

Thermodynamic Assessment of the Mg-Y and Mg-Ce System

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Abstract

The Mg-Y and Mg-Ce binary systems have been assessed with CALPHAD method. Liquid, Bcc and Fcc phases are treated as substitutional solution phases, of which the excess Gibbs energies are modeled by Redlich-Kister polynomial functions. The binary intermetallic compounds are treated as stoichiometric phases. Thermodynamic parameters of various phases have been optimized and the calculated results are in agreement with experimental data.

Keywords: Thermodynamic calculation; Mg-Y system; Mg-Ce system; Schwarzschild radius; Phase diagram

Introduction

Mg-based alloys with high strength and high electronic-conductivity have found wide application in high-speed train and electronic industry. However, high strength is usually incompatible with high electric conductivity in materials. Addition of rare earth elements into copper matrix and adoption of proper heat-treatment may help to achieve high strength while maintaining high conductivity. For example, it was reported that Y improves the strength and electronic-conductivity while the temperature coefficient of resistivity is negative [1,2]. Y is also a candidate element for improving the properties, such as magnetic moment, hall effect and magnetic resistivity, of some Mg-contained magnetic materials [3]. Generally, Y, Ce are found to be capable of improving resistivity of Mg-based alloys [4,5]. Knowledge of phase diagrams of the related multi-component Mg-alloys is essential to understand the role of these rare earth elements and do help in alloy design (optimal compositions) and fabrication (forming methods and heat-treatment conditions) for improving the material properties of Mg-alloys. The Mg-Y and Mg-Ce systems were assessed [6,7]. However, their assessments were only based on the phase diagram data and the lattice stabilities for Mg, Y and Ce were out-of-date [8]. Moreover, there are new thermodynamic data available since the previous calculation [9]. The purpose of this work is then to thermodynamic assess the Mg-Y and Mg-Ce systems with all the updated data.

Evaluation of Experiment Data

Mg-Y system

The melting points of Mg and Y in this work are accepted as 1084.87°C and 822°C, respectively [8,11,12]. Note, the melting point reported for Eu was 7°C lower than the accepted value due to impurity in their Y samples (99% Y) [10-12]. By thermal analysis found that the solid solubility of Mg in Y is negligible. Similarly, there was no evidence of terminal solid solubility of Y in Mg. According to there are four intermediate phases in this system: The Mg₅Y melts congruently at 847°C which is isostructural to CaCu₅; The Mg₂Y is a CeCu₂-structure intermediate phase formed peritectically from liquid at 597°C; and MgY of orthorhombic FeB-type crystal structure melts incongruently at 537°C, while MgY₂ of Ca₂Cu structure incongruently melts at 442°C [10]. The heat of mixing of liquid in copper-rich concentration region was measured using isoperibolic calorimetry [9]. It was found that the minimum enthalpy of mixing is correspond to the compound Ce₅Eu [9]. Other thermodynamic property of the Mg-Y system was not reported [9-18].

Mg-Ce system

The experimental information of the Mg-Ce system is limited. The phase diagram was studied based on Differential Thermal Analysis (DTA), metallography and X-ray diffraction. On the basis of lattice parameter measurements, determined that there is no appreciable terminal solid solubility in the Mg-Ce system. Later, reported that the maximum solid solubility of Ce in Mg is ~0.07 wt.% (~0.03 at.%) at the eutectic temperature. Of the five intermediate phases reported by, only Mg₉Ce₂ melts congruently at 937°C whereas Mg₅Ce, Mg₇Ce₂ and MgCe form incongruently at 879°C, 825°C, 757°C and 628°C respectively [19-22]. The (βCe)→(γCe) transformation temperature is accepted from 760°C, which is 35°C lower than that reported. The crystal structure of the three intermediate phases are listed in TABLE 1.

TABLE 1. Intermetallic crystal structure in Mg-Y and Mg-Ce system.

