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Microstructures and mechanical properties of extruded and aged Mg–Zn–Mn–Sn–Y alloys

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Abstract: The microstructures and mechanical properties of Mg-6Zn-1Mn-4Sn and Mg-6Zn-1Mn-4Sn-0.5Y alloys under extrusion and T6 aging conditions were investigated by optical microscopy (OM), X-ray diffraction (XRD), scanning electron microscopy (SEM) and tensile test. The results show that Y element refines the grains and improves the comprehensive mechanical properties of ZMT614-0.5Y both in as-extruded and T6 states. The phase compositions of Mg-6Zn-1Mn-4Sn-0.5Y are α -Mg, MgZn₂, Mn, Mg₂Sn and MgSnY phases. After T6 treatment, the ultimate tensile strength (UTS) and yield strength (YS) increase while the elongation decreases severely. For both of these alloys, the theoretical results combined with the experimental values demonstrate that the grain boundary strengthening and solid solution strengthening play an important role in enhancing the YS in the as-extruded state, while the precipitation strengthening is the key factor for the enhancement of YS in the T6 state. Key words: Mg-Zn-Mn-Sn-Y alloy; yttrium; extrusion; T6; microstructure; strengthening mechanism

1 Introduction

As the lightest green metallic structural materials, magnesium (Mg) alloys have great potential for applications in the fields of automobile, aerospace, electronic and telecommunication industries [1-3]. However, the low strength and poor ductility limit their applications [4]. Therefore, strong interests have been focused on the development of new wrought Mg alloys. Previous investigations have shown that rare earths (RE) could improve the comprehensive mechanical properties of Mg alloys by means of fine-grain strengthening, solid-solution strengthening and precipitation strengthening [5,6]. Yttrium (Y), as one of RE elements, has been widely used in improving the mechanical properties of Mg alloys. For Mg alloys, the solid solubility of Y element decreasing exponentially depends on the temperature decreasing, which indicates that the precipitation strengthening capability of Y-containing Mg is excellent [7].

The Mg–Sn alloy has been known as a precipitation hardenable system. Sn has a high solubility (3.35%, mole

fraction) at 834 K and low solubility at ambient temperature [8–10]. Recent researches have indicated that the addition of cost-effective Sn to Mg alloys could enhance the comprehensive mechanical properties since the formation of Mg₂Sn phase [11–13]. Combined addition of Y and Sn to Mg alloys could develop a new low cost high strength wrought Mg alloys. Therefore, many Y- and Sn-containing Mg alloys are researched, such as Mg–Sn–Y [14], Mg–Al–Sn–Y–Nd [15] and Mg–10Gd– 3Y–1Sn–0.5Zr [16] alloys. But up to now, the investigations of Mg–Zn–Mn–Sn–Y alloys are not carried out and the scientific understanding of the influence of Y on the microstructures and mechanical properties of this alloy is not clear.

The present work studied the effects of Sn and Y on the microstructures and mechanical properties of Mg–Zn–Mn–Sn–Y alloys in extrusion and T6 treated conditions.

2 Experimental

Commercial high-purity Mg (>99.9%, mass fraction), Zn(>99.95%), Sn(>99.9%) and two master

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alloys Mg-30.0%Y and Mg-5.01%Mn were used to prepare the experimental alloys. All alloys were melted at about 750 °C in a vacuum induction melting furnace under Ar atmosphere. Then the melts were poured into a steel mold with an ingot diameter of 90 mm. The chemical compositions were analyzed by XRF-1800 CCDE sequential X-ray fluorescence spectrometer, which were Mg-6.01Zn-0.88Mn-4.20Sn for ZMT614 and Mg-6.14Zn-0.91Mn-4.38Sn-0.50Y for ZMT614-0.5Y. The ingots were homogenized at 420 °C for 12 h and then under a controlled constant force by XJ-500 horizontal extrusion machine. The homogenized ingots were hot extruded to bars of 16 mm in diameter at 360 °C with the extrusion ratio of 25. After extrusion, the alloys were cooled in the open air. The extruded samples were solid-solution treated at 440 °C for 2 h followed by water quenching. Subsequently, the samples were age treated at 180 °C for 12 h followed by water quenching (T6).

Tensile tests were performed using tensile specimens with gauge length of 50 mm and gauge diameter of 5 mm. The tensile directions were parallel to the extrusion direction (ED). The tensile tests were performed on a SANS CMT-5105 electronic universal testing machine in air at a speed of 2 mm/min at room temperature. Tensile properties under each condition were obtained as the average values of three tests. The microstructures of specimens were observed with LEXT 2000 laser metallographic microscope and TESCAN VEGA II scanning electron microscope equipped with an INCA Energy 350 energy dispersive X-ray components spectrometer (EDS). Phase were characterized with a Rigaku D/max 2500PC X-ray diffractometer using Cu K_a.

