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Full Length Article

Experimental investigation of the isothermal section at 400 °C of the Mg—Ce—Sr ternary system

Songxiang Sun [a], Yuting Qin [a], Hua Zhou [b], Yong Du [b], Cuiyun He [a,*]

[a] College of Materials Science and Engineering, Guangxi University, Nanning 530004, China
[b] State Key Lab of Powder Metallurgy, Central South University, Changsha 410083, China

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Abstract

The objective of this study is to determine the isothermal section at 400 °C of the Mg—Ce—Sr system. In this study, the constitution of the Ce—Sr system and the Mg—Ce—Sr system have been investigated over the entire composition range using X-ray diffraction (XRD), field emission scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). No any new binary compound has been found in the Ce—Sr system and no ternary compound has been found in the Mg—Ce—Sr system also. Nine three-phase regions have been experimentally observed. Six binary phases Mg_2Sr, $Mg_{23}Sr_6$, $Mg_{38}Sr_9$, $Mg_{17}Sr_2$, $Mg_{12}Ce$, $Mg_{41}Ce_5$ are detected dissolving about 3–7 at.% the third element. This study first detected the experimental data of the Ce—Sr binary system and determined the isothermal section at 400 °C of the Mg—Ce—Sr ternary system.

Keywords: Ce—Sr system; Mg—Ce—Sr system; Isothermal section

1. Introduction

Magnesium alloys are attracting great attention as a light weight structural material used in various fields, such as construction of the body of portable electrical appliances including computer and mobile phone, and spare parts of automobiles [1,2]. The strontium and the rare earth are important additional elements for magnesium alloys. Baril et al. [3] studied the creep resistance, mechanical properties and the microstructure of magnesium alloys with less than 3 wt.% Sr. Hirai et al. [4] reported that Sr enhances mechanical properties of a cast AZ91 magnesium alloy at room and elevated temperature. It was found that the yield strength and the elongation at break were improved with increasing the amount of the intermetallic phase $Mg_{12}Ce$ under commercially pure Mg containing 5 wt.% Ce [5,6].

Despite the Sr and Ce are considered as benefitting elements for developing new magnesium alloys, however the phase diagram information of the Ce—Sr system and the Mg—Ce—Sr system are absent due to the samples are difficult to prepare since Mg has high evaporability and strontium is an extremely active element which can react with air very quickly.

There are no any experimental information about the Ce—Sr binary system and the Mg—Ce—Sr ternary system. Two boundary binary systems Mg—Sr and Mg—Ce of Mg—Ce—Sr system are well described in the literature. The Mg—Sr binary system [7] presents four line compounds: $Mg_{17}Sr_2$, $Mg_{38}Sr_9$, $Mg_{23}Sr_6$, Mg_2Sr. Two phases $Mg_{17}Sr_2$ and Mg_2Sr directly form from liquid at 606 and 680 °C, respectively. $Mg_{23}Sr_6$ peritectically forms from L + Mg_2Sr at 603 °C and $Mg_{23}Sr_6$ forms in a eutectoid reaction $Mg_{17}Sr_2$ + $Mg_{23}Sr_6$ at 592 °C. All the phases are stable until low temperature. The Mg—Ce system [8] contained six intermetallic compounds. Two binary compounds $Mg_{17}Ce_2$ and $Mg_{12}Ce$ are only stable at limited high temperature range and decompose at 611 and 615 °C, respectively. There are only four binary compounds: $Mg_{12}Ce$, $Mg_{41}Ce_5$, Mg_3Ce and MgCe are stable at 400 °C. $Mg_{12}Ce$ has two polymorphs (body-centered orthorhombic and tetragonal), although the exact phase transformation temperature is not known. The (δCe) dissolves large amount of Mg and stable at high temperature [9–14], the stable phase of Ce is (γCe) with fcc structure at 400 °C, which contain considerable amount of Mg also [15,16]. The crystal structure data for all phases of Mg—Ce—Sr system are listed in Table 1.

