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Thermodynamic modeling of the La–Mg–Zn, Pr–Mg–Zn and Sm–Mg–Zn system

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ABSTRACT

All available phase diagram data for the La–Mg–Zn, Pr–Mg–Zn and Sm–Mg–Zn systems have been collected and critically assessed. Critical thermodynamic evaluations and optimizations of the La–Mg–Zn, Pr–Mg–Zn and Sm–Mg–Zn systems were carried out and model parameters for the thermodynamic properties of all phases have been obtained.

1. Introduction

Magnesium being the lightest structural metal, Mg-based alloys have many applications. Zinc is one of the most commonly used alloying elements in Mg (AZ series), and the rare earth (RE) metals have been shown to improve creep resistance [1,2] and sheet formability (by reducing texture [3–6]).

Information on phase behavior is essential for the design of new RE–Mg–Zn alloys. However, few studies of the phase diagrams and thermodynamic properties of these systems have been made. The present study was thus undertaken to better define the phase diagrams of the RE–Mg–Zn ternary systems through the technique of critical thermodynamic assessment and optimization coupled with limited experimentation.

In a thermodynamic optimization, adjustable model parameters are calculated using all available thermodynamic and phase-equilibrium data in order to obtain one set of model equations as functions of temperature and composition. Thermodynamic data, such as activities, can aid in the evaluation of the phase diagrams, and information on phase equilibria can be used to deduce thermodynamic properties. With this technique, it is frequently possible to resolve discrepancies in the available data. From the model equations, all of the thermodynamic properties and phase diagrams can be back-calculated, and interpolations and extrapolations can be made in a thermodynamically correct manner. The thermodynamic properties and phase diagrams are thereby rendered self-consistent and consistent with thermodynamic principles, and the available data are distilled into a small set of model parameters, ideal for computer storage. Generally, in the optimization of a ternary system one begins by optimizing the three binary sub-systems. The binary model parameters are then used to estimate the properties of the ternary phases, and these estimates are then refined by introducing ternary model parameters where required to reproduce available ternary data.

Thermodynamic evaluations and optimizations have already been reported for the binary Mg–Zn system [7], all binary Mg–RE systems [8–11] and all binary RE–Zn systems (including Sc–Zn and Y–Zn) [12,13]. The liquid phase of the Mg–Zn system has been remodeled in the present work with the Modified Quasichemical Model (MQM) as will be discussed in Section 3. Evaluations, optimizations and experimental phase diagram studies of the Ce–Mg–Zn and Nd–Mg–Zn systems have been reported in our previous articles [14,15]. In the present article we report on our evaluations and optimizations of the La–Mg–Zn, Pr–Mg–Zn and Sm–Mg–Zn systems. In a subsequent article we shall report on our evaluations and optimizations of other ternary heavier-RE–Mg–Zn systems [16]. As expected, all RE–Mg–Zn systems are very similar. The present work on the La–Mg–Zn, Pr–Mg–Zn and Sm–Mg–Zn systems was greatly aided by our simultaneous assessments of the

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other RE–Mg–Zn systems.

Figs. 1–7 show the seven binary sub-systems of the La–Mg–Zn, Pr–Mg–Zn and Sm–Mg–Zn systems [7,8,12].

2. Phase equilibrium and thermodynamic data

The La–Mg–Zn, Pr–Mg–Zn and Sm–Mg–Zn systems have been investigated by several authors. Different ternary phase names were used by different authors. Phases with ternary phase fields considered in the present optimization are summarized in Table 1. All these phases (except the metastable ones) can also be seen in the calculated isothermal sections at 300 °C shown in Figs. 9, 14 and 17.

The same nomenclature as described in our previous report on the Ce–Mg–Zn system [14] is used here. The La–Mg–Zn system has been investigated over the entire composition range. None of the phases corresponding to phases τ1 to τ7 as considered in the Ce–Mg–Zn system [14] have been observed. However, although τ3 was not reported in the La–Mg–Zn system as a phase separate from $LaMg_3$, it is nevertheless assumed in the present study because it is a common phase observed in many other RE–Mg–Zn systems.

Phases corresponding to τ3, τ4 and τ5 were reported in the Pr–Mg–Zn and Sm–Mg–Zn systems, as will be discussed in section 2.2 and 2.3. Consequently, they are considered in the present study. Phases corresponding to τ1, τ2, τ6 and τ7 have not been reported. As mentioned previously [14,15], these phases could very well be stable in the Pr–Mg–Zn and Sm–Mg–Zn systems. However, no investigations have been carried out in the composition ranges where they might be found. Consequently, τ1, τ2, τ6 and τ7 are not assumed in the present study in the Pr–Mg–Zn and Sm–Mg–Zn systems.

The phase La(Mg,Zn), Pr(Mg,Zn) and Sm(Mg,Zn) in Table 1 are solid solutions of LaMg and LaZn, PrMg and PrZn and SmMg and SmZn, respectively. The phases $LaMg_3$, $PrMg_3$, $SmMg_3$, La_2Mg_{17}, $LaMg_{12}$ and $PrMg_{12}$ are solutions with limited solubility of Zn. The phases $LaZn_4$ and La_2Zn_{17} are solutions with limited solubility of Mg. The metastable binary $SmMg_{12}$ and $SmZn_{12}$ phases were considered and their thermodynamic parameters were estimated in previous work [8,12]. These two phases have the same crystal structure and thus are assumed to form a possible solution phase in the present study. As will be discussed in Section 4.3, the present calculations suggest that this phase is metastable. All other binary phases are assumed not to extend into the ternary systems. The prototypes, Pearson symbols and space groups of all binary phases were given previously [7,8,12].

