Original Article

Precipitation of secondary phase in Mg-Zn-Gd alloy after room-temperature deformation and annealing

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\textbf{A B S T R A C T}

Mg-Zn-RE alloys reinforced with quasicrystals have been investigated extensively because they show excellent balance in mechanical properties. Here, we perform deformation and annealing for Mg-1.50Zn-0.25Gd (at.\%) alloy at various temperatures, aimed to gain nanoscale precipitates. We find that after the room-temperature compression, the non-basal dislocation, stacking fault and twining are identified in the as-deformed samples, offering clear evidence that these deformation mechanisms can accommodate room-temperature deformation. We also perform systematic transmission electron microscopy observations of the precipitates in both the as-deformed and as-annealed samples. The results identify the formation of a large amount of secondary-phase precipitates, I-phase and MgZn\textsubscript{2}, when annealed at 200 °C, and precipitation of a small amount of W-phase when annealed at 400 °C.

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\section{Introduction}

In recent years, research and development of Mg alloys have been greatly promoted by the lightweight requirement in the automotive and aerospace industries [1–3]. Among these Mg alloys, Mg-Zn-RE (RE: rare earth element) alloys have been widely studied because of their excellent balance in mechanical properties [4–8]. To uncover the precipitation behavior of this alloy system, many studies have been done in the last two years, such as metastable phase formation [9], phase equilibria and transformations [10], precipitation phase [11–13] and slip systems activation [13]. It has been reported and confirmed that Zn/Y (in wt.\%) ratios of I-phase (Mg\textsubscript{5}Zn\textsubscript{3}Y) and W-phase (Mg\textsubscript{2}Zn\textsubscript{4}Y\textsubscript{2}) are 4.38 and 1.10, respectively [14]. When the Zn/Y ratio exceeds 4.38, the requirement to utterly form I-phase can be satisfied. However, when the Zn/Y ratio is between 1.10 and 4.38, the quantity of Zn is not high enough to meet the requirement to completely form I-phase, resulting in partial

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formation of W-phase [14,15]. Since the I-phase is superior to W-phase in grain refinement and strengthening effect [14], we previously designed Mg-Zn-Gd alloys with Zn/Gd (at.%) ratio of ~6 to obtain I-phase [16], and probed systemically secondary phases in these alloys [17–21]. To further improve mechanical properties, a large amount of nanoscale I-phase, which is distributed dispersively in α-Mg matrix, is highly preferred.

Thermal mechanical processing is usually applied to quasicrystal-reinforced Mg alloys to enhance nanoscale I-phase precipitation and grain refinement [22–26], e.g. hot compression [19,27], extrusion [28–31], rolling [25,30,32], equal channel angular extrusion (ECAP) [26,33–35] and cyclic extrusion and compression (CEC) [36–39]. Although the hot deformation behavior of Mg alloys reinforced with I-phase has been investigated widely, their room-temperature deformation behavior is scarcely studied, yet significant, because these structural materials are usually employed at ambient temperature.

The T10 treatment (i.e. heat treatment after deformation) can be used to further improve strength of the alloys by promoting secondary-phase precipitates [6]. On one hand, nanoscale I-phase can precipitate during annealing [20,40]. On the other hand, such T10 treatment is beneficial for secondary phase precipitation by promoting diffusion of alloying elements [6]. These lead us to think if there can precipitate large amount of dispersive nanoscale I-phase in the α-Mg matrix after T10 treatment. In addition, Kim et al. [40] investigated the precipitation behavior under various heat treatment conditions in both the as-cast and hot rolled Mg-Zn-Y alloys reinforced with quasicrystal. They proposed that the MgZn2 phase precipitates in the α-Mg matrix during annealing at 190 °C and the polygon-shaped I-phase precipitates are mainly formed during annealing at 350–420 °C. These indicate that the applied annealing temperature after deformation is also very important for determining the species of the secondary phase precipitation.

In this study, we select the Mg-1.50Zn-0.25Gd (at.%) alloys reinforced with I-phase for room-temperature compression. To gain insights into the room-temperature behavior and precipitation mechanisms after the T10 treatment, the microstructure of the samples after deformation and with/without annealing, especially the secondary phase precipitates were characterized by transmission electron microscopy (TEM).

