Experimental study of the crystal structure of the Mg$_{15-x}$Zn$_x$Sr$_3$ ternary solid solution in the Mg–Zn–Sr system at 300 °C

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A R T I C L E   I N F O

Article history:
Received 8 April 2015
Received in revised form 4 July 2015
Accepted 6 July 2015
Available online 15 July 2015

Keywords:
Ternary compound
Mg alloys
Phase diagram
Crystal structure
X-ray
SEM/EDS
EPMA

A B S T R A C T

A new ternary compound, Mg$_{15-x}$Zn$_x$Sr$_3$ with extensive solid solubility in the Mg–Zn–Sr system was observed and studied using electron probe microanalysis (EPMA), scanning electron microscopy SEM, and X-ray techniques. The solid solubility limits of this compound were found to be Mg$_{15-x}$Zn$_x$Sr$_3$ (0.24 ≤ x ≤ 10.58, at.%) at 300 °C using a diffusion couple and several equilibrated alloys. Analysis of the X-ray diffraction (XRD) patterns was carried out by Rietveld method. XRD data has shown that this solid solution crystallizes in the hexagonal P6$_3$/mmc (194) space group with the Ni$_1$Si$_4$Sc$_3$ prototype. The lattice parameters decrease linearly with decreasing Mg content. The fractional atomic occupancy of the 6h, 6g, 4f, 2b and 12k sites of this compound are function of Mg content.

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1. Introduction

Magnesium-based alloys are widely used in the automotive and aeronautic industries because magnesium is the lightest structural material with a density of about 1.80 g/cm$^3$. This interest in magnesium alloys arises from their low density, potentially high strength/weight ratios, good processing properties, and near complete recycling potential [1–4]. Actually, their high strength-to-weight ratio makes them even more attractive than steels [5] and plastics in many applications. The Mg–Zn series is the first hardenable Mg-based alloys developed for structural materials [6–9]. The solid solubility of Zn in the Mg (hcp) phase and the considerable amount of secondary precipitates in the Mg matrix can produce a very good age-hardening effect [10]. Unfortunately, the Mg–Zn series has the same problem as the Mg–Al series (but not the AE series), that is, poor mechanical properties at elevated temperatures which restrict their applications [2]. Recently, strontium has drawn much attention [11–14] as an important additive in Mg-based alloys for improving relatively high temperature mechanical properties. According to Baril et al. [14], the micro-alloying of strontium in magnesium alloys (e.g., Mg–Zn, Mg–Al based alloys) permits to obtain superior creep performance and excellent high-temperature properties. Moreover, Hirai et al. [15] reported that by adding Sr, high strength and improved creep resistance could be obtained for cast AZ91 magnesium alloy. For Nakaura et al. [16], Sr additions can also help to reduce the hot-cracking effect of Ca containing Mg–Al based alloys. Recently, Mg–Zn–Sr alloys were found to have a low degradation rate and moderate mechanical properties, which makes them potential biodegradable alloy candidates [17,18].

In the ternary Mg–Zn–Sr system, the phase diagrams of the three bounding binaries (Mg–Zn [19], Mg–Sr [20] and Zn–Sr [21]) have been satisfactorily investigated; the final accepted versions of each binary phase diagram are shown in Fig. 1. The phase diagram of the Mg–Zn binary system shows 5 intermetallic compounds, Mg$_2$Zn$_{11}$, Mg$_5$Zn$_{12}$, Mg$_{17}$Zn$_{13}$, Mg$_{51}$Zn$_{20}$, and two terminal solid solutions, hcp (Mg) and hcp (Zn). It is worth noting that the Mg$_{51}$Zn$_{20}$ compound is only stable between 325 and 342 °C. The phase diagram of the Mg–Sr binary system consists of 7 phases: hcp (Mg), fcc (Sr), bcc (Sr), Mg$_5$Sr$_7$, Mg$_{12}$Sr$_3$, Mg$_{51}$Sr$_{20}$, and two terminal solid solutions, hcp (Mg) and hcp (Zn), it is worth noting that the Mg$_{51}$Sr$_{20}$ compound is only stable between 325 and 342 °C. The phase diagram of the Mg–Sr binary system consists of 7 phases: hcp (Mg), fcc (Sr), bcc (Sr), Mg$_5$Sr$_7$, Mg$_{12}$Sr$_3$, Mg$_{51}$Sr$_{20}$, and two terminal solid solutions, hcp (Mg) and hcp (Zn), it is worth noting that the Mg$_{51}$Sr$_{20}$ compound is only stable between 325 and 342 °C. The phase diagram of the Mg–Sr binary system consists of 7 phases: hcp (Mg), fcc (Sr), bcc (Sr), Mg$_5$Sr$_7$, Mg$_{12}$Sr$_3$, Mg$_{51}$Sr$_{20}$, and two terminal solid solutions, hcp (Mg) and hcp (Zn).
Since Sr is promising as an important alloying element for Mg-based alloys (such as the Mg–Zn and Mg–Al series), a thorough understanding of the phase equilibria in the Mg–Zn–Sr ternary system is much needed. In this paper, the isothermal section at 300 °C is studied by a diffusion couple and several equilibrated key samples, as described in the following section. To this end, the solid solubility and crystal structure of the new Mg$_{15-\chi}$Zn$_\chi$Sr$_3$ ternary solid solubility limits at 300 °C is studied in the present work for the first time using EDS, EPMA, X-ray, and Rietveld techniques, which is a part of a wider thermodynamic database development project for the Mg–Zn–X (X: Ag, Ca, In, Li, Na, Sr, and Zn) multi-component systems [24–28].

