Effect of Zn, Cu and Ni addition on microstructure and mechanical properties of as-cast Mg-Dy alloys

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Abstract: This paper presents some research information on the effects of Zn, Cu and Ni on the microstructure and mechanical properties of as-cast Mg-2Dy (at.%) alloys. The Mg-2Dy alloy is composed of α -Mg and $\text{Mg}_{24}\text{Dy}_5$ phases. With the addition of 0.5at.%Zn, 0.5at.%Cu and 0.5at.%Ni, respectively, besides α -Mg, the long period stacking order (LPSO) phases containing Zn, Cu, and Ni precipitated in the α -Mg interdendritic boundary. The addition of Ni effectively refined the dendrite arm spacing. The as-cast Mg-2Dy-0.5Ni alloy exhibited the best tensile strengths and elongation. The better mechanical properties were mainly attributed to small secondary dendrite arm spacing (SDAS) and high volume fraction of LPSO phases.

Key words: Mg-Dy-Zn(Cu, Ni) alloys; LPSO phase; microstructure; mechanical properties

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Magnesium (Mg) alloys have been used as structural materials in aerospace, automobile and electronic industries due to their low density, high specific strength and good castability. However, low high-temperature strength and poor heat resistance limit their development and application. Recently, it was found that the Mg alloys with a long period stacking ordered (LPSO) phase exhibit high mechanical strength and heat resistance during the hot working processes, such as extrusion, rolling and forging^[1-3]. The excellent tensile properties of the alloys at room and elevated temperatures are mainly related to grain refinement and LPSO strengthening. The LPSO phase with different structural types (10H, 14H, 18R and 24R) was found in as cast or heat treated Mg-RE-Zn alloys (where RE represents rare earth element) when the RE/Zn ratio is about 0.5 or higher^[4]. The phase has a high melting point, hardness value and a coherent interface with α -Mg matrix^[5-6]. Thus the LPSO phase is known as an ideal heat resistant phase in Mg alloys. Furthermore, it was also found that the 10H, 14H and

18R-typed LPSO phases were formed in Mg-TM-Y (TM = Cu or Ni) alloys^[7-8]. The mechanical properties and formation of LPSO phase in Mg-TM-Y alloys have been systematically investigated.

More recently, our previous works have shown that the extruded Mg-2Dy-0.5Zn (at.%) alloy with LPSO phase has an excellent tensile strength at 300 °C^[9]. Peng et al.^[10] have investigated the age-hardening behavior and compressive properties of Mg-2.2Dy-Cu (at.%) alloy at elevated temperatures. These experimental results demonstrated that the Mg-Dy-Zn(Cu) alloys with LPSO phase are potential heat-resistant alloys. However, the microstructure and mechanical properties of Mg-Dy-Ni alloy with LPSO phase have not been reported until now. In order to further understand the effect of LPSO phase containing different TM elements on the microstructure and mechanical properties of Mg-Dy alloys, this research related to Mg-2Dy-0.5Zn, Mg-2Dy-0.5Cu and Mg-2Dy-0.5Ni (at.%) three alloys and studied the effect of LPSO phase containing Zn, Cu and Ni on the mechanical properties of the alloys.

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1 Experimental procedure

The three alloy ingots with normal compositions of Mg-2Dy-0.5Zn (alloy A), Mg-2Dy-0.5Cu (alloy B) and Mg-2Dy-0.5Ni (alloy C) (at.%) were prepared using pure Mg, high purity Zn, Cu, and Ni and Mg-20wt.%Dy master alloy. Melting was conducted in a graphite

crucible using an electric furnace at about 750 °C under the protection of antioxidant flux. The melts were homogenized at 720 °C for 0.5 h, and then cast into a steel mold with the size of 70 mm × 40 mm × 13 mm.

