THERMODYNAMIC MODELING AND EXPERIMENTAL INVESTIGATION OF THE MAGNESIUM-ALUMINUM-STRONTIUM-CALCIUM SYSTEM

M. Aljarrah[1], M. Medraj[1], J. Li[2] and E. Essadiqi[2]

[1]Mechanical Engineering Department, Concordia University, Montreal, Canada
[2] CANMET-MTL, Ottawa, Canada

Abstract

The phase equilibria and thermodynamic properties of the Mg-Al-Sr-Ca system were analyzed in this work and a thermodynamic description of the system was obtained using a computerized optimization procedure. The available thermodynamic and phase diagram data were critically assessed for all the binary and ternary sub-systems. Optimized thermodynamic properties of the binary systems were then used to construct a database and calculate the ternary phase diagrams. The phase equilibria in the Mg-Al-Sr and Mg-Al-Ca systems were investigated experimentally by differential scanning calorimetry (DSC), X-ray diffraction (XRD), scanning electron microscopy (SEM) and quantitative electron probe micro-analysis (EPMA). A new ternary solid solution, $Mg_xAl_{4-x}Sr$, was observed in the Mg-Al-Sr system, which is due to the substitution of Al by Mg atoms in the Al_4Sr compound. Maximum solubilities of 21.3 at.% Al in $Mg_{17}Sr_2$ and 11.4 at.% Al in Mg were observed. It was also noticed that $Mg_{38}Sr_9$ dissolved 12.5 at.% Al. In the Mg-Al-Ca ternary system, one of the invariant transformations, predicted by thermodynamic modeling, was verified experimentally and found to occur at 512°C with composition close to 10.8 at.% Ca, 79.5 at.% Mg and 9.7 at.% Al. Large solid solubility of Al in Mg_2Ca was observed. The Mg-Ca-Sr and Al-Ca-Sr phase diagrams were also calculated from the established database for the Mg-Al-Ca-Sr system.

Introduction

Magnesium has the best strength to weight ratio of common structural metals and has exceptional die-casting characteristics [1]. This makes magnesium alloys attractive for transportation applications such as automobiles and airplanes for weight reduction and higher fuel efficiency. To date, most Mg applications in the auto industry are in the form of die-cast parts. However, wrought magnesium applications, particularly sheet, and power train applications represent tremendous growth opportunities for magnesium. Unfortunately, magnesium alloys face a challenge for power train applications because of their limited creep resistance at higher temperatures [2].

Calcium and strontium are two important additives used in magnesium alloys. The alloying effects of 0.1 to 0.3 wt.% calcium on Mg-Al based alloys have been found to increase ductility through grain refinement [3]. Alloying magnesium with strontium, on the other hand, is suggested to improve creep resistance, strength and corrosion resistance of the alloy [4,5]. In recent years, Mg-Al-(Sr,Ca) systems have emerged as potential heat-resistant Mg-alloys. The development of Mg-Al-(Sr,Ca) was aimed to replace RE additions to Mg alloys. One of the main challenges of these alloy systems is to optimize the combinations of properties such as creep resistance, tensile yield strength and castability [2,6].

However, to date, little effort has been made to construct the phase relationships of Mg-Al-Sr and Mg-Al-Ca systems. The experimental work on the phase equilibria of the Mg-Al-Sr system was primarily originated from Makhmudov and coworkers [7-9]. Besides, inconsistency was noticed between their works. The solubility limits for the binary compounds determined by Makhmudov *et al.* [9] do not agree with the 400°C isothermal section given by Makhmudov *et al.* [8] in 1981. Baril *et al.* [10] investigated four samples in the Mg-rich region of the Mg-Al-Sr system and tentatively designated a ternary phase as $Al_3Mg_{13}Sr$. The chemical composition of this compound is not compatible with the ternary compound reported by Makhmudov *et al.* [8]. In 2003, Zhong *et al.* [11] modeled the Mg-Al-Sr system, and obtained results very similar to Chartrand and Pelton [12] except for the extent of the Mg_2Sr field. Recently, Janz *et al*. [13] investigated this system based on the work done by [14,15]. In their work, a consistent thermodynamic modeling of the Mg-Al-Sr system was done involving substitutional solid solubilities of Al and Mg in Mg-Sr and Al-Sr binary compounds and, a new ternary compound with Mg/Al ratio similar to that of $Mg_{17}Al_{12}$. The stoichiometry is not clearly identified and the chemical composition is not compatible with the ternary compounds reported by [8,10]. Czerwinski and Zielinska-Lipiec [16] investigated the microstructure evolution of a Mg-5Al-2Sr (wt.%) alloy and reported that the common feature of Sr-containing phases in the as-cast ingots is their location at grain or sub-grain boundaries. The presence of $Mg_{17}Al_{12}$ suggests an insufficient amount of Sr to bind all Al. At the same time, although Sr effectively suppressed the formation of the $Mg_{17}Al_{12}$, its traces existed as irregular shapes residing at the grain interiors.