* Corresponding author. College of Materials Science and Engineering, Guangxi University, Daxue Str. 100, Nanning, Guangxi 530004, China. Tel.: +86 771 3231441; fax: +86 771 3231441.
E-mail address: he-cy@gxu.edu.cn (C. He).

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Table 1
Crystallographic data of all phases in the Mg—Ce—Sr system [17].

Phase	Struktur-bericht	Pearson symbol/prototype	Space group	Lattice parameters (Å)		
				a	b	c
Mg	A3	*hP*2/Mg	$P6_3/mmc$	3.209		5.211
γCe	A1	*cF*4/Cu	$Fm\bar{3}m$	5.15		
MgCe	B2	*cP*2/ClCs	$Pm\bar{3}m$	3.906		
Mg_3Ce	$D0_3$	*cF*16/$AlFe_3$	$Fm\bar{3}m$	7.443		
$Mg_{41}Ce_5$	…	*tI*92	$I4/m$	14.78		10.43
$Mg_{12}Ce$	$D2_b$	*tI*26/$Mn_{12}Th$	$I4/mmm$	10.33		5.96
$Mg_{17}Sr_2$	…	*hP*38/$Ni_{17}Th_2$	$P6_3/mmc$	10.533		10.342
$Mg_{38}Sr_9$	…	*hP*94	$P6_3/mmc$	10.500		28.251
$Mg_{23}Sr_6$	$D8_a$	*cF*116/$Mg_{23}Th_6$	$Fm\bar{3}m$	14.914		
Mg_2Sr	C14	*hP*12/$MgZn_2$	$P6_3/mmc$	6.439		10.494
αSr	A1	*cF*4/Cu	$Fm\bar{3}m$	6.080		

Most recently, He et al. [18] measured the isothermal sections at 700 °C and 427 °C in the Al—Mg—Ni system by employing a powder metallurgy method to prepare alloys. This method is employed in the present work. The purpose of this study is to measure the isothermal section at 400 °C of the Mg—Ce—Sr system to provide phase diagram information for developing new commercial Mg alloys and for thermodynamic modeling the ternary system in the next step.

2. Experimental procedure

High-purity small piece metals: Mg 99.5 wt.%, Ce 99.5 wt.% and Sr 99.95 wt.% (supplied by Alfa Aesar China), were used as starting materials. Several steps were involved in preparing procedures. First, the small piece starting materials were weighed and put into tantalum tubes. Then these tubes were sealed. The above procedures were performed in a glove box (CL800S, Chengdu Dellix Industry Co., Ltd) under an argon atmosphere with less than 1 ppm of O_2 and H_2O. The sealed Ta tubes were sealed into vacuum silica tubes again. Then the samples were sintered in a resistance furnace. The heating processes were described as follows. Firstly, the samples were persevered at 600 °C about half an hour. Secondly, the samples were kept at 750 °C for 2 hours. Finally, the samples were stayed at 850 °C for 2 days and during the stage, these sealed tubes were shaken and inverted every couple hours in order to increase the homogenization of samples. After sintering, these samples were annealed at 400 °C for 30 days, and then quenched in ice water.

X-ray diffraction (XRD) investigations of the crushed and powdered samples were performed by Rigaku D-max/3015

