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Intermetallics and phase relations of Mg−Zn−Ce alloys at 400 °C

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Abstract: The crystal structures, compositions and phase relations of the intermetallics of Mg−Zn−Ce system in the Mg-rich corner at 400 °C were identified through equilibrium alloy method. For Mg−Zn−Ce system, there is a linear ternary compound (*T* phase), whose chemical formula is $(Mg_{1-x}Zn_x)_{11}Ce$. The range of Zn content in *T* phase is from 9.6% to 43.6% (molar fraction). The crystal structure of *T* phase is *C*-centered orthorhombic lattice with lattice parameters of a=0.96−1.029 nm, b=1.115−1.204 nm, c=0.940−1.015 nm. And the lattice parameters of *T* phase are decreasing a little with increasing Zn content. According to the results of composition and crystal structure, the maximal solubility of Zn in $Mg_{12}Ce$ is about 7.8% (molar fraction), and the chemical formula of the solid solution can be identified as $(Mg_{1-x}Zn_x)_{12}Ce$. The isothermal section of Mg−Zn−Ce system in Mg-rich corner at 400 °C was constructed.

Key words: Mg−Zn−Ce system; intermetallics; crystal structure; isothermal section

1 Introduction

Magnesium alloy is one of the lightest structural metal materials, and its application potential in automobile industry, aviation industry and electron industry has been focused [1, 2]. Mg−Zn binary system is one of the basic systems for magnesium alloy. Because of the low melting point, the alloys of Mg−Zn binary system cannot work at the elevated temperatures. However, the addition of rare earth elements can improve the mechanical properties of the alloys, especially at elevated temperature [3]. In recent years, the magnesium alloys with the addition of rare earth have been studied widely [4−7].

Cerium is one of the modifying elements for Mg−Zn binary alloys [8]. The forming of the intermetallics with cerium can improve the creep resistance and strength of Mg−Zn alloys at the elevated temperature. Nevertheless, the information about the intermetallics in Mg−Zn−Ce ternary system is limited [9], which restricts the development of the alloy design.

In the Mg-rich corner of Mg−Zn−Ce isothermal section at 300 °C, four main intermetallics have been reported by MELNIK et al [10, 11] and DRITS et al [12], which were $(Mg_{1-x}Zn_x)_{12}Ce(0\le x\le 0.08)$, $(Mg_{1-x}Zn_x)_{10}Ce$ (9.1%≤Zn≤45.5% (molar fraction)), $Mg_7Zn_{12}Ce$ and Mg_3Zn_5Ce. According to the data above, the isothermal section of Mg−Zn−Ce system at 300 °C was deduced by KOLITSCH et al [13]. The crystal structure of $(Mg_{1-x}Zn_x)_{12}Ce$ was reported as a body tetragonal lattice, which was identified as the solid solution of $Mg_{12}Ce$. The crystal structure of $(Mg_{1-x}Zn_x)_{10}Ce$ was identified as close-packed hexagon determined by X-ray powder diffraction [12]. All the crystal structures have not been confirmed by others. What's more, $(Mg_{1-x}Zn_x)_{10}Ce$ has been identified as the solubility of $Mg_{12}Ce$ by CHIU et al [14] recently. The two results of KOLITSCH et al [13] and CHIU et al [14] are conflict. In addition, the isothermal section of Mg−Zn−Ce at 350 °C was constructed by KEVORKOV and PEKGULERYUZ [15] using meaning of diffusion couple technology. It was only constructed according to the composition of phases, but the crystal structure of $(Mg_{1-x}Zn_x)_{10}Ce$ was not studied.

Compared with the results of other groups, the present work identified the phase relations of Mg−Zn−Ce system in the Mg-rich corner by studying the

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crystal structures of phases with different compositions in equilibrium alloys in detail. The crystal structures, compositions and phase relations of a linear ternary compound *T* phase ($(Mg_{1-x}Zn_x)_{11}Ce$) of Mg−Zn−Ce system were studied.

