Microstructure Evolutions of Rapidly-Solidified and Conventionally-Cast $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ Alloys

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Microstructure evolutions of rapidly-solidified (RS) ribbon and conventionally cast bulk $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloys have been studied by transmission electron microscopy (TEM), particularly focusing on formation process and phase stability of the long-period structures. It is found that there are significant differences in microstructural evolutions between the RS ribbon and the cast-bulk alloys, in terms of thermal stability of the long-period phases at temperatures higher than 673 K. For both the as-quench ribbon and the as-cast bulk specimens, 18R-type long-period phase is dominantly observed at grain boundaries. After annealing at temperatures higher than 673 K, the long-period phases at grain boundaries in the RS ribbon almost disappear to form Mg_{24}Y_5 and $\text{Mg}_3\text{Zn}_3\text{Y}_2$ compounds within the grain interiors, while the long-period phases remained stable in the cast-bulk alloy even at temperatures higher than 673 K. [doi:10.2320/matertrans.MC200763]

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1. Introduction

It was shown that nanocrystalline $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy (denoted as $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ hereafter), which is prepared through a non-equilibrium rapid solidification process, reveals mechanical properties with maximum tensile yield strength ~ 600 MPa and elongation $\sim 5\%$ at room temperature.^{1,2)} These properties seem to be originated from not only a grain refinement but also a novel long-period stacking structure formed in the alloy.²⁾ The long-period structure is found to be chemical-ordered as well as stacking-ordered;³⁾ a unique long-period ordered (LPO) structure. Formation of several types of long-period stacking structures have been reported for both rapidly-solidified (RS) ribbon⁴⁾ and conventionally-cast bulk⁵⁾ $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloys; four types (18R, 14H, 10H, 24R) are found in the RS ribbon, while just two types (18R, 14H) form in the bulk specimens. To establish an effective processing route for microstructure controls of the long-period structure based $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloys, it is necessary to understand phase evolutions through non-equilibrium or nearly equilibrium processes.

In this study, we investigate microstructure evolutions of the $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ RS ribbon and cast-bulk alloys using transmission electron microscopy (TEM) and Z-contrast scanning transmission electron microscopy (STEM), particularly focusing on formation and phase stability of the long-period structures. It should be noted here that details of the variant long-period structures have not been clarified yet; there are still some discrepancies between the model stacking structures,^{4,5)} and further none is known regarding their chemical ordered structures. Therefore, it will be of our following aim to determine the variant structures using Z-contrast scanning transmission electron microscopy.³⁾

2. Experimental Procedure

A master alloy ingot of $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ was prepared by high-frequency induction melting of pure metals in an argon atmosphere (see Ref. 5) for further details of sample preparations). RS ribbons were prepared by a single-roller melt spinning method with wheel rotating speed of 42.0 m/s. Conventionally cast bulk alloys were solution-treated at 823 K for 8 h, followed by quenching into water. The obtained RS ribbons and cast bulk alloys were annealed at 573 K for 120 h, 673 K for 48 h and 773 K for 12 h, respectively. All heat treatments were performed using a silica tube in an argon atmosphere after evacuation to pressures lower than 3×10^{-3} Pa. Thin foils for TEM observations were prepared by argon ion milling technique. Microstructures of these alloys were investigated with a JEM-2010F operating at 200 kV.

3. Results and Discussions

3.1 Microstructure evolutions in RS ribbons

Figures 1(a)–(d) show bright-field TEM images of the as-quench and annealed $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ RS ribbon specimens. In the as-quench RS ribbon, one sees that the microstructure is composed of fine α -Mg grains, approximately ~ 200 nm in average diameter, which are surrounded by the secondary phase at grain boundaries. Almost all of these grain boundary phases are identified as 18R-type long-period structure.⁵⁾ By annealing at 573 K for 120 h, the α -Mg grains grow and are coarsened into an average diameter of about ~ 500 nm. During this event, the grain boundary phase area also become thicker with its width of about 10–20 nm, and they are still found to be of 18R-type long-period structure. No significant precipitates were observed within α -Mg grain interiors.