In the Mg-Al-Ca system, Gröbner *et al.* [17] performed thermodynamic calculations of the phase diagram combined with experimental investigations carried out by DTA and XRD. In their investigation, a thermodynamic modeling of the ternary system was done involving an extended solid solubility of two binary intermetallic compounds; Mg_2Ca and Al_2Ca. Zhong *et al.* [11], and Islam and Medraj [23], however, calculated the ternary Mg-Al-Ca diagram by combining the data of the three binary systems, Al-Mg, Ca-Mg, and Al-Ca, assuming no ternary solubility between the binary compounds. Powell *et al.* [18] suggested the presence of a ternary solid solution in this system. Recent investigation [19] pointed out that Al_2Ca and Mg_2Ca are the primary precipitates responsible for the improvement of creep resistance in this system.

In this work, the phase equilibria and thermodynamic modeling of the Mg-Al-(Ca,Sr) systems were evaluated using the modified quasichemical model [21,22]. The phase equilibria in the Mg-Al-Sr and Mg-Al-Ca systems were investigated experimentally by DSC, XRD, SEM/EDS and EPMA.

Experimental

Thermal and analytical investigations and phase identification were carried out in the Mg-rich region of the Mg-Al-Sr and Mg-Al-Ca systems. For Mg-Al-Sr system, 22 alloys and for Mg-Al-Ca system, 21 alloys were chosen by critical assessment of the experimental and thermodynamic datasets that are available in the literature. The samples were prepared and analyzed chemically at MTL-CANMET and the

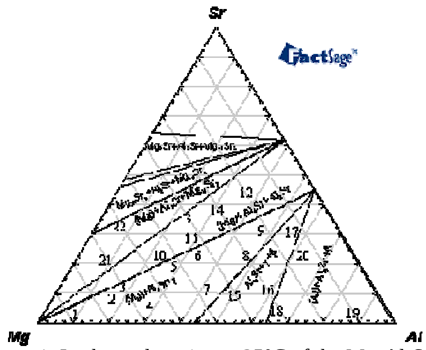


Figure 1: Isothermal section at 25°C of the Mg-Al-Sr system with the investigated compositions in wt.%.

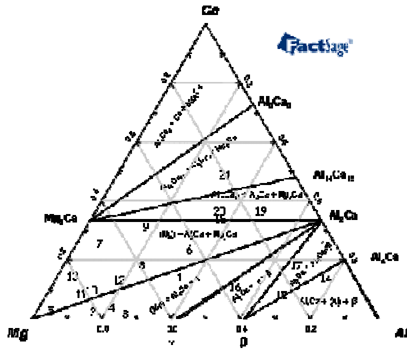
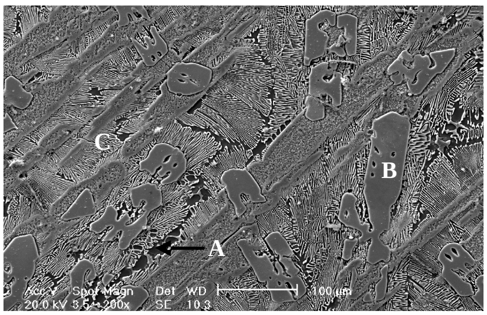


Figure 2: Isothermal section at 25°C of the Mg-Al-Ca system with the investigated compositions in wt.%.

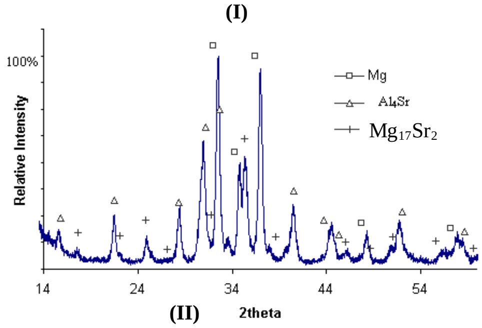
nominal sample compositions remained in very close proximity with the actual compositions. Mg-Al-Sr and Mg-Al-Ca ternary diagrams with the investigated compositions in weight percentage are given in Figures 1 and 2. Samples were prepared from 99.8 wt% magnesium, 99.9 wt.% aluminum, 99 wt.% strontium, and 99 wt.% calcium to achieve the target compositions. The charge was melted in a graphite crucible in an induction-melting furnace under argon with 1%SF_6 to protect the melt from oxidation. The samples were investigated by XRD, SEM and EPMA analyses. More details about the experimental procedure can be found in [14,15,20].

