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A transmission electron microscopy investigation of defects in an Mg-Cu-Mn-Zn-Y damping alloy

Xuefei Huang [a], Wenzheng Zhang [a,*], Jingfeng Wang [b,c], Wenwen Wei [b,c]

[a] Laboratory of Advanced Materials, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China
[b] National Engineering Research Center for Magnesium Alloys, Chongqing University, Chongqing 400044, China
[c] College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China

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ABSTRACT

A high number of dislocations have been observed in an as-cast high-damping Mg-3Cu-1Mn-2Zn-1Y (wt.%) alloy using transmission electron microscope (TEM). The majority of dislocations are distributed in parallel and uniform rows. Mg_2Cu particles in the matrix are often found to be associated with a number of parallel dislocations. Twins containing stacking faults are also frequently observed. The formation of eutectic phases occurring during casting is followed by precipitation of secondary intermetallic phases in supersaturated α-Mg with alloying elements upon annealing. The observed defect structures provide useful experimental evidence supporting the previously proposed damping mechanism for Mg alloys.

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1. Introduction

Magnesium alloys have attracted much attention nowadays not only for their competitive properties of low density and high specific strength, but also for their excellent damping properties [1,2]. Addtion of various soluble alloying elements, such as Al in the widely used AZ91, can remarkably improve the strength of the alloys, but adding some elements will result in poor damping capacity of the alloys [3,4]. Recently Srikanth [5] added copper to a AZ91 alloy and found that the overall damping capacity increased dramatically. High-strength damping Mg-Cu-Mn alloys have also been fabricated using powder metallurgy (PM) [6] or a severe plastic deformation (SPD) method [7]. However, these methods bring a high processing cost.

Generally, the high damping capacity of an Mg alloy requires the formation of a large number of dislocations that can vibrate freely to some extent in order to dissipate energy [8,9]. The Granato–Lücke(G–L) theory, i.e. the dislocation mechanism for damping, has been employed to rationalize the internal friction in Mg alloys such as Mg-Ni [10,11], Mg-Si [12], Mg-Cu [6] systems and Mg-matrix composites [13,14]. It has been proposed [8,9,15,16] that the damping of a magnesium alloy at room temperature is dependent on the applied strain amplitude. It is closely related to the movement of dislocations which are weakly pinned by point defects such as solute atoms or strongly pinned by precipitates, grain boundaries or junction points in a dislocation net. However, some deviations from the prediction of G–L theory have also been noticed in studies of sintered Mg-Cu-Mn and Mg-Ca alloys [6,15]. These deviations were speculated as originating from twins as another energy-dissipation source [6,15]. Nevertheless, to our best knowledge, little experimental evidence has been given on the microstructure features of these damping alloys, especially the dislocations and twins in the alloys mentioned above.

In a recent work, a high damping Mg-3Cu-1Mn (wt.%) alloy has been fabricated by conventional casting method and a proper amount of Zn and Y were added to further improve the damping capacity of the alloy without sacrificing its strength [17]. The damping property of the modified alloy is much higher than that of the base alloy in the high strain amplitude region and even close to that of pure Mg [17]. A deviation of the 'G–L' plot from a straight line also suggested new energy-dissipation sources in addition to the dislocations in this alloy [17]. However, the overall dislocation configurations, the distribution of the second phases and the microstructure change due to addition of Zn and Y remain unclear. A clear description of these microstructure features is essential to understanding the damping behavior of the alloy.

* Corresponding author. Tel.: +86 10 62773795; fax: +86 10 62771160.
E-mail address: zhangwz@tsinghua.edu.cn (W. Zhang).

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The present work reports an in-depth analysis of the microstructure in an as-cast high damping Mg-3Cu-1Mn-2Zn-1Y (wt.%) alloy using TEM. The dislocation and the twin structures are investigated. The results can provide useful insights toward understanding the damping mechanism of this alloy and guiding the design of damping Mg alloys with improved properties.

