

# EXPERIMENTAL DETERMINATION OF THE PHASE EQUILIBRIUM IN THE Mg-Ca-Y SYSTEM

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## Abstract

In the present work, isothermal section of the Mg-Ca-Y system at 400°C was studied using solid-solid diffusion couples and key alloys annealed for four weeks. The presence of phases, solubility limits and phase relations were determined by scanning electron microscope coupled with energy dispersive X-ray spectrometer. The solid solubility range of the phases present in the key alloys was ascertained by X-ray diffraction using Rietveld analysis and Pearson's crystal database. The solubility limit of Y in Mg<sub>2</sub>Ca was determined as 6.9 at.% where Ca is substituted by Y. The extended solid solubilities of Ca in Mg<sub>24</sub>Y<sub>5</sub> and Ca in MgY were determined as 3.4 at.% and 3.7 at.%, respectively. Based on the experimental results, partial isothermal section of the ternary system was constructed to provide useful information for aerospace, automotive and biomaterial applications.

Keywords: Mg alloys, Mg-Ca-Y, phase diagram, diffusion couple.

## 1. Introduction

Magnesium is the lightest structural metal with a density of 1.74 g/cm<sup>3</sup> as compared to other structural metals like Aluminum (2.70 g/cm<sup>3</sup>) and Iron (7.86 g/cm<sup>3</sup>). Apart from the low density, Mg possesses best strength to weight ratio and excellent die-casting characteristics. Due to these inherent properties, Mg based alloys are particularly attractive for transportation applications. Calcium was reported to be effective in promoting ductility, and strength, cast ability, creep and corrosion resistance [1-3] of Mg alloys. The ignition temperature of Mg is also increased by Ca addition [4], thereby providing safer materials for automobile and aerospace applications [5]. One of the disadvantages of alloying Mg with Ca alone is that ignition of Mg cannot be prevented completely while melting. This causes brittleness of the alloy [6]. Thus, in order to further improve the properties of binary Mg-Ca alloy, addition of Y was attempted in this work.

To date, no sufficient work on the experimental study of the phase diagram of Mg-Ca-Y ternary system could be found in the literature. However, Li et al. [7] studied the potential application of Mg-1Ca-1Y as a biomaterial. They compared microstructure, mechanical properties such as the compressive strength, elastic modulus, ductility, hardness and corrosion resistance of Mg-1Ca-1Y with the Mg-xCa (x = 0.5, 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 at.%) binary alloys. The biocompatibility of these two alloys was also tested in simulated body fluids (SBF) and modified minimal essential medium (MEM). It was concluded that the addition of less than 1 at.% Ca to Mg leads to improvement in compressive strength, elastic modulus and hardness while ductility decreased. In addition, the ductility could be improved by adding Y. These findings, however, revealed that, the addition of Y to Mg-Ca leads to lowering the corrosion resistance. It was also concluded by Steinemann et al. [8] that addition of Y to Mg-Ca leads to a reduction in the biocompatibility of the alloy. But Okazaki et al. [9] reported the successful in-vitro application of the Mg-Y based alloys. They investigated the short term effects of Mg-RE based alloys,

including Mg-Y alloys on the primary cells and cell lines. The performance of Y was found to be comparable to that of Dy and they did not observe any hypo toxicity. Hence, there are contradictions in the literature over the biocompatibility of Y based Mg alloys. As such, no experimental work or thermodynamic modelling was found in the literature which studied the phase diagram of this system.

## 2. Experimental Procedure

Four diffusion couples and twenty-two key samples were prepared to map the isothermal section at 400°C based on the critical assessment of preliminary thermodynamic model of the Mg-Ca-Y system. In particular, one solid-solid diffusion couple and two key samples were presented in this paper. The starting materials were Mg (purity 99.98%), Ca (99.99%) and Y (99.9%) ingots supplied by Alfa Aesar. The key alloys were initially prepared in water cooled arc-melting furnace in Copper crucible using a non-consumable tungsten electrode. In case of alloys with relatively less amount of Y (up to 30 at.%), The samples were crushed during the first two times melting and each sample was re-melted at least for five times to ensure the homogeneity. For alloys in Y rich corner of the phase diagram, binary master alloys of Mg and Y were prepared first in arc-melting furnace by melting the samples at least for four times. This could considerably reduce the melting temperature of Y by formation of intermediate binary intermetallic compound. Later on, Ca was added and mixed with the master alloy and the composition was re-melted in induction melting furnace to get a homogeneous alloy. To prepare solid-solid diffusion couples, the contacting surfaces were grinded down to 1200 grit SiC paper and polished using oxide polishing suspension (OPS) with 99% pure ethanol as lubricant. The two terminal members were carefully pressed together and clamped using a steel ring, wrapped in a Ta foil, and sealed in a quartz tube filled with argon. The encapsulated samples were then annealed at 400°C for 4 weeks followed by quenching in water.