2 Experimental

The Mg−Zn−Ce ternary alloys of different compositions were prepared from elemental metals of high purity (>99.9%, mass fraction), in the carbon crucibles in a vacuum induction furnace under Ar atmosphere. In order to get the homogeneous sample, the alloys were melted back three times, and cooled in the furnace to the room temperature. The as-cast samples wrapped with tantalum foils were sealed in a quartz tube under 10^{-2} Pa. The samples were equilibrium treated at 400 °C for 480 h, followed by ice water quenching.

The microstructure, the phase composition and the crystal structure were studied by scanning electric microscopy (SEM), electron probe microanalysis (EPMA), transmission electron microscopy (TEM) and X-ray diffraction analysis (XRD), respectively. Thin-foil specimens for transmission electron microscopy were prepared by using ion electron polishing.

3 Results and discussion

In order to study the intermetallics and the phase relations of Mg−Zn−Ce system in Mg-rich corner at 400 °C, thirteen equilibrium alloys were prepared. The composition places of the alloys prepared in this work are shown in Fig. 1.

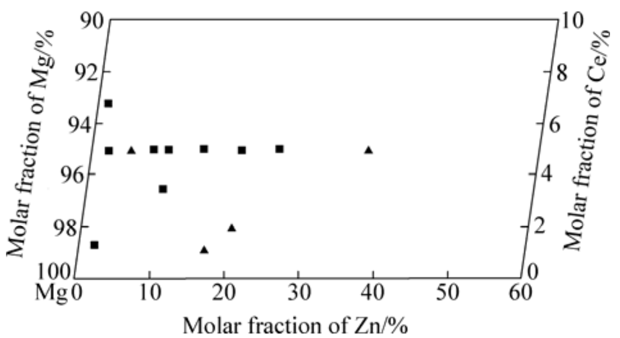

Fig. 1 Composition places of alloys prepared in this work (■ Two-phase equilibrium alloy; ▲ Three-phase equilibrium alloy)

3.1 Composition and crystal structure of *T* phase

The microstructures of 87Mg−8Zn−5Ce alloy, 85Mg−10Zn−5Ce alloy, 86Mg−10.5Zn−3.5Ce alloy, 80Mg−15Zn−5Ce alloy, 75Mg−20Zn−5Ce alloy and 70Mg−25Zn−5Ce alloy (molar fraction, %) are shown in Fig. 2. According to the results of compositions in Table1, the black phase is Mg solid solution, and the white one is ternary compounds. As shown in Table 1, all the ternary compounds (τ_1 to τ_6) contain about (8.5±0.2)% Ce, (12.68−34)% Zn and balanced Mg. With the increase of Zn, the Mg content is decreasing in the ternary compouds. The result suggests that the decrease of Mg content in the ternary compounds must be based on the substitution by Zn content. The results of the compositions from τ_1 to τ_6 suggest that all the ternary compounds should belong to a compound with a linear changing composition range. And the chemical formula of τ_1 to τ_6 can be identified as $(Mg_{1-x}, Zn_x)_{11}Ce$.

Table 1 Phase compositions of alloys with Mg+*T* two-phase equilibrium at 400 °C(molar fraction, %)

Composition of alloys	Compound	*T* phase			Mg solid solution		
		Mg	Zn	Ce	Mg	Zn	Ce
87Mg−8Zn−5Ce	τ_1	79.08	12.68	8.24	99.29	0.59	0.12
85Mg−10Zn−5Ce	τ_2	74.46	16.97	8.57	99.16	0.79	0.05
86Mg−10.5Zn−3.5Ce	τ_3	69.59	21.81	8.60	98.95	1.01	0.04
80Mg−15Zn−5Ce	τ_4	69.41	22.03	8.56	98.89	1.08	0.03
75Mg−20Zn−5Ce	τ_5	60.70	30.84	8.46	98.30	1.65	0.05
70Mg−25Zn−5Ce	τ_6	57.32	34.00	8.68	98.00	1.96	0.04