2. Experimental

Mg-1.50Zn-0.25Gd (at.%) alloy was fabricated by traditional gravity casting [16,41]. The as-cast samples were then machined into cylindrical rods of 10 mm in diameter and 15 mm in height for room-temperature compression. The compression was conducted at ambient with an initial strain rate of 0.001 s⁻¹ using the Zwick/RoellZ2020 testing machine until cracking. A portion of the deformed samples was annealed at 200 °C and 400 °C. Transmission electron microscopy (TEM) samples were obtained by cutting the samples near the crack plane of the compressed samples. Specimens for TEM observations were prepared by grinding, dimpling and argon ion-beam thinning.

Fig. 1 – Secondary phase precipitates and dislocations observed by TEM for the sample after room-temperature compression. (a) Needle-like secondary phase precipitated on (0001) plane of α-Mg matrix. (b) TEM image obtained under two-beam condition. (c) Diffraction pattern.

3. Results and discussion

3.1. Secondary phase and defects in the compressed sample

Fig. 1a shows TEM image of secondary phase precipitates. The needle-like secondary phase has the same morphology as the as-cast sample, and is confirmed to be Mg₄Zn₇ phase precipitated on the basal planes [17,19,20]. This secondary phase hence undergoes no change in room-temperature compression. Liu et al. [42] reported that non-basal dislocations are activated during deformation at elevated temperature for Mg-Zn-Gd alloys reinforced with quasicrystal. Fig. 1b and c shows TEM image and diffraction pattern taken at two-beam diffraction with g = 0002. The dislocation contrast is not extinguished for (0002) reflection, indicating that these dislocations are of type (a + c). Therefore, in addition to the basal slip, non-basal slip can also accommodate room-temperature deformation for Mg-Zn-Gd alloys reinforced with quasicrystal.

Some stacking faults can also be identified in the compressed sample, as shown in Fig. 2. Fig. 2a shows TEM image of the stacking faults parallel to the (0001) of α-Mg matrix, and Fig. 2b shows the corresponding diffraction patterns with incident electron beam parallel to [11–20] zone axis. The streaking along g = 0001 direction suggests that the stacking faults are basal (Fig. 2b) [43,44]. These results indicate that stacking faults can also accommodate room temperature deformation for Mg-Zn-Gd alloys reinforced with quasicrystal.

Fig. 3 shows TEM image of twins in the deformed sample. Fig. 3a shows the bright filed image, from which many dislocation traces can be identified. Fig. 3b shows selected area diffraction pattern (SADP) of the grain 1 marked in Fig. 3a. The zone axis can be identified to be [11–20] of α-Mg matrix. Fig. 3c shows SADP of the interfacial zone between grains 1 and 2. The grain 2 can be obtained by rotating grain 1 by ~29° along [11–20] zone axis. Fig. 3d and e shows SADP of the interface zone between grains 2 and 3 and between grains 3 and 4. The misorientation angle is determined to be ~86° between grains
2 and 3 and also between grains 3 and 4. The misorientation angle between grain 1 and 3 is thus determined to be $\sim 57^\circ$. Fig. 3f shows SADP of the grain 4, from which the grains 2 and 4 have the same orientation and the misorientation angle between grains 1 and 4 is $\sim 29^\circ$.

To extract atomic information, we conduct HRTEM imaging of the twinning zone, as shown in Fig. 4. The misorientation angle between grains 1 and 4 is determined to be $\sim 29^\circ$ (Fig. 4a and b) and the misorientation angle in Fig. 4c and d is determined to be $\sim 57^\circ$ and $86^\circ$, respectively, confirming further the diffraction analysis in Fig. 3. By looking at the atomic plane at the interface zone, one can see that the tension twinning interface is coherent (Fig. 4d), while semi-coherent or incoherent for compression and double twinning interface (Fig. 4b and c). The common twinning (e.g. tension, compression and double twining) can, therefore, also accommodate room-temperature deformation for Mg-Zn-Gd alloys reinforced with quasicrystal.