The phase compositions, phase relations and homogeneity ranges were studied using scanning electron microscope (SEM) (S-3400N) and energy dispersive X-ray spectrometer (EDS). The analysis of samples was carried out with a 15kV accelerating voltage and 50mA probe current. X-ray diffraction (XRD) was used for phase analysis and determination of the solubility limits in the key alloys. The XRD patterns were obtained using PANalytical X'pert Pro powder X-ray diffractometer with a  $\text{CuK}\alpha$  radiation at 45kV and 40mA. The XRD spectrum was acquired from 20 to 120° 2 $\theta$  with a 0.01° step size. XRD study of the samples was carried out using X'Pert HighScore Plus Rietveld analysis software in combination with Pearson's crystal database [10]. Standard Si was used to calibrate the zero shift and specimen displacement.

## 3. Results and Discussion

### 3.1 Determination of the Isothermal Section at 400°C via Diffusion Couple

Backscatter electron images (BSEI) of the solid-solid diffusion couple annealed at 400°C for four weeks are shown in Figs. 1a-d. One of the end members ( $\text{Mg}_{50}\text{Ca}_2\text{Y}_{48}$ ) is a two phase region consisting of  $\text{Mg}_2(\text{Ca},\text{Y})$  and MgY (Fig. 1b). The other end member ( $\text{Mg}_{74}\text{Ca}_{24}\text{Y}_2$ ) is also a two phase region comprising of Mg and  $\text{Mg}_2\text{Ca}$  (Fig. 1c). Extensive inter-diffusion of Mg, Ca and Y occurred and formed several layers during heat treatment. Spot analysis was carried out to identify the various formed phases present in the diffusion couple. Taking advantage of the local equilibrium at the interface of different layers, the sequence of phases formed (from right to left) was identified as:  $\text{Mg}_2\text{Y} + \text{MgY} \rightarrow \text{Mg}_2(\text{Y},\text{Ca}) \rightarrow \text{Mg}_2(\text{Ca},\text{Y}) \rightarrow \text{Mg} + \text{Mg}_2\text{Ca}$ .