Figure 3 shows the selected area electron diffraction (SAED) patterns of the zone axes of [111], [110], [210] and [310], which were obtained from the same area of one grain of τ_2. The results suggest that all the patterns agree to *C*-centered orthorhombic crystal structure with the lattice parameters of a=1.01 nm, b=1.15 nm, c=0.98 nm. Table 2 shows the theoretic and experimental angles between the zone axes of SAED patterns of τ_2. The theoretic angles were calculated according to the formula of the zone axis angle of orthorhombic crystal structure of τ_2. The data in Table 2 show that the experimental angles are consistent with the theoretic ones in the range of allowable error. It suggests that the crystal structure of τ_2 must be *C*-centered orthorhombic lattice.

Table 2 Included angles between zone axes of SAED patterns of τ_2

Zone axes	Angle/(°)	
	Theoretic value	Experimental value
From [111] to [110]	33	32.6
From [110] to [210]	18.7	18.5
Form [210] to [310]	9	9.2

The XRD pattern of 85Mg−10Zn−5Ce alloy is shown in Fig. 4(a). According to the results of the microstructure (Fig. 2(b)) and the compositions of phases (Table 1), the 85Mg−10Zn−5Ce alloy contains two phases, which are Mg solid solution and the ternary compoud τ_2. Therefore, in addition to the diffraction peaks of Mg, the rest peaks of the diffraction pattern can

