Morphologies of Microstructure in $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ Ribbon upon Ageing at Different Temperatures

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In order to clarify the morphology of the rapidly-solidified (RS)/melt-spun $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ (at%) alloy, which has the secondary phases of long-period stacking (LPS) structure, the ribbon was processed with the thickness of 60 μm and the width of 7 mm, and aged (T5 heat-treated) at different temperatures. The as-spun and aged ribbons were characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD) and laser optical microscopy, and micro-hardness measurement were conducted. It is found that there was a cellular/dendritic transition during melt-spinning process of $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy, and a mild age strengthening with the hardness of 113HV/0.05 at 573 K; more importantly, there was a different evolution of morphologies of the matrix and inter-metallic compounds from general secondary phase strengthened alloys when age temperatures up to the 773 K had been introduced to the as-spun alloy. [doi:10.2320/matertrans.MRA2008033]

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1. Introduction

Magnesium is one of the lightest of all metals as construction materials in practical use. Due to the strong demand for weight reduction of transportation vehicles for better fuel efficiency, magnesium alloys have recently received strong research interest for applications to various structural components of automobile and aircraft.

The Mg-Zn-RE-Zr system is regarded as high strength magnesium alloys because of the evident strengthening effect of rare earth (RE) addition on magnesium alloys. In a paper entitled "Investigation of the Mg-Zn-Y system" by E. M. Padezhnova *et al.*,¹⁾ three ternary equilibrium phases were found, *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. They reported that the $W\text{-Mg}_3\text{Zn}_3\text{Y}_2$ phase belongs to an isostructure of AlMnCu_2 . In recent years, Z. P. Luo *et al.* identified the $Z\text{-Mg}_3\text{Zn}_6\text{Y}$ as a stable icosahedral quasicrystalline phase,²⁾ and determined the $X\text{-Mg}_{12}\text{ZnY}$ phase as an 18R LPS structure by an electron diffraction technique.^{3,4)}

A. Inoue *et al.* fabricated an high strength Mg-based $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy with a novel LPS structure by rapid solidification (RS) techniques such as powder metallurgy and melt-spinning,⁵⁻⁷⁾ and later the variation and formation process of LPS structures were reported.⁸⁻¹⁰⁾ Now Mg alloys with LPS structures already become an important crystal alloy series besides ones with quasicrystallines in study. Whereas, the morphologies of $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy as spun and aged, which were only reported for the research of LPS structures,^{11,12)} as a basic study, have not been reported systemically had as conventional alloys been.

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 1048 K with protecting of $\text{SF}_6 + \text{CO}_2$ atmosphere, and adding pure Zinc particles and holding at 1048 K for 30 minutes, and then casting the alloy melt into a steel mould of $190 \times 95 \times 20 \text{ mm}^3$. Some small cuboids for processing RS ribbon were prepared from the ingot. The RS ribbon was processed by a melt-spinning apparatus at a speed of 34 m/s, and it is about 7 mm wide and 60 μm thick. Then the ribbon was divided into several groups. Seven groups were aged at 373, 473, 523, 573, 623, 673, 773 K respectively for 20 minutes with protecting of $\text{CO}_2 + \text{SF}_6$ atmosphere and cooled out of furnace at room temperature, and the sum of heating and holding time was approximately 30 minutes. Another two were kept as spun.

The as-cast alloy was characterized using X-ray diffractometer (40 kV and 200 mA, D/MAX 2000/PC, Rigaku), and a differential thermal analysis was conducted within a temperature range of 293–928 K with protecting of Ar atmosphere. A sample from a ribbon as spun was processed into an inset one, and it was mechanically polished on a succession of progressively finer abrasive papers, and final polishing was employed on a polishing machine. Following these processes, the sample was characterized under a laser optical microscope for metallographic morphology of transverse section. Some of the others as spun and aged 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). Some as-spun and aged ribbons were characterized by the above X-ray diffractometer and measured on a Vickers

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Fig. 1 DTA heating curve of the as-cast $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy.

micro-hardness equipment at a load of 50 g with holding time of 15 seconds.

3. Results and Discussion

3.1 Phase constitution and hardness after ageing at different temperatures

A differential thermal analysis (DTA) curve of the as-cast $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy is showed in Fig. 1. The as-cast alloy has α -Mg matrix (2H-Mg) and the ternary X- Mg_{12}ZnY (18R type hexagonal superlattice) secondary phase from Fig. 2(a). When the alloy was cast into the steel mould, a eutectic transformation, which was not perhaps only due to a micro-segregation during solidification, was finished at the late stage of liquid-solid phase transformation as the designated interval between point A and B. Thus the alloy containing the secondary phase will melt partly when it is heated at 823 K.

From Fig. 2(b), the alloy as spun has a solidification texture, and the melt solidified by the prior [0002] orientation. This results from that the solidification process occurred with great decreased temperature gradient from the interface with the wheel of the apparatus to the free surface of the ribbon by the rapid solidification technique, and that the α -Mg grew at the prior [0002] orientation from the liquid alloy. The as-spun alloy has a same phase constitution as as-cast one from XRD analysis, and when ageing up to 623 K a new peak at 28.343° appeared, and more peaks did at 773 K. This indicates the solid phase transformation of precipitation had been developing during ageing from 623 K to 773 K.

