

Thermodynamic assessment of Mg-Ga binary system

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Abstract: In order to obtain the thermodynamic description of the Mg-Ga binary system, the thermodynamic assessment of the system was carried out using the CALPHAD method through Thermo-calc[®] software package based on the evaluation of all available experimental data from the published literature. The solution phases, including liquid, hcp(Mg) and orthorhombic(Ga), were described by the substitutional solution model, of which the excess Gibbs energies were expressed with the Redlich-Kister polynomial. Meanwhile, all intermetallic compounds, Mg₅Ga₂, Mg₂Ga, MgGa, MgGa₂ and Mg₂Ga₅, were modeled as stoichiometric compounds. A set of self-consistent thermodynamic parameters formulating the Gibbs energies of various phases in the Mg-Ga binary system were obtained finally. The much better agreement is achieved between the calculated results and the reported experimental data.

Key words: Mg-based alloys; phase diagram; thermodynamic; CALPHAD method; Mg-Ga binary system

1 Introduction

Mg-based alloys as metal structure materials[1–3] and hydrogen storage materials[4] have been attracting considerable attention recently due to their good performances[5–8]. On the other hand, Mg-based alloys with different additives such as Al, Ga, Hg, Pb and Tl, have been widely used as anode materials due to their rapid activation, low density, low electrode potential and high current capacity[9–11]. For example, in the Mg/AgCl and Mg/CuCl seawater batteries[12–14], Mg-6Al-5Pb (mass fraction, %), Mg-5Al-7Tl (mass fraction, %) and Mg-Hg-Ga alloys as anode materials were investigated[15–18]. In order to better understand the activating mechanism of alloying elements, the selection of alloy compositions and the optimization of materials processing, thermodynamic properties and phase relations which can be obtained from the thermodynamic description of the related metal systems

are indispensable to design novel Mg-based alloys. The thermodynamic descriptions of many Mg-based systems have been well established, but there is no perfect one for the Mg-Ga system. Therefore, the purpose of the present work was to evaluate critically the measured phase diagram and thermodynamic data of the Mg-Ga binary system using the CALPHAD method[19–20] and Thermo-calc[®] software package[21] and then to obtain a consistent and reliable thermodynamic description of this binary system.

2 Experimental information

2.1 Phase diagram data

The available crystallographic data and phase equilibrium data of the Mg-Ga binary system in the literature up to 1985 had been critically reviewed by NAYEB-HASHEMI and CLARK[22]. PUSCHIN and MICIC[23] determined firstly the liquidus of the Mg-Ga alloys from 10% to 93% Ga (molar fraction) using thermal

analysis. The liquidus of the Mg-rich part was measured accurately by HUME-ROTHERY and RAYNOR[24] through thermal analysis and metallographic method. ELLNER et al[25] used differential thermal analysis to determine the liquidus of the Mg-Ga alloys from 50% to 85% Ga (molar fraction). The liquidus of the Ga-rich part was measured by FESCHOTTE and YVON[26] using thermal analysis. NOTIN et al[27] determined later the phase boundaries of the Mg-Ga binary system by means of differential enthalpic analysis. The experimental data of the liquidus reported by PUSCHIN and MICIC[23], HUME-ROTHERY and RAYNOR[24], ELLNER et al[25], FESCHOTTE and YVON[26] and NOTIN et al[27] are compatible and thus were employed in the present optimization.

The solubility of Ga in hcp(Mg) phase was measured only by HUME-ROTHERY and RAYNOR[24] using metallographic analysis. No experimental information concerning the solubility of Mg in orthorhombic(Ga) phase could be found in the literature. So, the solubility of Ga in hcp(Mg) phase was taken into account, while the solubility of Mg in orthorhombic(Ga) phase was negligible in the present optimization.