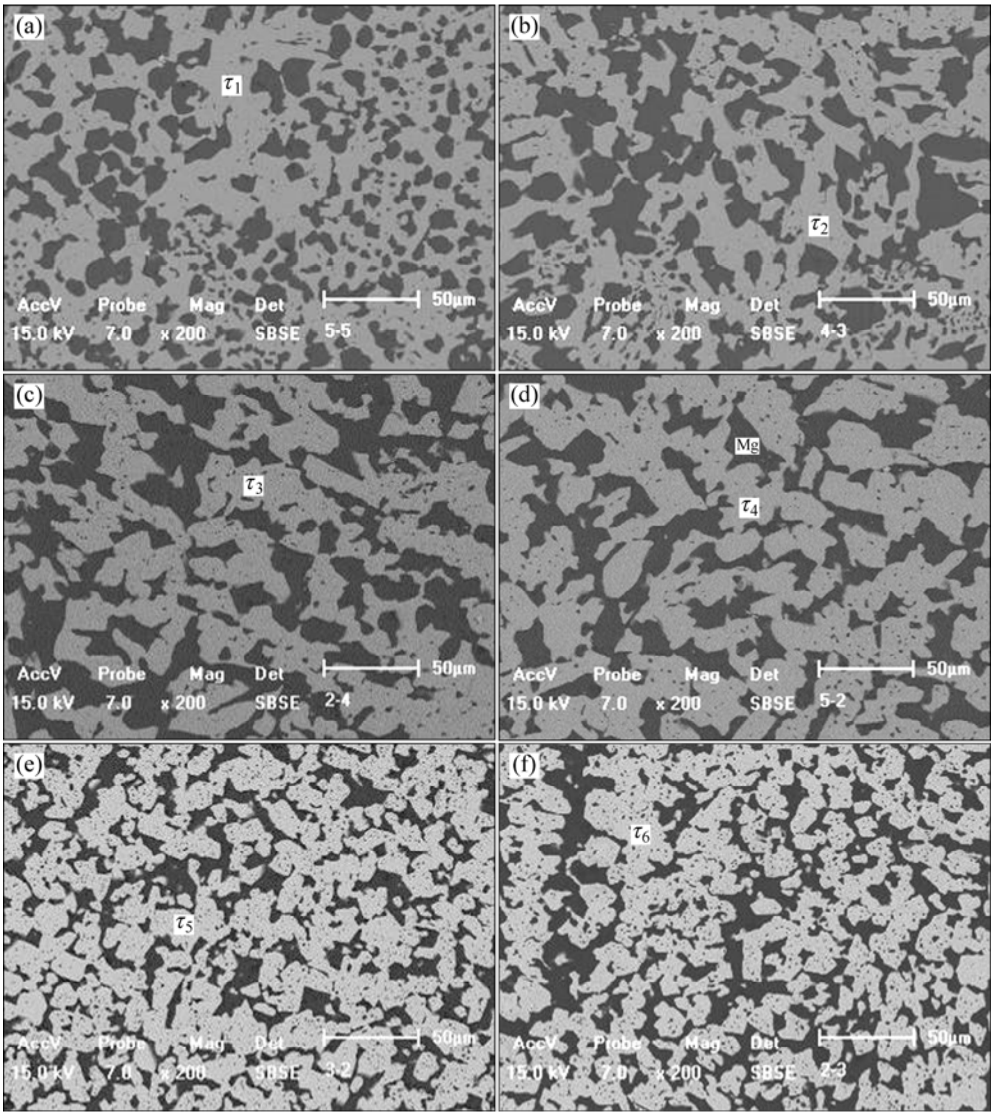

Fig. 2 Microstructures of Mg+T two-phase equilibrium alloys at 400 °C: (a) 87Mg−8Zn−5Ce; (b) 85Mg−10Zn−5Ce; (c) 86Mg−10.5Zn−3.5Ce; (d) 80Mg−15Zn−5Ce; (e) 75Mg−20Zn−5Ce; (f) 70Mg−25Zn−5Ce

be assigned to τ_2 phase. And it is well known that the crystal structure of Mg had been identified, so the diffraction peaks of Mg can be indexed easily. Except the diffraction peaks of Mg, all the rest diffraction peaks cannot be indexed by $Mg_{12}Ce$, but can be indexed by *C*-centered orthorhombic crystal structure with the lattice parameters obtained above. The results confirm further that the crystal structure of τ_2 is *C*-centered orthorhombic lattice.

In the report of CHIU et al [14], the crystal structure of the ternary compound τ_2 in the 85Mg−10Zn−5Ce alloy was not reported, and τ_2 was looked as the solid solution of $Mg_{12}Ce$, which has the body centered tetragonal lattice. But the results in this work show that the crystal structure of τ_2 is different from that of $Mg_{12}Ce$.

The XRD patterns of the alloys of 87Mg−8Zn−5Ce, 86Mg−10.5Zn−3.5Ce, 80Mg−15Zn−5Ce, 75Mg−20Zn−5Ce and 70Mg−25Zn−5Ce are shown in Fig. 4(b). The results suggest that the diffraction peaks of τ_1, τ_3, τ_4, τ_5 and τ_6 all nearly correspodence one to one with those of τ_2. This suggests that the compounds from τ_1 to τ_6 have the same crystal structure. According to the results in Fig. 4(b), the diffraction angles for the same (h k l) triplet shift to a little higher with the increase of Zn content in the ternary compounds. That is to say, the lattice parameters of the compounds are decreasing a little with the increase of Zn content. This is because the atomic radius of Zn is shorter than that of Mg.

According to the results of the compositions and crystal structures, the ternary compounds from τ_1 to τ_6 can be identified as one linear ternary compound called T phase here. The chemical formula of T phase is $(Mg_{1-x}, Zn_x)_{11}Ce$ and the crystal structure of T phase is *C*-centered orthorhombic lattice. The crystal structure is not the body centered tetragonal lattice and not the hexagonal lattice as reported [12, 14]. And the results