Phase	Composition, at.% Yb	Pearson symbol	Space group	Prototype	Reference
Mg ₅ Y	~16.67	<i>hp6</i>	<i>P6/mmm</i>	CaCu ₅	[13-14]
Mg ₂ Y	~33.3	<i>oI2</i>	<i>Imma</i>	CeCu ₂	[15-16]
MgY	~50	<i>oP8</i>	<i>Pnma</i>	FeB	[17-18]
MgY ₂	~66.67	<i>oP12</i>	<i>Pnma</i>	Ca ₂ Cu	[10]
Mg ₅ Ce	~16.67	<i>hP6</i>	<i>P6/mmm</i>	CaCu ₅	[21]
Mg ₂ Ce	~33.3	<i>oI12</i>	<i>Imma</i>	CeCu ₂	[22]
MgCe	~50	<i>oP8</i>	<i>Pnma</i>	FeB	[19]

Heats of mixing of liquid in copper-rich concentration region were measured using isoperibolic calorimetry [9]. It was found that heats of mixing are negative [9].

Thermodynamic Model

The lattice stabilities for element Mg, Y and Ce are referred [5]. An ordinary substitutional solution model is employed to describe liquid, Bcc and Fcc terminal solution. The molar Gibbs energy of a solution phase Φ (Φ = Liquid, Fcc, Bcc) can be represented as a sum of the weighted Gibbs energy for the pure components, the ideal entropy term describing a random mixing of the components, and the excess Gibbs energy describing the degree of deviation from ideal mixing, i.e.

$$G_m^\Phi = \sum x_i^0 G_i^\Phi + RT \sum x_i \ln(x_i) + G_m^E \quad (1)$$

where G_m^Φ is the molar Gibbs energy of a solution phase Φ , the Gibbs energy of pure element i , the mole fraction of component i (i = Mg, Y or Cu, Ce), R gas constant, T temperature, G_m^E the excess Gibbs energy. For ordinary substitutional solution, the excess Gibbs energy of phase Φ can be written in the form of a Redlich-Kister polynomial as follows:

$${}^E G_m^\Phi = x_{Mg} x_M \sum_{j=0}^n {}^{(j)} L_{Mg,M}^\Phi (x_{Mg} - x_M)^j \quad (2)$$

Here M is either Ce or Y; an interaction parameter and can be expressed as temperature dependent as follows:

$${}^{(j)} L_{Mg,M}^\Phi = A_j + B_j \times T + C_j \times T \ln(T) \quad (3)$$

where, and are model parameters to be optimized.

The intermetallic phases have been treated as stoichiometric phases Mg_pMg_q. Due to lack of heat capacity and according to the Neumann-Kopp rule, the Gibbs energy of Mg_pMg_q can be formulated as:

$$G_{Mg_pMg_q} = \frac{p}{p+q} \times {}^0 G_{Mg}^{Fcc} + \frac{q}{p+q} \times {}^0 G_M^S + A + BT \quad (4)$$

Where S is the stable phase of M at 298.15 K and S represents Body-Centered Cubic (BCC) for Ce, Face-Centered Cubic (FCC) for Y. A and B are the adjustable parameters being optimized in the present work.

Results and Discussion

On the basis of lattice stabilities cited [8]. The optimization of the two systems is carried out using the Parrot modules in the Thermo_Calc program developed [23]. Thermodynamic parameters of all phases in these 2 systems are obtained, as listed in TABLE 2. All experimental data including phase diagrams and thermodynamics are reasonably reproduced. Detailed analysis is given below.

TABLE 2. Thermodynamic parameters of the Mg-Y and Mg-Ce system.