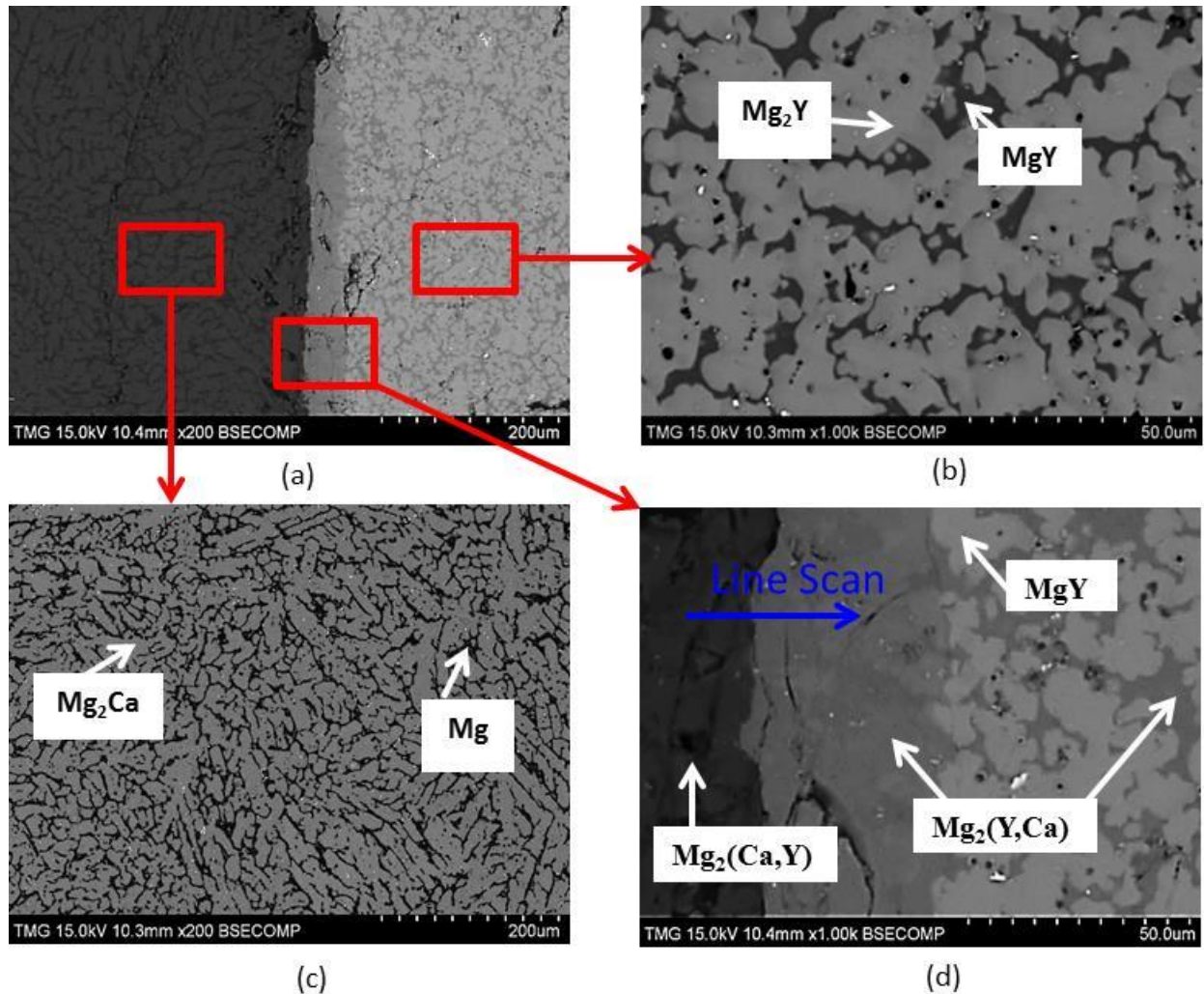


Fig.1(a) BSEI of DC after annealing for four weeks at 400°C,(b) BSEI of end member  $Mg_{50}Ca_2Y_{48}$ ,(c) BSEI of end member  $Mg_{74}Ca_{24}Y_2$  (d) Enlarged image of interface of the diffusion layer with the SEM line scan.

In this diffusion couple,  $Mg_2Ca$  and  $Mg_2Y$  were two binary compounds with extended solubility into ternary system. Due to similar atomic radius, electronegativity and valence electrons of Ca and Y, substitutional ternary solid solutions were formed in both the  $Mg_2Ca$  and  $Mg_2Y$  binary compounds, i.e.  $Mg_2(Ca,Y)$  and  $Mg_2(Y,Ca)$ , respectively. In order to determine the ternary solubility limits of the  $Mg_2Ca$  and  $Mg_2Y$  binary compounds, a 40  $\mu m$  length SEM line scan was carried out as shown in Fig.1d. The results of the line scan were studied by a least square approximation method, as shown in Fig. 2. It could be concluded that  $Mg_2(Ca,Y)$  forms substitutional solid solution in which Y substitutes Ca at constant Mg and the solubility limit of Y in  $Mg_2Ca$  is 6.9 at.%. Similarly, the solubility limit of Ca in  $Mg_2Y$  is 8.4 at.%.