3 Results and discussion

3.1 Microstructure of as-extruded alloys

Figure 1 shows the XRD patterns of as-cast and as-extruded ZMT614 and ZMT614-0.5Y alloys, which reveals that the phase compositions of both alloys are remained whether in as-cast or as-extruded conditions. The ZMT614 alloy is composed of α -Mg, MgZn₂, Mn and Mg₂Sn phases. After adding 0.5% Y, a new ternary phase MgSnY is formed. Therefore, the phase compositions of ZMT614-0.5Y alloy are α -Mg, MgZn₂, Mn, Mg₂Sn and MgSnY phases.

Figure 2 shows the optical micrographs in longitudinal extrusion direction of as-extruded samples. The fine grains in the longitudinal direction indicating that dynamic recrystallization (DRX) occurred during extrusion at 360 °C. The average grain sizes of these samples are 6 and 5 μ m, respectively. A small number



Fig. 1 XRD patterns of ZMT614 (a, b) and ZMT614-0.5Y (c, d) alloys at different states: (a, c) As-cast state; (b, d) As-extruded state



Fig. 2 Optical micrographs of as-extruded samples: (a) ZMT614; (b) ZMT614-0.5Y

of oval and rod shaped compounds lie in the as-extruded ZMT614 alloys, whose lengths are 5–10 μ m. However, for ZMT614–0.5Y alloy, a mass of irregular blocky compounds disperse in the matrix with a non-uniform manner. The size of these compounds reaches more than 10 μ m. Extrusion streamlines which consist of MgZn₂, Mn, Mg₂Sn and MgSnY phases parallel the extrusion

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direction in the alloys. Some unDRX grains around the extrusion streamlines reflect that the irregular blocky compounds restrain the DRX process.

Figure 3 and Table 1 show the SEM and corresponding EDS analysis of longitudinal extrusion direction of as-extruded samples. From Fig. 3(a), EDS analysis demonstrates that the fine oval and rod shaped compounds both are Mg₂Sn phase. From Fig. 3(b), a small quantity of oval shaped compound exists, and EDS analysis indicates that they are Mg₂Sn phase. The aspect ratio of Mg₂Sn phase in ZMT614–0.5Y is smaller than that of ZMT614 alloy. Based on the XRD and EDS analyses, the irregular blocky compounds are MgSnY



Fig. 3 SEM images of as-extruded samples: (a) ZMT614; (b) ZMT614–0.5Y

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Region -	Mass fraction/%					
	Mg	Zn	Mn	Sn	Y	
A	85.96	8.93	0.96	4.15	_	
В	50.18	3.18	_	46.64	-	
С	32.91	-	_	67.09	_	
D	87.54	7.52	0.78	4.43	_	
Ε	77.26	7.78	1.25	8.61	5.10	
F	62.46	2.83	-	34.72	_	

phase. It is obvious that the volume fraction of the Mg₂Sn phase in the ZMT614–0.5Y alloy is lower than that in the ZMT614 alloy. This is mainly due to the fact that the formation of MgSnY phase consumes a certain amount of Sn element. In addition, EDS analysis reveals that the MgSnY phase contains Mn element. According the calculated Mg–Mn–Sn and Mg–Mn–Y phase diagrams [17], a solid-solution reaction $L\rightarrow L+\alpha$ -Mn occurs at about 650 °C at the first stage of solidification. Then at the later stage, formed primarily Mn phase may act as heterogeneity nucleus of MgSnY phase. However, more details need further study.

3.2 Microstructure of T6 treated alloys

Figure 4 shows the optical micrographs in vertical section of T6 treated samples. The average grain sizes of ZMT614 and ZMT614–0.5Y alloys are 60.8 and 52.8 μ m, respectively. A mass of tiny precipitations dispersed in the matrix. EDS analysis indicates that they are Mg₂Sn and MgZn₂ phases. However, the density of the precipitations in ZMT614–0.5Y is much higher than that in ZMT614, explaining that the Y elements or its intermetallic could promote the precipitates nucleation and growth. Some big irregular blocky compounds disperse at triple points of the grain boundaries. EDS



Fig. 4 Optical micrographs of T6 treated samples: (a) ZMT614; (b) ZMT614–0.5Y

analysis reveals that they are MgSnY phase. The MgSnY ternary phase may act as crack source during deformation.