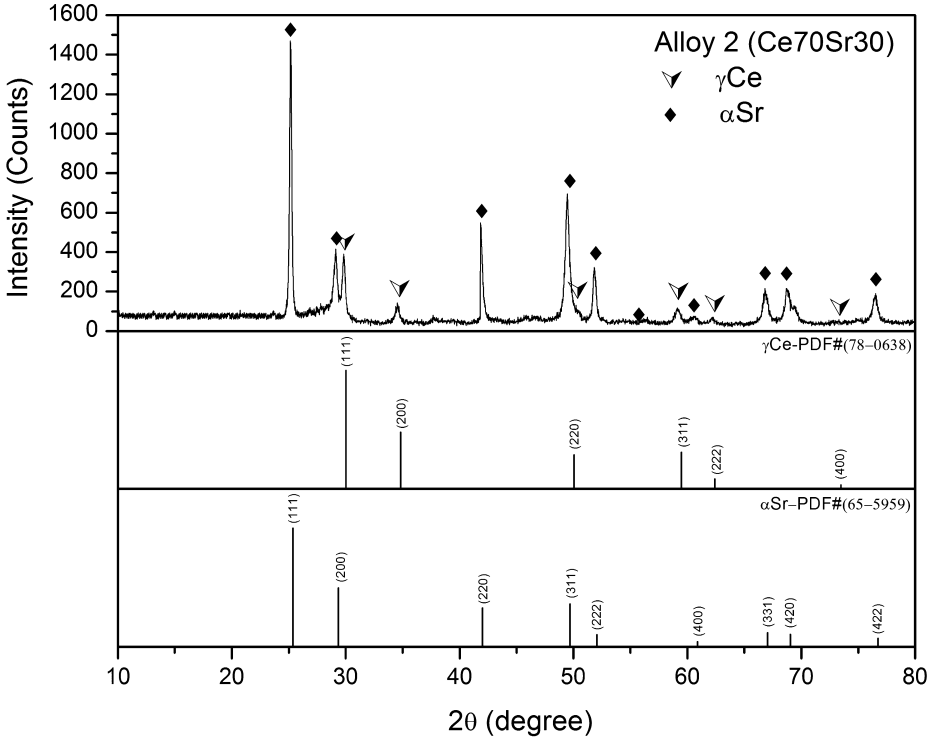

Fig. 1. XRD patterns of alloy 2 (Ce70Sr30) annealed at 400 °C for 30 days and it contains with (γCe) and (αSr) two phase.

Table 2
Summary the experimental results of the XRD and SEM/EDS measurements on alloys of the Ce—Sr system and the Mg—Ce—Sr system annealed at 400 °C for 1 month.