### 3.2. Precipitation after deformation and annealing

In our previous study, we found that different types of secondary phase are precipitated and distributed by partition in grains due to the composition segregation of the solute alloying elements [20]. The concentration of the alloying elements in the region near grain boundary is higher than that in the middle of grain. Here, we also investigate the precipitation behavior in different areas. Fig. 5 shows TEM images of the sample after compression and annealing at 200°C for 10 h. Fig. 5a shows the morphology of the precipitates in the middle.
of the grain, which is needle-like or ellipsoidal. Compared to Fig. 1a, the size of the needle-like secondary phase is much smaller and the ellipsoidal secondary phase is newly formed. The size of these newly formed secondary phases ranges from 10 to 20 nm. Fig. 5b shows precipitates of the region near grain boundary. As compared to Fig. 5a, the size of the secondary phase is larger and no needle-like secondary phase is found. We select the newly formed particle A to further conduct SADP analysis, as shown in Fig. 5c, which is a typical diffraction pattern for I-phase. The zone axis is 5-fold. The trace of defects can also be identified in this particle. In our previous study [21], we have characterized defects in I-phase particles for the Mg-Zn-Gd alloy after deformation at elevated temperature. This result may be further confirmed that defects can also be formed during deformation at room temperature. Fig. 5d shows SADP of the newly formed particle B. The shape of the particle B is approximately rod-like. After tilting by ~30°, we obtain another SADP, as shown in Fig. 5e. By analyzing the two SADPs, we conclude that the particle B is MgZn2 and the zone axis is [100] in Fig. 5d and [210] in Fig. 5e.

Fig. 6 shows TEM image of annealed sample at 400 °C. From the low magnification image in Fig. 6a, the needle-like secondary phase is confirmed to be also dispersed and only a few secondary-phase precipitates are in the α-Mg matrix. Fig. 6b shows an enlarged image of a particle with size of ~400 nm. Fig. 6c shows a SADP of the particle shown in Fig. 5b, from which this secondary phase can be confirmed to be W-phase (face-centered cubic structure, a = 0.768 nm) [45]. The as-cast alloy annealed at 400 °C for 8h has also been characterized in our precious study [46], verifying that crystalline secondary phase can be precipitated after heat treatment. Hence, deformation and annealing would retard precipitation of the secondary phase, possibly leading to solid solution of the secondary phase. Therefore, a large amount of secondary-phase precipitates, including I-phase and MgZn2, are formed during annealing at 200 °C, and a few W-phase precipitates are formed when annealing at 400 °C.

3.3. Deformation mechanism

Most of the wrought Mg alloys have a poor ductility due to their hexagonal close-packed structure, which allows an activation of only two independent basal slips at room temperature [47]. Since only two independent basal slip systems are available in Mg, other non-basal slip and/or twinning systems must be activated to satisfy the geometrical requirement of five independent deformation components for homogeneous deformation without crack formation [47]. These alloys has an extremely low critical resolved shear stress of basal slip (~0.6 MPa) as compared to that of non-basal slip (>38 MPa) [48–50], tension twinning (2.0–2.8 MPa), and contraction twinning (76–153 MPa) [50]. Hence, during deformation, a large amount of basal slips and tension twinning will be activated and Mg alloys exhibit a relatively low strength (tensile yield strength: ~100–250 MPa for commercial casting Mg alloys [43,51] and limited ductility (elongation: 2–8% [43,51]). Actually, twinning represents an important deformation mechanism for Mg alloys [52–57]. The most commonly observed three typical twinning are tension, compression and double twinning. Tensile twinning reorients around [11–20] zone axis by ~89° [50,58–62], while for contraction twinning and double twinning the rotating angle is 56° ± 5° [50,61,63,64] and 38° ± 5° [63–65], respectively. In addition, it has been reported that Gd lowers the stacking-fault energy of Mg [44]. Stacking fault is usually formed by the dissociation of a full dislocation into two partial dislocations on the basal plane during deformation [43]. The partial dislocation can then be separated by applying stress to form a wide planar stacking fault ribbon [66].
3.4. Precipitation behavior

According to the binary alloy phase diagram of Mg-Zn [67], there are five types of Mg-Zn phases: MgZn$_2$ (or Mg$_7$Zn$_{20}$), MgZn (or Mg$_{17}$Zn$_{13}$), Mg$_2$Zn$_3$ (or Mg$_8$Zn$_4$), Mg$_2$Zn$_2$ and Mg$_2$Zn$_1$, and the phase transition temperature is 340 °C, 347 °C, 416 °C, ~590 °C and 381 °C, respectively. Among them, MgZn$_2$ is the most thermally stable phase. The most common ternary secondary phases are I-phase and W-phase. For the I-phase, the phase transition temperature is 437 °C (I-phase partly transformed) and 470 °C (I-phase and α-Mg eutectic transition), while for W-phase, it is ~510 °C [16,68].