WECHERLE[28] reported firstly that there are four intermetallic compounds, Mg_5Ga_2 , Mg_2Ga , MgGa and MgGa_2 in the Mg-Ga binary system. Furthermore, Mg_2Ga has a homogeneity range from 31% to 37% Ga (molar fraction). PREDEL and STEIN[29] employed differential thermal analysis to measure the temperatures of invariant reactions in the Mg-Ga binary systems. Their experimental results show that the compound MgGa is not formed by a peritectic reaction between Mg_2Ga and liquid phase and Mg_2Ga_5 compound is not observed either. According to the experimental results reported by SMITH et al[30–31], there is a stable intermetallic compound Mg_2Ga_5 in the Mg-Ga binary system. Fortunately, FESCHOTTE and YVON[26] re-examined intermetallic compounds of the Mg-Ga binary system using X-ray powder diffraction, electron microprobe and thermal analysis. Five intermetallic compounds, Mg_5Ga_2 , Mg_2Ga , MgGa , MgGa_2 and Mg_2Ga_5 were identified and had a very narrow range of homogeneity (less than 0.1%, molar fraction). The intermetallic compounds Mg_5Ga_2 , MgGa and MgGa_2 melt congruently. Later, through differential enthalpic analysis, NOTIN et al[27] found that MgGa melts congruently while MgGa_2 melts incongruently. Mg_2Ga is a stoichiometric compound confirmed also by NOTIN et al[27]. Considering the experimental information of intermetallic compounds mentioned above[26–31], their crystal structure data in the Mg-Ga binary system are given in Table 1. In addition, PUSCHIN and MICIC[23], HUME-ROTHERY and RAYNOR[24], ELLNER et al[25], FESCHOTTE and YVON[26], NOTIN et al[27], SMITH et al[31],

PREDEL[32] and STAHLIN[33] also investigated the temperatures and compositions of invariant reactions in the Mg-Ga binary system using thermal analysis. Based on the latest experimental results by FESCHOTTE and YVON[26] and NOTIN et al[27], Mg_2Ga as a stoichiometric compound and MgGa_2 formed by a peritectic reaction were accepted in the present work. It was also considered that MgGa melts congruently from the experimental results by FESCHOTTE and YVON[26], NOTIN et al[27] and PREDEL and STEIN[29] during the present optimization. Table 2 summarizes all invariant reactions in the Mg-Ga binary system. Experimental information on temperatures and compositions of all invariant reactions for this binary system in Refs.[23–33] was taken into account in the present optimization.

Table 1 Crystal structure data of intermetallic compounds in Mg-Ga binary system

Phase	Prototype	Pearson symbol	Space group
Mg_2Ga_5	Mg_2Ga_5	<i>t</i> 128	<i>I4/mmm</i>
MgGa_2	MgGa_2	<i>o</i> P24	<i>Pbam</i>
MgGa	MgGa	<i>t</i> 132	<i>I4₁/a</i>
Mg_2Ga	Mg_2Ga	<i>h</i> P18	<i>P6₃2c</i>
Mg_5Ga_2	Mg_5Ga_2	<i>o</i> I28	<i>Ibam</i>

2.2 Thermodynamic data

PREDEL and STEIN[29] determined the enthalpies of mixing of the liquid Mg-Ga alloys using the high-temperature calorimeter at 1 023 K. The enthalpies of mixing of the liquid Mg-Ga alloys calculated from the electromotive force (EMF) data were reported by SLABY and TERPILOWSKI[34] at 923 K. Using calorimetry, MOSER et al[35] measured the enthalpies of mixing of the liquid Mg-Ga alloys at different temperatures (943 K, 969 K, 972 K and 973 K). The experimental data of mixing enthalpies of liquid alloys at different temperatures in Ref.[35] are almost independent of the temperature. However, there is very obvious discrepancy (about 2 500 J/mol) in the narrow temperature range (100 K) among the experimental data obtained by PREDEL and STEIN[29], SLABY and TERPILOWSKI[34] and MOSER et al[35]. During their measurements, MOSER et al[35] employed a calorimeter in a closed system with an argon atmosphere, while PREDEL and STEIN[29] used a calorimeter with dynamic system, leading to the oxidation of the bath or samples. Therefore, the experimental data in Ref.[35] are more reliable than other experimental data in Ref.[29] and were adopted only in the present optimization.