Based on abovementioned differential thermal analysis, and on reported Vickers hardness change of the ribbon which was attained by the induction melting the mixture of pure metals,⁹⁾ ageing treatments schemed of the ribbon were conducted. The Vickers micro-hardness was presented in Fig. 3 with maximum measurement error of 11HV/0.05. When the experimental materials were aged at different temperatures, a mild age hardenability of the ribbon was observed from 96HV/0.05 as spun to the maximum of 113HV/0.05 upon ageing at 573 K. The tendency of ageing hardening is consistent with the reported.

Fig. 2 XRD patterns/spectrums: (a) the ingot as cast, (b) XRD spectrums of the ribbons as spun and aged at 623 K, 773 K respectively.

Fig. 3 The effect of aging at different temperatures on Vickers hardness of the ribbon.

3.2 Morphologies of the as-spun alloy

The morphology of the transverse section of the ribbon is characterized from Fig. 4(a). The upside is the interface with the wheel of the melt-spinning apparatus and the downside is the free surface of the ribbon. From this micrograph

Fig. 4 Morphological images of the ribbon as spun: (a) laser optical micrograph, (b) TEM image of dendritic arrays, (c) TEM image of cellular arrays.

a distribution of microstructure is characterized, that is, dendritic arrays are near the interface for rapid cooling rate while cellular arrays are near the free surface for slow cooling rate. The cellular/dendritic transition or distribution according to cooling rate differentiates from the microstructures of Al-Mn-Be as-spun ribbons.¹³⁾ The dendritic and cellular arrays are showed in Figs. 4(b), 4(c). The size of dendritic arrays is about 15 μm and the second dendrite arm spacing or the size of the dendritic grains in the arrays is about 500 nm. The cellular spacing in the cellular arrays is about 320 nm. The secondary phase distributes on the boundaries of grains and cells, and of their arrays, and mainly along boundary edges. Only the LPS structure, *i.e.* $X\text{-Mg}_{12}\text{ZnY}$, was found in the cast and as-spun $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy from the XRD spectrums in Fig. 2. The cellular/dendritic transition or distribution can be understood the following. When the melt was ejected to the surface of the rotating copper wheel in the RS processing technique by melt-spinning, the thermal extraction occurred at high speed so that the thin layer of spreading liquid alloy was solidified at high velocity directionally from the interface to the free surface. In comparison with the cooling rate of the Al-20 mass% Si,¹⁴⁾ the cooling rate of a 10^5 order of magnitude (the unit, K/s) can be acquired. Thus a hypothesis that only diffusion could occur in

liquid phase near the interface and convection could not in the liquid can be proposed. Furthermore, cellular/dendritic transition is determined by constitutional super-cooling during a directional solidification with great decreased temperature gradient from the interface to the free surface. On one hand, the thermal gradient and the solidification rate were the highest in the interface, and two were decreased gradually towards the free surface; on the other hand, the ratio of thermal gradient to solidification rate was increased. The ratio was almost equal to the threshold of cellular/dendritic transition during the directional solidification in the processing, and then the pattern was transformed. As a result the as-spun alloy was characterized by the dendritic arrays followed the cellular ones.

3.3 Evolution of microstructures of the ribbon upon ageing at different temperatures

In as-spun alloy, there are supersaturated solid solution as matrix and Guinier-Preston (GP) zones and intermediate transition phase in the matrix, and stable long-period order phase on the boundaries according to solute concentration of Zn or Y and the ratio of Zn/Y in dendritic and cellular arrays. Upon ageing at 573 K, the transition phase in the dislocation areas is similar to the long-period order one. The acicular

Fig. 5 TEM images of the microstructures of the ribbon aged at 573 K in different acicular regions and respective SAED spectra: (a) one acicular region marked A, the electron beam was parallel to $[11\bar{2}0]$; (b) the other region and further magnified images, and its SAED spectrum in region marked B, the electron beam was parallel to $[1\bar{1}00]$.

secondary phase which is like a group of ordered lines and some areas like assemble of dislocations distribute within the dendritic arrays of the ribbon in Figs. 5(a) and 5(b) respectively. There are small quantities of short columns and they should distribute on the boundary edges and more at the corners, which is determined by the higher cooling rate of dendritic arrays. The two inset SAED spectra designate possible a same LPS phase with different incident directions. While the short columnar secondary phase distributes in the cellular arrays as the reported, and the edges of cell boundary are like long columns. Their circular and square sections are

visible universally. The size of the short columnar precipitates about 100 nm determined the peak of the mild age hardenability at 573 K. Upon ageing at 673 K, the circular and square sections of short columnar secondary phase are visible explicitly in morphology in the cellular arrays, and the prior extending orientation perpendicular to c axis of HCP structure can be discerned clearly. The blurred morphologies of dendritic and cellular arrays are distinguished in the ribbon aged at 673 K yet in Figs. 6(a) and 6(b), and though the dendritic arrays is not easy to found. This indicates Y atom has very poor diffusive mobility until to 673 K in