System	Phase	Thermodynamic parameters
Mg-Y	Liquid	${}^0 L_{Mg,Y} = -25402.860 + 89.739T - 11.941T \ln(T)$
		${}^1 L_{Mg,Y} = -15903.788 + 12.691T$
		${}^2 L_{Mg,Y} = -11787.219$
	Bcc	${}^0 L_{Mg,Y}^{Bcc} = +5000$
	Fcc	${}^0 G_Y^{Fcc} - GHSEY = +180000$
		${}^0 L_{Mg,Y}^{Fcc} = +5000$
	Mg ₅ Y	$G^{Mg_5Y} = 0.8333 {}^0 G_{Mg}^{Fcc} + 0.1667 {}^0 G_Y^{Bcc} - 4363.535 - 1.237T$
	Mg ₂ Y	$G^{Mg_2Y} = 0.6667 {}^0 G_{Mg}^{Fcc} + 0.3333 {}^0 G_Y^{Bcc} - 5968.325 + 0.235T$
	MgY	$G^{MgY} = 0.5 {}^0 G_{Mg}^{Fcc} + 0.5 {}^0 G_Y^{Bcc} - 6135.327 + 1.137T$
MgY ₂	$G^{MgY_2} = 0.3333 {}^0 G_{Mg}^{Fcc} + 0.6667 {}^0 G_Y^{Bcc} - 5912.367 + 3.156T$	
Mg-Ce	Liquid	${}^0 L_{Mg,Ce} = -41356.325 + 33.75T - 7.201T \ln(T)$
		${}^1 L_{Mg,Ce} = -30258.324 + 15.025T$
	Fcc	${}^0 L_{Mg,Ce}^{Fcc} = +10000$
		${}^1 L_{Mg,Ce}^{Fcc} = -10000$
	Mg ₅ Ce	$G^{Mg_5Ce} = 0.8333 {}^0 G_{Mg}^{Fcc} + 0.1667 {}^0 G_{Ce}^{Fcc} - 15339.485 + 2.2025T$
	Mg ₉ Ce ₂	$G^{Mg_9Ce_2} = 0.8182 {}^0 G_{Mg}^{Fcc} + 0.1818 {}^0 G_{Ce}^{Fcc} - 16248.917 + 2.0060T$
	Mg ₇ Ce ₂	$G^{Mg_7Ce_2} = 0.7778 {}^0 G_{Mg}^{Fcc} + 0.2222 {}^0 G_{Ce}^{Fcc} - 16841.985 + 1.4725T$
	Mg ₂ Ce	$G^{Mg_2Ce} = 0.6667 {}^0 G_{Mg}^{Fcc} + 0.3333 {}^0 G_{Ce}^{Fcc} - 17792.410 + 5.7701T$
MgCe	$G^{MgCe} = 0.5 {}^0 G_{Mg}^{Fcc} + 0.5 {}^0 G_{Ce}^{Fcc} - 14796.220 - 1.4309T$	

Note: Gibbs energies are expressed in J/mol. Lattice stabilities of elements Mg, Y and Ce are referred [8].

Mg-Y system

No Solubility is assumed in the bcc (Y) solution, which is realized by assigning a large positive interaction parameter, i.e.

$${}^0L_{Mg,Y}^{Bcc} = 5000 \text{ J/mol} \tag{4}$$

In this work, the lattice stabilities of Eu in fcc is +180000, which is assessed [24]. And the interaction parameter of fcc solution phase is just given a large positive, i.e.

$${}^0L_{Mg,Y}^{Fcc} = 5000 \text{ J/mol} \tag{5}$$

The thermodynamic data of liquid (the reference states are pure liquid Mg and Y) and the liquidus of terminal solution are first used to optimize simultaneously the binary interaction parameters of liquid. The parameters of various intermetallic phases are then optimized through fitting the phase diagram data, especially the invariant reactions. All the parameters were finally evaluated together to give a reasonable description of this system. **FIG. 1** shows the calculated phase diagram of Mg-Y system compared with experimental data.