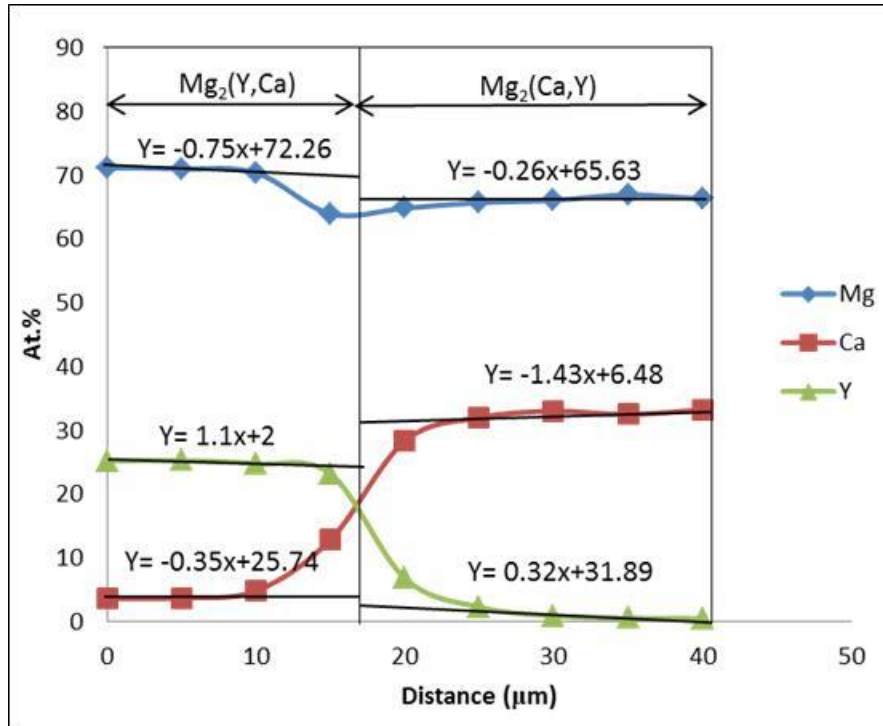


Fig.2 Composition profile of the line scan.

### 3.2 Determination of the Isothermal Section at 400°C Using Key Alloys

The diffusion couple approach is a high through-put technique. However, certain issues can happen during studying phase diagrams, such as the missing phase, which is not formed during nucleation or the formed layer is too thin to be detected by SEM [11]. This can result in inaccuracies in estimating tie-line compositions for these phases, because it is difficult to extrapolate to the interface based on a few data points. In order to overcome this uncertainty, a combined investigation with key alloys was followed. Key alloys provide a wide range of information regarding the phase identification, phase boundaries and phase relationships in a system. They also provide valuable information regarding the presence and solubility of ternary compounds. In the current work, nominal compositions of key alloys were used for the analysis. Based on the analysis of the preliminary thermodynamic model of the Mg-Ca-Y phase diagram, the compositions of key alloys were selected.

Fig. 3a shows the BSEI of Key alloy No. 1 with nominal composition of  $Mg_{63}Ca_{10}Y_{27}$  annealed for four weeks at 400°C. This sample was shown in a two-phase region, Mg+Mg<sub>2</sub>Ca. The Mg<sub>2</sub>Ca phase with primary dendrite structure was formed first and the solidification of this sample was terminated by forming Mg. Mg<sub>2</sub>Ca was found to have extended ternary solubility of Y. The solubility of Y in the binary compound Mg<sub>2</sub>Ca was found to be 4.2 at. %. The value determined from this sample is not the limit of ternary solubility of Mg<sub>2</sub>Ca as obtained from the previous finding of diffusion couple (i.e. 6.9 at.% of Y).

The XRD analysis of the alloy annealed at 400°C was carried out using powder technique. The XRD pattern is presented in (Fig. 3b). It could be seen that the results of XRD and SEM/EDS are in good agreement in terms of the phases present and phase amount. As shown in Fig. 3b, peak

shift was observed for the  $Mg_2Ca$  binary compound. The lattice parameters of the two phases present in this key alloy are presented in Table I. Compared to the standard binary  $Mg_2Ca$ , where  $a = 6.253\text{\AA}$  and  $c = 10.144\text{\AA}$  [12], the lattice parameters  $a = 6.228\text{\AA}$  and  $c = 10.087\text{\AA}$  were determined for this  $Mg_2(Ca,Y)$  solid solution, indicating the shift of peaks towards to the higher values of  $2\theta$ . This can be explained due to the formation of substitutional solid solution of  $Mg_2(Ca,Y)$ . Since the diameter of Y is smaller than that of Ca, when Y substitutes Ca, the lattice spacing  $d$  decreases. According to the Bragg's Law, as  $d$  decreases,  $2\theta$  tends to increase. The reliability factors for the XRD analysis were used to study the accuracy between the Rietveld analysis and the experimental XRD pattern, as listed in Table I. The  $R_e$  and  $R_{wp}$  factors were ascertained to be well within the permissible limits and goodness of fit  $s$  was simulated closed to 1 by Rietveld analysis.