2. Experimental procedures

The alloy for microstructure characterization was prepared using a conventional permanent-mold casting method. For making the alloy, Mg-30%Cu, Mg-4.1%Mn, Mg-30.30%Y (weight fraction) master alloys, pure Zn and pure Mg were melted in an electrical furnace using a mild steel crucible under the argon atmosphere at 850 °C, and then the melt was cooled in air after adequate stirring. The annealing treatment of the cast samples was carried out at 200 °C for 15 h. Thin foil specimens for TEM observations were prepared by twin-jet electropolishing in a solution containing 3 ml perchloric acid and 297 ml ethanol at −50 °C, with a voltage of 90 V and a polishing current around 20 mA. Characterizations of the microstructure and phase analysis were performed in the JSM-6301 scanning electron microscope (SEM) operated at 15 kV and JEOL 200CX and JEM-2011 TEM equipped with energy dispersive X-ray spectrometer (EDX), with an acceleration voltage of 200 kV. Specimens were tilted extensively for contrast analysis of dislocations with TEM. The TEM images were obtained at the diffraction conditions in which most of the dislocations are visible to reveal their factual configurations. In order to examine the typical defect microstructure in the alloy, at least 30 TEM samples from different part of the alloy have been examined with TEM.

3. Results and discussion

3.1. Microstructure of the as-cast alloy

Since the damping behavior of the alloy is sensitive to the defect microstructure, the following analyses focus on grain size, distribution of intermetallic phases (IMPs), solution of alloy atoms, dislocations and twins in the as cast alloy.

3.1.1. Grain sizes and distribution of IMPs

The SEM micrograph of the as-cast microstructure of the alloy is shown in Fig. 1a–c. The measurement shows that the grain size of the alloy is around 100–300 μm. A certain number of IMPs are distributed along the grain boundaries. From the enlargement of the microstructure in Fig. 1b, one can see that the IMPs exhibit a discontinuous morphology. The back-scattered electron (BSE) image shows that there are two components of different contrasts, bright and grey, in the discontinuous regions, as can be seen in Fig. 1c. This structure is probably due to a eutectic reaction from a non-equilibrium solidification process. In addition, it should also be noted that there are sparsely distributed precipitates within the grains, as indicated by the arrows. These precipitates are possibly formed during cooling after fast solidification, indicating that the matrix is highly supersaturated with solute atoms. TEM investigations with selected area electron diffraction (SAED) patterns revealed that the bright phase along the grain boundaries is Mg_2Cu, as shown in Fig. 1d. This agrees with the binary phase diagram of Mg-Cu, indicating that eutectic structure consists of α-Mg an Mg_2Cu. A 14H long-period stacking ordered (LPSO) structure has been identified from grey regions in the eutectic structure (Fig. 1e). According to an EDS analysis, the LPSO phase is enriched in Y, Cu and Zn (Fig. 1f). Detailed characterization of the LPSO structures is under investigation and will be reported in a separated publication.