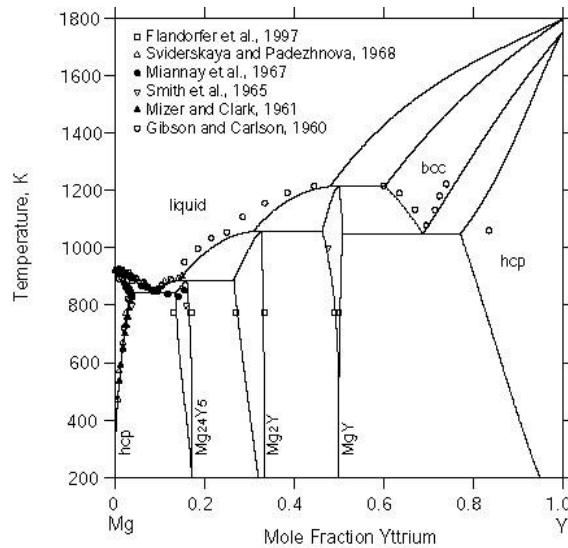


FIG.1. The calculated Mg-Y phase diagram with experimental data.

Combined with invariant reactions (as listed in **TABLE 3**), it is now clear that there is good agreement between the calculated values and the experimental phase diagram data.

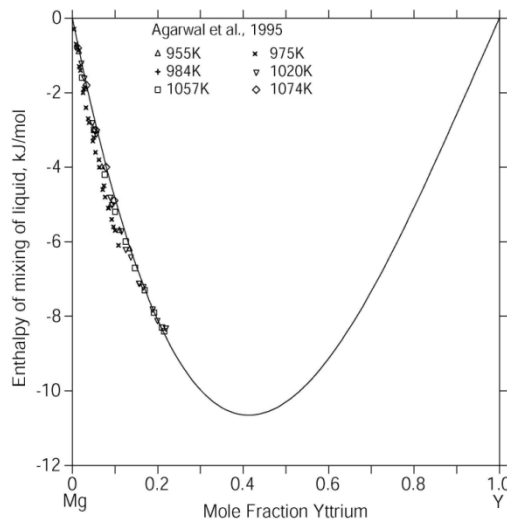


FIG. 2. Calculated enthalpy of mixing of liquid at 1480 K in Mg-Y system with the experiment data.

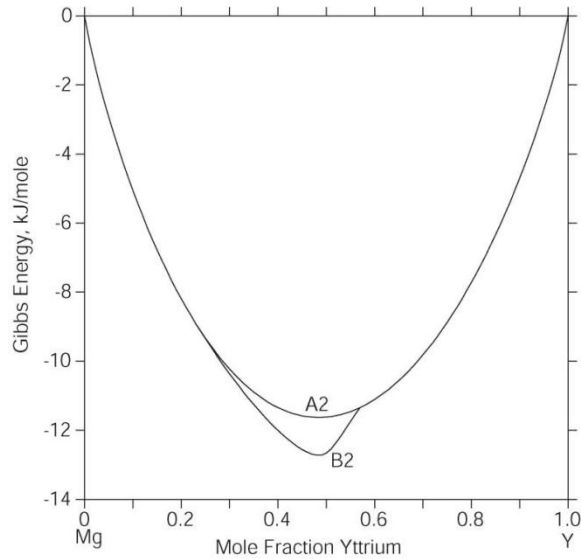


FIG. 3. Calculated partial enthalpy of Y in liquid Mg-Y alloys at 1480 K in comparison with experimental data.

TABLE 3. Invariant reactions in the Mg-Y system.

Reaction	Composition of liquid (at% Mg)	T/K	Reaction Type	Source
$L \Leftrightarrow \text{Fcc}(\text{Mg}) + \text{Mg}_5\text{Y}$	88.24	1109	Eutectic	This work
	87	1115	Eutectic	[10]
$L \Leftrightarrow \text{Mg}_5\text{Y}$	83.33	1122	Congruent	This work
		1120	Congruent	[10]
$L + \text{Mg}_5\text{Y} \Leftrightarrow \text{Mg}_2\text{Y}$	59.19	869	Peritectic	This work
	59	870	Peritectic	[10]
$L + \text{Mg}_2\text{Y} \Leftrightarrow \text{MgY}$	48.90	802	Peritectic	This work
	49	810	Peritectic	[10]
$L + \text{MgY} \Leftrightarrow \text{CuY}_2$	26.49	720	Peritectic	This work
	26.7	715	Peritectic	[10]
$L \Leftrightarrow \text{Bcc}(\text{Y}) + \text{MgY}_2$	25.97	717	Eutectic	This Work
	26	710	Eutectic	[10]

