Microstructure and mechanical properties of a compound reinforced $\text{Mg}_{95}\text{Y}_{2.5}\text{Zn}_{2.5}$ alloy with long period stacking ordered phase and W phase

Shou-zhong Wu, *Jin-shan Zhang, Chun-xiang Xu, Kai-bo Nie, Xiao-feng Niu, and Zhi-yong You

1. College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, China

2. Shanxi Key Laboratory of Advanced Magnesium-based Materials, Taiyuan 030024, China

Abstract: The microstructure evolution of $\text{Mg}_{100-2x}\text{Y}_x\text{Zn}_x$ ($x=2, 2.5, 3, 3.5$) alloys was investigated. Results show that the $\text{Mg}_{100-2x}\text{Y}_x\text{Zn}_x$ alloys are composed of α -Mg, long period stacking ordered (LPSO) phase and eutectic structure phase (W phase), and the $\text{Mg}_{95}\text{Y}_{2.5}\text{Zn}_{2.5}$ alloy has the best comprehensive mechanical properties. Subsequently, the microstructure evolution of the optimized alloy $\text{Mg}_{95}\text{Y}_{2.5}\text{Zn}_{2.5}$ during solidification and heat treatment processes was analyzed and discussed by means of OM, SEM, TEM, XRD and DTA. After heat treatment, the lamellar phase 14H-LPSO precipitated in α -Mg and W phase transforms into particle phase (Mg_7Zn_2). Due to the compound reinforcement effect of the particle phase and LPSO phase (18R+14H), the mechanical properties of the alloy are enhanced. The tensile strength and elongation of the $\text{Mg}_{95}\text{Y}_{2.5}\text{Zn}_{2.5}$ alloy is improved by 9.1% and 31.3% to 215 MPa and 10.5%, respectively, after solid-solution treatment.

Key words: magnesium alloys; $\text{Mg}_{95}\text{Y}_{2.5}\text{Zn}_{2.5}$ alloy; long period stacking ordered (LPSO); W phase; compound reinforcement

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Magnesium alloys as the lightest structure materials have attracted extensive concerns because of their low density, high specific strength, and good shielding characteristics. However, the disadvantages of lower strength and poorer formability in magnesium alloys seriously limit their extensive applications in industry.

Composite strengthening is an important means to improve the properties of the alloys. So, it is important to explore an effective strengthening phase. Recently, magnesium alloys with long period stacking ordered (LPSO) structure have attracted much attention due to their excellent mechanical properties. Luo et al.^[1] firstly identified that the 18R-LPSO phase was identical to the $\text{X-Mg}_{12}\text{YZn}$ phase. It was also found that there are other two phases (I phase and W phase) in Mg-Y-Zn alloys under conventional casting according to the different Zn/Y atomic ratio^[2-3]. Because of the composition fluctuation (segregation) and non-equilibrium solidification, LPSO

phase and W phase can coexist when the value of Zn/Y (at.%) was 1, as discussed in the study of Li et al.^[4]. A variety of high strength magnesium alloys containing LPSO phase have been developed. However, there was little research on the Mg-Y-Zn alloys containing LPSO phase and W phase in as-cast condition. Therefore, it is very necessary to study the effect of composite reinforcement of LPSO phase and W phase.

Meanwhile, mechanical properties are controlled by the content and morphology of α -Mg, LPSO phase and W phase in the Mg-Y-Zn (atomic ratio Zn/Y=1) alloys. In order to develop a compound reinforced magnesium alloy with LPSO phase and W phase, the present research investigated the effect of different Y and Zn contents on microstructure evolution and mechanical properties of the Mg-Y-Zn alloys with Zn/Y (at.%) ratio of 1. Subsequently, the formation of LPSO phase and W phase in the process of solidification and the effect of the microstructure after solid-solution treatment on mechanical properties in the optimized $\text{Mg}_{95}\text{Y}_{2.5}\text{Zn}_{2.5}$ alloy were studied.

*Jin-shan Zhang

Male, born in 1955, Ph.D., Professor. He is mainly engaged in research on wear resistant metallic materials, and strengthening-toughening and molding technology of magnesium alloy. He is an author of over 100 technical papers and 8 patents.