Possible ternary phases in RE–Mg–Zn systems, both stable and metastable, as assumed in the present project [14–16], are summarized in Table 2.

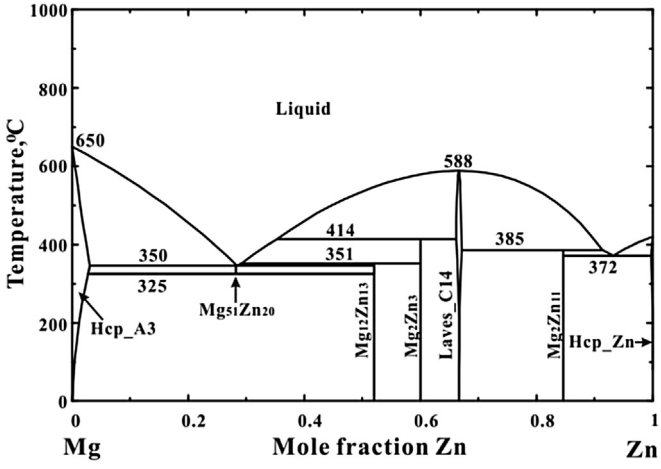

Fig. 1. Calculated optimized Mg–Zn phase diagram [7].

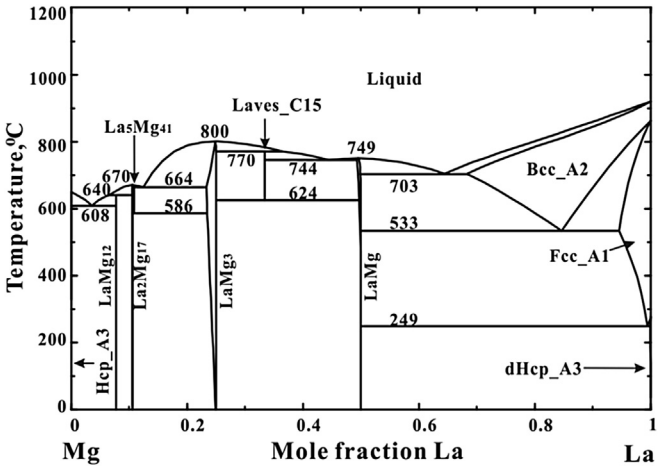

Fig. 2. Calculated optimized Mg–La phase diagram [8].

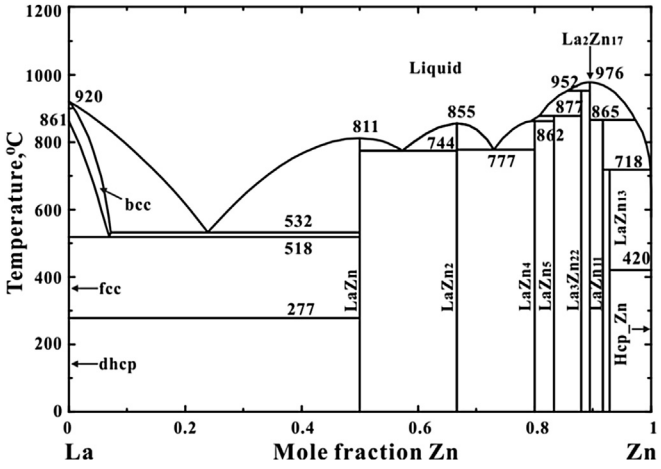

Fig. 3. Calculated optimized La–Zn phase diagram [12].

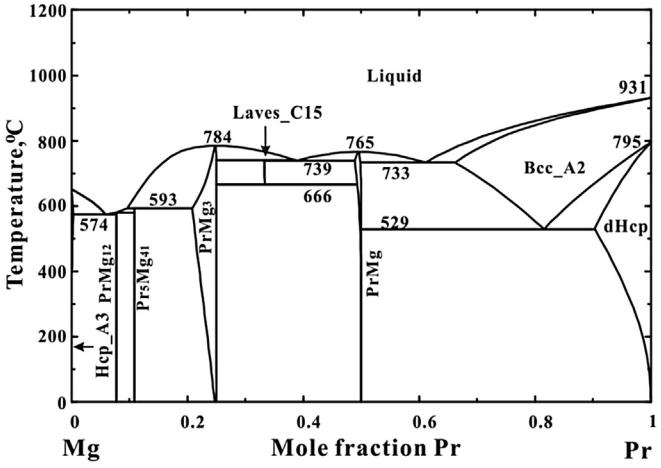

Fig. 4. Calculated optimized Mg–Pr phase diagram [8].

2.1. La–Mg–Zn

The La–Mg–Zn system was first investigated by Dobatkina et al. [17,18] by differential thermal analysis (DTA), electron probe microanalysis (EPMA), X-ray diffraction analysis (XRD) and micro-