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Isothermal section of Mg-Zn-La system in Mg-rich corner at 400 ℃

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Abstract: Alloys with different compositions in Mg-rich corner of Mg-Zn-La system at 400 ℃ were prepared, the phase equilibrium in the Mg-rich corner of Mg-Zn-La system was determined by scanning electron microscopy(SEM), electron probe microanalysis based on energy dispersive X-ray spectroscopy (EPMA-EDS) and X-ray diffraction(XRD), and the isothermal section at 400 ℃ was established. The results show that there exists a ternary compound (T-phase) with a constant La content and changable Mg/Zn contents in the Mg-Zn-La system. The mole fraction of La in T-phase is about 8%, and that of Zn is from 16% to 43%. There exist a two-phase equilibrium which consists of T-phase plus hcp-Mg and a three-phase equilibrium which is composed of T-phase, hcp-Mg and a liquid phase (L-phase) at 400 ℃. The L-phase consists of 70% Mg, 30% Zn and is free of La.

Key words: Mg-Zn-La system; isothermal section; T-phase; phase equilibrium

1 Introduction

As structural materials with low density, magnesium alloys are promising for use in aerospace and automobile industry in recent years[1−6]. But the application of magnesium alloys is limited at present because of its limited mechanical strength, especially at elevated temperature. The alloys of Mg-Zn system are applied earlier because of their high strength, but their founding properties are poor. The addition of rare earth (RE) metals to these alloys can improve the castability and elevate the creep resistant at higher temperatures[7−8], though it will reduce the ambient temperature strength to a certain extent.

The phase equilibrium of Mg-Zn-RE system is the basic information for alloys preparation, and the compounds are various from each other with different RE metal additions[9−13]. In the Mg-rich corner of Mg-Zn-RE system, there exist binary phases and ternary phases that can be in equilibrium with Mg solid solution.

The binary information of Mg-Zn-La system is nearly complete now. The intermetallic phases of Mg-La binary system are LaMg, $LaMg_2$, $LaMg_3$, La_2Mg_{17}, $LaMg_{12}$, and all phases are stoichiometric except $LaMg_3$ and $LaMg_{12}$ that show a narrow homogeneity range at high temperatures; there are five metallic phases in the La-Zn binary system, which are LaZn, $LaZn_2$, $LaZn_4$, $LaZn_8$ and $LaZn_{13}$; and there are five metallic phases in the Mg-Zn binary system, i.e. Mg_7Zn_3, MgZn, Mg_2Zn_3, Mg_2Zn, Mg_2Zn_{11}[14].

There is no isothermal section of Mg-Zn-La ternary system hitherto. Some investigations on the phase equilibrium in a narrow composition region of Mg-Zn-La system were made 20 years ago, and the existence of $(Mg, Zn)_{17}La_2$, $Mg_{42}Zn_{53}La_5$ and $Mg_{51}Zn_{20}$ with the primary α(Mg) solid solution has been reported[15]. So the aim of this work is to identify the phase equilibrium of Mg-Zn-La system in Mg-rich corner at 400 ℃, which can provide direction for the application of the alloys at higher temperatures.

2 Experimental

The alloys with different compositions were prepared. Different amounts of pure element Mg (99.99%, mass fraction), Zn (99.99%, mass fraction) and La(99.8%, mass fraction) were mixed and melted at

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750 ℃ in graphite crucibles in an induction furnace under Ar (99.999%, mass fraction) atmosphere with electromagnetic stirrer, and the vacuum degree in the furnace is 5×10^{-3}–7×10^{-3} Pa. The ingots were cooled with the furnace and then cut into small pieces. The samples were wrapped by Ta foil and annealed at 400 ℃ in the vacuum quartz tubes for two weeks, finally quenched by cold water. The microstructures of the alloys were observed by scanning electron microscopy. The chemical compositions of every phase were identified by electron probe microanalysis. X-ray diffraction was utilized for phase identification.

3 Results and discussion

Fifteen Mg-Zn-La samples were prepared and characterized after annealing at 400 ℃ for two weeks, and their compositions are depicted in Fig.1.