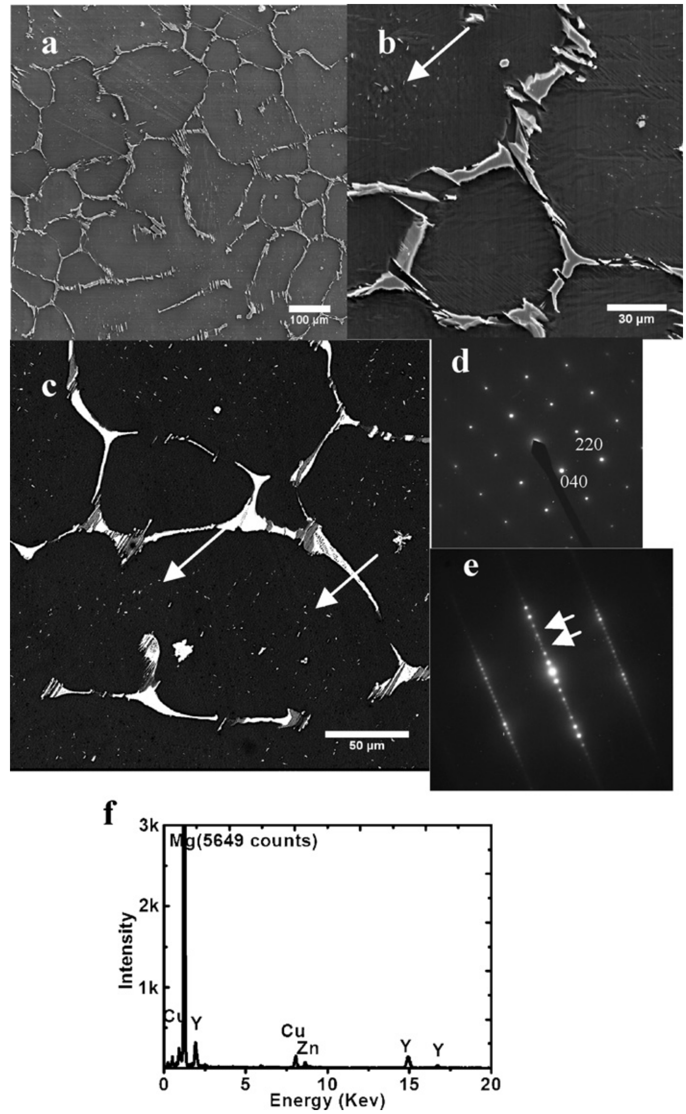

Fig. 1. Microstructure of the as-cast Mg-3Cu-1Mn-2Zn-1Y alloy. (a) SEM image of a low magnification, showing morphology of grains; (b) SEM image of a high magnification, showing eutectic structure at grain boundaries; (c) back-scattered electron image with SEM, with high light of LPSO (grey) component in the eutectic structure; (d) [0 0 1] zone axis of the Mg_2Cu diffraction pattern corresponding to the major (bright) phase in the eutectic structure; (e) [1 0 0] zone axis of the 14H LPSO structure, the additional spots between $g0002_{\alpha}$ and the direct spots are schematically marked by the white arrows; (f) EDS analysis of the LPSO structure.

3.1.2. Dislocation configurations in the matrix

Fig. 2 shows the typical dislocation features in different parts of the cast Mg-3Cu-1Mn-2Zn-1Y alloy. It is amazing to observe a large number of dislocations in the as-cast alloy. The configurations of these dislocations can be classified into three types. Firstly, the majority of the dislocations align nearly parallel to each other and they are arranged uniformly in rows as shown in Fig. 2a, which was obtained near the $[\bar{2}201]_{Mg}$ zone axis. These dislocations are distributed in only two rows. These rows are almost perpendicular to each other. The individual dislocations in each row usually exhibit a similar morphology. Parallelism or similar configuration of these dislocations suggests that these dislocations possibly lie in the same group of glide planes and intersections between them seldom occur. Therefore, they can readily vibrate to certain extent, so as to dissipate energy effectively. According to a rough estimation in TEM observation, the areas containing the parallel and uniform dislocations in rows occupy a proportion of approximate 70% in the total visible area in a TEM sample. It indicates a possible significant role of dislocation rows in damping property of the alloy. These major parallel dislocations are likely to move in response to stress and thus they play a key role in energy dissipation in damping process.

In addition to the above type of dislocations, there are also a few regions where tangles of many dislocations arrange in walls