Within the experiment errors, the present calculation of the mixing enthalpy looks reasonably good for Mg-rich side, as shown in FIG. 2 Partial mixing enthalpies of Y in the Mg-Y liquid alloys at 1480 K are further calculated in comparison with the experimental data, as shown in FIG. 3 It is demonstrated that the experimental data of thermodynamic properties can be well described by the present calculation with regards to experimental errors.

Mg-Ce system

Like in the Mg-Y system, we conduct the assessment of the Mg-Ce system. FIG. 4 shows the calculated Mg-Ce equilibrium phase diagram with experimental values used in the optimization. TABLE 2. gives the optimized parameters for this system. The calculated phase diagram is in good agreement with that reported [19]. All the assessed and experimental invariant equilibria in the Mg-Ce system are listed in TABLE 4. An agreement within 7 K between the temperature of calculated and experimentally determined invariant reactions has been obtained except for the congruent temperature of Mg_9Ce_2 phase, where the disagreement is 11 K. This reaction temperature, which is 1210 K, cannot be thermodynamically reproduced well despite great care taken in optimization, the phase equilibria measurements about this region need further clarify. FIG. 5 shows the calculated enthalpy of mixing of liquid in Mg-

Ce system at 1453 K with the experimental data [9]. From FIG. 4 and 5, we can see that the calculated phase diagram and thermodynamic properties of Mg-Ce system agree well with the experimental data.

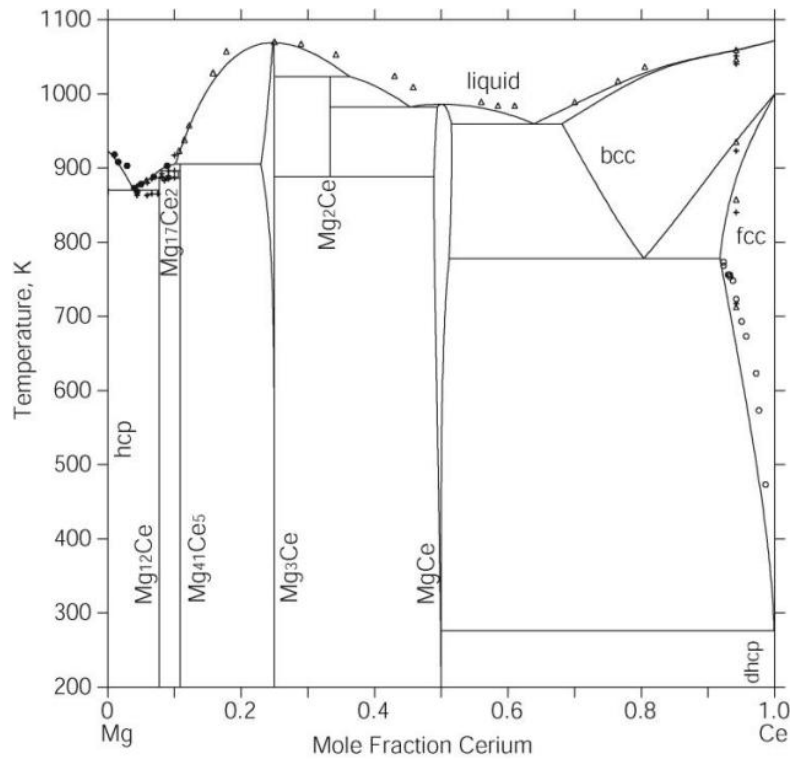


FIG. 4. The calculated Mg-Ce phase diagram with experimental data.