E-mail: jinshansx@tom.com

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1 Experimental procedure

$\text{Mg}_{100-2x}\text{Y}_x\text{Zn}_x$ ($x=2, 2.5, 3, 3.5$) alloys were prepared

by using pure Mg (99.95 wt.%), Y (99.95 wt.%) and Zn (99.95 wt.%). The metals were melted in an electric resistance furnace under the protective atmosphere of N_2 and CH_2FCF_3 at 760 °C for 20–30 min. When the temperature was down to 720 °C, the melt was poured into a preheated steel mold (inner diameter 21 mm, outer diameter 70 mm, high 160 mm) with the temperature of 200 °C. The collected cast samples were held at 500 °C for 8 h in a SX2-8-10 box type high-temperature electric resistance furnace, followed by air cooling. The actual chemical compositions of four Mg-Y-Zn alloys are listed in Table 1. The microstructures of the alloys were investigated using an optical microscope (OM, Leica DM2500M), a scanning electron microscope (SEM, TESCAN-MIRA3) equipped with an X-ray energy dispersive spectrometer (EDS OXFORD) and X-ray diffraction (XRD, Cu-K α , Y-2000). The samples for OM and SEM examination were taken from the bottom part of the ingot by wire cutting, then by polishing and etching with a solution of 4 ml nitric acid and 96 ml ethanol. Thin foils for TEM observation were prepared by cutting the bulk samples into about 0.3 mm slices and grinding them to the thickness of about 50 μm , followed by electropolishing with a solution of 30 ml nitric acid and 70 ml ethanol, and finally, by ion milling. Microhardness was measured using a HVS-1000A Vickers hardness testing machine, with a load of 10 g and a loading time of 15 s. Brinell hardness was measured by means of a HB-3000 Brinell hardness testing machine with a load of 62.5 kg and loading time of 30 s. The alloys were analyzed by differential thermal analysis (DTA, HCT-1) with a heating rate of 5 °C $\cdot$ min $^{-1}$. Tensile specimens were cut into sheet with a gauge dimension of 18 mm $\times$ 4 mm $\times$ 2.5 mm and tested on a DNS100 electronic universal testing machine with a crosshead speed of 0.5 mm $\cdot$ min $^{-1}$ at room temperature.

Table 1: Chemical compositions of experimental alloys (at.%)

Alloys	Y	Zn	Mg
A	1.98	2.03	Bal.
B	2.59	2.43	Bal.
C	3.10	2.89	Bal.
D	3.46	3.57	Bal.

2 Results and discussion

Figure 1 shows the morphology and microstructures of as-cast A, B, C, D alloys. It can be seen that all the alloys are composed of α -Mg, gray phase and dark phase. With the increase in the contents of Y and Zn, the following phenomena can be observed: (i) the amount of second phase increases obviously; (ii) α -Mg grains are refined and the length of secondary dendrites becomes shorter; (iii) the size of gray phase and dark phase becomes larger. Compared with alloy A, the grain size of α -Mg in alloy B is finer and the grain boundaries are smoother. The secondary dendrites in alloy A are developed, as shown in Fig. 1a, while only a few secondary dendrites can be observed in alloy B, and the growth of secondary dendrites is limited, as shown in Fig. 1b. The constitutional undercooling generated by the segregation of Y element in the front of liquid/solid interface can restrict the growth of α -Mg grains and the secondary dendrites [5-6]. The reason for having finer α -Mg grains in alloy C and D is that the growth of second phase requires a lot of Mg. The dark phase clearly presents typical eutectic structure morphology, as shown in Fig. 1c. The area fractions of the dark phase in the four alloys are about 9.6%, 15.8%, 19.4% and 21%, respectively. Xu et al [7] reported that eutectic structure can degrade the mechanical properties of the Mg-Zn-Y-Zr

Fig. 1: Microstructures of as-cast alloys: A (a), B (b), C (c), D (d) and tensile stress-strain curves (e)

alloys when area fraction of eutectic structure phase exceeds 17.5%. As can be seen from Fig. 1e, alloy B has the best tensile properties, which is in agreement with Xu's result. In order to investigate the microstructures of the four alloys, the optimized alloy $\text{Mg}_{95}\text{Y}_{2.5}\text{Zn}_{2.5}$ is chosen as the research object.