The microstructure, phase structure and compositions of the alloys were characterized using an optical microscope (OM), X-ray diffraction (XRD) and a scanning electron microscope (SEM) with an energy-dispersing spectrometer (EDS). The specimens for OM observation were prepared by the standard technology of grinding and polishing and etched by a solution of picric-ethanol-H₂O. The secondary dendrite arm spacing in alloys and volume fraction of LPSO phase were evaluated by image analysis technology using at least ten areas for each alloy. The micro-hardness (HV) was measured using a micro-hardness tester (HV-1000B) and at least 10 points for the hardness value of each sample. The load and dwelling time were 100 g and 15 s, respectively. Tensile tests were carried out on an Instron-type

tensile testing machine (Instron 1211) at room temperature with a strain rate of $1 \times 10^{-3} \text{ s}^{-1}$ for all of the specimens. The tensile specimens with a gage dimension of 16 mm in length, 5 mm in width and 1.8 mm in thickness were cut from the as-cast ingots. Three parallel tensile specimens were tested for each alloy.

2 Results and discussion

2.1 Microstructures

Figure 1 shows the optical microstructures of three as-cast alloys. The as-cast Mg-2Dy alloy was composed of α -Mg and Mg₂₄Dy₅ phase^[11]. With the addition of 0.5at.%Zn, 0.5at.%Cu and 0.5at.%Ni into Mg-2Dy alloy, some white particles and a great number of lamellar phases precipitated in the grain interior and at dendrite boundaries, as shown in Fig. 1(a), (b) and (c). In Fig. 1(d), (e) and (f) it was found that the fine lamellar phase

Fig. 1: SEM images of as-cast alloys at low and high magnifications: alloy A (a) and (d); alloy B (b) and (e); and alloy C (c) and (f)

Table 1: EDS results of phases in three alloys in Fig. 1 (d), (e) and (f)

Point	Phase	alloy A			alloy B			alloy C		
		Zn (at.%)	Dy (at.%)	Mg (at.%)	Cu (at.%)	Dy (at.%)	Mg (at.%)	Ni (at.%)	Dy (at.%)	Mg (at.%)
1	Mg	0.38	0.62	99.00	1.00	2.60	96.4	0.63	1.62	97.7
2	Mg ₁₂ ZnDy	4.14	5.41	90.45						
3	Mg ₁₂ CuDy				4.90	4.70	90.4			
4	Mg ₁₂ NiDy							3.00	4.37	92.63
5	Mg ₈ ZnDy	9.49	7.68	82.83	-	-	-	-	-	-
6	(Mg,Zn)Dy ₃	3.45	76.79	19.76	-	-	-	-	-	-
7	MgDy ₃	-	-	-	-	75	25	-	-	-
8	Dy	-	-	-	-			1.20	92.40	6.50

were parallel to each other and these lamellar phases appeared at a same orientation. It was noted that the lamellar phase was distributed more homogeneously in alloy C than that in alloy A and alloy B. This also contributes to improving the hardness and tensile properties of the alloy. In addition, the secondary dendrite arm spacing (SDAS) and the volume fraction of lamellar phase changed with the addition of Zn, Cu and Ni. The values of SDAS in alloy A, alloy B and alloy C were 45 μm , 52 μm and 26 μm , respectively. The volume fractions of the lamellar phase in alloy A, alloy B and alloy C were about 36%, 30% and 40%, respectively.

Table 1 shows EDS results of particles in the three alloys. For alloy B and alloy C, the chemical compositions of irregular particles are Mg₂₅-Dy₇₅(at.%) and Mg_{6.5}-Dy_{92.4}-Ni_{1.2} (at.%), respectively. The atomic ratio of Mg:Dy in point 7 is 1:3, Dy:Mg:Ni in point 8 is near 90:6:1. Thus it could be inferred that the two phases should be MgDy₃ in alloy B and Dy phase in alloy C, respectively. Notably, the compositions of the lamellar phase containing Ni or Cu are near to approaching that of Mg₁₂ZnDy with an 18R-LPSO structure. So, the lamellar phase in alloy B and alloy C should have an LPSO structure as