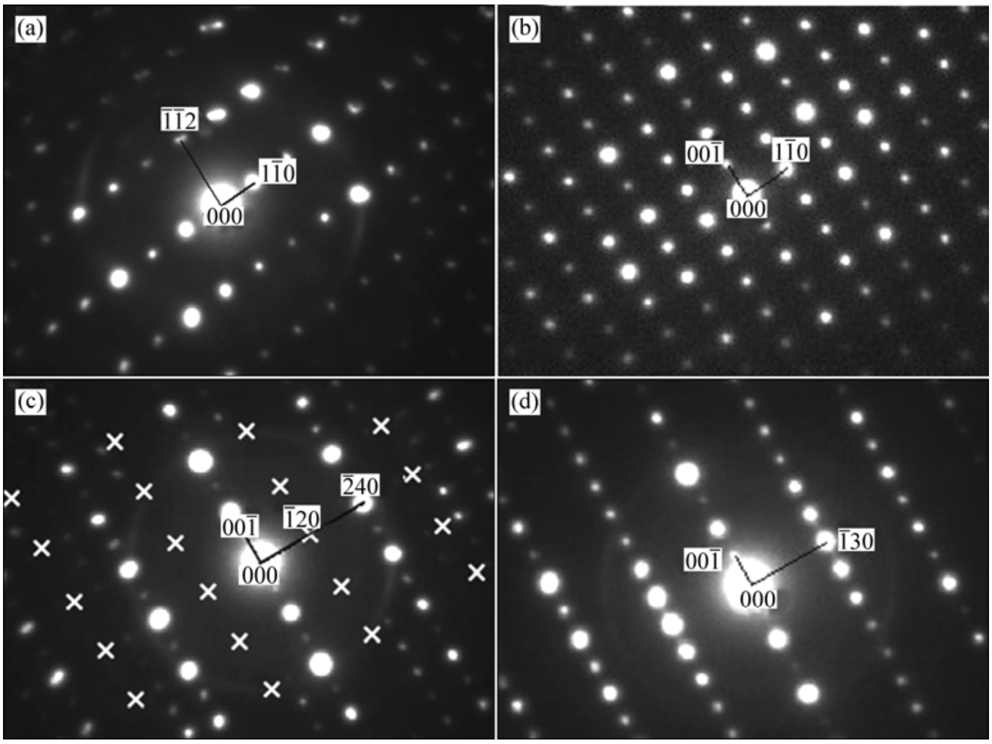

Fig. 3 SAED patterns of τ_2: (a) [111] zone axis; (b) [110] zone axis; (c) [210] zone axis; (d) [310] zone axis (× Stands for positions of extinct diffraction spots)

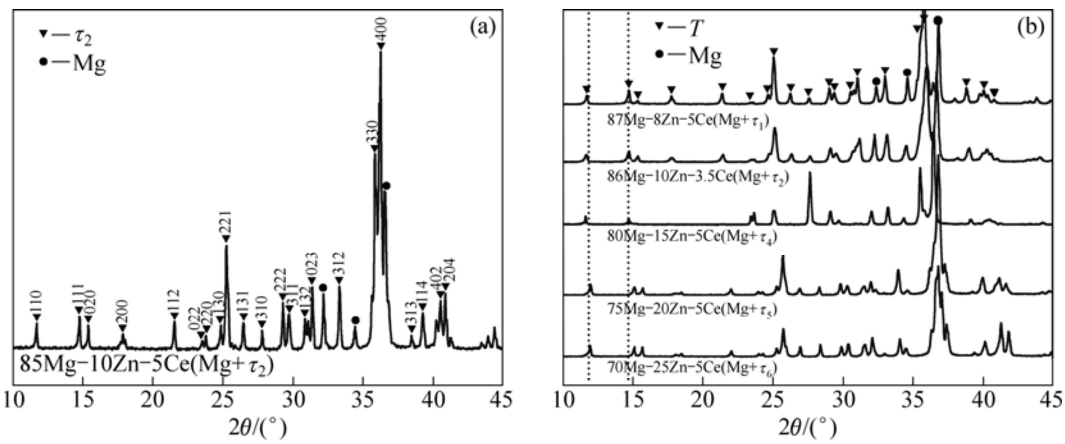

Fig. 4 XRD patterns of Mg+*T* two-phase equilibrium alloys

also suggest that, there is a two-phase region of Mg+*T* in Mg−Zn−Ce system at 400 °C, and this two-phase region is broad.

3.2 Three-phase equilibrium of Mg+*T*+$Mg_{12}Ce$ at 400 °C

The scanning electron microscopy microstructure of 90Mg−5Zn−5Ce alloy is shown in Fig. 5(a). The microstructure contains two different color blocks. The black block is Mg solid solution, which contains 0.5% Zn, ignored Ce and balanced Mg.