The activities of Mg in the liquid Mg-Ga alloys were measured by SLABY and TERPILOWSKI[34] using the EMF method in the temperature range of

673–920 K. MOSER et al[35] employed the EMF method to determine the activities of Mg in the liquid Mg-Ga alloys in the temperature range from 760 K to 900 K. NEBELL[36] determined the activities of Mg in the liquid Mg-Ga alloys at 923 K through the EMF method. The activities of Mg in the liquid Mg-Ga alloys obtained by SLABY and TERPILOWSKI[34] and NEBELL[36] are more negative than the data reported by MOSER et al[35] in the composition range from 35% to 65% Ga (molar fraction). MOSER et al[35] pointed out that the enthalpies of mixing of the liquid Mg-Ga alloys calculated from EMF measurements agree well with those obtained directly from calorimetry. It is believed that the activities of Mg in the liquid Mg-Ga alloys measured by MOSER et al[35] are more accurate. The experimental data reported by SLABY and TERPILOWSKI[34] and NEBELL[36] were compared only in the present work and thus the experimental data measured by MOSER et al[35] were employed during the optimization.

The enthalpies of formation of the supersaturated hcp(Mg) solid solution and intermetallic compounds Mg_5Ga_2 , Mg_2Ga , MgGa and MgGa_2 in the Mg-Ga binary system have been determined by PREDEL and HÜLSE[37] using the sensitive differential scanning calorimeter. MOSER et al[35] determined the enthalpies of formation of all intermetallic compounds in the Mg-Ga binary system by solution calorimetry. The formation enthalpies of intermetallic compounds obtained by MOSER et al[35] are more negative than the data give by PREDEL and HÜLSE[37]. In the present work, the experimental data in Refs.[35, 37] were also considered.

3 Thermodynamic modeling

3.1 Pure elements

The stable forms of the pure elements at 298.15 K and 10^5 Pa were chosen as the reference states of the system. For the thermodynamic functions of the pure elements in their stable and metastable states, the phase stability equations for the element i in ϕ phase are given as

$${}^0G_i^\phi(T) = G_i^\phi(T) - H_i^{\text{SER}} = a + b \cdot T + c \cdot T \ln T + d \cdot T^2 + e \cdot T^3 + f \cdot T^{-1} + g \cdot T^7 + h \cdot T^{-9} \quad (1)$$

where H_i^{SER} is the molar enthalpy of the so-called “standard element reference” (SER), i.e., the enthalpies of the pure elements in their defined reference phase at 298.15 K and 10^5 Pa; T is the absolute temperature in K; $G_i^\phi(T)$ is the absolute molar enthalpy of the element i with structure of ϕ ; ${}^0G_i^\phi(T)$ is the molar Gibbs energy of the element i with the structure of ϕ referred to the

enthalpy of its stable state at 298.15 K and 10^5 Pa. In the present work, the Gibbs energy functions of the pure elements Mg and Ga, ${}^0G_{\text{Mg}}^\phi(T)$ and ${}^0G_{\text{Ga}}^\phi(T)$ are taken from the Scientific Group Thermodata Europe (SGTE) database compiled by DINSDALE[38].

3.2 Solution phases

The substitutional solution model is employed to describe the solution phases including liquid, hcp_A3(Mg) and orthorhombic(Ga), respectively. The molar Gibbs energy of the solution phase ϕ (ϕ =Liquid, hcp_A3 and orthorhombic) can be expressed as

$$G_m^\phi = x_{\text{Mg}} {}^0G_{\text{Mg}}^\phi + x_{\text{Ga}} {}^0G_{\text{Ga}}^\phi + RT(x_{\text{Mg}} \ln x_{\text{Mg}} + x_{\text{Ga}} \ln x_{\text{Ga}}) + {}^E G_m^\phi \quad (2)$$

where R is the gas constant; x_{Mg} and x_{Ga} are the mole fractions of Mg and Ga, respectively; and ${}^E G_m^\phi$ is the excess Gibbs energy expressed by the REDLICH-KISTER polynomial functions[39]:

$${}^E G_m^\phi = x_{\text{Mg}} x_{\text{Ga}} \sum_{i=0}^n {}^i L^\phi (x_{\text{Ga}} - x_{\text{Mg}})^i \quad (3)$$

where ${}^i L^\phi$ is the interaction parameter between elements Mg and Ga, which is formulated as temperature dependent:

$${}^i L^\phi = A_i + B_i \cdot T \quad (4)$$

where A_i and B_i are model parameters to be optimized in the present work.