Figure 2a shows the SEM image of as-cast $\text{Mg}_{95}\text{Y}_{2.5}\text{Zn}_{2.5}$ alloy. The corresponding EDS results of points A and B are shown in Fig. 2c and Fig. 2d, respectively. It can be concluded that the $\text{Mg}_{95}\text{Y}_{2.5}\text{Zn}_{2.5}$ alloy is composed of α -Mg, LPSO phase and fishbone-like W phase based on EDS and XRD (Fig. 2b)

analysis. The LPSO phase in the as-cast $\text{Mg}_{95}\text{Y}_{2.5}\text{Zn}_{2.5}$ alloy was confirmed as 18R-LPSO phase from Fig. 2e. W phase and 18R-LPSO phase correspond to the dark phase and gray phase, respectively in Fig. 1, and alternately locate at the grain boundaries. The results of Ref. [2–3] showed that 18R-LPSO phase was easier to form when the value of Zn/Y (at.%) was less than 1, and W phase was easier to form when the value of Zn/Y (at.%) was between 1 and 6. Thereby, the 18R-LPSO phase and W phase can coexist when the value of Zn/Y (at.%) was 1 because of the composition fluctuation in the melt.

Fig. 2: SEM image (a), XRD (b), EDS result of LPSO phase (c) and W phase (d), and bright-field TEM image of 18R-LPSO phase (e) in as-cast $\text{Mg}_{95}\text{Y}_{2.5}\text{Zn}_{2.5}$ alloy, and corresponding SEAD pattern is shown in insets

Figure 3a shows DTA curve of the as-cast $\text{Mg}_{95}\text{Y}_{2.5}\text{Zn}_{2.5}$ alloy. According to the reports [8–9], the melting peaks of α -Mg, 18R-LPSO phase and W phase are 632 °C, 535 °C and 489 °C, respectively. It is well-known that the high melting point phase will precipitate from the liquid prior to the low melting point phase during solidification process. When the temperature dropped to 632 °C, α -Mg firstly formed from the melt and phase transformation reaction occurred: $L \rightarrow \alpha\text{-Mg}$. As primary crystal α -Mg grew gradually, the concentration of Y and Zn solute atoms increased in the liquid, leading to the enrichment area of Y and Zn. With the decrease of temperature in the melt, the content of Y and Zn in the remaining liquid increased continuously. Then, the phase transformation reaction

$L \rightarrow \alpha\text{-Mg} + \text{Mg}_{12}\text{YZn}$ (18R-LPSO phase) occurred at 535 °C. Meanwhile, the residual Y and Zn were further enriched in the unsolidified liquid phase, and phase transformation reaction occurred at 489 °C: $L \rightarrow \alpha\text{-Mg} + \text{Mg}_3\text{Y}_2\text{Zn}_3$. At 489 °C, α -Mg firstly precipitated and promoted the growth of W phase as the core of heterogeneous nucleation. W phase and α -Mg alternately grew, resulting in the formation of fishbone-like eutectic structure. The isothermal section of Mg-Y-Zn ternary system phase diagram [10] at 400 °C is shown in Fig. 3b. It can be seen that the compositions of the four alloys locate at the Mg + W + X region. Therefore, the microstructures of the $\text{Mg}_{100-2x}\text{Y}_x\text{Zn}_x$ ($x=2, 2.5, 3, 3.5$) alloys are composed of α -Mg, 18R-LPSO phase and fishbone-like W phase.

Fig. 3: DTA curve of as-cast $Mg_{95}Y_{2.5}Zn_{2.5}$ alloy (a) and isothermal section of Mg-Y-Zn ternary system phase diagram at 400 °C^[10] (b)

Figure 4 shows the Brinell hardness of the as-cast alloys. It can be seen that Brinell hardness of the alloys increased with X value. The results of microhardness testing indicate that the microhardness of α -Mg matrix and 18R-LPSO phase are 80.6 $HV_{0.01}$ and 108.9 $HV_{0.01}$, respectively, while the microhardness of W phase is 150.5 $HV_{0.01}$. Microhardness of LPSO phase and W phase also increased with X value. W phase and 18R-LPSO phase with high microhardness together improve the hardness of the alloys. However, the W phase is a hard and brittle phase, which can strengthen the alloys to some extent but is not conducive to the deformation^[7]. Solid solution treatment can not only make the composition uniformity, but also dissolve certain phases that are not conducive to improve the mechanical properties of the alloys. Thus, solid solution treatment is necessary for the alloys.

