Computational Thermodynamics and Experimental Investigation of the Mg-Al-Ca-Sr Alloys

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ABSTRACT

The thermodynamic properties of the quaternary Mg-Al-Ca-Sr system are investigated by combining the six binary systems, i.e. the Al-Ca, Al-Mg, Al-Sr, Ca-Mg, Ca-Sr and Mg-Sr. The constructed quaternary database is used to understand the microstructures and phase relationships of the two alloys (Mg-5.7%Al-3.1%Ca-0.15%Sr and Mg-5.0%Al-3.1%Ca-0.07%Sr). Scheil simulations and equilibrium calculations were performed for the solidification process of the alloys and compared with experimental observations.

INTRODUCTION

The light-weight magnesium alloys are particularly attractive for transportation applications such as automobiles and helicopters for weight reduction and higher fuel efficiency (1-3). Mg-Al alloys are one group of these magnesium-based alloys that are under development. Their use, however, is limited to low temperature applications. Therefore, a large amount of effort has been made to increase the service temperature of these alloys. The addition of alkaline earth elements into Mg-Al alloys has been found to be beneficial not only to keep the costs low but also to improve the mechanical properties, especially the creep resistance at elevated temperatures (>150^{o}C)(4). Ca and Sr have been found to be the two alkaline earth elements which affect high temperature performance positively. Parallel to the experimental investigations, there is a great need for an efficient route of alloy development with reduced cost and time. The emerging concept of system materials design provides such opportunities(5). In the system materials design, the essential component is the computational thermodynamics, often referred to as CALculation of PHAse Diagrams, or CALPHAD.

The current project was initiated with the interactions between the Pennsylvania State University and General Motors and supported by the National Science Foundation. In the previous paper, the results for the Mg-Al-Ca ternary system were reported(6). In the present paper, our preliminary results in the Mg-Al-Ca-Sr system are presented and compared with the experimental data. The ultimate objective is to study the fundamental thermodynamics and kinetics of Mg-Al-Ca-Sr based alloys and to provide understanding and guidance of system design of magnesium alloys through computational modeling and experimental investigations.

THEORETICAL APPROACH

CALPHAD has been under development since early 1970's(7). The development of CALPHAD techniques in the past three decades was discussed by Saunders and Miodownik(8). This technique was briefly summarized in a previous publication by one of the authors(9). In this paper, only the general procedure for the development of the thermodynamic description of the Mg-Al-Ca-Sr system will be discussed, as the detailed evaluation of the thermodynamic database is still under development and will be published in the near future.

The thermodynamic descriptions of the pure Mg, Al, Ca and Sr elements are taken from the SGTE database(10). The Mg-Ca(11) and Mg-Al(12) binary systems are obtained from the literature. The Mg-Sr, Al-Ca, Al-Sr and Ca-Sr binary systems are carefully assessed in the present work by using critically reviewed experimental data in the literature. There are 15 binary compounds in these binary systems and they are listed in Table 1 with their crystal structures shown.

Table 1: The binary compounds and their crystal structures in the Mg-Al-Ca-Sr system.

Phase	Space Group	Crystal Structure	Prototype
Al_4Ca	I4/mmm	bct ($D1_3$)	Al_4Ba
Al_2Ca	$Fd\bar{3}m$	fcc (C15)	Cu_2Mg
AlCa	---	---	---
Al_3Ca_8	P1	triclinic	Tl_3Yb_8
$Mg_{17}Sr_2$	$P6_3/mmc$	---	Th_2Ni_{17}
$Mg_{38}Sr_9$	$P6_3/mmc$	---	---
$Mg_{23}Sr_6$	$Fm\bar{3}m$	$D8_a$	$Mn_{23}Th_6$
Mg_2Sr	$P6_3/mmc$	(C14)	$MgZn_2$
Mg_2Ca	$P6_3/mmc$	(C14)	$MgZn_2$
AlMg-□	$R\bar{3}$	---	$Co_5Cr_2Mo_3$
AlMg-□	$Fd\bar{3}m$	---	Cd_2Na
AlMg-□	$I\bar{4}3m$	cbcc (A12)	□-Mn
Al_4Sr	I4/mmm	bct ($D1_3$)	Al_4Ba
Al_2Sr	Imma	---	$CeCu_2$
A_7Sr_8	$P2_13$	---	Al_7Sr_8