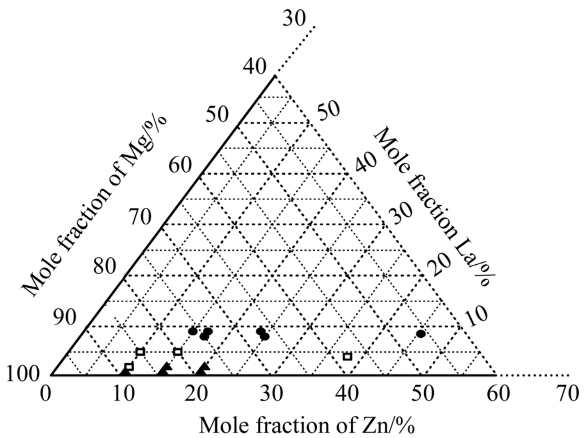

Fig.1 Compositions of Mg-Zn-La alloys at 400 ℃ (● Single phase sample; □ Two-phase samples; ▲ Three-phase samples)

3.1 Equilibrium of T-phase alloy at 400 ℃

Fig.2 shows the typical microstructures of the alloys in this research. Figs.2(a) and (b) show the microstructures of the single phase alloys, indicating that the single phase is a ternary compound. The composition of the ternary compound in Fig.2(a) is 67%Mg, 25%Zn and 8%La; and that of the ternary compound in Fig.2(b) is about 46%Mg, 45.5%Zn and 8.5%La.

Figs.2(c) and (d) show the typical microstructures of two-phase equilibrium alloys with T-phase+hcp-Mg. The bright block is T-phase, and the black phase is Mg matrix. According to the data shown in Table 1, the composition of T-phase in the two-phase equilibrium alloys also shows a linear character as that of the single-phase alloys. With the increase of Zn content in the alloys, the La content of T-phase is constant, and the Zn substitutes for Mg. In the Mg matrix, the solubility of Zn also increases with the increase of Zn content in the alloys.

Figs.2(e) and (f) show the microstructures of three-phase (T-phase+hcp-Mg+L-phase) equilibrium alloys. The bright block is the T-phase, whose composition(mole fraction) is about (8±0.4)%La, 43% Zn and 49% Mg. In the T-phase of the three-phase equilibrium alloys, Mg, Zn and La contents are constant. The grey phase consists of 70% Mg, 30% Zn and is free of La. In Mg-Zn binary system at 400 ℃, the composition of the grey phase is under liquid state[14]. So the grey phase must be L-phase though it is in Mg-Zn-La ternary system. The black phase is the Mg matrix containing 3%Zn content.

Fig.3 shows the XRD patterns of $Mg_{46}Zn_{45.5}La_{8.5}$ and $Mg_{67}Zn_{25}La_8$ single phase alloys. The diffraction peaks of $Mg_{46}Zn_{45.5}La_{8.5}$ and $Mg_{67}Zn_{25}La_8$ single phase alloys are nearly the same, and only the values of 2θ are different. The values of 2θ of $Mg_{46}Zn_{45.5}La_{8.5}$ alloy are larger than those of $Mg_{67}Zn_{25}La_8$ alloy. With the increase of Zn content in the ternary compound, 2θ shifts to larger values. At the same time, these two ternary compounds have a constant La content and a substitution of Mg/Zn content. That is to say, the ternary compound called T-phase has a linear characteristic in composition and a continuous characteristic in lattice structure.

Fig.4 shows the characteristic diffraction peaks of T-phase. The Zn contents of T-phase for the patterns a to d are 16%, 23.7%, 43%, and 43%, respectively. Because $Mg_{46}Zn_{45.5}La_{8.5}$ alloy consists of the single T-phase, so pattern d can be regarded as the standard T-phase XRD pattern compared with the other patterns in Fig.4. For pattern a and pattern b, in addition to hcp-Mg, the other diffraction peaks can be assigned to T-phase according to pattern d. In addition to hcp-Mg in pattern c, the other diffraction peaks should be assigned to T-phase, and no peaks corresponding to the L-phase could be found in pattern c. The reason may be that the liquid phase in $Mg_{84}Zn_{15}La_1$ alloy might be amorphous by quick cooling. The peaks of Mg in the patterns a, b and c are indexed exactly as shown in Fig.4. The existing principles of the

Table 1 EPMA analysis compositions of two-phase (T-phase+hcp-Mg) equilibrium alloys by EPMA (mole fraction, %)

Alloy	Hcp-Mg EDS			T-phase EDS		
	Mg	Zn	La	Mg	Zn	La
$Mg_{85}Zn_{10}La_5$	99.2	0.8	0	76.1	16	7.8
$Mg_{80}Zn_{15}La_5$	98.8	1.2	0	68.3	23.7	8.0