Results and Discussions

It can be seen in Figure 1 that composition 10 (22.78/54.39/22.83 Sr/Mg/Al wt.%) is located in the Mg-rich corner close to composition 5. But these two alloys belong to two different phase fields. SEM image, as shown in Figure 3(I), shows that the size of the plate-like phase is relatively smaller than in alloy 5 [15] and distributed more evenly in the microstructure. (Mg), (Al_4Sr) and ($Mg_{17}Sr_2$) were identified in the diffraction patterns and by the EPMA analysis that is located in regions (A), (B) and (C), respectively, as shown in Figure 3(I). From the EPMA analysis shown in Figure 3(III), Al_4Sr dissolves 14.1 at.% Mg. In contrast, 11 at.% of Mg was dissolved in Al_4Sr in alloy 5 [15]. In the present EPMA analysis, the light grey precipitate is identified as $Mg_{17}Sr_2$ dissolving 21.3 at.% Al which is the maximum solubility of Al in $Mg_{17}Sr_2$. The details of the rest of the samples are described in [14,15].



(I)



(II)

Location	at.% Mg	at.% Al	at.% Sr	Phases
A	88.6	11.2	0.2	(Mg)
B	14.1	64.5	21.4	(Al_4Sr)
C	70.0	21.3	8.7	($Mg_{17}Sr_2$)

(III)

Figure 3: (I) SEM Image, (II) XRD spectra and (III) EPMA analysis of sample 10 (22.78/54.39/22.83 Sr/Mg/Al wt.%).

Based on the current experimental results, a new Mg-Al-Sr isothermal section at 300K has been drawn (Figure 4) and compared with that calculated from thermodynamic modeling of [12]. Sample 10 is located in three phase regions; (Mg), (Al_4Sr) and ($Mg_{17}Sr_2$) which was, however, not predicted correctly by [11] and [12].

In the Mg-Al-Ca system, a eutectic point in the Mg-Mg_2Ca-Al_2Ca field has been investigated through compositions 10 to 13 shown in Figure 2. Sample 10 was prepared with

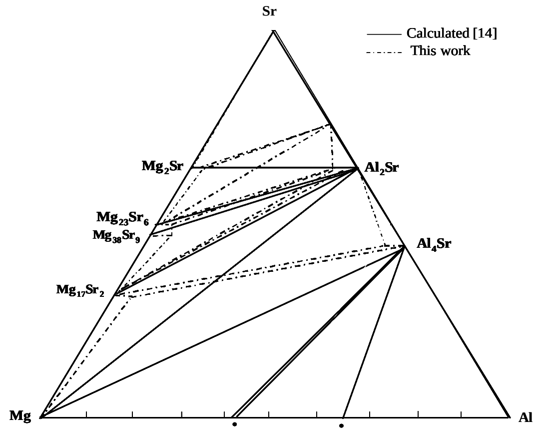


Figure 4: Isothermal section of Mg-Al-Sr at 300K.

the calculated composition of the eutectic point predicted by thermodynamic modeling of [23]. The phase assemblage diagram in Figure 5(II) shows the eutectic transformation, i.e. liquid phase transforms during cooling into three phases simultaneously: (L/(Mg) + Al_2Ca + Mg_2Ca). DSC spectra of sample 10 in Figure 5(I) show a sharp, narrow and unique peak. This indicates that the infinite heat transfer occurs during an invariant transformation. The optical micrograph of sample 10 in Figure 5(III) shows typical lamellar eutectic feature and some plate-like precipitates. This indicates that the sample is quite close to the eutectic composition. The XRD pattern in Figure 5(IV) shows the coexistence of the (Mg), Al_2Ca and Mg_2Ca phases. This is in agreement with the phase assemblage diagram shown in Figure 5(II). Therefore, it is concluded that this eutectic transformation takes place at 512°C. Detailed discussions of the other alloys are described in [20].

Thermodynamic modeling of Mg-Al-(Sr,Ca) systems

A self-constituent database was established based on the optimized binary parameters by the modified quasichemical model with the symmetric approximation. The database was then used to calculate polythermic projections of the ternary sub-systems shown in figures 6 to 9. For the Mg-Al-Sr system, the established database predicted eight quasi-peritectics and three ternary eutectics, for the Mg-Al-Ca system, predicted two quasi-peritectics, six ternary eutectics and five saddle points, for the Mg-Ca-Sr system, predicted three quasi-peritectics, three saddle points and three ternary eutectics, for the Al-Ca-Sr system, predicted eight quasi-peritectics and two ternary eutectics.