There are four ternaries in the system, i.e. Mg-Al-Ca, Mg-Al-Sr, Mg-Ca-Sr and Al-Ca-Sr currently under investigations. As can be seen in Table 1, some of binary compounds have the same crystal structure, which indicates that they are the same phase and will have extensive solubility into each. However, due to the incompleteness of our work in these aspects, in the present paper, the thermodynamic properties of the ternary systems are predicted simply from the combination of those of their constitutive binary systems.

EXPERIMENTAL PROCEDURE

Two alloys, Mg-5.7%Al-3.1%Ca-0.15%Sr and Mg-5.0%Al-3.1%Ca-0.07%Sr, (all in weight percent unless otherwise specified), were supplied by General Motors R&D Center. The alloys were made by die casting at Lexington Die Casting, Lakewood, NY. The melt temperature was controlled at around 677°C with the die surface temperature maintained at 350°C. Chemical analysis using ICP/AES (Inductively-Coupled Plasma/Atomic Emission Spectroscopy) techniques was performed, and the other alloying elements and impurities are typically as 0.27%Mn, 0.003%Fe and 0.002%Cu.

Samples were cut from the 6mm diameter, die-casting tensile-test bar and prepared for optical (Nikon Epiphot) microscopy and SEM (Philips XL 20) observations under either polished only or polished and etched conditions. When etched, the etchant was 5% HNO_3 in methanol. The volume fractions of phases were measured using the Image-Pro Plus Version 4.5 image analysis software on photos taken from the optical microscope with at least ten areas randomly chosen for each sample.

RESULTS AND DISCUSSIONS

To view phase equilibrium in a quaternary system, one typically uses isopleth sections. In Fig. 1, the isopleth sections at 5%Al and 3.1%Ca withrespect to the temperature and the Sr content was calculated, to depict the effect of the Sr content on phase equilibria and phase relationships at different temperatures.

For the two Mg-Al-Ca-Sr alloys, the equilibrium phase fractions (dotted lines) and the phase fractions from Scheil simulations (solid lines) are plotted in Fig. 2 as a function of the temperature. In the Scheil simulations, it is assumed that the liquid phase is homogenous all the time, and there is no diffusion in the solid phases. Therefore, the equilibrium calculations and the Scheil simulations represent two extreme situations.

In both alloys, the hcp phase solidifies first from the liquid phase, followed by the hcp+Al_2Ca eutectic solidification. The liquidus temperature of the Mg-5%Al-3.1%Ca-0.07%Sr alloy is about 3 degree higher than that of the Mg-5.7%Al-3.1%Ca-0.15%Sr alloy, but the eutectic temperatures are only about 0.61 degree apart in the Scheil simulations and about 0.91 degree in the equilibrium calculations.

The equilibrium amounts of the Al_2Ca phase are 5.74% and 5.75% in the Mg-5%Al-3.1%Ca-0.07%Sr and Mg-5.7%Al-3.1%Ca-0.15%Sr alloys, respectively, while the amount in the Scheil simulations, they are 5.96% and 6.75%, respectively. There are 0.99% and 0.23% Mg_2Ca phase formed in the Mg-5%Al-3.1%Ca-0.07%Sr and Mg-5.7%Al-3.1%Ca-0.15%Sr