2. Experimental procedures

The solid solubility limits of the Mg$_{15-\chi}$Zn$_\chi$Sr$_3$ phase were determined using a diffusion couple with Mg–Mg$_{25}$Zn$_{55}$Sr$_{20}$ (at.%) alloy as end-members and with 9 key samples; it is should be noted that all the compositions of samples and their constituted phases were designated in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Alloy nominal composition (at.%)</th>
<th>Phase equilibria</th>
<th>Measured equilibrium phase compositions determined by EPMA (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phase 1/Phase 2/Phase 3</td>
<td>Phase 1 (Mg$<em>{11}$Zn$</em>\chi$Sr$_3$)</td>
<td>Phase 2</td>
</tr>
<tr>
<td>A1</td>
<td>Mg$_{82}$Zn$<em>3$Sr$</em>{15}$</td>
<td>Mg$<em>{15-\chi}$Zn$</em>\chi$Sr$<em>3$/Mg$</em>{17}$Sr$<em>2$/Mg$</em>{38}$Sr$_9$</td>
<td>81.6</td>
</tr>
<tr>
<td>A2</td>
<td>Mg$_{82}$Zn$<em>3$Sr$</em>{12}$</td>
<td>Mg$<em>{15-\chi}$Zn$</em>\chi$Sr$<em>3$/Mg$</em>{17}$Sr$_2$</td>
<td>81.4</td>
</tr>
<tr>
<td>A3</td>
<td>Mg$_{82}$Zn$<em>3$Sr$</em>{10}$</td>
<td>Mg$<em>{15-\chi}$Zn$</em>\chi$Sr$<em>3$/Mg$</em>{17}$Sr$_2$</td>
<td>77.0</td>
</tr>
<tr>
<td>A4</td>
<td>Mg$<em>{82}$ZnxSr$</em>{15}$</td>
<td>Mg$<em>{15-\chi}$Zn$</em>\chi$Sr$<em>3$/Mg$</em>{17}$Sr$_2$</td>
<td>73.2</td>
</tr>
<tr>
<td>A5</td>
<td>Mg$<em>{82}$ZnxSr$</em>{15}$</td>
<td>Mg$<em>{15-\chi}$Zn$</em>\chi$Sr$<em>3$/Mg$</em>{17}$Sr$_2$</td>
<td>69.0</td>
</tr>
<tr>
<td>A6</td>
<td>Mg$_{30}$Zn$<em>3$Sr$</em>{15}$</td>
<td>Mg$<em>{15-\chi}$Zn$</em>\chi$Sr$<em>3$/Mg$</em>{17}$Sr$_2$</td>
<td>60.0</td>
</tr>
<tr>
<td>A7</td>
<td>Mg$_{25}$Zn$<em>3$Sr$</em>{15}$</td>
<td>Mg$<em>{15-\chi}$Zn$</em>\chi$Sr$<em>3$/Mg$</em>{17}$Sr$_2$/IM2*</td>
<td>39.6</td>
</tr>
<tr>
<td>A8</td>
<td>Mg$_{25}$Zn$<em>3$Sr$</em>{15}$</td>
<td>Mg$<em>{15-\chi}$Zn$</em>\chi$Sr$_3$/IM2*</td>
<td>33.8</td>
</tr>
<tr>
<td>A9</td>
<td>Mg$_{25}$Zn$<em>3$Sr$</em>{15}$</td>
<td>Mg$<em>{15-\chi}$Zn$</em>\chi$Sr$_3$/IM4*/IM5*</td>
<td>24.9</td>
</tr>
</tbody>
</table>