After annealing at temperatures higher than 673 K, we find a remarkable change of microstructures; see Figs. 1(c) and

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Fig. 1 Bright-field TEM images of the $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ RS ribbon (a) as quench, (b) annealed at 573 K for 120 h, (c) annealed at 673 K for 48 h and (d) annealed at 773 K for 12 h. (e), (f) representative EDS spectra obtained from the precipitates in (c) and (d), respectively. Small peaks indicated by grey arrows are due to the copper grid used as a support of the ribbon specimens during TEM experiments.

1(d). For the specimen annealed at 673 K for 48 h (Fig. 1(c)), the pre-existing 18R-type phase at grain boundaries mostly disappear, and the α -Mg grains grow into $\sim 1\mu\text{m}$ in an average diameter. Within the grain interiors, one can see the rectangular-shape precipitates (10–100 nm), some of which are significantly grown into about several hundred nanometers as indicated in Fig. 1(c). These precipitates are identified as Mg_{24}Y_5 intermetallic compounds,²⁾ based on energy-dispersive X-ray spectroscopy (EDS) (Fig. 1(e)) and electron diffraction analyses. We note that, not depending on their size, almost all the rectangular-shape precipitates are found to be the Mg_{24}Y_5 compound. Besides the Mg_{24}Y_5 precipitates, it is also noticeable that dim (grey) contrasts appear within the grain interiors; these morphologies are basically the same as those reported by Matsuda *et al.*⁴⁾ as a consequence of ‘coagulation’ of the pre-existing long-period phases. These coagulated regions are found to involve several types of long-period structures. As described later, lamellar packets composed of several types of long-period structures are formed within the present specimen (Fig. 3(c)).

Annealing at 773 K for 12 h has further promoted grain growth of the α -Mg matrix, coarsening the grains into more than a few micrometers in diameter (Fig. 1(d)). The grain boundary phase seem to entirely disappear, and instead fine precipitates appear within the grain interiors, like the same

Fig. 2 (a) Bright-field TEM image and (b) Z-contrast STEM image of the grain interior of the $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ RS ribbon annealed at 573 K for 1 h. (c) Z-contrast STEM image of the long-period phase region adjacent to the grain boundary of the $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ RS ribbon annealed at 673 K for 48 h.

manner that observed for the case of annealing at 673 K (Fig. 1(c)). However, in the specimen annealed at 773 K, a $\text{Mg}_3\text{Zn}_3\text{Y}_2$ intermetallic compound precipitates as well as the Mg_{24}Y_5 compound within the grain interiors,⁶⁾ which were definitely identified by EDS analysis as shown in Fig. 1(f) (they are rather easily distinguishable since Zn can hardly solute into Mg_{24}Y_5 compound²⁾). As indicated in Fig. 1(d), relatively larger precipitates, more than a few tens nanometers, are mostly found to correspond to the Mg_{24}Y_5 compound, whereas those smaller ($< \sim 20\text{ nm}$) are frequently identified to be of $\text{Mg}_3\text{Zn}_3\text{Y}_2$ type.

It was reported that four types of long-period structures, 18R, 14H, 10H and 24R, are all observed in the RS ribbon specimen annealed at 573 K for 1 h.⁴⁾ With this in mind, we prepare the ribbon specimen annealed with the same manner and have carefully investigated it using Z-contrast STEM. However, we could find only the 10H-type long-period structures within the specimen, in addition to the 18R-type phase that exist at grain boundaries (almost similar distributions as of Fig. 1(a)). As shown in Fig. 2(a), for some grains the 10H-type phase precipitates within the grain interiors with their size less than $\sim 200\text{ nm}$, distributions of which are clearly seen in the corresponding Z-contrast STEM image (Fig. 2(b)). This immediately indicates that the 10H-type phase contains a certain amount of Zn and Y. It should be mentioned here that the fine precipitations of 10H-phase do not occur for all the grains; the grains such as shown in Fig. 2(a) are rarely observed within the ribbon specimen annealed at 573 K for 1 h. As already described, no precipitates are observed after the long-time annealing at the same temperature (573 K $\times$ 120 h, Fig. 1(b)), so that the present 10H-type long-period phase is considered to be metastable at this temperature for the ribbon specimens.