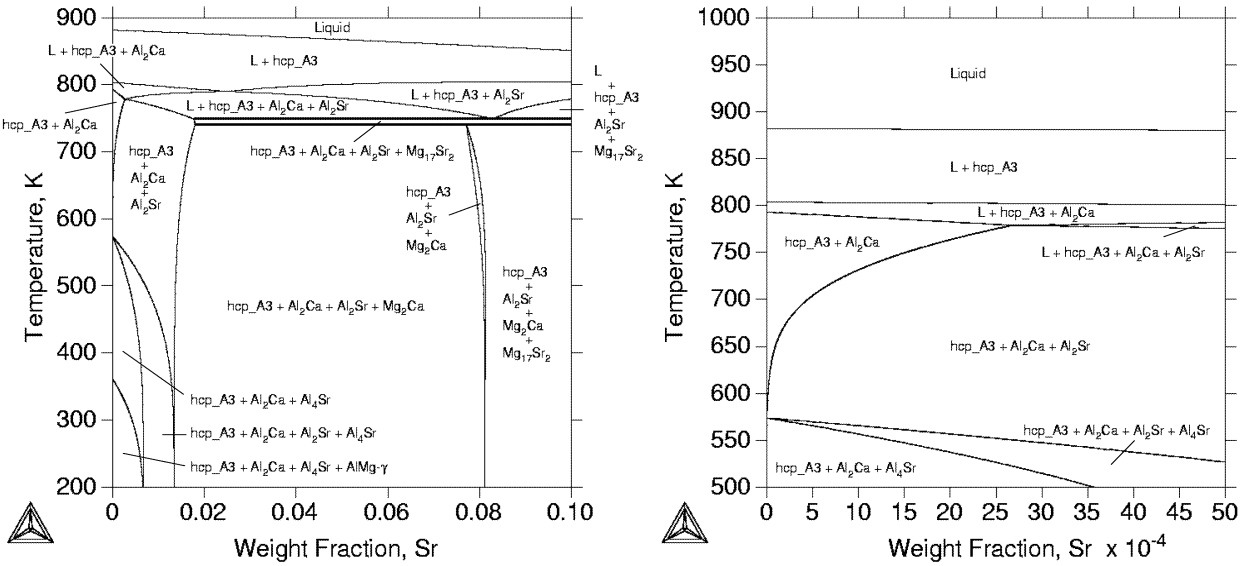

Figure 1: Calculated isopleth sections of the Mg-Al-Ca-Sr system with 5%Al-3.1%Ca. The righ diagram is an enlargement to show the phase diagram with low Sr contents.

alloys in the Scheil simulation, respectively. While in the equilibrium calculations, the Mg_2Ca phase is not stable, but the Al_2Sr phase.

The weight fraction of the eutectic structures are about 24.8% and 26.9% for the Mg-5%Al-3.1%Ca-0.07%Sr and Mg-5.7%Al-3.1%Ca-0.15%Sr for the equilibrium calculations, respectively. While in the Scheil simulations, they are 26.9% and 29.1% for the Mg-5.7%Al-3.1%Ca-0.15%Sr, respectively, i.e. there is about 2% more eutectic structure in the Mg-5.7%Al-3.1%Ca-0.15%Sr alloy.

The microstructures of both alloys are very similar to each other. Optical micrographs from the two alloys are shown in Figure 3.

The SEM micrograph and the EDS result of the intermetallic phase in the Mg-5.7%Al-3.1%Ca-0.15%Sr alloy are shown in Fig. 4. The measured volume fractions of the white areas are 17.4±1.5% and 19±1.3% for the Mg-5%Al-3.1%Ca-0.07%Sr and Mg-5.7%Al-3.1%Ca-0.15%Sr, respectively.

With the densities of the hcp and Al_2Ca being 1.738 and 2.395g/cm^3, the calculated volume fractions of the eutectic structure, using the Scheil simulation results, are 21.1% and 23% for the two alloys, respectively.

The comparison between the calculated and experimental results on eutectic fractions in the two die cast alloys is summarized in Table 2. The difference between the experimental and