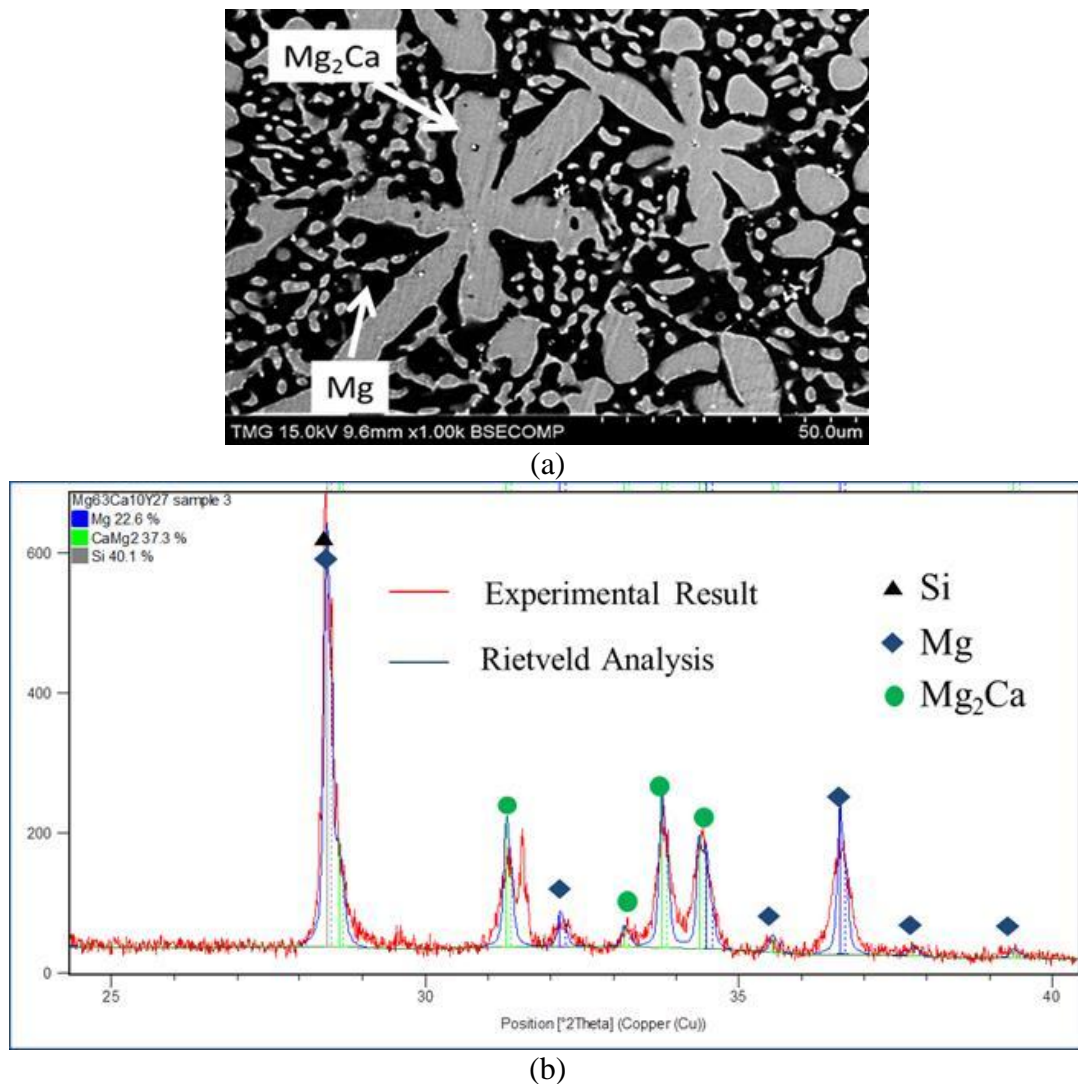


Fig. 3 (a) BSEI of Key alloy  $Mg_{63}Ca_{10}Y_{27}$  annealed for four weeks at  $400^\circ\text{C}$ . (b) XRD analysis of the key alloy.

