Study on the compounds of Mg$_{12}$La and (Mg,Zn)$_{11.5}$La

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Abstract: The composition, crystal structure and phase relationship of the main intermetallics of the Mg-Zn-La system on the low La side have been studied. The results show that there exists a binary solid solutions of Mg$_{12}$La as (Mg,Zn)$_{12}$La and a linear ternary compound (Mg,Zn)$_{11.5}$La. Though the composition formula of the two phases are similar, but the composition of Zn in them are different. The maximum Zn content of (Mg,Zn)$_{12}$La is 7.2at% and the minimum Zn content of (Mg,Zn)$_{11.5}$La is 8.5at%. What’s more, the crystal structures of (Mg,Zn)$_{12}$La and (Mg,Zn)$_{11.5}$La phase are also totally different. (Mg,Zn)$_{12}$La have the body centered tetragonal lattice structure, but the crystal structure of (Mg,Zn)$_{11.5}$La is C-centered orthorhombic lattice structure.

1. Introduction
Magnesium alloys are one of the lightest structural metal materials, and its application potential in automobile industry, aviation industry and electron industry has been focused [1-6]. Mg-Zn system is the basic system for Mg alloys, but the system exhibits a low eutectic temperature. For this reason, the mechanical properties of the Mg-Zn alloys are poor at elevated temperature. It is known that the addition of rare earth element can not only refine the grains of the Mg-Zn system alloys, but can also improve the creep resistance at elevated temperature[7-12], because of the formation of high melting-point compounds.

According to the literature [13], the phases in Mg-Zn-La system are Mg based solid solution, binary phases and ternary phases. The metallic phases in this system often play an important role on elevating the mechanical properties especially on the creep resistant property. From this point of view, the information of the intermetallic phases in Mg-Zn-La system must be the important for alloying.

2. Experimental
The experimental alloys with different composition were prepared in this work. The pure alloying elements of Mg (purity about 99.99wt.%), Zn (purity about 99.99wt.%) and La(purity about 9.98wt.%) were mixed up and melted in an induction furnace under Ar (purity about 99.9wt.%) atmosphere, then cooled to room temperature with the furnace. In order to achieve a relative equilibrium state, the as-cast alloys were annealed at 400°C for 1800 h, and then quenched in ice water.

Microstructure of each alloy was studied by scanning electron microscopy (SEM). The compositions of equilibrium phases in alloys were studied by electron probe microanalyzer (EPMA) with a beam size of 1µm and a voltage of 15kV. The high pure Mg, Zn, and La were served as standards to revise the characteristic radiations with ZAF4 correction. The crystal structures of phases were studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM) respectively. Thin foil specimens for TEM were prepared by ion polishing.
3. Results and discussion

3.1. The analysis of (Mg,Zn) \(_{1.2}\)La

The microstructure and XRD pattern of Mg\(_{93}\)La\(_{7}\) alloy are shown in Fig. 1. The results suggest that Mg\(_{93}\)La\(_{7}\) is a two-phase alloy with Mg\(_{12}\)La and Mg solid solution. As shown in Fig. 2b, the diffraction peaks of Mg\(_{12}\)La can be indexed as a body-centered tetragonal lattice structure. According to the result of EPMA, the large light area in Fig. 2a is pro-eutectic Mg\(_{12}\)La, and the region having the alternating light and dark lamellar structure is (Mg+Mg\(_{12}\)La) eutectic structure.

![Figure 1. The microstructure (a) and X-ray diffraction pattern (b) of Mg\(_{93}\)La\(_{7}\) alloy](image)