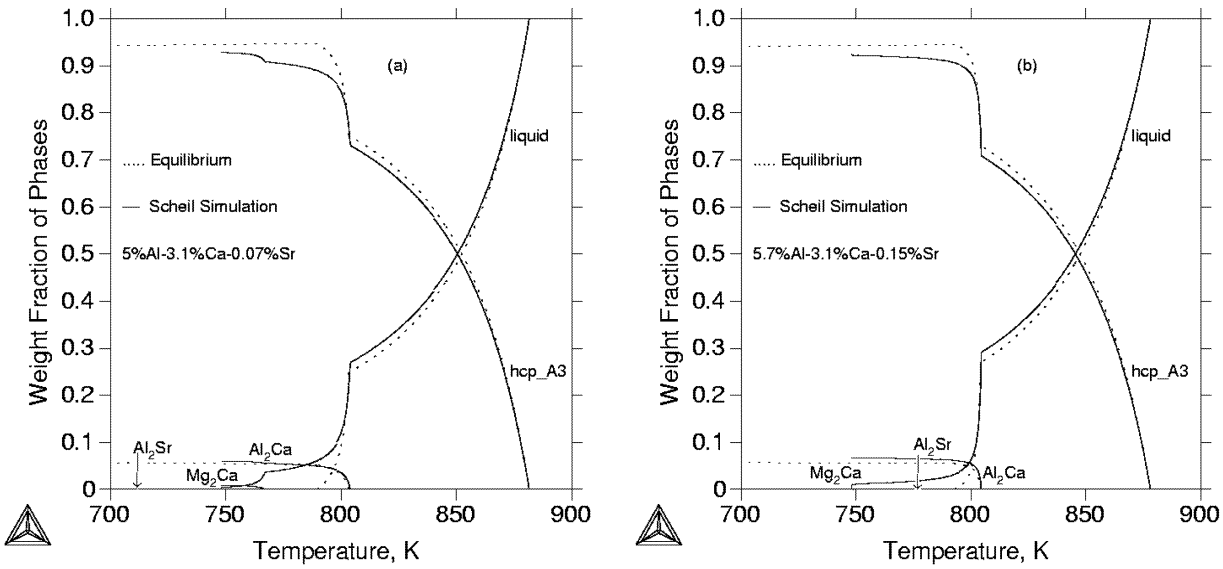

Figure 2: Phase fractions as a function of the temperature for the two alloys.

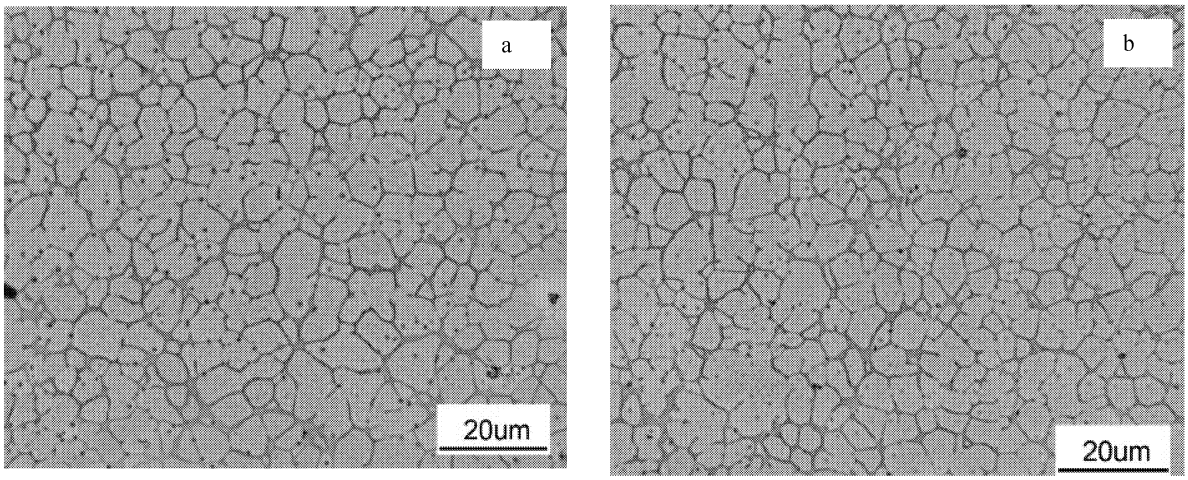

Figure 3: Optical micrographs of the two alloys. (a) Mg-5%Al-3.1%Ca-0.07%Sr and (b) Mg-5.7%Al-3.1%Ca-0.15%Sr.