No.	Nominal composition (at.%)			Phase identified by XRD	Phase composition from EDS (at.%)			Lattice parameter (Å)		
	Mg	Ce	Sr		Mg	Ce	Sr	a	b	c
1	0	90	10	Ce	–	–	–			
				Sr	–	–	–			
2	0	70	30	Ce	–	–	–	5.175(3)		
				Sr	–	–	–	6.098(2)		
3	0	50	50	Ce	–	–	–	5.148(2)		
				Sr	–	–	–	6.079(2)		
4	0	30	70	Ce	–	–	–	5.154		
				Sr	–	–	–	6.098(3)		
5	0	5	95	Ce	–	–	–			
				Sr	–	–	–			
6	93.5	2.5	4	Mg	96	2.5	1.5	3.202(6)		5.201(4)
				$Mg_{17}Sr_2$	91.0	3.4	5.6	10.539(7)		10.354(9)
7	88.5	2.5	9	$Mg_{17}Sr_2$	–	–	–	10.470		10.402
				$Mg_{38}Sr_9$	–	–	–	10.600		28.256
8	77.5	2.5	20	$Mg_{23}Sr_6$	–	–	–	14.914		
				Mg_2Sr	–	–	–	6.385(7)		10.600
9	69.5	2.5	28	$Mg_{23}Sr_6$	–	–	–	14.904		
				Mg_2Sr	–	–	–	6.490(4)		10.485(3)
10	57.5	2.5	40	Mg_2Sr	–	–	–	6.502		10.483(6)
				Ce	–	–	–	5.147(4)		
				Sr	–	–	–	6.084		
11	90.2	6	3.8	$Mg_{12}Ce$	90.8	5.1	4.1	10.344(2)		5.920(8)
				$Mg_{17}Sr_2$	89.9	3.4	6.7	10.533(5)		10.357(9)
				$Mg_{41}Ce_5$	–	–	–	14.835		10.421
12	86.4	9.6	4	$Mg_{38}Sr_9$	82.9	4.2	12.9	10.434(1)		28.22
				$Mg_{41}Ce_5$	88.9	7.5	3.6	14.628		10.238(1)
				Mg_3Ce	77.2	22.8	0	7.451(1)		
13	79.3	14.5	6.2	$Mg_{38}Sr_9$	82.7	4.1	13.2	10.379		28.184
				$Mg_{23}Sr_6$	79.2	3.7	17.1	14.889(1)		
				Mg_3Ce	74.6	25.4	0	7.445		
14	74	18	8	Mg_3Ce	74.9	25.1	0	7.433(1)		
				$Mg_{23}Sr_6$	79.2	3.7	17.1	14.867(2)		10.516(5)
				Mg_2Sr	67.7	2.8	29.5	6.429(4)		
15	55.7	31	13.3	MgCe	47.7	51	1.3	3.8981		
				Mg_2Sr	64.9	6.7	28.4	6.473(2)		10.417(5)
16	43.3	39.7	17	MgCe	49.3	49.5	1.2	3.9165(1)		
				Mg_2Sr	–	–	–	6.4384(8)		10.513
				Ce	6.1	93.9	0	5.120(3)		
17	41	48	11	MgCe	–	–	–	3.928(1)		
				Mg_2Sr	–	–	–	6.414(6)		10.533
				Ce	–	–	–	5.134(1)		
18	64	25	11	Mg_3Ce	–	–	–	7.476(1)		
				Mg_2Sr	–	–	–	6.417(3)		10.351
				MgCe	–	–	–	3.896		
19	74	11	15	Mg_3Ce	–	–	–	7.430(1)		
				Mg_2Sr	–	–	–	6.452(6)		10.461(7)
				$Mg_{23}Sr_6$	–	–	–	14.860(2)		
20	89	5	6	$Mg_{38}Sr_9$	–	–	–	10.487(3)		28.177(5)
				$Mg_{17}Sr_2$	–	–	–	10.525(6)		10.346
				$Mg_{41}Ce_5$	–	–	–	14.790(4)		10.425(4)

(Japan) with Cu-Kα radiation at 40 kV and 200 mA of current. Si powders (99.9 wt.% purity) were added into each sample as an internal standard to calculate the lattice parameter of the observed phases. The XRD patterns of alloys were analyzed by Jade 5.0 with the PDF database [17].

Field emission scanning electron microscope with energy dispersive spectroscopy (SEM/EDS) measurement was carried out using a Hitachi/Oxford SU-8000/X-MAX80 (Japan/Britain). Phase compositions were determined according to the average value of 5–10 EDS data per phase.

3. Results and discussion

Five binary alloys in the Ce—Sr system and 15 ternary alloys annealed at 400 °C were analyzed by XRD and SEM/

