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A thermodynamic description of the Gd–Mg–Y system

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Abstract

Thermodynamic modeling and optimization of the Gd–Mg, Mg–Y, Gd–Y binary systems and the Gd–Mg–Y ternary system have been critically carried out by means of the CALPHAD (CALculation of PHAse Diagrams) technique. The solution phases (liquid, body-centered cubic, and hexagonal close-packed) are modeled with the Redlich–Kister equation. The Compound Energy Model has been used to describe the thermodynamic functions of the intermetallic compounds in these systems. The compounds Mg_2Y, Mg_5Gd, Mg_3Gd, Mg_2Gd and $Mg_{24}Y_5$ in the Gd–Mg–Y system have been treated as the formulae (Mg, Y)$_2$(Gd, Mg, Y), Mg$_5$(Gd, Y), Mg$_3$(Gd, Y), Mg$_2$(Gd, Y) and Mg$_{24}$(Gd, Mg, Y)$_4$Y, respectively. A model (Gd, Mg, Y)$_{0.5}$(Gd, Mg, Y)$_{0.5}$ has been applied to describe the compound MgM formed by MgGd and MgY in order to cope with the order–disorder transition between the body-centered cubic solution (A2) and MgM with CsCl-type structure (B2) in the Gd–Mg–Y system. A set of self-consistent thermodynamic descriptions of the Gd–Mg–Y system have been obtained. The projection of the liquidus surfaces and the entire reaction schemes for the Gd–Mg–Y system have been constructed.

Keywords: Gd–Mg–Y system; CALPHAD technique; Thermodynamic properties; Order–disorder transition; Mg-based alloys

1. Introduction

Magnesium alloys have received considerable attention in recent years due to their potential applications as hydrogen storage material and because they are the lightest metal structural material [1–3]. The optimization of alloy composition and heat-treatment conditions is impossible without knowledge of their phase equilibria. In addition, the experimental determination of a ternary phase diagram is very time consuming. An advanced method for the design of multi-component alloys with specific properties is the thermodynamic calculation of phase diagrams (CALPHAD) [4]. The thermodynamic properties of a system are analyzed by using mathematical models for the Gibbs energy of the individual phases. The models involve empirical parameters, which are defined or estimated from the experimental information. Once a self-consistent thermodynamic description of a system is obtained, any kind of phase diagram and thermodynamic property of interest can be calculated. The results help to define and plan further key experiments, which need to be performed to understand the system comprehensively and to allow further refinement of the thermodynamic descriptions.

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2. Experimental information

2.1. Mg–Y system

Gibson and Carlson [5] first investigated the Mg–Y phase diagram using thermal analysis, X-ray diffraction, and microstructure analysis in the temperature range of 400–950 °C. Five invariant reactions were reported: liq. → (Mg) + ε(Mg$_{24}$Y$_5$) at 566 °C; β(Y) → α(Y) + γ(MgY), 775 °C; liq.+δ(Mg$_2$Y) → ε, 650 °C; liq.+γ → δ, 780 °C and liq. + β(Y) → γ, 935 °C. Mizer and Clark [6] determined the phase relationships in the range of 200–650 °C and 0–20 wt% Y by metallography and thermal analysis. Miannay et al. [7] measured the phase diagram at 8–40 wt% Y and 500–650 °C and the homogeneity range of the ε-phase by metallography and thermal analysis. The compositions of the ε and δ phases were reported as near to Mg$_{24}$Y$_5$ and MgY, respectively. Smith et al. [8] determined the structure and composition of the intermetallic compounds γ, δ and ε. The homogeneity ranges of the γ and ε phases were reported to be 50–52 at.% Mg for γ-MgY and 84–87.5 at.% Mg for ε-Mg$_{24}$Y$_5$.

The Mg–Y system in the composition range of 0–40 wt% Y and at 650 °C was studied by Sviderskaya and Padezhnova [9]

using metallography and thermal analysis. Lashko et al. [10] investigated the non-equilibrium Mg–Y phase diagram in the Mg-rich region (0.6–3.6 at.% Y). They detected a metastable compound Mg_5Y with hexagonal structure, which had been reported earlier by Anderko et al. [11] as an Mg-rich compound in the equilibrium phase diagram. A metastable eutectic reaction liq. → hcp(Mg) + Mg_5Y at 563 °C was shown in the Mg-rich non-equilibrium phase diagram. Mizer and Peters [12] and Drits et al. [13] investigated solid solution precipitation in the Mg–Y system.

In addition, Buschow [14], Chao and Duwez [15] and Newman [16] studied the magnetic properties of MgRE CsCl-type compounds. Buschow [17] studied the magnetic properties of Mg_2RE compounds in the temperature range 1.5–300 K.

Based on the above experimental information, the Mg–Y system was reviewed by Nayeb-Hashemi and Clark [18]. Three solutions, i.e., liquid, hcp(Mg, Y) and bcc(Y), and three intermetallic compounds, i.e., $Mg_{24}Y_5$, Mg_2Y, and MgY were presented. Lately, Giovannini et al. [19] and Flandorfer et al. [20] have determined the homogeneity ranges and the lattice parameters of the intermetallic compounds in the Mg–Y system, while the La–Mg–Y system was investigated by them. A wider homogeneity range for Mg_2Y 66.7–74 at.% Mg was reported.

