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Phase equilibria, thermodynamics and solidification microstructures of Mg–Sn–Ca alloys, Part 1: Experimental investigation and thermodynamic modeling of the ternary Mg–Sn–Ca system

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Abstract

The phase equilibria of the Mg–Sn–Ca system for the entire composition and temperature ranges have been clarified based on the Calphad method. To obtain a reliable thermodynamic description, we performed key experiments for the phase boundary data and also utilized the first-principle results of the finite-temperature properties for the binary and ternary compounds. Experimental works for the phase equilibria, which consist of thermal, crystallographic and microstructural analyses, and the thermodynamic modeling combined with finite-temperature first-principle calculations are reported. The satisfying agreements between the experimental and calculated results support the reliability of the proposed thermodynamic description. The phase diagram for overall composition and temperature ranges of the ternary system based on the thermodynamic calculations is presented. In a second study this result is applied to obtain details of the phase formation during solidification for practically important Mg-rich as-cast alloys.

Keywords: A. Ternary alloy systems; B. Phase diagrams; B. Thermodynamic and thermochemical properties; E. Phase diagram, prediction; F. Electron microscopy, scanning

1. Introduction

In recent years, magnesium alloys have become a center of interest among material engineers and scientists. The combination of lightweight, high specific strength and good castability makes Mg alloys a promising engineering material of the automotive and aviation industries [1,2]. Most commercial Mg alloys are Mg–Al based (AZ and AM series) with additions of Zn, Mn and/or Ca, Sr, Si, RE (RE: rare earth mischmetal), which demonstrate good room-temperature strength and ductility with satisfying salt-spray corrosion resistance and excellent castability [3]. On the other hand, Al-free Mg alloys are currently attracting attention as a next generation of commercial Mg alloys, in the light of the fact that grain refinement can effectively be realized by the addition of Zr, which is not possible in the Al-containing AZ and AM series because of detrimental Al–Zr compound formation. Mg–Sn–Ca (TX series) as well as Mg–Zn–Zr (ZK series) is among the most important systems for the Al-free Mg alloys. It has been suggested in Ref. [4] that the addition of Sn improves strength at the expense of ductility in Mg alloys. Some precipitates involving Ca could be considered relevant to this behavior.

The effects of additional elements on the phase equilibria in alloys are of great importance in material design and manufacture. The focused optimization of alloy composition and heat treatment conditions is virtually impossible without the knowledge of pertinent phase equilibria. Therefore phase diagrams of

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multi-component Mg-systems are indispensable information. Despite its importance mentioned above, the phase diagram of the ternary Mg–Sn–Ca system has not been established yet. Even isolated equilibrium phase boundary data could not be found in the literature. The aim of this work is to clarify the phase equilibria of this important ternary system over the entire composition and temperature ranges, for the first time, based on a combination of the Calphad methodology, first-principle calculations and own key experiments.

The Calphad method has been recognized as a powerful method to provide the phase equilibria and thermodynamic quantities in multi-component systems with high accuracy [5,6]. Within this approach, the Gibbs free energies for all the phases involved in the system of interest are quantified with relatively simpler mathematical expression and/or statistical mechanics formula based on various kinds of experimental data. Hence, the reliability of the Calphad method is largely dependent on the available experimental data. As mentioned above, however, little has been clarified for the Mg–Sn–Ca phase equilibria. Therefore, we performed our own painstaking experiments for the determination of the phase equilibria by means of X-ray diffraction (XRD), scanning electron microscopy with energy-dispersive X-ray analysis (SEM/EDX), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). These experimental results are then fully employed in the Calphad modeling. In order to obtain a highly reliable thermodynamic description, furthermore, we utilize the finite-temperature first-principle results as detailed below.

Alloys with considerable content of Ca often involve the difficulty to realize true equilibrium, due to the high reactivity and high vapor pressure and also the low purity of commonly used Ca. A recent work on the Calphad modeling of the Ca–Sn system by the present authors [7] has clarified that the formation enthalpy of compounds from Ca-rich part experimentally determined in the early work [8] is unrealistic. In Ref. [7] the authors performed two types of Calphad modeling, one is based only on the experimental data and the other is based on the first-principle output of finite-temperature properties of compounds and, then, the detailed comparison between them indicates that the latter description is more realistic than the former one. In this regard, careful attention should be paid to the present ternary system where, in addition to the Ca–Sn binary compounds, a Mg–Ca binary compound (Mg_2Ca) and two ternary compounds exist, as described in the next section. The finite-temperature properties of these compounds should be subjected to the first-principle investigation. Especially, there have been no thermodynamic data available for two reported ternary compounds. In the present work, therefore, we extend the combined approach of the Calphad and finite-temperature first-principle methods recently attempted in Ref. [7] to the present ternary system. The details of the methods for the present first-principle calculations are found in Refs. [9,10] and also in Ref. [7] for the Ca–Sn binary phases, and the main concern of this study is the thermodynamic modeling based on these outputs.

As mentioned above, this is the first investigation of phase equilibria of the Mg–Sn–Ca ternary system over a wide range of composition and temperature, consisting of the detailed experiments on phase equilibria and the Calphad modeling combined with finite-temperature first-principle calculations and, furthermore, the solidification process for the Mg-rich alloys.

We report our extensive work on Mg–Sn–Ca alloys in a series of two publications. In this paper (part I of this series), the Calphad modeling combined with finite-temperature first-principle calculations and the experimental work on the phase equilibria are presented, using ternary key samples selected at strategic intermediate compositions (16–67 at.% Mg). This is followed by the comparison between the calculated and experimental results concerning liquidus surface, isothermal sections at various temperatures, invariant reactions and sequence of phase formation during solidification process to demonstrate the consistency of the constructed thermodynamic description.

The second report [11] (denoted ‘‘part II’’ here) is devoted to an application to practically important Mg-rich (92–96.5 wt.% Mg) as-cast alloys, demonstrating the satisfying consistency between the phase formation obtained by computational thermochemistry using the constructed description and the solidification behavior revealed in an experimental investigation.

2. Literature data

2.1. Binary subsystems

Successful Calphad modeling for each of the constituent binaries Mg–Ca, Mg–Sn and Ca–Sn has been already performed. In the following, we briefly refer to the Calphad modeling relevant to the present work and demonstrate the calculated phase diagrams for the discussion of ternary phase equilibria given in Section 6.

The Calphad modeling of the Mg–Sn system was reported in Ref. [12] and subsequently corrected in Ref. [13]. In the Mg–Sn system, the existing phases are liquid, hcp-(Mg), bct-αSn, diamond-βSn, and the intermediate compound Mg_2Sn. No solubility of Mg in βSn has been experimentally observed, but there is a small amount of solubility of Sn in (Mg). There are two eutectic reactions: one is $L \leftrightarrow (Mg) + Mg_2Sn$ at 563 °C on the Mg-rich side and the other is $L \leftrightarrow \beta Sn + Mg_2Sn$ at 204 °C on the Sn-rich side. The congruent melting of Mg_2Sn occurs at 774 °C. Fig. 1 shows the calculated phase diagram for the Mg–Sn system based on the corrected version [13].

The thermodynamic modeling of the Ca–Sn system has been recently reported by the present authors [7]. In that work, due to a discrepancy between the experimental and first-principle data of formation enthalpy of compounds, two types of thermodynamic modeling were attempted: one is based on the first-principle output (model I) and the other based on the experimental data (model II). The detailed comparison between the several types of experimental data and the corresponding calculated results revealed that model I is superior to model II. Shown in Fig. 2 is the phase diagram calculated by model I. One sees that there are seven compounds in