When the annealing temperature is 200 °C, all these Mg-Zn binary phases and Mg-Zn-Gd ternary phases are thermally stable. However, TEM observation indicates that the newly formed precipitates are MgZn$_2$ and I-phase. Kim et al. [40] probed the precipitates in a ternary Mg-Zn-Y alloy, and also found that low-temperature precipitate is MgZn$_2$ phase, which is also consistent with that obtained in the binary Mg-Zn alloy [69]. The difference is, however, that we find I-phase precipitates for Mg-Zn-Gd alloy, while there is no I-phase precipitates for Mg-Zn-Y alloy. In our previous study on the precipitation behavior for as-cast Mg-Zn-Gd alloy annealing at 350 °C [20], we find that the formation of I-phase requires a high concentration of alloying elements, otherwise the MgZn$_2$ will be precipitated in α-Mg matrix. Hence, in this study, the newly formed I-phase, which precipitates in α-Mg matrix, may be due to the high concentration of alloying elements. In addition, deformation also introduces a large amount of defects into the alloys, which benefit the diffusion of alloying elements [19,70–72]. The diffusion coefficient of Gd in α-Mg matrix is enhanced, which may be another reason for the precipitation of I-phase in α-Mg matrix.

When the annealing temperature increases to 400 °C, only four types of secondary phases (Mg$_2$Zn$_3$, Mg$_2$Zn$_2$, I- and W-phase) have a higher transition temperature than annealing temperature. Hence, only these four secondary phases are likely to be newly formed. On the other hand, with the increase of temperature, the solid solution ability of the alloying elements increases accordingly. The solubility limits of the Zn and Gd in α-Mg matrix is ~6.2 wt.% at ~340 °C and 23.49 wt.% at ~548 °C, respectively [67,73]. In addition, solubility of Zn and Gd in α-Mg matrix at 400 °C is ~5.5 wt.% and 11 wt.%, respectively [67]. The concentration of Zn and Gd in our studied alloy is 3.88 wt.% and 1.56 wt.%, respectively. Because the solubility is higher than the concentration, it is likely that the secondary phase decomposes and is then dissolved into α-Mg matrix by annealing at 400 °C. Especially for Mg$_2$Zn$_3$ and I-phase, the phase transition temperatures are only a little higher than the annealing temperature. Although both MgZn$_2$ and W-phase are thermally stable at this annealing temperature, maybe W-phase is easier to form due to the addition of Gd. The best proof is that W-phase formed instead of MgZn$_2$ in as-cast Mg-Zn-Gd alloys [16]. It may also have a very small amount of MgZn$_2$ phase, which is undetected, precipitated in the samples after deformation and annealing. Therefore, in this study, the TEM observation reveals that the needle-like Mg$_2$Zn$_2$ (Mg$_2$Zn$_3$) phase was disappeared and only a small number of W-phase is found.

4. Conclusions

We have conducted room-temperature compression of Mg-1.50Zn-0.25Gd (at.%) alloys reinforced with I-phase and performed a systematic TEM analysis of the microstructure of the alloys, especially the secondary-phase precipitates. We find that during the room-temperature deformation, the non-basal slipping, stacking faults and twining are activated to accommodate the deformation strain and there is no secondary-phase transition. When annealed at 200 °C after deformation, the needle-like Mg$_2$Zn$_2$ phase is dispersed and a large amount of I-phase and Mg$_2$Zn$_2$ phase are precipitated. However, when annealed at 400 °C after deformation, only a small amount of W-phase is found in the α-Mg matrix, though the needle-like Mg$_2$Zn$_2$ phase is also dispersed.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

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