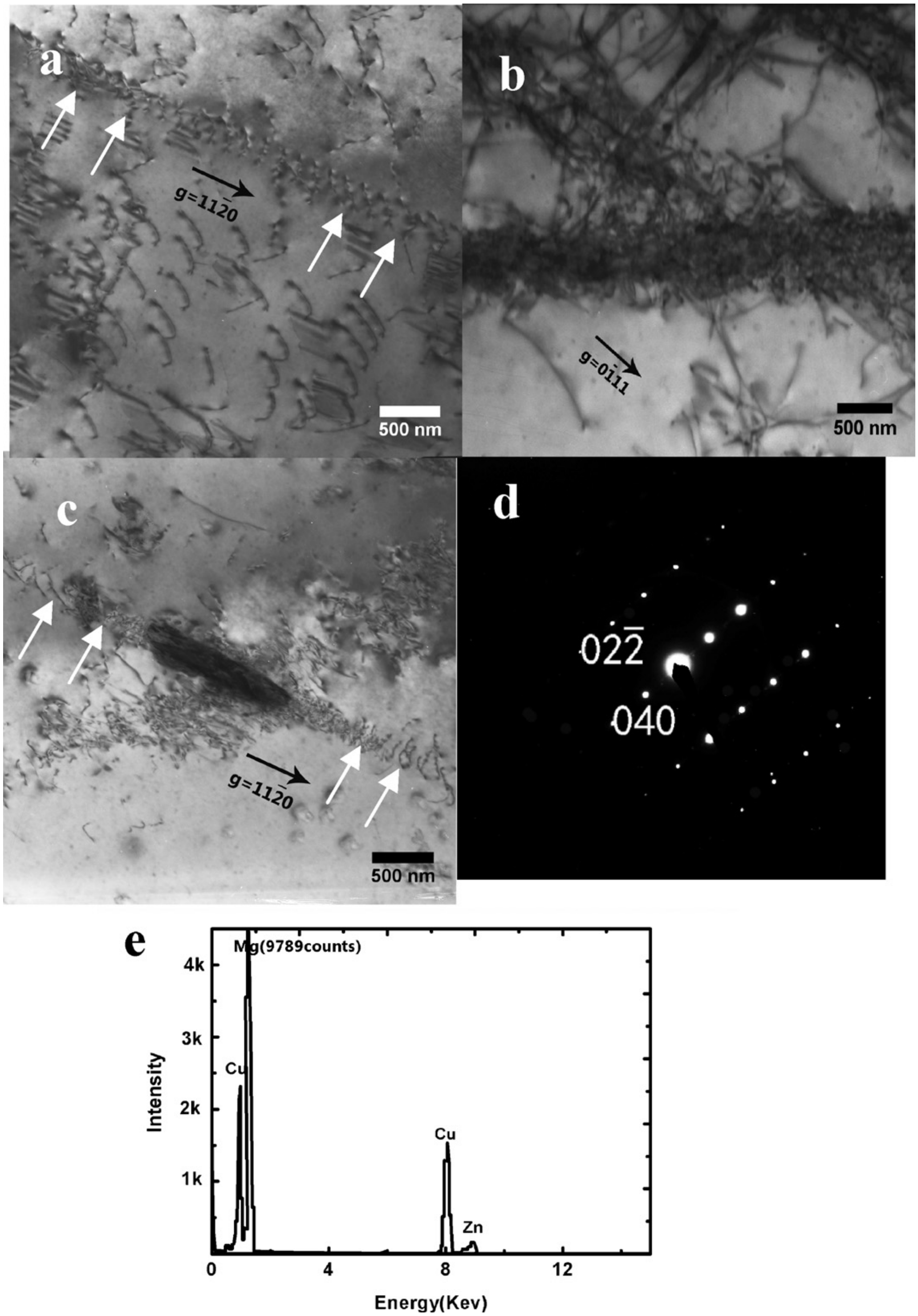

Fig. 2. TEM bright-field micrographs show the three distinguished dislocation configurations in an as-cast Mg-3Cu-1Mn-2Zn-1Y alloy. (a) Dislocations arranged uniformly in rows; (b) dislocation walls; (c) dislocations around a Mg_2Cu particle with SAED pattern of the particle shown in (d) and; (e) EDS analysis of the Mg_2Cu particle.

across each other (Fig. 2b). Tangles of these dislocations suggest that several sets of dislocations exist in different glide planes and these dislocations can intersect each other. These dislocations walls likely present barriers for the dislocation movement [18]. Therefore they are unfavorable for damping capacity of the alloy. However, some locally vibration of these dislocations within the walls may contribute to internal friction.

The third characteristic configuration of the dislocations was observed near the interfaces regions between the matrix and the sparsely distributed secondary phases. A typical example of the dislocations associated with a secondary phase is shown in Fig. 2c. The SAED pattern from the secondary phase is given in Fig. 2d, while its corresponding EDX analysis is shown in Fig. 2e. The diffraction pattern was indexed as [1 0 0] zone axis of Mg_2Cu compound. As seen from Fig. 2c, a large number of dislocations surround the Mg_2Cu particle. It seems that the interface acts as a dislocation source from which the parallel dislocations emerge one by one. Much like the situation in the damping Mg-matrix composites

[2], the nucleation of these dislocations is most probably resulted from the stress concentrated around the secondary phase particles caused by the large different thermal expansion coefficients (TEC) of the matrix and the secondary phase during cooling or by the mismatch strain between these two phases. The regular dislocations formed around the Mg_2Cu particles are probably the same as the first type. The irregular dislocations around the particles may also affect internal friction. The association of parallel dislocations with the secondary particles provides clear evidence of these particles being the origins of parallel dislocations. In this sense, presence of these sparsely distributed particles is in favor of increasing the damping capacities. Since the particle spacing is rather large, their resistance to the dislocation motion is relatively weak.