The XRD patterns of solid-solution and T6 treated samples are shown in Fig. 5. After being solution treated, the diffraction peaks of $MgZn_2$ disappear, indicating that the phase dissolved into the matrix completely. Due to the fact that the melting temperature of MgSnY phase is much higher than the solution temperature, the phase cannot dissolve into the matrix during solution treatment and precipitate in the following T6 treated process [18]. The solid solubility of Zn and Sn declines dramatically as the temperature decreases [19]. As a result, large amount of Mg₂Sn and MgZn₂ precipitate during the aging.



Fig. 5 XRD patterns of ZMT614 (a, b) and ZMT614-0.5Y (c, d) alloys at different states: (a, c) Solid-solution treated state; (b, d) T6 treated state

Figure 6 shows the SEM micrographs in vertical section of T6 treated samples. The extremely fine MgZn₂ and Mg₂Sn precipitates dispersed in the grains and at boundaries. The T6 treated sample has been not changed in the macro-morphology of the MgZn₂ and Mg₂Sn phase obviously. Nevertheless, the macro-morphology of MgSnY phase changes obviously, transforming from irregular blocky to petal shape. The MgSnY phases are much bigger than the others.

3.3 Mechanical properties

Table 2 shows the tensile results of as-extruded and T6 treated ZMT614 and ZMT614–0.5Y alloys. It is interesting to note that the ultimate tensile strength (UYS) and elongation (EL) of as-extruded ZMT614–0.5Y increased obviously compared with ZMT614. While the yield strengths (YS) of both alloys are almost the same. The UTS and YS of T6 treated sample increase, while the EL decreases obviously. Under T6 treatment, the EL of ZMT614–0.5Y alloy increases by 1.68% compared with ZMT614 alloy. In conclusion, the YS, UTS and EL of ZMT614–0.5Y alloy are improved by adding Y element both in as-extruded and T6 states.



Fig. 6 SEM micrographs of T6 treated samples: (a) ZMT614; (b) ZMT614–0.5Y

 Table 2 Tensile properties of as-extruded and T6 treated

 ZMT614 and ZMT614-0.5Y alloys

Alloy	State	UTS/MPa	YS/MPa	EL/%
7 MT(1)	As-extruded	338	254	15.7
ZIVI1014	Т6	367	353	5.27
7MTC14 0 5V	As-extruded	350	259	18.3
ZM1014-0.5 Y	T6	372	367	6.93

For the as-extruded alloys, the YS improvement consists of grain boundary strengthening and solid solution strengthening. Therefore, the YS of as-extruded alloy is expressed as [16]

$$\sigma_{\rm ys} = \sigma_{\rm Mg} + \sigma_{\rm gb} + \sigma_{\rm ss} \tag{1}$$

where σ_{Mg} =21 MPa [16] for a pure Mg; σ_{gb} and σ_{ss} are grain boundary strengthening and solid solution strengthening, respectively. The grain boundary strengthening σ_{gb} can be estimated by the Hall–Petch law:

$$\sigma_{\rm gb} = \sigma_{\rm Mg} + kd^{-1/2} \tag{2}$$

where *k* is a parameter determined by the polycrystalline materials, and *k*=220 MPa· μ m^{1/2} for Mg alloys [16]; and *d* is the average grain size. Then, σ_{gb} is calculated to be 110 and 119 MPa for ZMT614 and ZMT614–0.5Y alloys, respectively.

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Considering that Zn and Sn are the main solid solution strengthening elements in the alloys, the solid solution strengthening σ_{ss} can be described by

$$\sigma_{\rm ss} = (k_{\rm Zn}^{3/2} C_{\rm Zn} + k_{\rm Mn}^{3/2} C_{\rm Mn} + k_{\rm Sn}^{3/2} C_{\rm Sn})^{2/3}$$
(3)

where k_{Zn} , k_{Mn} and k_{Sn} are the strengthening constants, k_{Zn} = 905 MPa/%^{2/3} and k_{Mn} =196 MPa/%^{2/3} [20] in the alloys. It is linear combination of the atomic size, shear modulus and valency difference. The atomic size, shear modulus and valency difference of Sn are almost to Zn, thus, k_{Sn} =905 MPa/%^{2/3} is estimated. The C_{Zn} and C_{Sn} are the concentration of the solution in mole fraction (%). The assumption is that no interaction exists between Zn and Sn. Substituting k and C (see Fig. 3) into Eq. (3), the calculative solid solution strengthening values of ZMT614 and ZMT614–0.5Y alloys are 117 and 105 MPa, respectively.

The theoretical calculation values of YS of ZMT614 and ZMT614–0.5Y alloys are 248 and 245 MPa, respectively, which are quite close to the experimental values of the as-extruded alloys. The discrepancy may be concerned with the inaccurate parameters and simplified solid solution elements interaction models used for prediction. However, the theoretical calculated values combined with experimental values state that the YS enhancement of as-extruded alloys originates from grain boundary strengthening and solid solution strengthening.