During the Z-contrast STEM investigations, we find a local trace of long-period phase region adjacent to grain bounda-

Fig. 3 Bright-field TEM images and the corresponding electron diffraction patterns of the grain boundary of the $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ cast-bulk alloy (a) as quench, (b) annealed at 573 K for 120 h, (c) annealed at 673 K for 48 h and (d) annealed at 773 K for 12 h.

ries in the ribbon specimen annealed at 673 K for 48 h, as shown in Fig. 2(c), where the 18R, 14H and 24R-type different period structures are found to coexist at several unit cell scales. Details of atomic structures of these variant long-period phases will soon be described elsewhere. We note that the feature shown in Fig. 2(c) is rarely observed and not common for all grains in the specimen. Concerning that the initial 18R-type phase at grain boundaries almost vanish, and formation of alternative Mg_{24}Y_5 compounds and coagulation of LPO structures has been progressed in the specimen, unique packets composed of different long-period structures are likely to be attributed as the transient state of this microstructural reconstruction. Namely, during the reconstruction, re-distribution of Zn and Y atoms may cause some microstructure instabilities due to local concentration fluctuations, producing metastable phases at several places. Therefore, the present LPO phases those found in local lamellar packets that include 18R, 14H and 24R-type are all considered to be metastable in the RS ribbon specimen annealed at 673 K. However, as described in the next section, 18R and 14H-type LPO phases are found to be highly stable in the cast-bulk specimen even at temperatures higher than 673 K.

3.2 Microstructure evolutions in conventionally cast bulk alloys

Itoi *et al.* reported that 18R-type phase dominantly forms at grain boundaries in the conventionally-cast bulk $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy.⁵⁾ We find that the long-period phase does not completely disappear and still exists (though its volume fraction has been significantly reduced) even after the solution heat-treatment at 823 K for 8 h, indicating a highly stable nature of the LPO phase in the bulk specimen. With this situation, present solution treatment does not mean to form a single α -Mg phase with Zn and Y in solution. It should be noted here that this is in sharp contrast to the case of RS ribbon $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloys, for which the pre-existing 18R-type phase almost vanishes after annealing at temperatures

higher than 673 K. After the solution treatment of the conventionally-cast bulk $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy, average grain size of the α -Mg matrix becomes larger than $\sim 50 \mu\text{m}$, which is beyond the conventional TEM imaging area. Hence the microstructures of the cast-bulk alloy specimens will be described with respect to the grain boundaries and the interiors respectively in the following.

Figures 3(a)–(d) show bright-field TEM images and the corresponding electron diffraction patterns obtained from grain boundaries in the $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ cast-bulk specimens. For the as solution-treated alloy, it was found that there still remain a small amount of grain boundary phases, which are mostly found to be the 18R-type long-period structure. A small amount of the 10H-type long-period phase is also rarely observed and coexists with the 18R-type phase, as indicated in Fig. 3(a). In the cast-bulk specimen, the 18R-type long-period phase at the grain boundaries remained stable at temperatures up to 673 K. Figs. 3(b) and 3(c) represent identifications of the grain boundary phase in the specimens annealed at 573 K and 673 K, respectively, within which the trace of 10H-type phase is hardly observed. After annealing at 773 K for 12 h, 18R-type long-period phase is found to transform into the 14H-type phase at grain boundaries.⁴⁾

Figures 4(a)–(d) show bright-field TEM images and the corresponding electron diffraction patterns of the grain interiors in the $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ cast-bulk alloys. By the solution treatment, the α -Mg matrix has been well homogenized, and no significant features such as fine precipitates or faults are recognized within the grain interiors. After annealing at 573 K for 120 h, a high density of dark-line contrasts appears along the c -plane of the α -Mg matrix (Fig. 3(b)). Strong streaks are recognized along the c^* -directions in the corresponding diffraction pattern, but no significant intensity maxima along it. This means that no long-period structures but stacking faults are densely formed within the grain interiors after annealing at 573 K. Preliminary Z-contrast STEM observation has confirmed that these stacking faults accompany the enrichment of Zn and Y around them, similar

Fig. 4 Bright-field TEM images and the corresponding electron diffraction patterns of the grain interior of the $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ cast-bulk alloy (a) as quench, (b) annealed at 573 K for 120 h, (c) annealed at 673 K for 48 h and (d) annealed at 773 K for 12 h.