* Note: IM2 to IM5 are new found phases which have been analyzed, and the identification results will be published in an upcoming paper.
in the present work using atomic percentage at.%. their nominal compositions are shown in Fig. 1 and given in Table 1. The diffusion end-members and key alloys were prepared from pure Mg (99.8 wt.%), Zn (99.5 wt.%), and Sr (99 wt.%) and melted in a frequency induction furnace under high purity argon atmosphere. The Sr pieces were kept in oil after weighing due to their high reactivity with oxygen. Before melting, each Sr piece was washed with 99 wt.% ethanol to remove the oil. In order to minimize the interaction of the samples with the crucibles, cubic-shaped crucibles were made using Ta foil (99.5 wt.% purity, 0.15 mm thickness). All the samples were melted in the induction furnace under

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**Fig. 2.** Backscattered electron image of the diffusion couple annealed at 300 °C for 3 weeks: a) overall diffusion microstructure of diffusion couple, (b) microstructure of end-member Mg$_{25}$Zn$_{55}$Sr$_{20}$, (c) magnification of the selected diffusion layers, and (d) compositions of the elements in the constituted phases analyzed by EDS.
argon atmosphere using this crucible. All samples were re-melted at least 3 times in order to obtain a homogenous microstructure. The Mg–Zn–Sr diffusion couple and all key samples were then sealed into quartz capsules under argon atmosphere and equilibrated at 300 °C for 21 and 35 days, respectively. Quenching was carried out in water without breaking the quartz tubes to prevent the oxidation of sample with water.

EPMA of the annealed samples was performed with JEOL 8900 probe using wavelength-dispersive spectroscopy (WDS). An accelerating voltage of 15 kV was used with a 20 nA beam current, a spot size of 2 μm and counting times of 20 s on peaks and 10 s on backgrounds. Raw data were reduced with the Phi-rho-Z (PRZ) correction using pure Mg, Zn metal and SrO standards. Phase relationships and constitutions of diffusion couples were determined using SEM equipped with energy-dispersive spectroscopy (EDS).

Crystal structures of the phases present in the annealed samples were identified by X-ray analysis. XRD patterns were obtained with the PANanalytical X’pert Pro powder X-ray diffractometer using CuKα radiation at 45 kV and 40 mA. The XRD patterns were acquired from 20 to 120° (2θ) with a 0.02° step size. Then the collected patterns were analyzed with the X’Pert HighScore plus Rietveld analysis software in combination with the Pearson’s crystal database[29]. The Si was used as an internal calibration standard enabled correcting the zero shift and specimen surface displacement which are the most serious systematic errors in X-ray powder diffraction patterns.

![Diagram](image)

**Fig. 3.** Diffusion paths, solid solubility and partial phase equilibrium relationships of Mg15−xZnxSr3 compound as determined in the present work (thin black lines present the tie(s) line between/among the equilibrated phases, and thick black lines present each single phase with extend solid solubility).

![Back-scattered images](image)

**Fig. 4.** Back-scattered (BSE) electron images of the typical ternary Mg–Zn–Sr alloys: (a) A4 (Mg78Zn7Sr15), (b) A8 (Mg35Zn55Sr10), (c) A1 (Mg83Zn1Sr16), and (d) A9 (Mg20Zn65Sr15) annealed at 300 °C for 35 days.
3. Results and discussions

3.1. Solid solution analysis

In order to obtain some knowledge of the equilibrium phase relationships in the Mg–Zn–Sr rich side (Sr ≤ 33 at.%) of the Mg–Zn–Sr ternary system at 300 °C, a solid–solid diffusion couple (designated D1) was prepared with end-members of Mg–Mg25Zn55Sr20 as can be seen in Fig. 1. Backscattered electron images of this diffusion couple annealed at 300 °C for 3 weeks are depicted in Fig. 2. As shown in Fig. 2a, several diffusion layers can be clearly observed. Unfortunately, the diffusion layer(s) at the Mg25Zn55Sr20 side was/were lost due to cracks that could not be avoided. However, the two-phase eutectic Mg15−xZnxSr3 + Zn2Sr could be observed in the end-member Mg25Zn55Sr20 (Fig. 2b). The magnification of the selected diffusion layers is shown in Fig. 2c. As can be seen in Fig. 2c, another new phase designated as IM1, which is equilibrated with Mg15−xZnxSr3 and Mg17Sr2, could also be observed in this diffusion couple. Compositions of the elements in the constituted phases were analyzed by EDS as shown in Fig. 2d. According to the acquired line scan results, the Mg15−xZnxSr3 compound forms a substitutional solid solution from 29 to 37 at.% Zn at a constant Sr content of about 16.7 at.%

As illustrated in Figs. 2 and 3, the diffusion path, Zn2Sr + Mg15−xZnxSr3 ↔ Mg15−xZnxSr3 ↔ Mg17Sr2 + IM1 ↔ Mg17Sr2 + Mγ + hcp (Mg) → hcp (Mg), was identified in the diffusion couple D1.

