THERMODYNAMIC DATABASE OF Mg-Al-Ca-Sr: A RESOURCE FOR ALLOY DEVELOPMENT AND IMPROVEMENT

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Abstract

A thermodynamic database of Mg-Al-Ca-Sr, a basic quaternary for a number of commercial magnesium alloys such as AXJ530 (Mg-4.5Al-3.0Ca-0.14Sr, weight percent hereafter, unless noted otherwise) was developed. Calculated isopleth from Mg-5Al-3Ca to Mg-5Al-3Sr agrees with experimental data reported in the literature. Moreover, using this database and a simple kinetic model proposed by Scheil, the calculated solidification paths of several alloys are likewise in accord with experimental data. Thus, the availability of this database enables one to exploit new alloy compositions for promising properties which can be rapidly validated with few experiments.

Introduction

Magnesium alloys with the lowest density among the structural metals has innate advantage for the application in the transportation industry when conservation of the energy consumption and minimization of the environmental degradation become crucial. However, as compared to most aluminum and ferrous alloys, the limited creep resistance hinders the application of Mg alloys in the powertrain components, such as engine blocks and transmission cases, where the service temperature can be as high as 175°C~250°C. Therefore, during the last decade, there has been a great deal of effort to develop creep-resist Mg alloys. It was found that the additions of Ca and Sr or both to Mg-Al based alloys can significantly improve the creep resistance [1-4], such as AJ62 and AXJ530 with a base composition of Mg-6Al-2Sr and Mg-4.5Al-3Ca-0.14Sr respectively. Therein, Ca and Sr are two promising elements not only because of their low density and low cost, but also improving their properties for practical applications. However, the thermodynamic database available in the literature was obtained from an extrapolation from those of the constituent binaries [5]. It is known that such a thermodynamic database is not reliable [6]. For instance the ternary C36 Laves phase is not included in that database for Mg-Al-Ca.

In the present study, a thermodynamic description of the quaternary Mg-Al-Ca-Sr system was developed. This database focuses primarily on the Mg-rich phase equilibria. An isopleth from Mg-5Al-3Ca-0Sr to Mg-5Al-0Ca-3Sr, was calculated, which is in good agreement with the experimental data reported in the literature. Moreover, using this database and a simple kinetic model proposed by Scheil, the calculated solidification paths of several alloys are likewise in accord with experimental data. Thus, the availability of this database enables one to exploit new alloy compositions for promising properties which can be rapidly validated with few experiments.

Thermodynamic Modeling

In Mg-Al-Ca-Sr quaternary system, there are four constituent ternaries. The two key ternaries, Mg-Al-Ca [7] and Mg-Al-Sr [8], containing both Mg and Al, have been experimentally investigated and thermodynamically modeled in our previous work. For Mg-Al-Ca ternary system, we have obtained a thermodynamic description, which is in excellent agreement with our own experimental data, as well as data in the literature [9, 10]. Using this description, coupled with Scheil simulation, we have successfully proved the ternary eutectic reaction in the Mg-rich corner with clear experimental evidences obtained with the help of thermodynamic calculations. [7]. In addition, two saddle points (temperature maximum) were predicted thermodynamically and confirmed experimentally [11]. For the Mg-Al-Sr ternary system, a thermodynamic description was obtained by us based on the experimental data from three designated alloys [8]. It is also in good agreement with the experimental data from a subsequent study [12], though we did not use their data for optimization of model parameters. The thermodynamic description of Mg-Ca-Sr was obtained by extrapolation of the constituent binaries [13]. Zhong et al [14] performed first principles calculations on the end members of the Laves C14 phase, $Mg_2(Ca,Sr)$, by assuming binary solubilities of C14-Mg_2Ca and C14-Mg_2Sr. However there is no experimental data to support their assumption. Therefore, in the present study, C14 was still treated as a line compound in both Mg-Ca and Mg-Sr binaries.

