Microstructure Evolution in the Rolled $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ Alloy with Long-Period Stacking Phase upon Annealing

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$\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy (at%) has been studying nearly ten years as an elevated temperature creep resistant Mg-based alloy with long-period stacking (LPS) phase. The deformation processing had been performed upon the alloy so that a highly non-equilibrium state was looked forward to provide particularly advantageous material property profiles for it. Thus the texture evolutions in $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy processed by rolling and annealing the as-cast alloy at different temperatures, are investigated thoroughly. The microstructures of the alloy had been examined using general optical microscopy (OM), laser optical microscopy (LOM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM); the textures were analyzed by X-ray diffraction (XRD). The result shows that the second recrystallization texture had developed primarily when a preliminary annealing treatment of 500°C for 2 hours was performed to the rolled alloy and that part of the LPS phase had evolved into another phase with hexagonal superstructure which is an approximant to a quasicrystal and even the quasicrystal.

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1. Introduction

Lightweight magnesium alloys have attracted significant interest in the last decade due to their potential applications in automotive, personal electronics and aerospace industries.

E. M. Padezhnova *et al.*, found three ternary equilibrium phases, i.e. $W\text{-Mg}_3\text{Zn}_3\text{Y}_2$, $Z\text{-Mg}_3\text{Zn}_6\text{Y}$ and $X\text{-Mg}_{12}\text{ZnY}$ phases.¹⁾ Z. P. Luo *et al.* identified the $Z\text{-Mg}_3\text{Zn}_6\text{Y}$ as a stable icosahedral quasi-crystalline phase,²⁾ and determined the $X\text{-Mg}_{12}\text{ZnY}$ phase as an 18R LPS structure by an electron diffraction technique.^{3,4)} In recent years, A. Inoue *et al.* fabricated a high strength Mg-based $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy with a LPS structure by rapid solidification (RS) techniques.⁵⁾ The Mg-Zn-RE-Zr system as high strength creep resistant magnesium alloys was furthermore researched. The deformation treatment for $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ (at%) alloy can give the conventionally cast alloy a complementarity of room temperature strength. Currently, the investigation to improve the mechanical property of the elevated temperature creep resistant Mg alloys with LPS structures has been advanced toward refining LPS structures or deformation treatment.^{6,7)} But some characteristics about the rolled alloy with LPS phase have been not reported. The microstructure evolutions of the $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy processed by rolling and annealing conventionally cast alloy have been deeply investigated in this research work.

2. Experimental Procedure

The nominal composition of the alloy in this study is $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ (at%). The ingot was prepared by melting intermediate alloy Mg-19.9 mass%Y and pure magnesium in a graphite crucible at 775°C with protecting of $\text{SF}_6 + \text{CO}_2$ atmosphere, and adding pure Zinc particles and holding at

775°C for 30 minutes, and then casting the alloy melt into a steel mould of $190 \times 95 \times 20 \text{ mm}^3$. The as-cast alloy specimen and plate type of samples for rolling were cut from the ingot.

A preheating treatment at 400°C for 30 minutes was performed before every rolling pass. The plates were reduced from a thickness of 6.0 mm to about 1.5 mm (74.8% reduction) through nine passes by 12–17% rolling deformation strain per one pass. Seven samples with 74.8% rolling reduction were annealed at 150, 200, 250, 300, 350, 400, 450°C respectively for 30 minutes with protecting of $\text{CO}_2 + \text{SF}_6$ atmosphere and cooled out of furnace at room temperature; two samples were annealed at 500°C for 30 and 120 minutes respectively.

The as-cast specimen was prepared by grinding and polishing, followed by etching in a solution of 4% (v/v) nitric acid alcohol, and the rolled alloys were prepared by insetting in polyester at about 145°C for 8 minutes and then etched with acetic-picric acid solution (5.5 mL CH_3COOH , 2.1 g picric acid, 5 mL water, 2 mL nitric acid and 90 mL alcohol). The microstructures of the as-cast and deformed specimens were characterized by optical microscope and laser optical microscope and scanning electron microscope. The phase constitutions of these specimens were identified using an X-ray diffractometer (D/MAX 2000/PC, Rigaku), and the texture analysis was conducted on X' Pert Pro MRD (PW3040/60, PANALYTICAL B. L.) respectively. Some as-rolled and annealed samples were polished on very fine abrasive papers, and ion polished and thinned again on a precision ion polishing system. The thinned samples were characterized using transmission electron microscope (JEM-2000EX, JEOL).

3. Results and Discussion

3.1 Microstructure of the as-cast $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy

The phase constitution of the as-cast $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy was

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Fig. 1 Micrographs of the as-cast $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy using OM and SEM: (a) OM image of overall dendrite morphology, (b) SEM image of LPS phase.