Based on the phase equilibria relationships obtained from this diffusion couple, nine additional alloys (A1–A9) were prepared to determine the solid solubility limits and crystal structure of the new found compound Mg15−xZnxSr3 at 300 °C.

A few backscattered electron (BSE) images of such typical ternary Mg–Zn–Sr alloys are shown in Fig. 4. The microstructures of the two phase equilibria Mg15−xZnxSr3 + Mg17Sr2 in samples A4 (Mg75Zn15Sr10) and A8 (Mg20Zn55Sr10) are shown in Fig. 4(a) and (b). The gray phase (labeled IM3) shown in Fig. 4(b) is another new ternary compound which will be discussed in future paper. The minimum solid solubility limit of Zn was obtained to be 1.3 at.% from the sample A1 (Mg83Zn15Sr10), where three-phase equilibrium Mg15−xZnxSr3 + Mγ + Mδ was observed as shown in Fig. 4(c). The maximum solid solubility limit of Zn in Mg15−xZnxSr3 was obtained to be 58.8 at.% from the sample A9 (Mg20Zn55Sr10), where a three-phase equilibrium Mg15−xZnxSr3 + IM3 + IM5 was observed as shown in Fig. 4(d). Moreover, the phases, light gray (named IM4) and deep dark (named IM5), are also new phases in this system which will be discussed in details in a future paper.

Furthermore, the constituted phases in all equilibrated samples were identified by XRD analysis. The XRD patterns obtained for samples A4 (Mg75Zn15Sr10) and A8 (Mg20Zn55Sr10) are shown in Fig. 5. As can be seen in Fig. 5, a series of the same peaks with a little angle shift were observed in samples A4 and A8, which corresponds to Mg15−xZnxSr3. In Fig. 5(a), the phases Mg17Sr2 and Mg15−xZnxSr3 were identified according to their characteristic peaks, which are in agreement with the observed results from the equilibrated sample A4 with metallographic method (see Fig. 4a). In Fig. 5(b), series of uncertain peaks were observed which shall belong to IM3.
All the compositions of the constituent phases of the equilibrated Mg–Zn–Sr ternary equilibrated samples are analyzed by EPMA and listed in Table 1. A nearly constant composition value of 16.7 in atomic percentage of Sr in the Mg$_{15-x}$Zn$_x$Sr$_3$ compound was obtained in all key samples A1–A9 within the measurement error limits. The phase equilibrium relationships of Mg$_{15-x}$Zn$_x$Sr$_3$ compound in the isothermal section of the Mg–Zn–Sr ternary system at 300 °C obtained in the present work are shown in Fig. 3.

Combining the measurement results of diffusion couple and equilibrated samples using EPMA and SEM/EDS techniques, the solid solubility limits of Mg$_{15-x}$Zn$_x$Sr$_3$ were obtained in the present work. The formula of this compound is presented as Mg$_{15-x}$Zn$_x$Sr$_3$ ($0.24 \leq x \leq 10.58$) at 300 °C.

### 3.2. Crystal structure analysis for Mg$_{15-x}$Zn$_x$Sr$_3$

Full patterns refinement of samples A1 and A4–A9 has been carried out by the Rietveld method. Combining Pearson's crystallographic database [29] with the Rietveld analysis, the new Mg$_{15-x}$Zn$_x$Sr$_3$ compound was found to crystallize in hexagonal P6$_3$/mmc (194) space group and has the Ni$_1$Si$_4$Sc$_3$ prototype. This is the same structure type as Mg$_{11}$Zn$_4$Ca$_3$ (IM1) compound in the Mg–Zn–Ca ternary system reported by Zhang et al. [30,31]. The sites of 6h (1) ($x = 0.5618, y = 0.1236, z = 0.25$), 4f, 2b, and 12k are occupied with Mg and Zn atoms to form the continuous solid solubility, and the site of 6h (2) ($x = 0.192, y = 0.384, z = 0.25$) are occupied with Sr.
The lattice parameters of the Mg\textsubscript{15} - xZn\textsubscript{x}Sr\textsubscript{3} powder XRD diffraction are summarized in Fig. 7. According to the solid obtained by EPMA.