For the non-Mg containing Al-Ca-Sr, since the current alloys development is centered in the phase equilibria of Mg-rich region and experimental data are very sparse in the literature, the thermodynamic description was obtained by extrapolation. Once the thermodynamic descriptions of the four constituent ternary systems are obtained, the thermodynamic description of the Mg-Al-Ca-Sr quaternary can be readily achieved by extrapolation from the descriptions of the four constituent ternaries. In most cases, the extrapolation usually works quite well, and the only exception is that in some rare cases when quaternary phases do exist in the system, where optimization of the model parameters for the quaternary phases in question is necessary [6]. It is worth while to note that since the descriptions of Mg-Ca-Sr and Al-Ca-Sr are obtained by extrapolation, the description of this quaternary may only give the topological features when going to higher Ca and Sr contents. In this study, all the phase diagram calculations were performed using the software Pandat [15].

Results and Discussion

Different from binary and ternary systems, it is difficult to directly visualize the phase equilibria and phase transformation information for a quaternary system. A vertical section of the quaternary system, i.e., an isopleth is usually used to view the phase equilibria relations. Figure 1 shows the calculated isopleth with constant Mg and Al content (92 wt.% Mg, 5 wt.% Al) and Sr contents varying from 0-3 wt.%. Also shown in this diagram, the reported data from [16] on the liquidus and solidus temperatures of seven Mg-Al-Ca-Sr quaternary alloys detected by thermal analysis. The squares denote the liquids temperatures, while the circles correspond to the solidus temperatures. It is clear that there is excellent agreement between our calculation and the

experimentally measured temperatures. With the increasing Sr concentration, the liquidus temperatures increase slightly, while the corresponding solidus temperatures decrease initially, reach a minimum and then increase again.

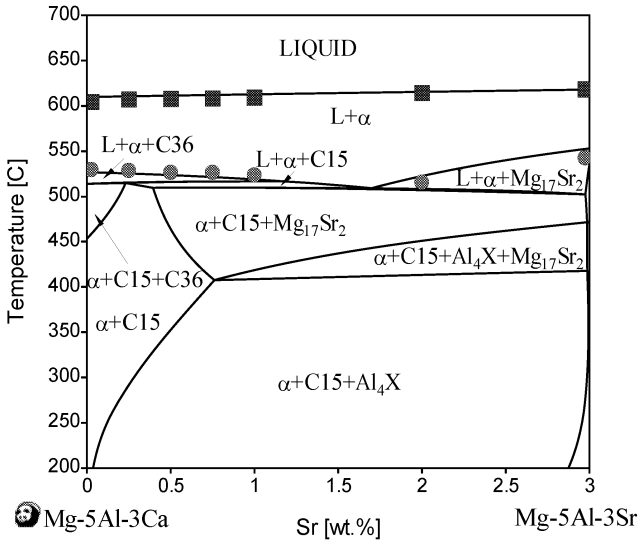

Figure 1. Calculated isopleth (temperature-composition) of the Mg-Al-Ca-Sr quaternary system with 92 wt.% Mg and being 5 wt.% Al, Ca and Sr exchanging with each other. Also shown in this diagram, the reported data from [16] on the liquidus and solidus temperatures of seven Mg-Al-Ca-Sr quaternary alloys detected by thermal analysis during the solidification. The squares denote the liquids temperatures, while the circles correspond to the solidus temperatures.

