pairs with strongly negative mixing heats. Strongly affinitive atomic pairs such as the Ln-Zn pair¹⁸⁾ are important for an increase in the stability of the long-period atomic configurations by the segregation of Ln and Zn elements into the misfit atomic array region in the long-period layered structure. Although the formation mechanism of the novel structure was described for the Mg-Y-Zn alloy with the fourteen layered region which was obtained in the as-quenched state, it is important to discuss the formation mechanism of the six layered structures in the Mg-Gd-Zn and

Mg-Sm-Zn alloys subjected to annealing treatments. That is, no long-period structure in Mg solid solution phase is seen in the as-spun state of the alloys and the annealing induces the formation of the six layered structure region, accompanying the precipitation of Y-Zn, Gd-Zn and Sm-Zn clusters at the misfit atomic array sites. This result suggests that the formation of the long-period hexagonal structure can be regarded as a kind of structural change through the formation of Ln-Zn clusters with strongly negative mixing heats. This interpretation is consistent with the mechanism for the Mg-Y-Zn alloys in which the segregation of Y and Zn elements is clearly revealed by the HAADF analyses and their segregation stabilizes the long-period structure. In addition, the existence of two kinds of long-period layered hexagonal structures with six and fourteen layers also implies the spontaneous formation of a nanoscale-controlled distribution of the Ln-Zn rich clusters. Consequently, the new cluster-controlled method is expected to be employed as a new type of cluster dispersion method which is important for the future development of high strength materials.

5. Summary

We examined the formation tendency of a Mg-based solid solution phase including a long-period hexagonal atomic configuration region in melt-spun and annealed states of Mg-Ln-Zn (Ln=Y, La, Ce, Gd or Sm) alloys by using the high-resolution TEM and HAADF techniques. The results obtained are summarized as follows.

(1) The as-spun $\text{Mg}_{97}\text{Y}_2\text{Zn}_1$ alloy consisted of an hcp phase including long-period hexagonal phase regions with fourteen layered packing. The enrichment of Y and Zn elements was found to occur at the two misfit atomic array sites in the fourteen period hexagonal structure.

(2) The fourteen layered packing of the Mg-Y-Zn alloy changed to a six layered packing by annealing at 573 K for 1.2 ks, accompanying the similar enrichment of Y and Zn elements at the two misfit atomic array sites. The decrease in the periodicity interpreted to result from the decrease in the hexagonal structure for the annealed alloy appears to reflect the decrease in the strains caused by the reinforced solid solution of Y and Zn elements into the Mg phase.

(3) A similar six layered hexagonal structure is also formed in melt-spun $\text{Mg}_{97}\text{Gd}_2\text{Zn}_1$ and $\text{Mg}_{97}\text{Sm}_2\text{Zn}_1$ alloys subjected

to annealing at 573 K for 1.2 ks, though no long-period hexagonal structure is identified in their as-spun alloys.

(4) The $\text{Mg}_{97}\text{La}_2\text{Zn}_1$ and $\text{Mg}_{97}\text{Ce}_2\text{Zn}_1$ alloys in as-spun and annealed states also consist of hcp-Mg and compound phases and the Mg phase does not include any appreciable long-period hexagonal phase regions.

(5) The long-period hexagonal structure was found to be formed in the Mg-Ln-Zn alloys which satisfy the following three factors; (1) significant atomic size ratios of Ln/Mg above 1.10, (2) lower precipitation tendency of Mg-Ln intermetallic compounds, and (3) higher formation tendency of Mg-based reinforced solid solution including Ln and Zn elements.

(6) The findings of the novel long-period hexagonal atomic configurations in the Mg-Ln-Zn alloys as well as the atomic scale enrichment of Ln and Zn elements into the misfit atomic array sites indicate the possibility that a high-strength Mg-based alloy is developed by the control of the novel structure and the atomic scale segregation mode.

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