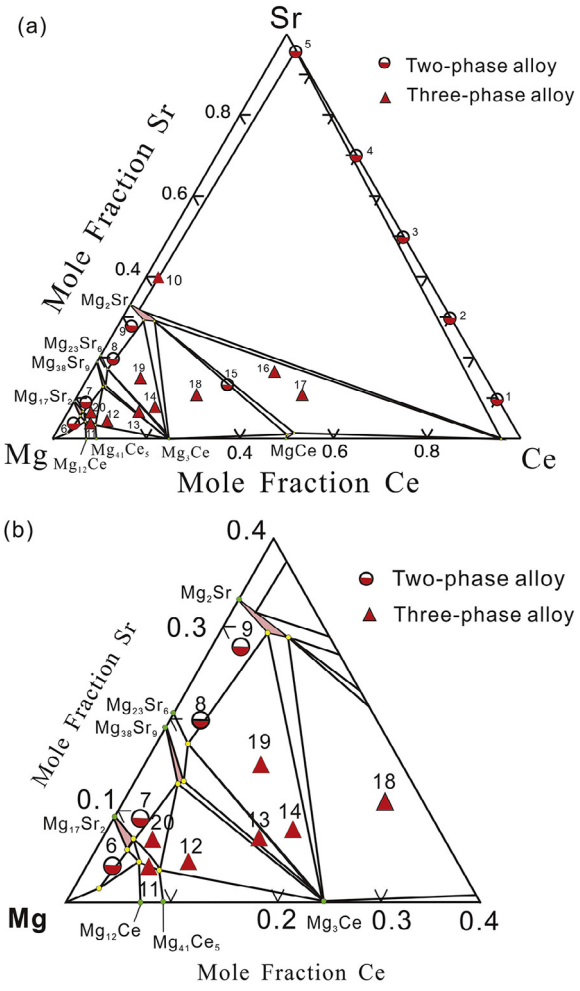

Fig. 2. Experimental isothermal section at 400 °C of the Mg—Ce—Sr system: (a) whole composition range, (b) enlarged part in Mg-rich corner.

EDS. The nominal compositions of the investigated alloys are listed in Table 2 together with all phases identified by XRD and composition of phase measured by EDS.

Five binary alloys were prepared in the Ce—Sr system. These samples were performed with XRD measurement and their XRD patterns showed the five samples all consisting of (γCe) and (αSr) only. A representative XRD pattern of Ce—Sr binary alloys (the alloy 2# Ce70Sr30) is presented in Fig. 1 which shows the XRD patterns consisting of (γCe) and (αSr) phases. No any new binary compound was observed in the Ce—Sr system.

Among the 15 alloys in Mg—Ce—Sr system, 5 ternary alloys were located at two-phase region and 10 ternary alloys were located at three-phase region. No any ternary compound was detected in the Mg—Ce—Sr system at present work. Based on all the present experimental data listing in Table 2, the isothermal section of the Mg—Ce—Sr system at 400 °C was deduced and presented in Fig. 2. The whole isothermal section with experimental data is shown in Fig. 2(a), the half full round dot represents two-phase alloys and the full triangle represents three-phase alloys. Fig. 2(b) shows the enlarge phase diagram of Mg-rich corner at 400 °C with experimental data.

The most striking feature of the phase diagram is (αSr) equilibrium with (γCe) and Mg_2Sr, which occupies large area in Sr-rich phase. This phase region was first proved by XRD pattern of alloy 10 and it consisted of Mg_2Sr + (αSr) + (γCe), but the patterns of (γCe) are weak since the amount of (γCe) in alloy 10 was small. The phase region was further indirectly proved by the alloys 16 and 17. Fig. 3 presents the XRD patterns of alloy 16 and it clearly shows that this alloy consists of MgCe, Mg_2Sr and γCe three phases.

The other six of three-phase regions at Mg-rich corner were directly detected by the other alloys, such as: $Mg_{12}Ce$ +