As one can see that for alloys in this particular composition range, the preferable primary phase of solidification is the α(Mg) phase. This is also consistent with the microstructure observations by Suzuki et al [16], where all the seven cast alloys solidify with the primary phase of α(Mg). According to the calculation, when Sr concentration of an alloy is 0-1.16 wt.%, the second solidified phase is C36-$(Mg,Al)_2Ca$; when Sr content is 1.16-1.70 wt.%, the second phase is C15-Al_2Ca; when Sr content is higher than 1.70 wt.%, the second phase is $Mg_{17}Sr_2$. This is also in line with the identified intermetallic phases in the as-cast microstructure by Suzuki et al. According to [16], the major intermetallic compound observed at the primary α(Mg) dendrite cell boundary region changes from the Al-rich C36-$(Mg,Al)_2Ca$ phase to the Mg-rich $Mg_{17}Sr_2$ phase with increasing Sr concentration. In addition, the calculation also provides that several different solid phases will be stable at lower temperatures, such as α(Mg) + C15, α(Mg) + C15 + Al_4X, etc. Here it should be noted that the Al_4X actually denotes $Al_4(Ca,Sr)$, a combination of Al_4Ca and Al_4Sr. Since these two binary phases have exactly the same crystal structure, i.e. the body center tetragonal structure, it is reasonable and also necessary to combine these two into one phase in the quaternary thermodynamic description.

For all the seven alloys reported in [16], solidification paths have been calculated based on the Scheil model and the thermodynamic description obtained in the current study. The Scheil model, with the assumptions of complete mixing in the liquid but no diffusion in the solid, can be used with reasonable confidence to predict the phase formation sequence for substitutional alloys.

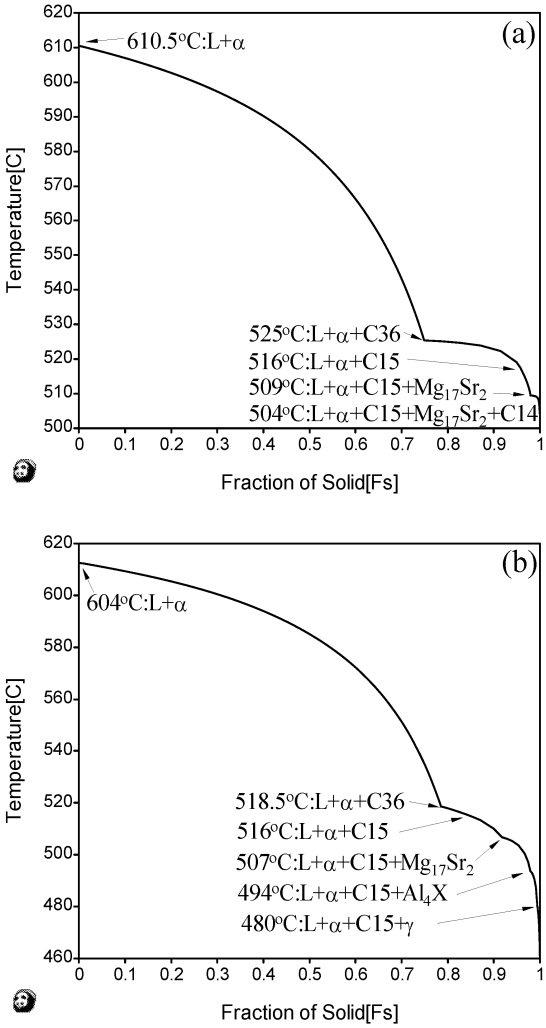

Figure 2. Calculated volume fraction of solid as a function of temperature under Scheil solidification condition for two typical quaternary alloys: (a) Mg-5Al-2.75Ca-0.25Sr, (b) Mg-5Al-2Ca-1Sr.

Figure 2 shows the calculated solidification paths for two typical Mg-Al-Ca-Sr quaternary alloys, (a) Mg-5Al-2.75Ca-0.25Sr, (b) Mg-5Al-2Ca-1Sr. According to the calculation, solidification consists of multiple stages. For both alloys the primary phase, i.e. the first phase to form from the liquid upon solidification, is α(Mg), usually a coarse dendrite. The second and third stages of solidification would be the eutectic-like α+C36 and α+C15-Al_2Ca. For a quaternary system, these phases do not freeze at a fixed temperature and generally are found surrounding the primary phase in the microstructure. The subsequent solidification stage $Mg_{17}Sr_2$ will form. After that, for alloy Mg-5Al-2.75Ca-0.25Sr, the solidification will end at the quaternary eutectic invariant reaction: $L \rightarrow \alpha + C15 + Mg_{17}Sr_2 + C14\text{-}Mg_2Ca$. While for alloy Mg-5Al-2Ca-1Sr, there will be negligible amount of Al_4X (about 0.2%) and γ-$Mg_{17}Al_{12}$ (about 0.4%) phase formed in the final solidification stage. From above discussion, it can be seen that there is a fairly good agreement between the calculated solidification paths and the experimentally observed