3.1.3. Twins and stacking faults in the as-cast alloy

The linear behavior of the 'G–L' plot is often used to check whether the damping behavior is caused only by dislocation movement [6,9,15]. A 'G–L' plot of the as-cast Mg-3Cu-1Mn-2Zn-1Y alloy (Fig. 3) shows that it deviates from a straight line. This deviation has also been observed in other Mg alloys and twins were suggested as another energy dissipation source, though no experimental evidence has been given [6,15]. In the present alloy, twin structures were frequently observed. Fig. 4a shows a typical twin structure in the matrix. It should be noted that heavy stacking faults exist in these twins. The twinning plane is $(\bar{1}\,0\,1\,\bar{2})_{Mg}$ and the direction of the faults fringes are parallel to $[1\,1\,\bar{2}\,0]_{Mg}$. Additionally, some dislocations were also observed in the interfaces between the twins and matrix, as shown in Fig. 4b. The frequently observed twins and stacking faults suggest low stacking fault energy in this alloy, indicating that the shear of close-packed atomic planes is easily activated. Many shape memory alloys are known to have excellent damping capacity. The origin of the high damping capacity in these alloys is associated not only with the presence and the hysteretic mobility of interphase and intervariant interfaces, but also with the internal defects within martensite variants such as dislocations, twin structures and stacking faults [19,20]. Much like the sintered Mg-Cu-Mn [6] and Mg-Ca [15] alloys, the 'G–L' plot of this alloy clearly deviates from the straight line. Twinning has been suggested to be responsible for this deviation because the twin interface is also another energy-dissipative source [6,15]. Frequently observed twins in the present Mg alloy provide experimental support to the above suggestion. In addition to the possible mobile interfacial dislocations together with the twin-matrix interfaces, the stacking faults within the twins also possibly contribute to the deviation from the dislocation mechanism.

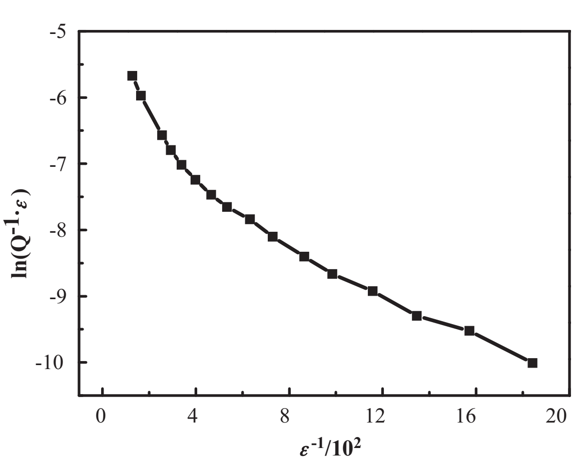

Fig. 3. A 'G–L' plot of the as-cast Mg-3Cu-1Mn-2Zn-1Y alloy.

3.2. Effect of annealing on the alloy phase configuration

Generally, the movement of dislocations was not only obstructed by the secondary phases, the grain boundaries or the dislocation net, but the soluble atoms in the matrix can also pin the dislocations by solute-dislocation interactions [8,9]. In this alloy, fast solidification during the casting process may cause significant supersaturation of solute atoms in the matrix. As mentioned early, a certain amount of intragranular precipitates have formed due to supersaturation. However, since the precipitation occurs during fast cooling, one would expect that the precipitation is incomplete. In order to verify remaining supersaturation in the cast alloy, an annealing treatment has been carried out at 200 °C for 15 h. Fig. 5a shows the typical microstructure of the heat-treated alloy. One can see that numerous precipitates formed along the dislocations (Fig. 5a), indicating that dislocations serve as heterogeneous sites for nucleation of precipitates. A higher magnification in Fig. 5b shows that most precipitates exhibit rod morphology but a few blocky precipitates also exist. The axis of the rod is along the $[0\,0\,0\,1]_{Mg}$ direction (see the diffraction pattern inserted in Fig. 5b). The rod precipitates usually have a width of 10 nm and a length of 50 nm. It is interesting to note that the rod precipitates are often associated with a particle at its end as seen in Fig. 5c. The EDX spectra recorded from the "blocky precipitates", "rod precipitates" and "end-particles" are provided in Fig. 5d, e and f, respectively. Both the "blocky" precipitates and "end-particles" are enriched with Mn, while the rod precipitates are enriched with Cu and Zn. According to the Mg-Cu and Mg-Mn binary phase diagrams [21], the solubility of Mn is less than 0.1 wt.% and Cu has nearly no solubility in α-Mg matrix at 200 °C. The fast cooling in the solidification process may have cause a large amount of Mn and Cu atoms to supersaturate at 200 °C. However, the solubility of Zn in the α-Mg matrix is about 3 wt.% at 200 °C according to the Mg-Zn phase diagram [21]. While this solubility is above the content of Zn in the alloy, the identification of Zn in the precipitates may indicate that the solubility of Zn in the present alloy is lower than the binary alloy. In addition, possible segregation of Zn in the as-cast alloy may also lead to local supersaturation of Zn in the matrix. In addition, the dislocation lines (Fig. 5a) and twin grain boundaries (Fig. 4c) decorated by these precipitates can serve as experimental evidence to confirm that these defects exist before annealing treatment, i.e. they formed during casting process other than introduced by TEM sample preparation.