reported in Mg-Cu-Y alloy^[7] and Mg-Ni-Y alloy^[8]. Figure 2 shows the XRD patterns of three as-cast alloys of alloy A, alloy B, and alloy C. According to previous investigations^[9-12], alloy A is composed of diffraction peaks of α -Mg, Mg₁₂ZnDy and Mg₈ZnDy phases. It can be seen from Fig. 2 that besides α -Mg, the diffraction peaks of the Mg₁₂CuDy phase and Mg₁₂NiDy phase are also indexed in alloy B and alloy C, respectively. In addition, the diffraction peak of MgDy₃ phase appeared in alloy A and alloy B, but that of Dy phase in alloy C was not detected due to a low amount. It can be seen that those phases in Fig. 1 agree fairly well with the XRD results in Fig. 2.

2.2 Mechanical properties

The mechanical properties of the three as-cast alloys are shown in Fig. 3. The corresponding tensile properties and hardness of alloys are listed in Table 2. It can be seen that the tensile strengths vary with the addition of Zn, Cu and Ni. Alloy C exhibits the highest ultimate tensile strength (R_m), yield strength ($R_{0.2}$) and elongation (A). The values of R_m , $R_{0.2}$ and A of alloy C are 176 MPa, 120 MPa and 15.5%, respectively. In addition, the hardness values of the three alloys are shown in Fig. 4. For the three as-cast alloys, the hardness value of α -Mg

Fig. 2: XRD patterns of as-cast alloys: alloy A, alloy B, and alloy C

Fig. 3: Mechanical properties of as-cast alloys

Table 2: Tensile properties and hardness values of as-cast alloys

Alloy	R_m (MPa)	$R_{0.2}$ (MPa)	A (%)	HV (α -Mg)	HV (LPSO)
alloy A	145	100	5.2	72	90
alloy B	170	110	12.7	68	81
alloy C	176	120	15.5	59	82

Fig. 4: Hardness values of Mg matrix and LPSO phase region in as-cast alloys

matrix in alloy A is higher than that in alloy B and alloy C. The mechanical properties of three as-cast alloys are mainly related to the microstructures. For the three as-cast alloys, besides small amounts of particles, the LPSO phase is a main precipitate phase. The average hardness value of the LPSO phase region is higher than that of the Mg matrix. It is worth noting that the average hardness value (HV 90) of the LPSO phase region containing Zn is slightly higher than that of the LPSO phase region containing Cu (HV 81) and Ni (HV 82).

The different average hardness values of the LPSO phase region in the three alloys should be mainly related to the following four aspects: i) alloying element contents of LPSO phase; ii) volume fraction of LPSO phase; iii) atomic-bonding energy of LPSO phase; and iv) distribution of LPSO phase. Usually, the high alloying element content, large volume fraction, more homogenous distribution and high atomic-bonding energy could result in a high average hardness value for the phase region or intermetallic compound region. For the present alloys, the content of (Zn+Dy) (9.55at.%) of LPSO phase in alloy A is nearly the same as that of (Cu+Dy) (9.6at.%) of LPSO phase in alloy B, which is higher than that of (Ni+Dy) (7.37at.%) of LPSO phase in alloy C. In addition, the calculated value of cohesive energies (2.175 eV) of Mg-Dy-Zn alloy using first-principle is higher than that of Mg-Dy-Cu alloy (-1.291 eV) and Mg-Dy-Ni alloy (-3.972 eV) [13]. Conversely, the volume fraction (40%) of LPSO phase region in alloy C is higher than those in alloy A (36%) and alloy B (30%), as shown in Fig. 1. Thus, it can be inferred that the LPSO phase region in alloy A should have the highest average hardness compared with those in alloy B and alloy C, although it had small volume fraction. Moreover, compared with the LPSO phase region in alloy B,