microstructures from the ac-cast alloys [16]. The only exception is that the calculations predict that there will be small amount of C15 phase formed in both alloys, about 0.4 % and 3 % respectively. However, Suzuki et al did not report the existence of C15 in any of their as-cast microstructures. The possible reason, which might account for this, could be two folds. On the one hand, it is possible that there is indeed very small amount of C15 phase, but it is very difficult to detect experimentally in the as-cast alloys. On the other hand, it is also possible that solidification path calculation is not accurate enough due to the fact that the descriptions of the two constituent ternary systems were obtained by extrapolation, as mentioned early, or the assumption of no diffusion in solid for the Scheil model is not fully valid.

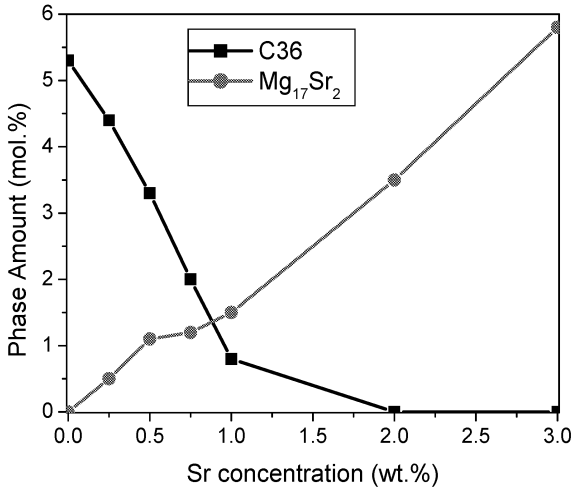

Figure 3. Phase amounts of C36 and $Mg_{17}Sr_2$ as a function of the Sr content from the Scheil calculation for the series of alloys with compositions of Mg-5Al-(3-x)Ca-xSr.

Figure 3 shows the amounts of the C36 and $Mg_{17}Sr_2$ phases as functions of Sr content calculated based on Scheil model and the Mg-Al-Ca-Sr thermodynamic description obtained in the present study. It is clear that in this series of alloys with compositions of Mg-5Al-(3-x)Ca-xSr, the amount of C36 decreases while that of $Mg_{17}Sr_2$ increases when Sr concentration increases. The exact same trend was observed by Suzuki et al [16].

Base on the above discussion, the good agreement between the calculation and the experimental data leads us to conclude that the current Mg-Al-Ca-Sr thermodynamic description can be used as a viable guidance for new alloys development or improvement of the existing alloys. In the future, it would be desirable to have the other two ternary systems, Mg-Ca-Sr and Al-Ca-Sr modeled thermodynamically, when some key thermochemical or phase equilibria data become available, rather than just extrapolation from the corresponding constituent binaries.

Summary

A thermodynamic database of Mg-Al-Ca-Sr was developed based on the descriptions of the constituent binaries and key ternaries. Using this description, the calculated isopleth with 92 wt.% Mg and 5 wt.% Al is in good accordance with the experimental data in the literature. It is very useful to understand the equilibrium phase relationships at low temperatures. The calculated solidification paths based on the Scheil model is also in line with the microstructure observations in the as-cast alloys. The good agreement between the calculation and the experimental data suggests that the present thermodynamic description is reliable for the Mg-rich region of Mg-Al-Ca-Sr system and can be considered as a useful tool for alloys development and improvement.

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