Microstructural Characterization of a Mg–9%Li–1%Zn Alloy

Chui-Hung Chiu^{1,2}, Jian-Yih Wang³ and Horng-Yu Wu²

¹Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan 31015, R. O. China

²Institute of Engineering Science, Chung Hua University, Hsinchu, Taiwan 30012, R. O. China

³Department of Materials Science and Engineering, National Dong Hua University, Hualien, Taiwan 97401, R. O. China

A Mg–9%Li–1%Zn alloy was investigated by transmission electron microscopy and microdiffractometry. The alloy had a dual phase structure with dispersed particles of ZnO and MgO oxides. The Wurtzite structure of ZnO exhibited a good orientation with respect to the Mg matrix, but the MgO did not. The peak aging at a temperature of 100°C occurred at 10 h. At 50°C, the hardness reached the maximum value after an aging period of around 100 h. The appearance of the extra bump adjacent to the main peak of $\alpha(002)$ after aging at 50°C/100 h and 100°C/10 h, was thought to correspond to a precipitate phase or spinodal decomposition.

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1. Introduction

Magnesium is almost the lightest metal that can be utilized in structural applications when it is alloyed with other elements. Magnesium alloys have recently been used to make portable electronic devices because these alloys are light and can be recycled. However, magnesium exhibits poor formability because it has the hexagonal close-packed structure. Haferkamp *et al.*¹⁾ reported new magnesium–lithium alloy systems with lower density, improved ductility and corrosion resistance recently. Alloying magnesium with lithium, which has an extremely low density, 0.534 g/cm³, can overcome these shortcomings and further reduce the weight. Ultralight Mg–Li alloy has a density that is similar to that of plastics, so it has only half the weight of aluminum alloys. The Mg–Li phase diagram²⁾ reveals that when the Li content is between ~5.5 and 11.5 mass%, the BCC-structured β phase of the Li solid solution co-exists with the HCP α phase of the Mg solid solution (Fig. 1). Moreover, the notorious typical HCP crystalline structure of the general magnesium alloys, which has inherently poor formability, can be modified to improve its manufacturability markedly.^{3–5)} Cold working and precipitation hardening^{6,7)} have been suggested to improve the poor mechanical characteristics of magnesium–lithium alloy. However, most such investigations have focused on mechanical behaviors, perhaps because preparing foil specimens for TEM is difficult. Understanding microstructural changes during processing is important to the development of a magnesium–lithium alloy with appropriate mechanical properties. The authors made TEM observations of the magnesium–lithium alloys, and this work explores the variations in the microstructures of a dual-phase Mg–9%Li–1%Zn alloy. The microstructure and hardness of the as-cast ingot and the age-hardened specimen were measured using an electron microscope and a microhardness tester.

2. Materials and Experimental Procedures

This Mg–Li alloy was melted in a high-frequency electric induction furnace equipped with vacuum capability, and inert

Fig. 1 Binary magnesium–lithium phase diagram of the Mg–9 mass%Li alloy, comprising α and β phases.²⁾

argon gas was employed. The cast alloy was analyzed using an induction coupled plasma (ICP) apparatus, and its chemical composition was 9.6 mass%Li and 1.1 mass%Zn (designated as LZ91). Subsequent rolling was performed at room temperature. The initial 37 mm-thick flat ingot was thinned down to a final 2 mm; each pass of the rolling reduced the thickness by ~5%. Before aging treatment, the alloy was maintained in silicon oil at 300°C for 30 min. and quenched in water. Aging treatments were performed in an ambient furnace at 50 or 100°C. Microstructural analysis was conducted using a 400 kV high-resolution transmission electron microscope (HR-TEM) and a 200 kV field-emission TEM. Micro-hardness was measured to evaluate the effects of aging. X-ray diffraction (XRD) and X-ray energy dispersive spectrometry (EDS) were employed to identify any second phases.

3. Results and Discussion

3.1 TEM analyses of as-cast LZ91

The as-cast microstructure of LZ91 comprises a mixture of α and β phases (bright and dark regions, respectively) with

Fig. 2 α phase on the top of the photograph is almost free of dislocations, while the β phase, on the bottom has a high density of dislocations.

Fig. 3 TEM analysis of as-cast specimen; oxide particles were distributed in the α matrix, and were identified as ZnO (granular particles) and MgO (faceted particle).

Fig. 4 Granular particles (a) and matrix (b) identified by EDS. The particles contain Zn and O, and are ZnO.

Fig. 5 Faceted particle (a) and matrix (b) identified by EDS. The particles contain Mg and O, and are MgO.