The enthalpies of mixing of liquid Mg–Y at 955, 975, 984, 1020, 1057 and 1074 K were obtained by Agarwal et al. [21] by drop calorimetry in the Mg-rich side of the Mg–Y system. The activity of Mg in the liquid phase was derived by Ganesan and Ipser [22] from vapor pressure measurements using an isopiestic method. The enthalpies of formation of compounds $Mg_{24}Y_5$, Mg_2Y and MgY were determined calorimetrically by Smith et al. [8] and Pyagai et al. [23].

2.2. Gd–Mg system

The Gd–Mg system was first investigated by Savitskii et al. [24] and four compounds MgGd, Mg_2Gd, Mg_3Gd and Mg_9Gd were reported. The solubility of Mg in α(Gd) was reported by Joseph and Gschneidner Jr. [25]. Rokhlin and Nikitina [26] determined the solubility of Gd in hcp(Mg), and reported a eutectic reaction liquid → Mg_9Gd + hcp(Mg) at 544 °C and at the composition of liquid 90.7 at.% Mg. Manfrinetti and Gschneidner Jr. [27] investigated the Gd–Mg phase diagram once more, and confirmed the existence of four compounds Mg_5Gd, Mg_3Gd, Mg_2Gd and MgGd, which are formed by peritectic reactions, MgGd at 868 °C, Mg_2Gd at 756 °C, Mg_3Gd at 720 °C and Mg_5Gd at 658 °C. The Mg-rich eutectic reaction liquid → Mg_5Gd + hcp(Mg) occurred at 91.2 at.% Mg for liquid and 548 °C, in good agreement with the values of 90.7 at.% Mg and 544 °C reported by Rokhlin and Nikitina [26].

Based on the above experimental data, the Gd–Mg system was reviewed by Nayeb-Hashemi and Clark [28]. In their assessment of the Gd–Mg system, it consists of liquid, bcc(Gd), hcp(Mg, Gd) and four intermetallic compounds Mg_5Gd, Mg_3Gd, Mg_2Gd and MgGd. The maximum solubility of Gd in hcp(Mg) and Mg in α(Gd) are shown as 4.53 at.% Gd and 14.4 at.% Mg, respectively.

The enthalpies of formation of compounds in the Gd–Mg system were determined by Pahlman and Smith [29], and Cacciamani et al. [30].

2.3. Gd–Y system

The Gd–Y phase diagram was determined by Spedding et al. [31] using differential thermal analysis, metallographic observations, and X-ray diffractography. In the Gd–Y system, there are only three solution phases: liquid, bcc, and hcp.

2.4. Gd–Mg–Y system

Drits et al. [32] determined the isoplethic sections of the Gd–Mg–Y system, $w(Gd)/w(Y) = 3$, $w(Gd)/w(Y) = 1$ and $w(Y)/w(Gd) = 3$. The $w(Y)$ and $w(Gd)$ are the weight fractions of Y and Gd, respectively. In their work, the compounds $Mg_{24}Y_5$ and Mg_6Gd were considered as one liner compound β-Mg_6(Gd, Y). Giovannini et al. [33] determined the isothermal section at 773 K, and found that both compounds $Mg_{24}Y_5$ and Mg_5Gd exist. No new ternary compounds were reported.

3. Thermodynamic model

3.1. Unary phases

The Gibbs energy function $G_i^{0,\phi}(T) = G_i^{\phi}(T) - H_i^{\mathrm{SER}}$ (298.15 K) for the element i (i = Gd, Mg, Y) in the phase ϕ (ϕ = liquid, body-centered cubic (bcc), or hexagonal close-packed (hcp)), is described by an equation of the following form:

$$G_i^{0,\phi}(T) = a + bT + cT\ln T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} \quad (1)$$

where H_i^{SER} (298.15 K) is the molar enthalpy of the element i at 298.15 K in its standard element reference (SER) state, hcp for Gd, Mg and Y. The Gibbs energy of the element i, $G_i^{\phi}(T)$, in its SER state, is denoted by GHSER_i, i.e.,

$$\mathrm{GHSER}_i = {}^{0}G_i^{\mathrm{hcp}}(T) - H_i^{\mathrm{SER}}(298.15). \quad (2)$$

In the present work, the Gibbs energy functions are taken from the SGTE compilation of Dinsdale [34].

3.2. Mg–Y system

3.2.1. Solution phases

In the Mg–Y system, there are three solution phases: liquid, bcc(Y), and hcp(Mg, Y). Their Gibbs energies are described by the following expression:

$$G_m^{\phi} = x_{\mathrm{Mg}}G_{\mathrm{Mg}}^{\phi}(T) + x_{\mathrm{Y}}G_{\mathrm{Y}}^{\phi}(T) + RT(x_{\mathrm{Mg}}\ln x_{\mathrm{Mg}} + x_{\mathrm{Y}}\ln x_{\mathrm{Y}}) + {}^{E}G_m^{\phi} \quad (3)$$