3.2. The analysis of (Mg,Zn)\(_{11.5}\)La

Fig. 2 shows the microstructures of alloys of Mg\(_{85}\)Zn\(_{10}\)La\(_{5}\), Mg\(_{67}\)Zn\(_{25}\)La\(_{8}\), Mg\(_{88}\)Zn\(_{10}\)La\(_{2}\) and Mg\(_{46}\)Zn\(_{46}\)La\(_{8}\) at 400°C. As shown in Fig. 2, the alloys Mg\(_{85}\)Zn\(_{10}\)La\(_{5}\) and Mg\(_{88}\)Zn\(_{10}\)La\(_{2}\) all consist of two phases. According to the results of Table 1, the black region is the solid solution of Mg, and the white phase of each alloy is a ternary compound. Mg\(_{67}\)Zn\(_{25}\)La\(_{8}\) and Mg\(_{46}\)Zn\(_{46}\)La\(_{8}\) alloys are nearly the single phase alloys. The single phase in each alloy is a ternary compound as shown in Table 1. It is not difficult to find that the compositions of the four ternary compounds in the key alloys all contain about 8at% La, and the Zn content in them are increasing with the decreasing of the Mg contents from 16at% to 44.3at%. The compounds in Mg\(_{85}\)Zn\(_{10}\)La\(_{5}\), Mg\(_{67}\)Zn\(_{25}\)La\(_{8}\), Mg\(_{88}\)Zn\(_{10}\)La\(_{2}\) and Mg\(_{46}\)Zn\(_{46}\)La\(_{8}\) were identified as \(\tau_1\), \(\tau_2\), \(\tau_3\), \(\tau_4\) respectively. The results show that the formation of the ternary compounds is on the substitution of Mg atom by Zn atom.

| Table 1. Phase compositions of the alloys in Figure 2. by EPMA (at%) |
|-------------------|--------|--------|--------|--------|--------|--------|
| Alloys            | Ternary compound (T-phase) | Mg     | Zn     | La     | Mg     | Zn     | La     |
|                   |        |        |        |        |        |        |        |
| Mg\(_{85}\)Zn\(_{10}\)La\(_{5}\) | \(\tau_1\) | 76.2   | 16.0   | 7.8    | 99.2   | 0.8    | 0.0    |
| Mg\(_{67}\)Zn\(_{25}\)La\(_{8}\) | \(\tau_2\) | 66.9   | 25.2   | 7.9    |        |        |        |
| Mg\(_{88}\)Zn\(_{10}\)La\(_{2}\) | \(\tau_3\) | 54.3   | 37.8   | 7.9    | 98.4   | 1.6    | 0.0    |
| Mg\(_{46}\)Zn\(_{46}\)La\(_{8}\) | \(\tau_4\) | 48.7   | 43.3   | 8.0    |        |        |        |
**Figure 2.** The microstructures of alloys: (a) Mg$_{85}$Zn$_{10}$La$_5$; (b) Mg$_{67}$Zn$_{25}$La$_8$; (c) Mg$_{88}$Zn$_{10}$La$_2$; (d) Mg$_{46}$Zn$_{46}$La$_8$

Fig. 3 is the XRD patterns of Mg$_{85}$Zn$_{10}$La$_5$ alloy, Mg$_{67}$Zn$_{25}$La$_8$ alloy, Mg$_{88}$Zn$_{10}$La$_2$ alloy and Mg$_{46}$Zn$_{46}$La$_8$ alloy. It shows that the law of the appearance of the diffraction patterns of the ternary compounds and the intensity of the diffraction peaks of the other ternary compounds $\tau_1$, $\tau_2$, $\tau_3$, $\tau_4$ are coherent. That is to say, the four ternary compounds have the same crystal structure. According to the analysis of the single phase alloy of Mg$_{67}$Zn$_{25}$La$_8$, the crystal structure of $\tau_2$ have been identified as the C-centered orthorhombic crystal structure. The results of Table 1 and Fig. 3a suggest that all the ternary compounds belong to one phase, and it has the C-centered orthorhombic crystal structure. According to the result in Table 1, The ternary compounds from $\tau_1$ to $\tau_4$ have the characterization of the linear compound in composition, and the chemical formula is about (Mg,Zn)$_{11.5}$La, it is a typical replacement solid solution.

Fig. 3b is enlargement of Fig. 3a, which shows that the diffraction angles for the same ($h$ $k$ $l$) triplet of the ternary compound shift to a little higher with the increase of Zn content in it. It is well known that the radius of Zn is shorter than that of Mg. Therefore, the phenomenon must be due to the substitution of Mg by Zn according to Bragg Equation and Crystal plane spacing equation.

**Figure 3.** The XRD patterns of the alloys Mg$_{85}$Zn$_{10}$La, Mg$_{67}$Zn$_{25}$La$_8$, Mg$_{88}$Zn$_{10}$La$_2$ and Mg$_{46}$Zn$_{46}$La$_8$:

(a) $2\theta$ from 10$^\circ$ to 45$^\circ$; (b) $2\theta$ from 10$^\circ$ to 20$^\circ$
The composition and the crystal structure characteristic of the ternary compounds from \( \tau_1 \) to \( \tau_4 \) suggests that all the compounds belong to one ternary linear phase which identified as \((\text{Mg,Zn})_{11.5}\text{La}\) here.