Fig. 2 Inverse pole figures of the alloy as cast and deformed with 74.8% rolling reduction and annealed: (a) as-cast, (b) rolled, (c) annealed at 400°C for 30 minutes, (d) at 500°C for 30 minutes, (e) at 500°C for 120 minutes.

identified as α -Mg (2H-Mg) and the ternary $\text{X-Mg}_{12}\text{ZnY}$ (18R type hexagonal super-lattice) secondary phase had been presented to other paper in this study. The α -Mg dendrites in Fig. 1(a) as matrix and the $\text{X-Mg}_{12}\text{ZnY}$ phase as showed by Fig. 1(b) distributing on the grain boundaries make up of the microstructure of the as-cast $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy. The acicular $\text{X-Mg}_{12}\text{ZnY}$ intermetallic compound in different dendrites can be observed and the different orientation of $\text{X-Mg}_{12}\text{ZnY}$ with the α -Mg can be distinguished according to the orientation relationship provided according to the reference.⁴⁾

3.2 Texture evolution of the $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy upon rolling and annealing

The phase constitutions of the rolled and annealed $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy can be analyzed through XRD spectrums and compared to the spectrum of the as-cast alloy, the results is that the phase constitution was not altered with comparison to No. 65-3365 (1940) and No. 36-1273 (1982) PDF card, but the deformation and annealing textures can be found through observing peak intensity of (0002) and (10 $\bar{1}$ 1) and (1120) of 2H-Mg with comparison to No. 65-3365 PDF card. An

expression that the {0001} rolling texture evolved gradually toward the $\{12\bar{1}0\}$ annealing texture is presented when heat treatments were performed with increasing temperature and prolonging time. Thus, furthermore observing inverse pole figures of the texture analysis of the as-cast and rolled and annealed alloys is necessary, as showed in Fig. 2. A deformation texture of {0001} as showed in Fig. 2(b) by comparison with the texture of the as-cast alloy in Fig. 2(a) was obtained when the as-cast alloy was hot rolled to a reduction of 74.8% through nine passes by 12–17% rolled deformation strain per one pass and a preheat treatment at 400°C for 30 min before every rolling pass. Two accessory texture of $\{12\bar{1}4\}$ $\langle 10\bar{1}0 \rangle$ and $\{01\bar{1}4\}$ $\langle 2\bar{1}10 \rangle$ can be found to belong to the rolled $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy. Such a texture constitution is connection with the prepared alloy and the deformation mode during rolling upon it. When annealing treatment at 400°C and 500°C for 30 minutes like Fig. 2(c) and Fig. 2(d) and at 500°C for 120 minutes like Fig. 2(e) respectively upon the rolled alloy, the deformation texture was gradually weakened according to decreasing maximum strength and scattered distribution of contours. Below 400°C, the annealing treatment did not induce obviously weakening

Fig. 3 LOM Micrographs of the deformed alloy with 74.8% rolling reduction its annealed ones at different temperatures for 30 minutes: (a) as-rolled, (b) annealed at 400°C, (c) 450°C, (d) 500°C.

for texture. This kind of feeble change of texture maybe results from a primary recrystallization process of continuous recrystallization (or called as recrystallization *in situ*).⁸⁾ Such continuous recrystallization is mainly contributed by the formation of subgrains via dislocation rearrangement and growth and coarsening of cells and subgrains. The occurrence of continuous recrystallization or extended recovery is consistent with a heightened level of stacking fault energy of Mg-Y-Zn alloy.

3.3 Microstructure evolution of the bulk $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy during rolling and annealing

The microstructure of the rolled $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy with rolling reduction of 74.8% and ones of the $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy annealed at 400, 450 and 500°C for 30 minutes after rolling are showed by LOM micrographs in Fig. 3. The deformation texture of the as-cast $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy with LPS structure during plastic deformation can be observed to be along rolling direction. But deformation twins are not found and deformation bands can nearly be visible after hot working in Fig. 3(a). A verdict, that the partial recrystallization behavior and extended recovery as mentioned annealing texture analysis occurred during cooling after hot rolling at an elevated temperature of 400°C in the α -Mg matrix, can be ascertained by the existing weak contrast in the deformation microstructure in Fig. 3(a). The recrystallized grains are difficult to be discerned because of small orientation difference between them and secondary phase distribution in the microstructure yet. Plastic deformation at the elevated temperature of 400°C increases the number of slip systems

in the 2H-Mg phase in principle. The basal plane slip is retarded because of the Y solid solution in 2H-Mg, and the $\mathbf{c} + \mathbf{a}$ dislocation was observed in the TEM images of the annealed specimen in the reference.⁹⁾ So the non-basal slip is the main deformation mechanism in the $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy during rolling after heating up to 400°C. Moreover, the $\mathbf{c} + \mathbf{a}$ dislocation as a main non-equilibrium lattice defect exist in the deformed alloy. The deformation twins were restricted by more slip systems start-up, while the LPS structure retarded the extending of the formed twins too.¹⁰⁾ The above mentioned deformation mechanism markedly improved the deformation unevenness of the HCP structure of magnesium alloy. The LPS structure in the rolled alloy was fragmented fundamentally by non-basal slip, and its shrinking resulted basically from the Zn and even Y diffusion into dislocation, which developed into Cottrell atmosphere.