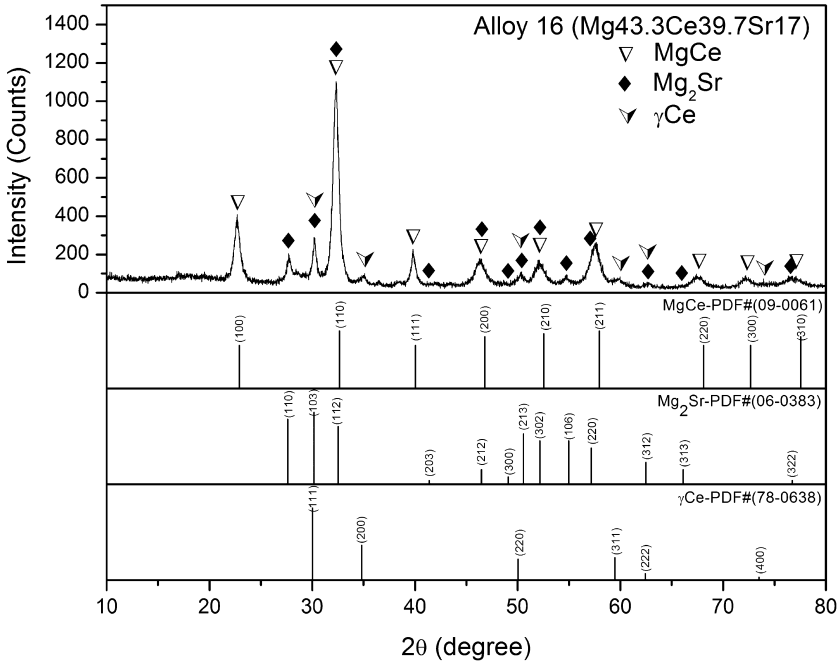

Fig. 3. XRD patterns of alloy 16 (Mg43.3Ce39.7Y17) annealed at 400 °C for 30 days, consist of MgCe, Mg_2Sr and γCe three phase.