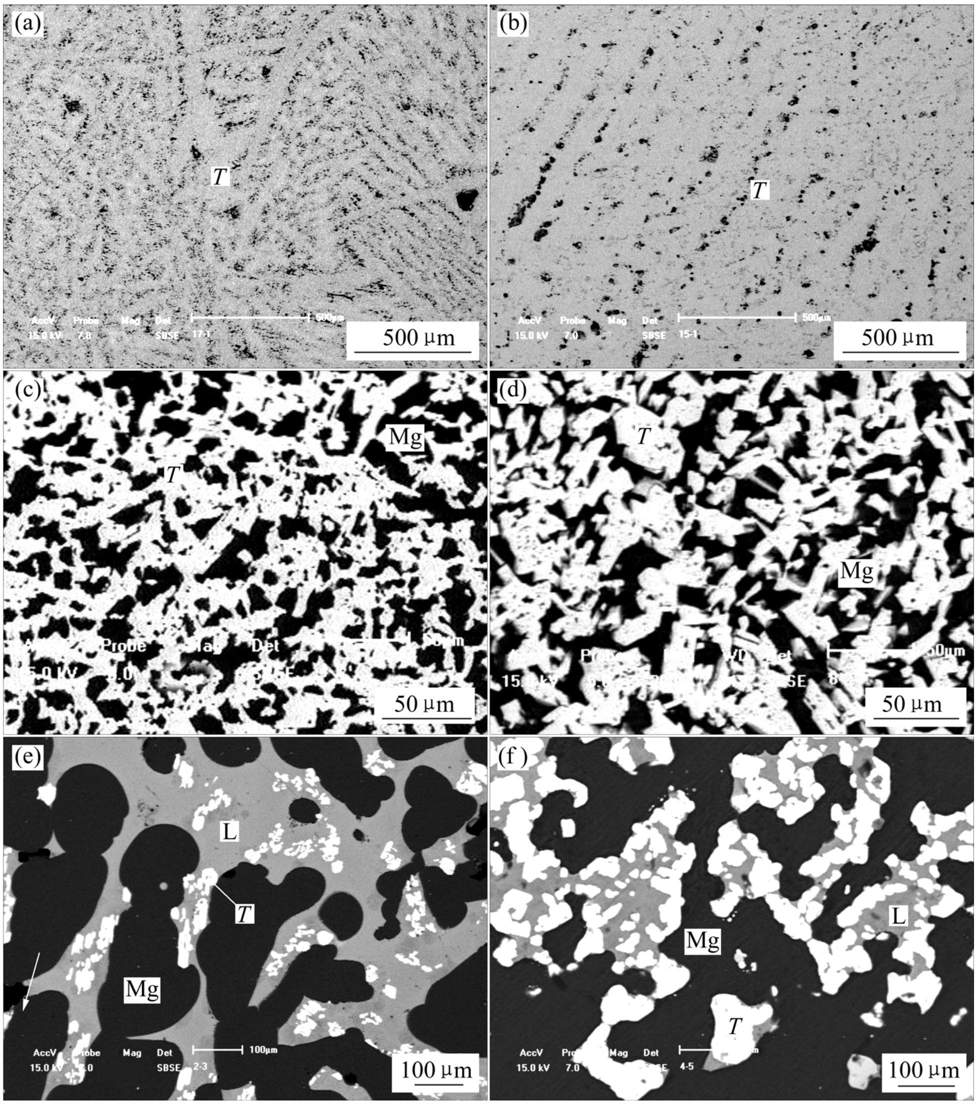

Fig.2 Equilibrium microstructures of alloys with T-phase at 400 ℃ (SEM): (a) $Mg_{67}Zn_{25}La_8$ alloy; (b) $Mg_{46}Zn_{45.5}La_{8.5}$ alloy; (c) $Mg_{85}Zn_{10}La_5$ alloy; (d) $Mg_{80}Zn_{15}La_5$ alloy; (e) $Mg_{84}Zn_{15}La_1$ alloy; (f) $Mg_{83}Zn_{15}La_2$ alloy