Fig. 4: Brinell hardness of as-cast alloys

Figure 5a shows the microstructure of the solid-solution treated $Mg_{95}Y_{2.5}Zn_{2.5}$ alloy. It can be seen that there are three different phases: the particle phase, the block shaped phase and the lamellar phase. At the high temperature of 500 °C, the solute atoms Y and Zn broke away from W phase and diffused into α -Mg matrix, leading to the eutectic phase disconnected and transformed into the particle phase. The chemical composition (as shown in Fig. 5b) of the particle phase is $Mg_{26.8}Y_{25.7}Zn_{47.5}$ with the atomic ratio of Mg: Y: Zn being about 1:1:2. Thus, it can be concluded that the particle phase is $MgYZn_2$. The

thermodynamically stable phase, LPSO, still maintains the block morphology. The lamellar phase in as-annealed $Mg_{95}Y_{2.5}Zn_{2.5}$ alloy is confirmed as the 14H-LPSO phase from Fig. 5c. The reports^[11-12] showed that simultaneous addition of Y and Zn in magnesium alloys could decrease the formation energy of stacking faults (SF) on basal planes of Mg alloys. The solute atoms Y and Zn concentrated at the grain boundaries during the non-equilibrium solidification and diffused into the α -Mg matrix during high temperature treatment. When Y and Zn diffused into the SF area, the lamellar phase 14H-LPSO precipitated^[13]. The 14H-LPSO phase would grow along the direction of basal plane and appear in a thin strip shape^[14], as shown in Fig. 5a.

The tensile stress-strain curves of the as-cast and solid-solution treated $Mg_{95}Y_{2.5}Zn_{2.5}$ alloys are shown in Fig. 5d. The tensile strength and elongation of the as-cast $Mg_{95}Y_{2.5}Zn_{2.5}$ alloy are 197 MPa and 8%, respectively, which are improved remarkably by 9.1% and 31.3% to 215 MPa and 10.5%, respectively, after solid-solution treatment. As compared with W phase in as-cast condition, the stress concentration caused by the particle phase is relatively weak. The crack is not easy to form, which is conducive to deformation of alloy. The 14H-LPSO phase has precipitation strengthening effect, hinders the dislocation motion and improves the deformability of the alloy. The thermodynamically stable phase, 18R-LPSO, still maintains the block morphology, and strengthens the alloy. The improvement in tensile properties of the alloy after the solid-solution treatment is the result of the coordination of the above factors.

3 Conclusions

According to the above experiment, the following conclusions can be drawn:

(1) The microstructures of $Mg_{100-2x}Y_xZn_x$ ($x=2, 2.5, 3, 3.5$) alloys are composed of α -Mg, 18R-LPSO phase and fishbone-like W phase under conventional casting condition. The contents of Y and Zn have a significant effect on the microstructure of Mg-Y-Zn alloys. With an increase in contents of Y and Zn, the amount of secondary phase in the alloys increases, and the grain size of α -Mg decreases. Element Y plays a significant role in refining α -Mg grains. The $Mg_{95}Y_{2.5}Zn_{2.5}$ alloy has the best tensile

Fig. 5: Microstructure of as-annealed $Mg_{95}Y_{2.5}Zn_{2.5}$ alloy (a); EDS of particle phase (b); bright-field TEM image of 14H-LPSO phase (c) in as-annealed $Mg_{95}Y_{2.5}Zn_{2.5}$ alloy, corresponding SEAD pattern is shown in insets; tensile stress-strain curves (d) of as-cast and solid-solution treated $Mg_{95}Y_{2.5}Zn_{2.5}$ alloy

properties in as-cast condition.

(2) The fishbone-like W phase transforms into the particle phase $MgYZn_2$, and the lamellar 14H-LPSO phase precipitates in α -Mg matrix after solid-solution treatment in the $Mg_{95}Y_{2.5}Zn_{2.5}$ alloy. The particle phase ($MgYZn_2$) and the (18R+14H) LPSO phase jointly improve the mechanical properties of the alloy. The tensile strength and elongation of the $Mg_{95}Y_{2.5}Zn_{2.5}$ alloy is improved by 9.1% and 31.3% to 215 MPa and 10.5%, respectively, after solid-solution treatment.

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