Fig. 6(a) shows the XRD patterns refinement result of sample A1 (Mg\textsubscript{83}Zn\textsubscript{20}Sr\textsubscript{17}), which contains three phases Mg\textsubscript{17}Sr\textsubscript{2} + Mg\textsubscript{38}Sr\textsubscript{9} + Mg\textsubscript{15} - xZn\textsubscript{x}Sr\textsubscript{3}. It demonstrates the Rietveld analysis for the Mg\textsubscript{17}Sr\textsubscript{2}, Mg\textsubscript{38}Sr\textsubscript{9}, and Mg\textsubscript{15} - xZn\textsubscript{x}Sr\textsubscript{3} phases in sample A1, and the analyzed volume fractions of each phase with Rietveld analysis are in reasonable agreement with the results observed by SEM as shown in Fig. 4(c). Fig. 6(b) shows the Rietveld analysis results of sample A9 (Mg\textsubscript{20}Zn\textsubscript{65}Sr\textsubscript{15}). The identified phase composition and the lattice parameters of the Mg\textsubscript{15} - xZn\textsubscript{x}Sr\textsubscript{3} compound obtained from seven samples by XRD Rietveld analysis and EPMA analysis are summarized in Table 2. The phase relations obtained from XRD after refinement analysis show great consistency with the results obtained by EPMA.

The XRD patterns of samples A1, A4, A6, A7 and A9 obtained by powder XRD diffraction are summarized in Fig. 7. According to the solid solubility measured by EPMA in the present work, the Mg and Zn substitu-tion on another at a constant Sr composition in the Mg\textsubscript{15} - xZn\textsubscript{x}Sr\textsubscript{3} compound. The substitution of Mg by Zn, which has a smaller atomic radius, decreases the unit cell parameters. This is con-sistent with the observed changing size with Mg concentration, as shown in Fig. 7. A ss h o w ni n Fig. 8, where substitution of Mg by Zn decreases the unit cell parameters.

The variations of cell parameters with Mg concentration are shown in Fig. 8, where substitution of Mg by Zn decreases the unit cell parameters a and c, this is also shown in more details in Table 2. The linear relation between the lattice parameters and Mg clearly indicating the occurrence of substitutional solid solubility of Mg and Zn.

Table 3 shows the refined structural parameters of the Mg\textsubscript{15} - xZn\textsubscript{x}Sr\textsubscript{3} compound and the reliability factors. The fractional atomic occupancy of 6h, 6g, 4f, 2b, and 12k sites of Mg\textsubscript{15} - xZn\textsubscript{x}Sr\textsubscript{3} compound have been determined as a function of the Mg content, as shown in Fig. 9. The current experimental results obtained by Rietveld analysis of crystallographic and the site occupany show similar results compared to the previous results reported for Mg\textsubscript{11}Zn\textsubscript{4}Ca\textsubscript{3} [30] compounds, which have the same crystal structure.

### 4. Conclusions

The solid solubility limits and crystal structure of the ternary compound Mg\textsubscript{15} - xZn\textsubscript{x}Sr\textsubscript{3} in the Mg-Sr-Sr system have been deter-mined for the first time. The formula of this compound is suggested to be Mg\textsubscript{15} - xZn\textsubscript{x}Sr\textsubscript{3} (0.24 ≤ x ≤ 0.58) according its solid solubility limits at 300 °C. It has hexagonal P\textsubscript{6}\textsubscript{3}/mmc structure, 194 space group and Ni\textsubscript{11}Si\textsubscript{4}Sc\textsubscript{3} prototype.

The site occupany of Mg\textsubscript{15} - xZn\textsubscript{x}Sr\textsubscript{3} was obtained using Rietveld analysis of XRD patterns. The site occupanies of 6h (1) (a = 0.5618,
Fig. 9. The fractional atomic occupancy of 6h, 6g, 4f, 2b, and 12k sites variations with Mg content.

\[ b = 0.1236, c = 0.25 \], 4f, 2b, and 12k have been presented as a function of Mg concentration.

Acknowledgments

Financial support from General Motors of Canada Ltd., and The Natural Sciences and Engineering Research Council of Canada through the CRD grant program is gratefully acknowledged. The support in the experimental part from Mr. Tian Wang, Mr. Xin Zhang, and Dr. Dmytro Kevorkov from Concordia University, and Dr. Shi Lang from McGill University is acknowledged by the authors.

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