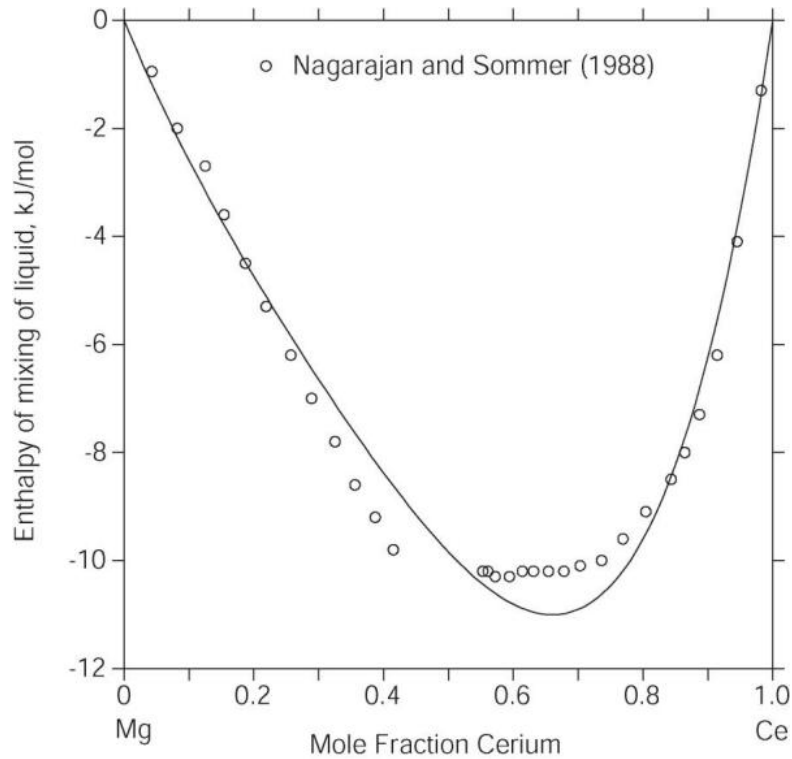


FIG. 5. Calculated enthalpy of mixing of liquid at 1453 K in Mg-Ce system with the experiment data.

TABLE 4. Invariant reactions in the Mg–Ce system.

Reaction	Composition of liquid (at% Cu)	T/K	Reaction Type	Source
Bcc(Ce) \leftrightarrow Fcc(YCe)	0	1033	Allotropic	This Work [8]
		1033	Allotropic	
L \leftrightarrow Fcc(Ce)+MgCe	25.5 26.5	750	Eutectic	This Work [19]
		745	Eutectic	
L+Mg ₂ Ce \leftrightarrow MgCe	47.39 49	901	Peritectic	This Work [19]
		901	Peritectic	
L+Mg ₇ Ce ₂ \leftrightarrow Mg ₂ Ce	62.08 64	1028	Peritectic	This Work [19]
		1030	Peritectic	
L+Mg ₉ Ce ₂ \leftrightarrow Mg ₇ Ce ₂	68.39 70	1098	Peritectic	This Work [19]
		1098	Peritectic	
L \leftrightarrow Mg ₉ Ce ₂	81.82	1195	Congruent	This Work [19]
		1210	Congruent	
L+Mg ₉ Ce ₂ \leftrightarrow Mg ₅ Ce	88.74 88	1151	Peritectic	This Work [19]
		1150	Peritectic	
L \leftrightarrow Fcc(Mg)+Mg ₅ Ce	89.81 90	1139	Eutectic	This Work [19]
		1132	Eutectic	

Conclusions

The Mg-Y and Mg-Ce binary systems have been assessed thermodynamically based on reported experimental data of phase diagrams and thermodynamic properties. Reasonable agreement between calculated and experimental data has realized and thermodynamic parameters for various phases in these two binary systems are obtained.

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