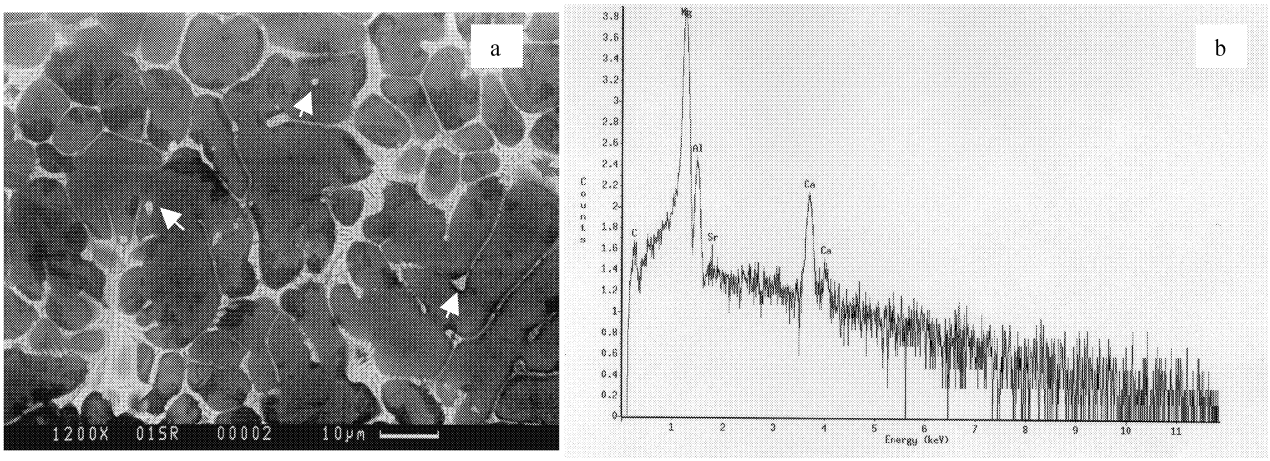

Figure 4: The SEM micrograph (a) and the EDS analysis of the intermetallic phase (b) of the Mg-5.7%Al-3.1%Ca-0.15%Sr alloy.

calculated values is about 4%. This discrepancy can be due to several reasons. First, the thermodynamic database is a simple combination of all binary system as the key ternary systems are still under development. Secondly, there are many degenerated eutectic structure as shown by arrows in Fig. 4 where the hcp phase in the eutectic structure is part of the hcp matrix. For example, assuming 20% of the hcp phase in the eutectic structure becomes part of the hcp matrix, the calculated fraction of the eutectic structure would be reduced by about 4%. Therefore, it is desirable to experimentally measure the amount of the intermetallic phases only so a more direct comparison can be made.

Therefore, the agreement between the calculated and experimental volume fractions of the eutectic structure can be considered satisfactory. Furthermore, the EDS analysis indicates that the intermetallic compound is rich in Al and Ca, indicating the existence of the Al_2Ca phase in accordance with the calculation. The significant Mg peak in the EDS result is probably from the hcp phase in either the matrix or the eutectic structure.

Table 2. Calculated and Experimental Results on Eutectic Fractions in Two Die Cast Alloys

Alloy	Equilibrium Simulation		Scheil Simulation		Experimental
	Wt.%	Vol.%	Wt.%	Vol.%	Vol. %
Mg-5%Al-3.1%Ca-0.07%Sr	24.8	19.5	26.9	21.1	17.4±1.5
Mg-5%Al-3.1%Ca-0.07%Sr	26.5	21.2	29.1	23.0	19.0±1.3

In the future work, the details of the structure and composition of the intermetallic compounds in the eutectic structure will be examined by TEM equipped with an EDS system to determine the solubility of Mg in the Al_2Ca phase and Al in the Mg_2Ca phase. With these data, the addition of the third component into

the Al_2Ca and Mg_2Ca phases will be considered. Together with available data of various ternary systems in the literature, a more complete thermodynamic database of the Mg-Al-Ca-Sr system will be developed to better describe the phase equilibria in the alloys.

SUMMARY

The thermodynamic description of the Mg-Al-Ca-Sr has been developed with the data of the six binary in the present work. Using this database, various calculations have been made to understand the phase relationships during the die-casting process and the effect of the Sr content on the microstructures. The calculated results and experimental observations carried out in the present work are in reasonable agreement. More work is underway to refine the thermodynamic database and experimentally determine the structure and composition of the intermetallic phases.

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