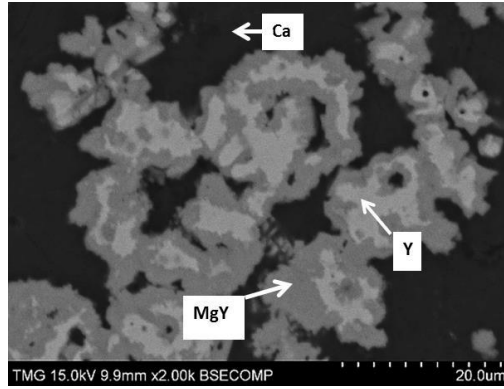
Table I. SEM/EDS data on selected Mg-Ca-Y samples compared with XRD results.

Sample No.	Nominal Composition (at. %)			Phases Identified by SEM	Phases Identified by XRD	Lattice parameters (Å)		Reliability Factors		
	Mg	Ca	Y			<i>a</i>	<i>c</i>	<i>R<sub>e</sub></i>	<i>R<sub>wp</sub></i>	<i>s</i>
1	63	10	27	Mg Mg <sub>2</sub> Ca	Mg Mg <sub>2</sub> Ca	3.209 6.228	5.207 10.087	17.156	21.729	1.604
2	20	30	50	Ca MgY Y	Ca MgY Y	5.431 3.807 3.655	5.431 3.807 5.762	16.723	27.59	2.721

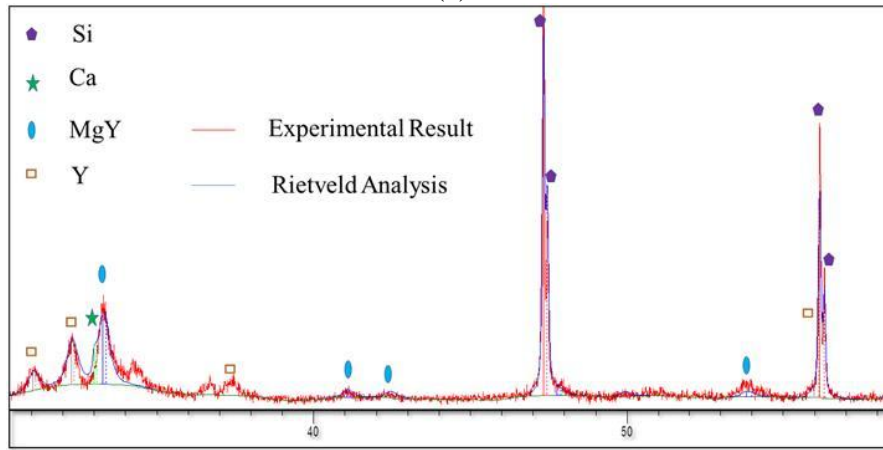
<sup>a</sup>Reliability factors: *s* is the goodness of fit, *R<sub>wp</sub>* is the weighted summation of the residuals of the least-squares fit and *R<sub>e</sub>* is the statistically expected value.

In order to study the Y-rich corner of the phase diagram, the key alloy (No. 2) with nominal composition Mg<sub>20</sub>Ca<sub>30</sub>Y<sub>50</sub>(Table I) was prepared and annealed for four weeks at 400°C. Fig. 4a shows the BSE image of this alloy. The equilibrium microstructure consists of three phases Ca, MgY and Y. Among the three phases present in this alloy, the Y phase with composition of Mg<sub>6.2</sub>Ca<sub>3.3</sub>Y<sub>90.5</sub> was solidified first followed by the formation of MgY during peritectic reaction, and then the solidification ends up with the formation of Ca. The MgY phase formed substitutional solid solution where Ca substitutes Y. Spot analysis of the alloy revealed that the solubility of Ca in MgY is 3.9 at. %.