Fig. 6 Morphological images of the ribbon aged at 673 K: (a) TEM image of dendritic arrays, (b) TEM image of cellular arrays.

comparison with very much high one of Zn atom before 573 K. Figure 7 shows the morphology of the $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy aged at 773 K. The precipitates ripped and grew into many acicular clusters which are parallel to each other in a dendritic or cellular array. Some are a same smaller order of magnitude at latitude direction, which includes c_{LPS} axial direction, and up to the array size at longitude direction which is possibly $[1\bar{1}00]$ orientation. This can be concluded from SAED spectrums of LPS structures in many reports and in this study, and an $a_{\text{LPS}} \parallel a_{2\text{H}}$ and $b_{\text{LPS}} \parallel b_{2\text{H}}$ and $c_{\text{LPS}} \parallel c_{2\text{H}}$ axe-axe orientation relationship between LPS phases and 2H-Mg matrix, and the expand dislocation which consists of stacking and Shockley part dislocations in 2H-Mg. From Fig. 8(a) and the inset SAED spectrums, a LPS phase and 2H-Mg distribute in a grain, which is an array in the alloy before ageing. The LPS phase had ripen according to Ostwald's step rule. The new cells on the grain boundaries have a different structure showed in Fig. 8(b), which is similar to the L-phase among the approximants in the Zn-Mg-rare earth alloys reported.¹⁵⁾ When the ribbon was heated at 823 K and held for 20 minutes, a very small quantity of LPS phase was remained and the eutectic structure appeared on the boundary edges or corners. The eutectic structures can be found similar to ones of the as-cast microstructure

Fig. 7 Morphological TEM image of grains of the ribbon aged at 773 K.

of $\text{Mg}_{68}\text{Zn}_{28}\text{Y}_4$ and the precipitates in as-cast ZYA1261 alloy and the as-cast microstructure of Mg-5.49 mass%Zn-3.08 mass%Y-0.82 mass%Zr,^{16–18)} the compound has not been determined whether the decagonal quasi-crystal phase or $W\text{-Mg}_3\text{Zn}_3\text{Y}_2$. But from the evolution upon ageing the phase should be a quasi-crystal one.

The evolution of the melt-spun $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy upon ageing at different temperatures can be understood as mixed effects. They include different micro-segregation of Y and Zn atoms during solidification in melt-spinning process, and multi-stage and very great amount of binary or ternary compounds in ternary Mg-Zn-Y alloys during precipitation. The compound data of binary Mg-Zn and Mg-Y alloys can be reference to Binary Alloy Phase Diagrams by American Society of Metals. The new stable phases, such as LPS structure and stable quasicrystalline phases of the ternary Mg-rich Mg-Zn-Y alloy have been being under work by many research teams since 1980s.^{1–4,8,10,15,19–21)} The segregation and partition behavior of Zn and Y during rapid solidification,^{22,23)} and the effect of their respective concentrations and ratio on the energy of the periodic structures in the local,²⁴⁾ and the rate high enough to prevent the normal process of nucleation and growth of equilibrium phases,²⁵⁾ and the effect of non-equilibrium vacancies on Ostwald ripening,²⁶⁾ result in only a few out of the large quantity of options to occur at special types of distribution,²⁷⁾ in a special situation such as during rapid solidification or upon ageing at different temperatures in this study. The number of options is the product of number of phases and varieties of defects and possibility of discontinuous or continuous mode. By combination with XRD analysis and TEM observation, no cells on the boundaries of arrays developed in the reported,⁹⁾ possibly because the process of melting the pure metals including the low melt point of Zn increased its lose.

4. Conclusions

(1) The RS/melt-spun technique had not completely prevented the normal process of nucleation and growth of equilibrium phases at the cooling rate of a 10^5 order of magnitude (the unit, K/s) during solidification in the

Fig. 8 TEM images of the microstructures of the ribbon aged at 773 K in different regions and respective SAED spectrums: (a) the LPS structure in region marked A, the electron beam was parallel to $[11\bar{2}0]$; (b) the cell in region marked B, the electron beam was parallel to $[0001]$.

$\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ alloy. The processed alloy has a morphology including not only the fine microstructure but also cellular/dendritic transition according to the solidification rate. Dendritic and cellular arrays were scribed to two regions adjacent each other. The LPS phase, which is Mg_{12}ZnY , distributes on the boundaries of dendritic grains and cells and their arrays, and mainly along the boundary edges.

(2) The precipitates developed mainly into short columnar shape on cell boundaries in the cellular arrays and mainly into the acicular clusters in the dendritic arrays during aging before/at 673 K. In the end the precipitates grew into the many acicular clusters, which is parallel, in a dendrite or cellular array, some are a same order of magnitude at latitude direction, which includes c axial direction, and up to array

size at longitude one. Part of the boundaries of dendritic and cellular arrays evolved from thickened ones before 673 K, to cells which structure is different from the LPS structures at 773 K. That is to say, a dendritic or cellular array evolved into a grain respectively, but also the 2H-Mg and LPS phase distribute in the one grain with cell precipitates on the boundary upon ageing at 773 K.

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