Under T6 treated state, most of Zn, Mn, Sn and Y elements are consumed to form precipitates. Consequently, the solid solution strengthening is substituted by the precipitation strengthening. The YS of T6 treated alloys is expressed as

$$\sigma_{\rm ys} = \sigma_{\rm Mg} + \sigma_{\rm gb} + \sigma_{\rm ppt} \tag{4}$$

where σ_{ppt} is the contribution of precipitation strengthening. The σ_{gb} values of ZMT614 and ZMT614–0.5Y treated by T6 are 49 and 51 MPa, respectively. The Orowan mechanism is operative for precipitation strengthening, so σ_{ppt} is described by

$$\sigma_{\rm ppt} = \frac{Gb}{2\pi\sqrt{1-\nu}(0.825\sqrt{(d_{\rm t}t_{\rm t}/f_{\rm v})} - 0.393d_{\rm t} - 0.886t_{\rm t})} \times \ln\frac{0.886\sqrt{d_{\rm t}t_{\rm t}}}{b}$$
(5)

where G is the shear modulus of the pure Mg; b is the magnitude of the Burgers vector; v is the Poisson ratio; d_t is the mean diameter of the precipitations; t_t is the average thickness of the precipitations; and f_v is the volume fraction of the precipitates.

As shown above, the precipitation values of d_t , t_t and f_v in ZMT614–0.5Y alloy are higher than those of ZMT614 alloy. And the σ_{ppt} is proportional to d_t , t_t and f_v . So, the YS of ZMT614–0.5Y alloy is much higher than that of ZMT614 alloy. The YS of T6 treated ZMT614 alloy is σ_{ppt} +70 MPa and the ZMT614–0.5Y is σ_{ppt} +72 MPa. As a result, the precipitation strengthening exerts the dominating effects on YS enhancement of these alloys in T6 treated state.

Figure 7 shows the fracture surface morphologies of the T6 treated samples. Some deep cracks are observed (marked by arrows in Fig. 6). Furthermore, there are a quite large number of cleavage facets on the surface of ZMT614 alloy, the fracture of the alloy belongs to cleavage regime. Many cleavage facets besides small-sized dimples are on the surface of ZMT614–0.5Y alloy, which reflects that the fracture of the alloy belongs to quasi-cleavage regime. The cleavage facets of ZMT614–0.5Y alloy are much smaller than those of ZMT614 alloy. This indicates that a large amount of dispersed precipitations inhibit the dislocation motion and cracks propagation. In consequence, adding Y element can change the fracture mode and improve the comprehensive mechanical properties.



Fig. 7 SEM micrographs of fracture surface of T6 treated samples: (a) ZMT614; (b) ZMT614–0.5Y

4 Conclusions

1) After adding Y element to ZMT614 alloy, a new MgSnY ternary phase is formed. The T6 treated sample cannot change the phase compositions. The phase compositions of ZMT614–0.5Y in as-extruded and T6

states both are α -Mg, MgZn₂, Mn, Mg₂Sn and MgSnY phases.

2) The Y element refines the grains of ZMT614–0.5Y alloy in as-extruded and T6 treated states. Compared with ZMT614 alloy, the UTS, YS and EL of ZMT614–0.5Y alloy in as-extruded and T6 states are improved.

3) For the ZMT614 and ZMT614–0.5Y alloys, the grain boundary strengthening and solid solution strengthening make the same contribution to the YS enhancement in as-extruded state. However, the precipitation strengthening exerts the dominating effect on the YS enhancement in T6 treated state.

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挤压态和时效态 Mg-Zn-Mn-Sn-Y 合金的组织性能

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摘 要:利用光学显微镜、X 射线衍射和扫描电镜等对挤压态和时效态 Mg-6Zn-1Mn-4Sn 和 Mg-6Zn-1Mn-4Sn-0.5Y 镁合金的微观组织和力学性能进行研究。结果表明:与 ZMT614 镁合金相比,添加 Y 元素后,ZMT614-0.5Y 晶粒得到细化,综合力学性能得到提高。Mg-6Zn-1Mn-4Sn-0.5Y 合金的相组成为 α-Mg、MgZn₂、Mn、Mg₂Sn 和 MgSnY 相。经过 T6 热处理后,合金的抗拉强度和屈服强度明显得到提高,伸长率明显被降低。理论计算表明,在挤压态合金中,细晶强化和固溶强化产生重要的作用,而在 T6 热处理态合金中,析出强化产生决定作用。 关键词: Mg-Zn-Mn-Sn-Y 合金; Y;挤压; T6;显微组织;强化机制