The XRD pattern for the alloy is shown in Fig. 4b. As seen in Table I, the XRD results show a good consistency with the SEM findings. The lattice parameters of the two phases present and the reliability factors in this key alloy are also presented in Table I. Peak shift was observed for the MgY binary compound (Fig. 4b). Compared with the standard binary MgY, where *a* = 3.797 Å [13], the lattice parameter *a* = 3.807 Å for this Mg(Y,Ca) solid solution is slightly increased, indicating the shift of peaks towards to the lower values of 2θ. This can be explained due to the formation of substitutional solid solution of Mg(Y,Ca). Since the diameter of Ca is larger than that of Y, when Ca substitutes Y, the lattice spacing *d* increases and 2θ decreases. In addition, the phase Mg<sub>6.2</sub>Ca<sub>3.3</sub>Y<sub>90.5</sub> consists of solubility of Mg and Ca in Y. The SEM analysis revealed that this phase has a complex solid solution, where Y is substituted by both Ca and Mg. Based on the results of the diffusion couples and key alloys, the partial isothermal section of Mg-Ca-Y system at 400°C was constructed as shown in Fig. 5.



(a)



(b)

Fig. 4 (a) BSEI of Key alloy  $Mg_{20}Ca_{30}Y_{50}$  annealed for four weeks at  $400^{\circ}C$ . (b) XRD analysis of the key alloy.

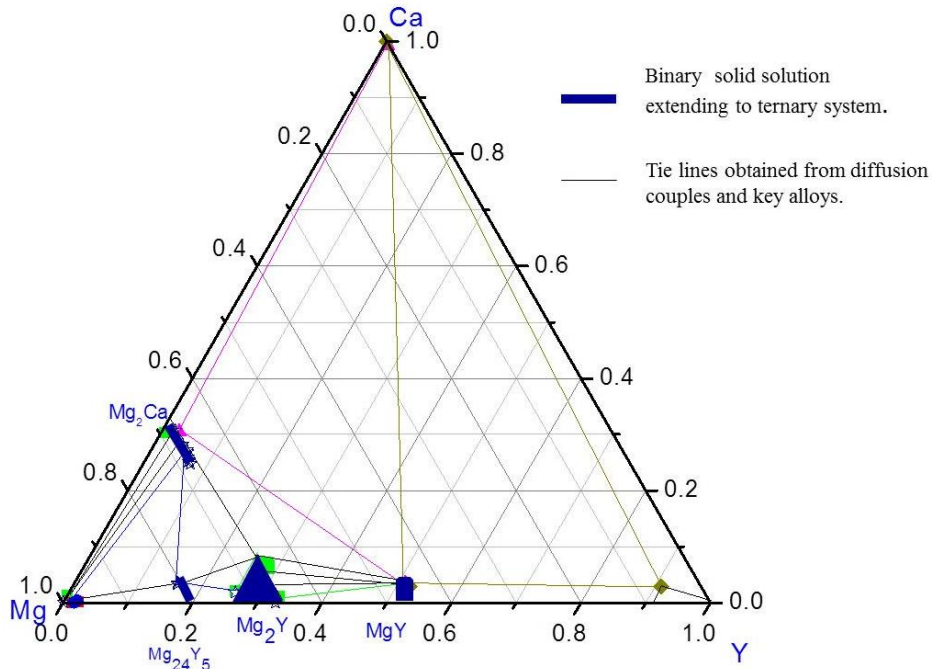


Fig. 5 Partial Isothermal section of Mg-Ca-Y at  $400^{\circ}C$ .

#### 4. Summary

A comprehensive investigation of the Mg-Ca-Y system was studied by a high-throughput diffusion couple technique combined with equilibrated key alloys. SEM and XRD were used to determine the phase relations and solubility limits. Rietveld analysis has been carried out for the XRD results. Four binary compounds, Mg<sub>2</sub>Ca, Mg<sub>24</sub>Y<sub>5</sub>, Mg<sub>2</sub>Y and MgY were found to have solid solution extending to ternary system. The extended solubility of Mg<sub>2</sub>Ca and Mg<sub>2</sub>Y was determined and the solubility limit of Ca in MgY was established. Based on the results of diffusion couples and key alloys, the partial isothermal section was constructed at 400°C.

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