the LPSO phase in alloy C distributed more homogeneously in α -Mg matrix and had a higher volume fraction. This also led to a slightly high hardness value (HV 82) of LPSO phase in alloy C, despite the phase containing lower contents of the alloying elements and a small atomic-bonding energy (Table 2). However, it was noted that the hardness was not in direct proportion with tensile strength for the present alloy. That is, the alloy A had the highest hardness value (HV 90) but exhibited the lowest R_m (145 MPa) and $R_{0.2}$ (100 MPa). This abnormal phenomenon was mainly related to the different microstructures of the above three alloys. The addition of Ni significantly refined the dendrite microstructure of Mg-Dy alloy, and the alloy C exhibited the smallest value of SDAS (26 μ m) (Fig. 1). According to the Hall-patch relationship ($\sigma_y = \sigma_0 + k_y d^{-1/2}$, where σ_y is the yield strength, σ_0 and k_y are constants for a given polycrystalline material, the yield strength of alloy increases with a decrease in grain size [14]. The smaller the SDAS, the higher the yield strength; thus the alloy C exhibits the highest yield strengths (Fig. 3 and Table 2).

Additionally, the LPSO phase could act as an effective reinforced fiber in the Mg/LPSO composite [15]. During tension, the load can transfer from the Mg matrix to the LPSO phase. Simultaneously, the LPSO phase having a high hardness and good interface coherent with α -Mg matrix [5-6] bends and forms the kink bands which hinder dislocation movement [16-17]. In this paper, the LPSO phase region in alloy C has the highest volume fraction (40%) and distributes more homogeneously, although its average hardness value is low. Additionally, the homogeneous distribution of the phase could effectively enhance the load transfer mechanism effect [18]. Thus, the alloy C exhibits high tensile strengths. Also, a good interface of the LPSO phase with the α -Mg matrix could delay crack initiation resulting from stress concentration to further improve ductility of the alloy. Therefore, alloy C exhibits the highest tensile strengths and best elongation (15.5%). To further understand the crack initiation of the alloys, the fracture lateral surfaces of three tensile specimens after tensile testing are shown in Fig. 5. It can be seen that the fracture surface of alloy A appears smoother than those of alloy B and alloy C. The fracture direction of alloy A is near 90° to the tensile direction but those of alloy B and alloy C are near 45° with the tensile axis. This indicates that the fracture of alloy A occurs under normal stress but those of alloy B and alloy C do under shear stress. Thus, the alloy B and alloy C exhibit better elongation than alloy A (Fig. 3 and Table 2). Furthermore, the typical micro cracks form around the hard particles in alloy B and alloy C as shown in Fig. 5 (b) and (c).

3 Conclusions

(1) The microstructure of as-cast Mg-2Dy (at.%) alloy is composed of α -Mg and $Mg_{24}Dy_5$ phase. With the addition of Zn, Cu or Ni, the long period stacking order (LPSO) phases containing Zn, Cu or Ni precipitate in the α -Mg interdendritic boundary.

(2) The addition of Ni effectively refines the dendrite arm

Fig. 5: Fracture lateral surfaces of tensile specimens of (a) alloy A, (b) alloy B and (c) alloy C

spacing and results in the highest volume fraction of LPSO phases. The values of secondary dendrite arm spacing of as-cast Mg-2Dy-0.5Zn, Mg-2Dy-0.5Cu and Mg-2Dy-0.5Ni alloys are 45 μm , 52 μm and 26 μm , respectively.

(3) The as-cast Mg-2Dy-0.5Ni alloy exhibits the highest tensile strengths and elongation. The values of R_m , $R_{0.2}$ and A of the alloy are 176 MPa, 120 MPa and 15.5%, respectively. The improved mechanical properties are mainly attributed to small secondary dendrite arm spacing and high volume fraction of the LPSO phases.

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