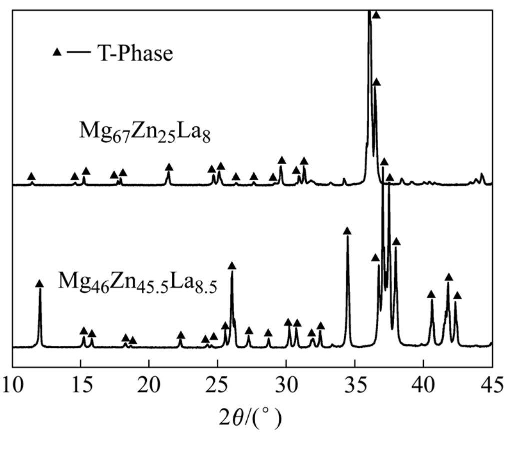

Fig.3 XRD patterns of single T-phase alloys at 400 ℃

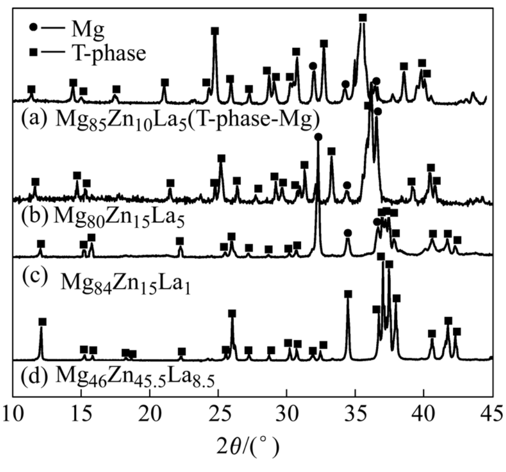

Fig.4 Comparison of T-phase XRD pattern in different alloys at 400 ℃

characteristic diffraction peaks of T-phase with different compositions are concordant, and with the increase of Zn content. Fig.4 shows that the values of 2θ shift to higher.

The results agree with those from Fig.3.

The results from Fig.2 show that the T-phase is a linear compound, in which the mole fraction of La is (8±0.4)% constantly, and the Zn content changes from 16% to 43%. The T-phase in single-phase equilibrium and in two-phase equilibrium has the change in composition, and that in the three-phase region has no change in composition. The composition of T-phase in the three-phase is 7.6%−8.4%La , 43% Zn and the Mg in balance. So the stoichiometry of T-phase is about $(Mg, Zn)_{92}La_8$. The results of Figs.3 and 4 suggest that the lattice structure of T-phase does not change with the increase of Zn in it, and the change only happens on the parameters of the lattice structure.

The ternary compound T-phase was found to exist in the Mg-Zn-La system at 400 ℃, in which the mole fraction of La content is at constant of (8±0.4)%, and those of Mg and Zn change in a large region. The Zn content is from 16% to 43%. This result suggests that the T-phase forms by the Mg/Zn substitution. The stoichiometry of T-phase is about $(Mg, Zn)_{92}La_8$. The results show that there exist two types of phase equilibriums: T-phase+hcp-Mg, and T-phase+hcp-Mg+ L-phase.

3.2 Isothermal section at 400 ℃

Fig.5 shows the isothermal section of Mg-Zn-La system in Mg-rich corner at 400 ℃, which is drawn based on the data above. As a result, there are a single phase region of T-phase, a two-phase region of T-phase+ hcp-Mg and a three-phase region of T-phase+hcp-Mg+ L-phase. The broad region of T-phase+ hcp-Mg is shown clearly in Fig.5 because of the change of composition of T-phase.

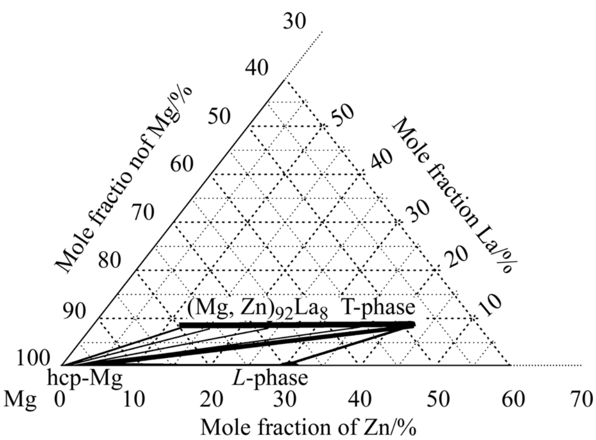

Fig.5 Isothermal section of Mg-Zn-La system in Mg-rich corner at 400 ℃

4 Conclusions

1) There is a linear ternary compound T-phase in the Mg-Zn-La system at 400 ℃, and the stoichiometry of T-phase is about $(Mg, Zn)_{92}La_8$. The composition of T-phase is (7.6%−8.4%)La, (16%−43%)Zn and the rest Mg. In three-phase equilibrium alloys, the composition of T-phase contains (8±0.4)% La, 43% Zn and the Mg in balance.

2) The characteristic peaks of T-phase's XRD pattern are identified. With the increase of Zn content in T-phase, the values of 2θ of the same crystal plane shift to higher. And the crystal structure of the T-phase does not change with the composition change of T-phase.

3) There are a narrow single-phase region of T-phase, a broad two phase region of T-phase+hcp-Mg and a three-phase region of T-phase+hcp-Mg+L-phase in the Mg-rich corner of Mg-Zn-La ternary system at 400 ℃.

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