The TEM microstructure of the white block in Fig. 5(a) is shown in Fig. 5(b). According to the results of Fig. 6, the white block contains two phases. One phase contains 7.8% Ce, 7.8% Zn and balanced Mg, whose composition is close to that of *T* phase. But the result of SAED pattern of it in Fig. 6(a) shows that the crystal structure of it is the body centered tetragonal lattice with the parameters of a=b=1.03 nm and c=0.59 nm. It suggests that this phase is $Mg_{12}Ce$, and the solubility of Zn in it is about 7.8%.

The other phase in Fig. 5(b) is a ternary compound called τ_0 here, which contains 8.4% Ce, 9.6% Zn, and balanced Mg. The composition of τ_0 agrees to the chemical formula of *T* phase too. Figure 6(b) shows the SAED pattern of [100] zone axis of τ_0, and the result

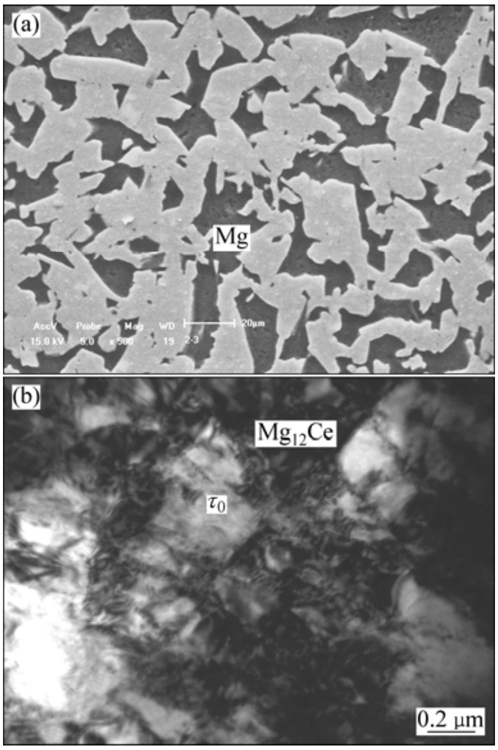

Fig. 5 Microstructures of 90Mg−5Zn−5Ce alloy at 400 °C: (a) SEM image; (b) TEM image

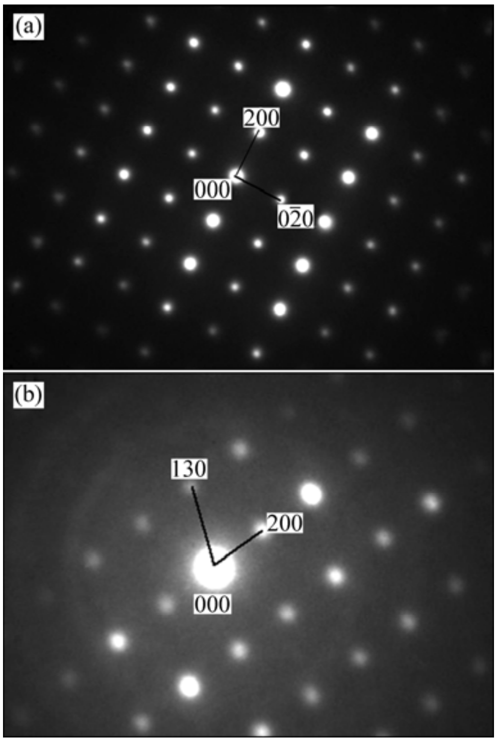

Fig. 6 SAED patterns of ternary compounds of 90Mg−5Zn−5Ce alloy: (a) [011] zone axis of $Mg_{12}Ce$; (b) [100] zone axis of τ_0

suggests that the crystal structure of τ_0 is *C*-centered orthorhombic lattice with the lattice parameters of *a*=1.029 nm，*b*=1.204 nm and *c*=1.015 nm. The results of composition and crystal structure suggest that τ_0 belongs to *T* phase.