3.3. Discussions on the damping mechanisms of the alloy

Based on the above investigations, the microstructure of the high damping permanent-mold casting Mg-3Cu-1Mn-2Zn-1Y alloy can be described as follows: The as-cast Mg-3Cu-1Mn-2Zn-1Y alloy have a relatively larger grain size of 100–300 μm, with an Mg_2Cu and LPSO eutectic structure distributed along the grain boundaries. The alloy also contains some dilute Mg_2Cu precipitates within the grains. The large grain size means that the dislocations can move to a large extent in the matrix. Many sets of parallel and regular-spaced dislocations exist in the most areas of the matrix and some dislocations tangle together locally. The dislocations pie up near the interface regions between Mg_2Cu precipitates and α-Mg matrix. Besides, Cu, Mn and Zn are supersaturated at least locally in the cast alloy. According to the G–L theory [8,9], the damping behavior of these alloys can be interpreted as follows. When the strain-amplitude is small, the dislocation movement is restricted in the distance defined by the point defects such as solution atoms. It was found that in the low strain region, Mg-Cu-Mn-Zn-Y alloy has a lower damping capacity than the Mg-Cu-Mn alloy [17]. This is possibly because certain amount of Zn atoms in the solid solution can pin the dislocation movement through the

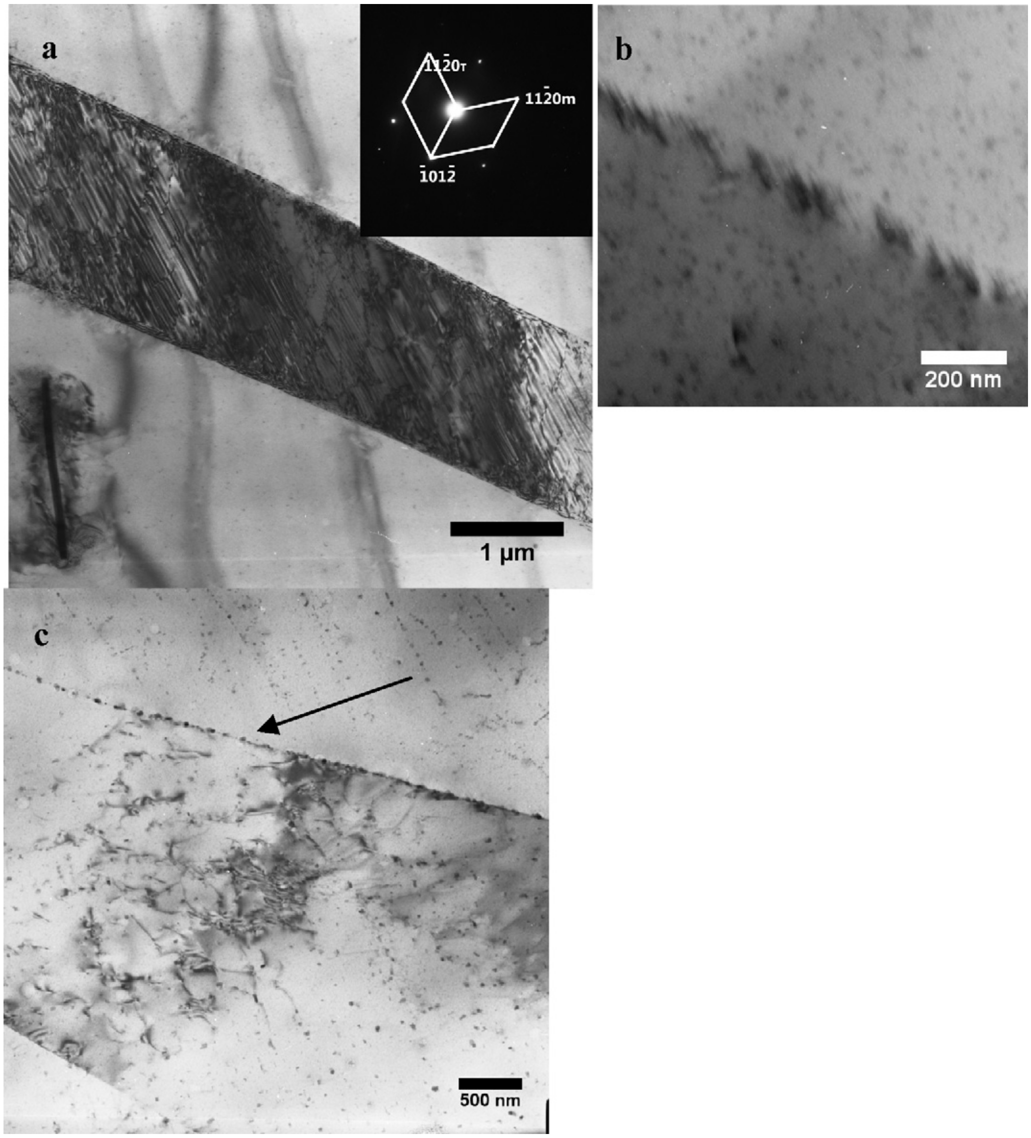

Fig. 4. (a) TEM bright-field image of the twins in the matrix in the as-cast alloy. The common zone axis is [$\bar{2}$ 2 0 1] (insert in the upright). (b) Interface dislocations between the twin and the matrix. (c) The twin grain boundary decorated by precipitates in the annealed alloy.

Cottrell mechanism. As the strain amplitude increases to a critical value, dislocations will breakaway from the weakly pinned solute atoms and move at a large extent, so the damping capacity will increase [8,9]. The higher damping capacity of the modified alloy compared to the Mg-Cu-Mn alloy in the high strain-amplitude regions may be caused by the Y addition. The addition of Y has