### 3.3. Discussion about Mg\(_{12}\)La and \((\text{Mg,Zn})_{11.5}\)La

Fig.4 is the microstructures of alloys as Mg\(_{93}\)Zn\(_2\)La\(_5\), Mg\(_{90}\)Zn\(_5\)La\(_5\) and Mg\(_{85}\)Zn\(_{10}\)La\(_5\). All the alloys contain two areas, the black and the light. According to the results of composition shown in Table 2, the black area is Mg solid solution, and the light one is a ternary compound. The TEM microstructures in Fig.5 show that the light region in Mg\(_{93}\)Zn\(_2\)La\(_5\) and Mg\(_{85}\)Zn\(_{10}\)La\(_5\) contains the big complete grain, with straight boundaries. But that in Mg\(_{90}\)Zn\(_5\)La\(_5\) contains large numbers of fine grains. The fine grains in light regions of Mg\(_{90}\)Zn\(_5\)La\(_5\) are formed from one another. But the compositions of the fine grains ternary compounds have slight difference as shown in Table 2.

#### Table 2. The phase composition of alloys as Mg\(_{93}\)La\(_5\)Zn\(_2\), Mg\(_{90}\)La\(_5\)Zn\(_5\) and Mg\(_{85}\)La\(_5\)Zn\(_{10}\) (at %)

| Composition of alloys | Compounds Mg | Zn | La | Mg solid solution |
|----------------------|--------------|----|----|------------------|
| Mg\(_{93}\)La\(_5\)Zn\(_2\) | 88.7 | 3.1 | 8.2 | 99.8 | 0.2 | ignored |
| Mg\(_{90}\)La\(_5\)Zn\(_5\) | 84.5 | 7.2 | 8.3 | 99.5 | 0.5 | ignored |
| Mg\(_{85}\)La\(_5\)Zn\(_{10}\) | 83.3 | 8.5 | 8.2 | 99.2 | 0.8 | ignored |

Fig.6 is the X-ray diffraction patterns of the alloys in Table 2. Fig.5a and Fig.6c shows that the diffraction patterns of the compounds in Mg\(_{93}\)Zn\(_2\)La\(_5\) and Mg\(_{85}\)Zn\(_{10}\)La\(_5\) are different to each other, though the microstructures and phase compositions of the two compounds are resemble. That is to say, the two ternary compounds are not the same phase. Through analysis of the diffraction patterns (Fig.6), the compound in Mg\(_{93}\)Zn\(_2\)La\(_5\) alloy is Mg\(_{12}\)La with body-centered tetragonal lattice structure and that in Mg\(_{85}\)Zn\(_{10}\)La\(_5\) alloy is \((\text{Mg,Zn})_{11.5}\)La with C-centered orthorhombic lattice structure.
Figure 6. The XRD patterns of Mg$_{93}$La$_5$Zn$_2$ (a), Mg$_{90}$La$_5$Zn$_5$ (b) and Mg$_{85}$Zn$_10$La$_5$ (c)

Fig. 6b shows that, Mg$_{90}$Zn$_5$La$_5$ alloy consists two compounds and a Mg solid solution. One of the compounds is a binary solid solution of Mg$_{12}$La, the other being a ternary compound (Mg,Zn)$_{11.5}$La. Because the composition of the two compounds are close to each other as shown in Table 2, so no phase interface between them has been observed in the black electron images as shown in Fig. 4b. However, according to the TEM microstructures (Fig. 5), the compound bulk in Mg$_{85}$Zn$_10$La$_5$ alloy is composed by so many small grains which is different from those in Mg$_{93}$Zn$_2$La$_5$ and Mg$_{85}$Zn$_10$La$_5$. The result in Fig. 6b also suggests that the small fine grains consist two phases, such as Mg$_{12}$La with maximum Zn content and (Mg,Zn)$_{11.5}$La with minimum Zn content.

4. Conclusions
- There is a binary substitutional solid solution solid of Mg$_{12}$La as (Mg,Zn)$_{12}$La, the maximum Zn must be Less than or equal to 7.2at%.
- A ternary linear compound (Mg,Zn)$_{11.5}$La has been identified, the Zn content of it must be Greater than or equal to 8.5at%, and the Zn content in this compound at least up to 43.3at%.
- The crystal structure of Mg$_{12}$La is the body-centred tetragonal lattice structure, and that of (Mg,Zn)$_{11.5}$La is C-centered orthorhombic lattice structure.

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