The results suggest that though having nearly the same composition, *T* phase and $Mg_{12}Ce$ solid solution are not the same phase because of the difference of the crystal structure. The three-phase region of Mg+($Mg_{12}Ce$)+*T*(τ_0) of Mg−Zn−Ce system at 400 °C was identified. And the minimum content of Zn in *T* phase of Mg+*T* two-phase region is about 9.6%.

3.3 Three-phase equilibrium of Mg+*T*+Liqiuid at 400 °C

The microstructure of 81Mg−17.5Zn−1.5Ce alloy is shown in Fig. 7(a). The black phase contains 3.6% Zn, ignored Ce and balanced Mg, which must be the Mg solid solution. The grey phase contains about 32.1% Zn, ignored Ce and balanced Mg. According to the Mg−Zn binary diagram, this composition must be in liquid condition at 400 °C. So, the grey phase must be liquid phase remaining from 400 °C by ice water quenching. The composition of the white phase is about 8.2% Ce, 43.6% Zn and balanced Mg, which agrees to the chemical formula of *T* phase. In the XRD pattern of 81Mg−17.5Zn−1.5Ce alloy (Fig. 7(b)), the characteristic diffraction peaks of *C*-centered orthorhombic lattice, with the lattice parameters of *a*=0.96 nm, *b*=1.115 nm and *c*=0.94 nm, can be indexed. The results of the composition and the crystal structure suggest that the

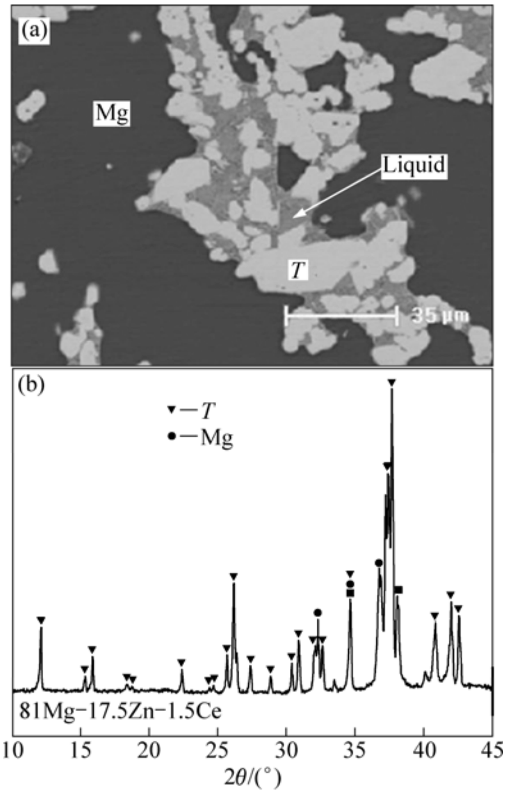

Fig. 7 Microstructure (a) and XRD pattern (b) of 81Mg−17.5Zn−1.5Ce alloy at 400 °C

white ternary compound belongs to *T* phase called as τ_7.

According to the results, *T* phase has equilibrium with Mg solid solution and liquid phase at 400 °C. So, the three-phase region of Mg+*T*+liquid of Mg−Zn−Ce system at 400 °C was identified. And the results also suggest that the maximal content of Zn in *T* phase in Mg+*T* two-phase region is about 43.6%.

According to the results all above, the range of Zn content of *T* phase in Mg+*T* two-phase region from 9.6% to 43.6% can be deduced, and that of Ce is at nearly constant of 8.5%. The crystal structure is *C*-centered orthorhombic lattice. The lattice parameters of τ_0 to τ_7 are decreasing a little with increasing Zn content in *T* phase, as shown in Table 3.