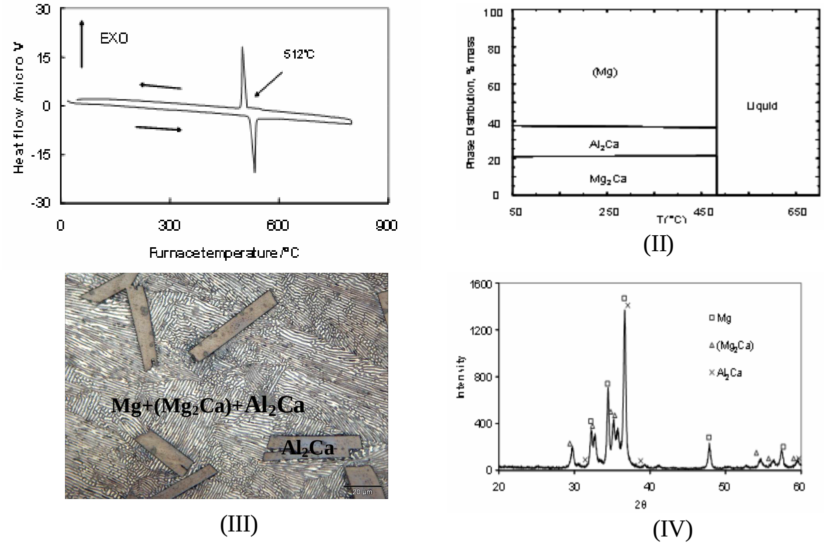


Figure 5: (I) DSC spectra, (II) Phase assemblage diagram, (II) Optical micrograph and (III) XRD pattern of sample 10 (*16.44/73.61/9.95 Ca/Mg/Al wt%)*.

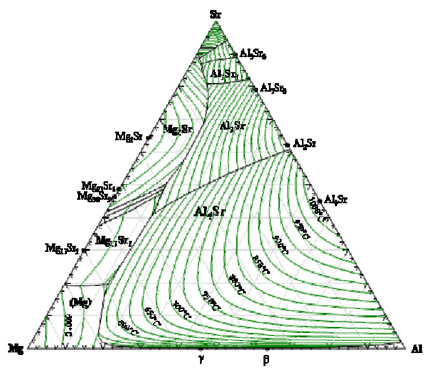


Figure 6: Liquidus projection of the Mg-Al-Sr system in wt.%.

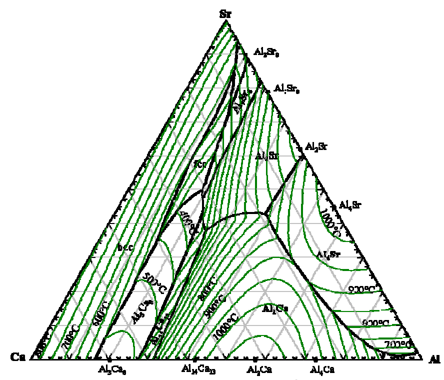


Figure 8: Liquidus projection of the Al-Ca-Sr system in wt.%.

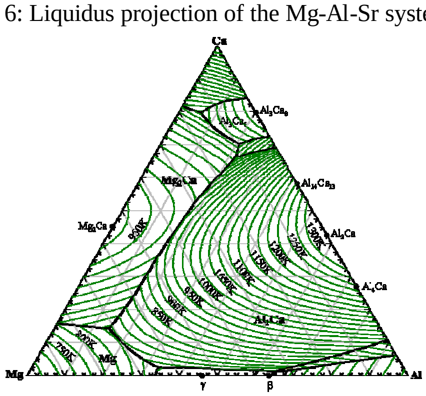


Figure 7: Liquidus projection of the Mg-Al-Ca system in wt.%.

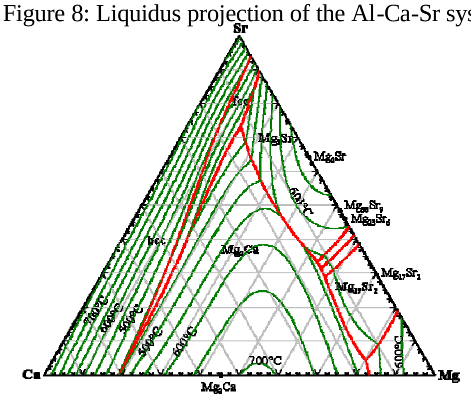


Figure 9: Liquidus projection of the Mg-Ca-Sr system in wt.%.

Conclusion Remarks

Thermodynamic modeling and experimental investigation have been carried out for the Mg-Al-Ca and Mg-Al-Sr systems using DSC, XRD SEM/EDS and EPMA analysis. In the present investigation, ternary solid solubility of three binary compounds which extended into the ternary system has been reported and denoted as: (Al_4Sr), ($Mg_{17}Sr_2$) and ($Mg_{38}Sr_9$). In the Mg-Al-Ca system, a ternary eutectic point in the Mg-rich corner was verified. The eutectic temperature is determined as 512°C. It was found that Mg_2Ca dissolves significant amount of Al, Al_2Ca and Al_3Ca_8 dissolve significant amount of Mg.

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