yielded formation of LPSO structure, and high-density stack faults in the LPSO structure may contribute to damping effect. The twins interface together with the stacking faults within them can act as another energy-dissipation source in all stress regions. In the as-cast state, the supersaturated solute atoms act only as weakly pinning spots for dislocation movements, and the distribution of IMPs is very sparse in the matrix. However, when the alloy was annealed, the supersaturated solute atoms precipitate from the matrix. Thus, the number density of the precipitates increased significantly within the grains. The high density precipitates acts as the strong pining spots for the dislocation movements [8]. So the damping capacity of the annealed alloy can be expected to be poor. A similar condition can be found in the heat-treated Mg-Si alloy [12].

4. Summary

In summary, microstructures of high-damping Mg-3Cu-1Mn-2Zn-1Y alloys have been investigated using TEM. The as-cast alloy has a grain size around 100–300 μm. A large amount of Mg_2Cu is distributed along the grain boundaries as part of eutectic structure. The other phase in the eutectic structure is mainly a LPSO phase. Precipitates were also found to be sparsely distributed within the grains. Many sets of parallel or isolated dislocations with similar morphology have been observed in most areas of the α-Mg matrix in the as-cast alloy. Some dislocations tangle locally to form dislocation walls. Parallel dislocations were found to be associated with the interface between Mg_2Cu particles and the matrix, indicating that the secondary particles are sources of the dislocations in the as-cast alloy. The observations of high density of parallel dislocations support the dislocation mechanisms of internal friction. This study also provides evidence of twin structures together with inner stacking faults and interface dislocations, which may be account for the deviation from the Granato–Lücke (G–L) theory. A large number of precipitates were generated from annealed alloy, indicating