Table 3 Lattice parameters of *T* phase with different compositions

Compound	*T* phase			Lattice parameter of *T* phase		
	x(Mg)/%	*x*(Zn)/%	*x*(Ce)/%	*a*/nm	*b*/nm	*c*/nm
τ_0	82.00	9.60	8.40	1.029	1.204	1.015
τ_1	79.08	12.68	8.24	1.020	1.200	0.990
τ_2	74.46	16.97	8.57	1.010	1.150	0.98
τ_3	69.59	21.81	8.60	0.999	1.146	0.976
τ_4	69.41	22.03	8.56	0.999	1.146	0.976
τ_5	60.7	30.84	8.46	0.980	1.130	0.963
τ_6	57.32	34.00	8.68	0.977	1.126	0.961
τ_7	48.2	43.60	8.20	0.960	1.115	0.940

3.4 Isothermal section of Mg−Zn−Ce system in Mg-rich corner at 400 °C

According to all the results obtained above, the main intermetallics of Mg−Zn−Ce system in the Mg-rich corner are $Mg_{12}Ce$ and *T* phase. The structure and the composition of *T* phase were identified. And the results suggest that *T* phase is not the solid solution of $Mg_{12}Ce$. The maximal solubility of Zn in $Mg_{12}Ce$ is about 7.8%. Therefore, the phase relations of Mg−Zn−Ce system in the Mg-rich corner at 400 °C were determined (Fig. 8).

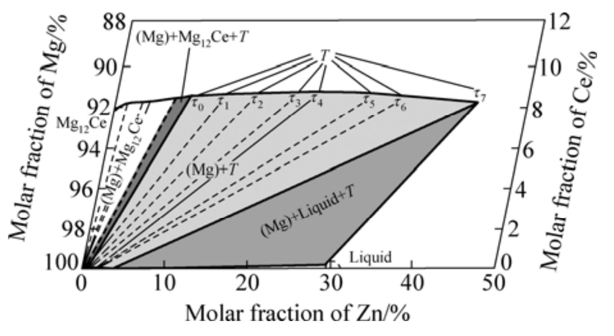

Fig. 8 Isothermal section of Mg−Zn−Ce system in Mg-rich corner at 400 °C

4 Conclusions

1) A linear ternary compound called *T* phase was identified in Mg−Zn−Ce system at 400 °C. The chemical formula of *T* phase is $(Mg_{1-x}, Zn_x)_{11}Ce$. The range of Zn content in *T* phase is from 9.6% to 43.6%.

2) The crystal structure of *T* phase is *C*-centered orthorhombic lattice with the parameters of *a*=0.96−1.029 nm, *b*=1.115−1.204 nm, *c*=0.940−1.015 nm. The lattice parameters are decreasing with the increase of Zn content in *T* phase.

3) *T* phase and the binary solubility of $Mg_{12}Ce$ are not the same phase, and the maximal solubility of Zn in $Mg_{12}Ce$ is about 7.8%.

4) The phase equilibria of Mg+($Mg_{12}Ce$), Mg+*T*, Mg+*T*+Liquid, and Mg+*T*+($Mg_{12}Ce$) were identified and the isothermal section of Mg−Zn−Ce system in Mg-rich corner at 400 °C was constructed.

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400 °C 时 Mg−Zn−Ce 系金属间化合物及相平衡

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摘 要：利用平衡合金法研究 Mg−Zn−Ce 系富镁角在 400 °C 时各金属间化合物的相成分、相结构及相关系。研究表明，Mg−Zn−Ce 系富镁角丰在一个线性化合物 *T* 相，其化学式为$(Mg_{1-x}Zn_x)_{11}Ce$。*T* 相中 Zn 的含量为 9.6%~43.6%(摩尔分数)。*T* 相的晶体结构为 *C* 底心正交晶格，其晶格参数随着 Zn 含量的增加而略有减小，分别为 a=0.96~1.029 nm，b=1.115~1.204 nm，c=0.940~1.015 nm。$Mg_{12}Ce$ 能够固溶 7.8%的 Zn 元素，其化学式为$(Mg_{1-x}Zn_x)_{12}Ce$。确定了 400 °C 时 Mg−Zn−Ce 系相图富镁角的相关系。

关键词：Mg−Zn−Ce 系；金属间化合物；晶体结构；等温截面

(Edited by YANG Hua)