Upon annealing at 200°C, the microstructure of the alloy was not obviously changed to the recrystallization one. From Fig. 3(b), a great amount of precipitates exist in the microstructure of the alloy annealed at 400°C. The many fine particles among those can be understand as which precipitated in the alloy when an age temperature was up to 400°C. The density of precipitated particles was decreased as showed in Fig. 3(c) when the deformed alloy was annealed by a higher temperature of 450°C. When annealed at 500°C, the alloy has only a small quantity of remnant compound particles (showed in Fig. 3(d)). Because the coarse particles and fine precipitated ones were dissolved or ripped during annealing at 500°C, a small quantity of LPS phase was remained as distorted or rounded striation region; at the same

Fig. 4 TEM images and SAED patterns of the deformed alloy with 74.8% rolling reduction and its annealed ones: (a), (b), (c) as-rolled, (d), (e), (f) annealed at 400°C for 30 minutes, (g), (h) at 500°C for 30 minutes, (i) at 500°C for 120 minutes.

time second recrystallization grains of 2H-Mg came to being. This indicates that grain growth proceeded during annealing at 500°C for 30 minutes in the rolled $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy and the final grain size is almost similar to the dendritic grain size of the as-cast alloy. A furthermore extended annealing time to 120 minutes did not alter the overall annealing microstructure including grain size of the alloy. Understanding for obtaining such second recrystallization grain size can be deduced from that the different deformation mechanics between LPS structure and 2H-Mg results in the increased atom mismatch among dendritic subgrains and $\text{X-Mg}_{12}\text{ZnY}$ phase distribution on the grain boundaries within same a dendritic array.

By combining the furthermore annealing texture evolution as showed from Fig. 2(d) to Fig. 2(e) after the second recrystallization finished, the mechanism can not be understand from the principles such as recrystallization orientational nucleation and preferred growth theories.

The phase constitution was not altered through analyzing the XRD spectrums of the rolled and annealed $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy. Furthermore TEM observation on particles in the rolled and annealed alloy from Fig. 4 indicates that a different structure coexists in the alloys. Such as that dislocation substructure and distortion LPS phase and new evolved L-type of hexagonal superstructure (an approximant of icosahedral quasicrystal¹¹) distribute in the α -Mg matrix of the rolled alloy (as showed in Figs. 4(a), 4(b) and 4(c) respectively), and that the different SAED pattern of LPS phase and the approximant of icosahedral quasicrystal represent the structure change of vicinal regions within same a particle for the rolled alloy annealed at 400°C (as showed in Figs. 4(d), 4(e) and 4(f) respectively), and that the hexagonal superstructure of a spherical particle is almost substitute for the LPS for the rolled alloy annealed

at 500°C for 30 minutes (as showed in Figs. 4(g) and 4(h) respectively), an evolution about substructure and compounds exists. After annealing the rolled alloy at 500°C for 120 minutes, a SAED pattern of quasicrystal was obtained as showed in Fig. 4(i). Thus an evolution about ternary Mg-Y-Zn compound may be summarized as following:

LPS phase (a hexagonal superstructure, by Zn and Y atoms holding several special layers of hexagonal compacted planes with long periods such as 6, 10, 14, 18, 24 layers) $\rightarrow$ an L-type approximant of icosahedral quasicrystal (a further-developed hexagonal superstructure towards a more complex spatial structure and with a stoichiometric composition similar to one of icosahedral quasicrystal $\text{Mg}_3\text{Zn}_6\text{Y}$) $\rightarrow$ a modulated icosahedral quasicrystal (deduced from the L-type approximant, and twofold axes and the Fibonacci numbers characteristic of icosahedron¹²).

The experimental fact confirms that a quasicrystal can be solid state transformed by thermodynamics and kinetics.^{13–15}

4. Conclusions

$\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy as an elevated temperature creep resistant Mg-based alloy was rolled, which brought any amount of thermodynamic non-equilibrium lattice defects on a space scale that ranges from angstroms (e.g. non-equilibrium solute atoms and vacancy) to meters (e.g. sample surface) during rolling, and was then annealed, the following results are acquired in this study:

- (1) An annealing texture evolution proceeded before and after second recrystallization process finished.
- (2) A microstructure evolution about ternary Mg-Y-Zn compound from a LPS phase to an L-type approximant of icosahedral quasicrystal to an icosahedral quasicrystal developed during rolling and annealing.

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