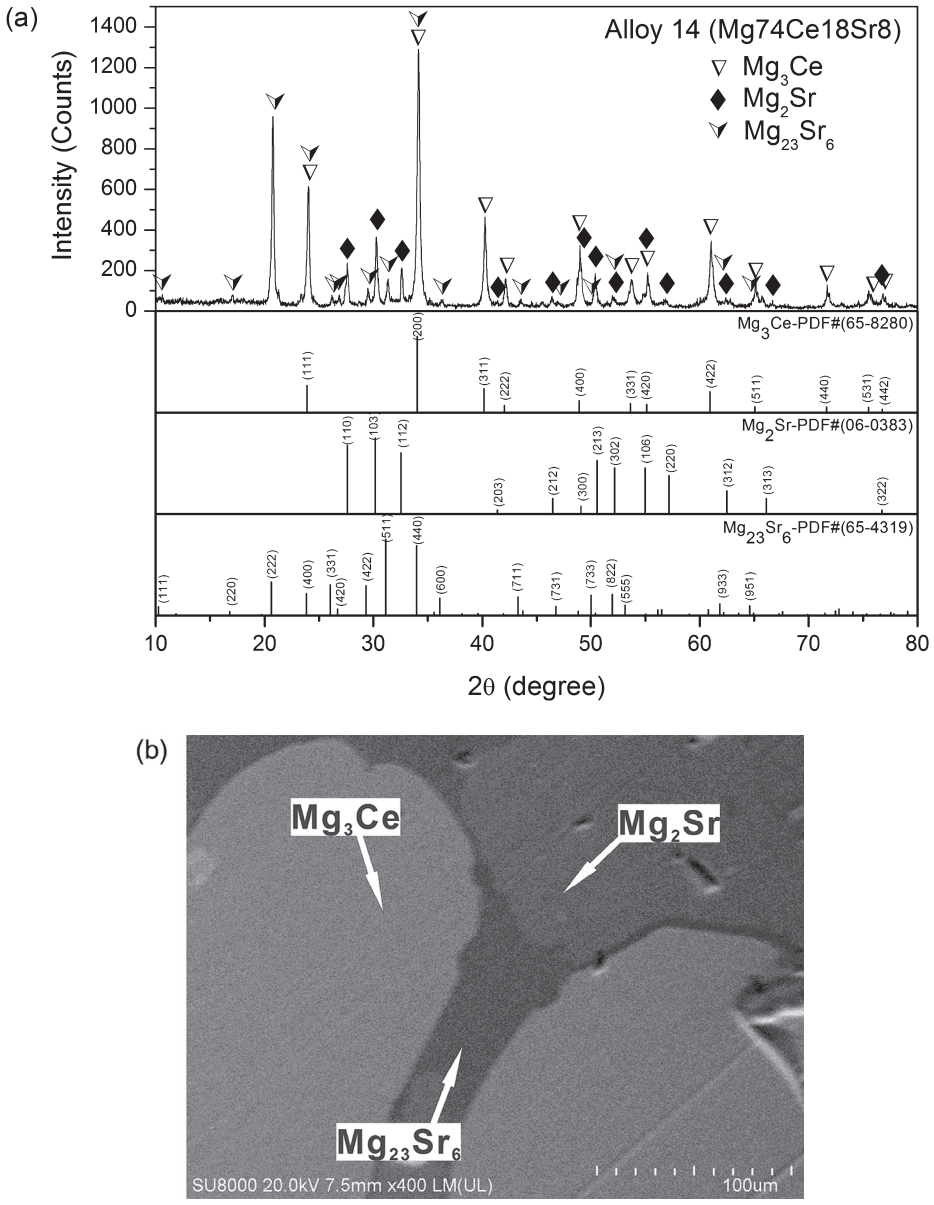

Fig. 4. Alloy 14 (Mg74Ce18Y8) annealed at 400 °C for 30 days: (a) XRD patterns contain with Mg_3Ce, Mg_2Sr and $Mg_{23}Sr_6$; (b) micrograph picture of alloy 14 show Mg_3Ce (gray), Mg_2Sr (dark gray) and $Mg_{23}Sr_6$ (black) three phase coexistence.

$Mg_{17}Sr_2 + Mg_{41}Ce_5$ (alloy 11), $Mg_{38}Sr_9 + Mg_{41}Ce_5 + Mg_3Ce$ (alloy 12), $Mg_{38}Sr_9 + Mg_{23}Sr_6 + Mg_3Ce$ (alloy 13), $Mg_2Sr + Mg_{23}Sr_6 + Mg_3Ce$ (alloy 14 and 19), $Mg_2Sr + Mg_3Ce + MgCe$ (alloy 18), $Mg_{38}Sr_9 + Mg_{17}Sr_2 + Mg_{41}Ce_5$ (alloy 20). The $Mg_{17}Sr_2 + (Mg) + Mg_{12}Ce$ were not observed directly and deduced from binary phase and present experimental data.

The XRD patterns and SEM micrograph image of a reprehensive ternary alloy 14 are shown in Fig. 4(a) and (b), respectively. The XRD patterns show this alloy consisted of $Mg_2Sr + Mg_{23}Sr_6 + Mg_3Ce$ phases and its SEM picture showing that the alloy contain three phase as Mg_3Ce (gray phase), Mg_2Sr (dark gray phase) and $Mg_{23}Sr_6$ (black phase).

The Mg_2Sr (Mg64.9Ce6.7Sr28.4) were detected to contain 6.7 at.% Ce from EDS data of alloy 15 and from the composition we could deduce that Ce can substitute Sr in Mg_2Sr phase. The other binary phases $Mg_{23}Sr_6$, $Mg_{38}Sr_9$, $Mg_{17}Sr_2$ in Mg—Sr system were observed dissolving about 3–4 at.% Ce and Ce mainly substituting Sr also. Two binary phases $Mg_{12}Ce$ and $Mg_{41}Ce_5$ in Mg—Ce system were detected to contain about 3–4 at.% Sr and Sr mainly substitutes Ce. The solubility of Sr in MgCe (Bcc_B2) is small and only about 1 at.% Sr was detected.

4. Conclusions

The isothermal section at 400 °C of the Mg—Ce—Sr system over the entire composition range is established. No any new binary compound and ternary compound were observed in the Ce—Sr binary system and the Mg—Ce—Sr ternary system, respectively. However, nine three-phase regions have been experimentally observed. Six binary phases Mg_2Sr, $Mg_{23}Sr_6$,

$Mg_{38}Sr_9$, $Mg_{17}Sr_2$, $Mg_{12}Ce$, $Mg_{41}Ce_5$ are detected dissolving about 3–7 at.% the third element.

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