Fig. 6 TEM morphology of the cold-worked and solution-treated LZ91 specimen.

some dispersed fine particles in the α phase, as presented in Fig. 2. The top α phase is almost free of dislocations, whereas the β phase on the bottom has a high density of dislocations. The α phase has the HCP structure, so it tends not to deform plastically during the preparation of the TEM specimen. In contrast, plastic deformation during the preparation of the specimen increases the density of dislocations in the softer β phase which has the BCC structure. Figure 2 depicts the two shapes of the ultrafine dispersed particles—spherical and faceted. All such particles are smaller than 40 nm, as presented in Fig. 3. The ultrafine particles were analyzed by FE-TEM equipped with EDS. The electron beam size was reduced to approximately 10 nm to make ensure the accuracy of the analysis of the ultrafine particles. Figure 4 reveals that the rounded particles contain Zn and O, indicating that this particles should be ZnO. EDS analysis of the faceted particles showed that the Mg and O elements

Fig. 7 Nano-beam diffraction pattern of as-cast LZ91 specimen, revealing that the orientation of the Wurtzite structure of ZnO is strongly related to that of the Mg matrix.

were present, as displayed in Fig. 5, suggesting that the faceted particles were the oxide, MgO. The oxidation potentials of Mg and Li exceed that of Zn, so when oxides formed during melting, Li oxides should be observed in the as-cast ingot. However, no particle was found to be an Li oxide in this investigation. Hence, the oxide detected in the as-cast ingot must have been present before melting. The presence of dispersive nano-sized ZnO and MgO oxides strengthens the LZ91 alloy.

3.2 Solution-treated structures

Figure 6 presents the microstructures of the cold-worked and solution-treated (as-quenched) specimen. The TEM micrograph shows the same oxide particles as were observed in the as-cast ingot, but aligned by cold working. A nano-beam diffraction technique was then employed to elucidate the structure of the ultrafine particles. The nano-beam diffraction pattern demonstrates that ZnO has a Wurtzite structure, as presented in Fig. 7. The relationship between the orientations, displayed in Fig. 7, also reveals that the ZnO has a coherent structure with the magnesium matrix. Figure 8 concerns the tri-point of the grain boundaries and displays faceted MgO nearby. The nano-beam diffraction pattern indicates that the structure of MgO is not very coherent with the magnesium matrix, as shown in Fig. 9.

3.3 Precipitation and microstructures

The solution-treated specimens were aged at 50 and 100°C. Changes in hardness were plotted against aging time, as presented in Fig. 10. When aged at 100°C, the hardness reached a maximum at 10 h. However, at 50°C, the corresponding time was around 100 h. These phenomena differ from the those of the dual-phase Mg–8.2 mass%Li–4.6 mass%Zn alloy, which exhibited softening at 348 and 383 K.⁷⁾ X-ray diffraction was utilized to analyze the constituents and thus relate the hardness to the microstructure. All

Fig. 8 TEM images of solution-treated LZ91 alloy. Faceted particles are present in the grain boundary area.

aged specimens were analyzed using XRD. Figures 11(a) and (b) display typical X-ray spectra obtained from LZ91, suggesting the presence of the two detectable phases— α and β . An extra bump (side band, indicated by arrows in the figures) adjacent the main peak of $\alpha(002)$ is observed in the specimens aged at 50°C/100 h and 100°C/10 h. The appearance of the extra bump in X-ray diffraction pattern implies that spinodal decomposition may be responsible for age hardening.⁸⁾ The aging curves, plotted in Fig. 10, also reveal that hardness and precipitation were maximal when the extra bump was present. However, the precipitate is an unstable phase because its diffracted peak disappeared in the XRD spectra after a long period of aging.

Figure 12 depicts a typical TEM micrograph of the specimen aged at 100°C for 10 h. It shows the particle-like structure. Although no clear precipitate was observed, the high-resolution TEM micrograph in Fig. 13 demonstrated

Fig. 9 Nano-beam diffraction pattern of faceted particle (a), matrix (b) and as-quenched LZ91 alloy (c). The orientation of the cubic MgO is not related to that of Mg.

Fig. 10 Peak aging is posited to be associated with precipitate phases or to be caused by spinodal decomposition.

fine fringes in the particle-like structure. The structure is similar to that of the short-range structural modulation, perhaps because of spinodal decomposition. Fourier transformation of the image [Fig. 13(b)] reveals the sticks that correspond to the modulation structure. The structure was further analyzed using nano-beam EDS and was found to be easily vanished when electron beam radiation is applied. It was found not to be stable.

4. Conclusions

Microstructural characteristics of a Mg–9%Li–1%Zn alloy were investigated by TEM and XRD analysis. The following results were obtained.

- (1) The TEM results reveal that the as-cast and as-quenched specimens exhibit α and β dual phases with many ultra fine particles, which were identified as ZnO and MgO oxides.
- (2) The orientation of the Wurtzite structure of ZnO, but not that of MgO, was closely related to that of the magnesium matrix.
- (3) XRD analysis revealed the presence of an extra bump adjacent to the main peak $\alpha(002)$ after aging at 50°C/100 h and 100°C/10 h, suggesting that age-hardening is

Fig. 11 XRD images following aging at 50°C (a) and 100°C (b) present an extra bump adjacent to the main peak of $\alpha(002)$ as indicated by arrows in the figures. This result was supported by linking the hardness to the XRD results. This bump was associated with an unstable phase since it disappeared after a longer period of aging.

Fig. 12 TEM image of the specimen aged at 100°C for 10h, indicating a particle-like structure.

Fig. 13 HRTEM image of the particle-like structure (a) demonstrates the short-range structural modulation. Fourier transformation of the image (b) presents many sticks that correspond to the modulation structure.

attributable to spinodal decomposition. The precipitate is an unstable phase because it disappeared after long aging.

- (4) The specimen under peak aging conditions at 100°C underwent short-range structural modulation could be caused by spinodal decomposition.

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