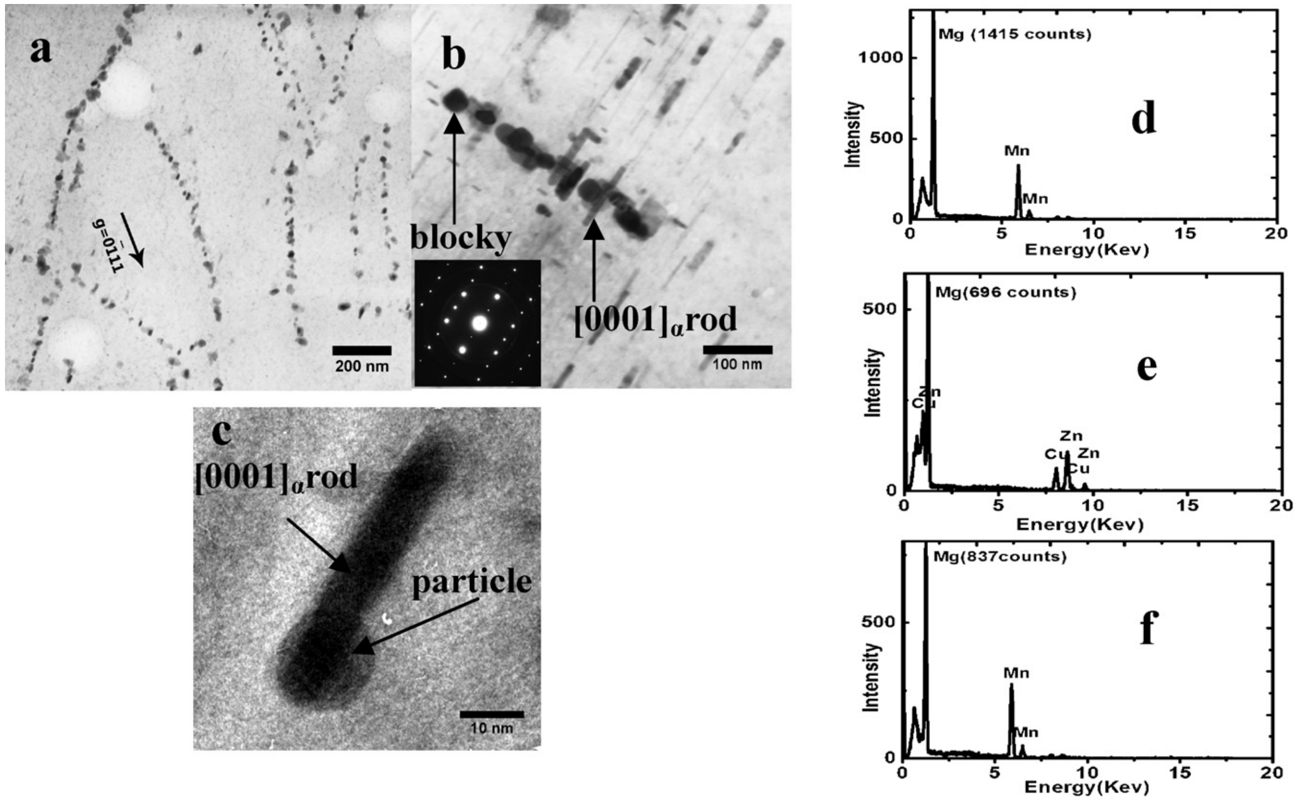

Fig. 5. (a) Bright-field TEM image of the 15-h heat-treated Mg-3Cu-1Mn-2Zn-1.0Y alloy. (b) A higher magnification of the precipitates obtained at the $[1\ 1\ \bar{2}\ 0]_{Mg}$ zone axis shown in the lower left of Fig. 2b. Most blocky precipitates in Fig. 2b are arranged in a straight dislocation line. (c) A rod precipitates with a particle at its end. EDX spectrum from the blocky precipitates (d), the rod precipitates (e) and the particles adjacent to the rod precipitates (f).

the supersaturation or local supersaturation of the solute atoms Cu, Mn and Zn in the as-cast alloy. These solute atoms together with the Mg_2Cu particles in the as-cast alloy are expected to act as weak and strong pinned spots to the dislocation movement, respectively.

Acknowledgments

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