Table 1 Phase evolutions of $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ RS ribbons and cast-bulk alloys.

Heat treatment condition	RS ribbon		Cast bulk	
	Grain boundary	Grain interior	Grain boundary	Grain interior
773 K $\times$ 12 h	disappeared	$\alpha + \text{Mg}_{24}\text{Y}_5$ + $\text{Mg}_3\text{Zn}_3\text{Y}_2$	14H	$\alpha + 14\text{H}$
673 K $\times$ 48 h	disappeared	$\alpha + \text{Mg}_{24}\text{Y}_5$ (+18R+14H+24R)	18R	$\alpha + 14\text{H}$
573 K $\times$ 120 h	18R	α	18R	$\alpha + \text{stacking faults}$
573 K $\times$ 1 h	18R	$\alpha + 10\text{H}$	—	—
As quench	18R	α	(18R+10H)	α

to the manner that observed for the LPO structure.³⁾ Details will be described elsewhere.

By annealing at temperatures above 673 K, 14H-type long-period phase precipitates within the α -Mg grain interiors,⁵⁾ and the superlattice reflections along the c^* -directions clearly appear in the corresponding diffraction patterns. As seen in Figs. 3(c) and 3(d), precipitations of the long-period structure proceed by lateral growth of the plate, and the size (thickness) and distributions of the plates can be controlled simply by annealing temperature. Similar precipitation behaviors have been also confirmed for the Mg-Zn-Gd alloys.⁷⁾

3.3 Formation and stability of the long-period phases

On the basis of the above observations, formation of the long-period phases both in the RS ribbon and the cast-bulk $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloys are summarized in Table 1. The phases denoted within the brackets mean that they are minor phases (rarely observed/small volume fraction) or those considered to be metastable configurations. In Table 1, there are significant differences in phase evolutions between the RS ribbon and the cast-bulk alloys, especially in terms of thermal stability of the long-period phases at temperatures higher than 673 K. For the RS ribbon alloys, intermetallic compounds, Mg_{24}Y_5 and $\text{Mg}_3\text{Zn}_3\text{Y}_2$, appear to replace the pre-

existing long-period phases, while the 18R-type and 14H-type long-period structures are given as thermodynamically stable configurations for the cast-bulk alloys. At this stage, we cannot find any specific reasons that cause the observed differences. We presume that a quite small amount of impurities such as oxygen, which is likely to be incorporated during a melt spinning procedure, may significantly affect the phase stability in the RS ribbons, even though we could not detect a certain amount of oxygen from the α -Mg matrix and the compounds using electron energy-loss spectroscopy (EELS).

4. Summary

Microstructure evolutions of the RS ribbon and conventionally cast-bulk $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloys have been investigated by TEM, particularly focusing on formation process and phase stability of the unique long-period structures. We find that the 18R-type long-period phase is dominantly formed at grain boundaries both in the as-quench ribbon and the as-cast bulk specimens. The long-period phases are found to be thermodynamically stable up to ~ 823 K in the bulk alloys, while those in the RS ribbon specimens almost disappear by annealing at temperatures higher than ~ 673 K, and instead

Mg₂₄Y₅ and Mg₃Zn₃Y₂ compounds precipitate within the grain interiors. Present investigation summarized in Table 1 will provide useful information for further development of the novel Mg-alloys based on long-period phases, through the effective microstructural controls. Details of variant long-period structures, particularly of their unique chemical order, will soon be described elsewhere.

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