3.3 Intermetallic compounds

Five intermetallic compounds, Mg_5Ga_2 , Mg_2Ga , MgGa , MgGa_2 and Mg_2Ga_5 , in the Mg-Ga binary system are all treated as stoichiometric compounds Mg_aGa_b because of their narrow homogeneity ranges determined by FESCHOTTE and YVON[26] and NOTIN et al[27]. Furthermore, due to the lack of heat capacities of these intermetallic compounds and with the NEUMANN-KOPP rule, the molar Gibbs energies of Mg_aGa_b are expressed as

$$G_m^{\text{Mg}_a\text{Ga}_b} = \frac{a}{a+b} {}^0G_{\text{Mg}}^{\text{hcp}} + \frac{b}{a+b} {}^0G_{\text{Ga}}^{\text{Ort}} + C_i + D_i \cdot T \quad (5)$$

where the parameters C_i and D_i are parameters to be optimized in the present work.

4 Results and discussion

Using the lattice stabilities of Mg and Ga cited from DINSDALE[38], the model parameters for various phases in the Mg-Ga binary system were optimized using the PARROT module in the Thermo-calc[®] software package developed by SUNDMAN et al[21]. This

module works with minimizing the square sum of the differences between the experimental data and calculated values. During the optimization, each set of experimental data was given a certain weight. The weights were changed systematically during the optimization until most of experimental data were accounted for within the claimed uncertainty limits.

The model parameters of the liquid phase were optimized firstly because many experimental data such as mixing enthalpies, activities and related phase boundaries are readily available. Then, it was followed by modeling the parameters for terminal solution phases and intermetallic compounds. The evaluation was conducted one by one using the step-by-step optimization procedure. Finally, all condensed phases were optimized simultaneously considering all of the selected experimental information.

Thermodynamic parameters for all condensed phases in the Mg-Ga binary system obtained eventually in the present work are summarized in Table 2. Table 3 lists the calculated temperatures and compositions of all invariant reactions compared with the reported experimental data[22–33] in this binary system. The calculated results in the present work are also compared with the reported experimental data and the assessed results by FENG et al[40].

Fig.1 shows the calculated phase diagram of Mg-Ga binary system in the present work. Fig.2 compares the present calculated phase diagram with the experimental

Table 2 Thermodynamic parameters of Mg-Ga binary system

Phase	Thermodynamic parameters	Reference
Liquid	$^{(0)}L^{\text{Liq}} = -46\,077.22 + 16.693T$ $^{(1)}L^{\text{Liq}} = +8\,953.22 - 6.992T$ $^{(2)}L^{\text{Liq}} = +5\,248.59$	This work
hcp(Mg)	$^{(0)}L^{\text{hcp}} = -24\,803.83 + 6.461T$	This work
Orthorhombic (Ga)	$^0G_{\text{Ga}}^{\text{Ort}}$ cited from SGTE database	[38]
Mg ₅ Ga ₂	$G_{\text{m}}^{\text{Mg}_5\text{Ga}_2} = 0.714\,3G_{\text{Mg}}^{\text{hcp}} + 0.285\,7G_{\text{Ga}}^{\text{Ort}} -$ $11\,998.00 + 0.330T$	This work
Mg ₂ Ga	$G_{\text{m}}^{\text{Mg}_2\text{Ga}} = 0.666\,7G_{\text{Mg}}^{\text{hcp}} +$ $0.333\,3G_{\text{Ga}}^{\text{Ort}} - 13\,155.68 + 0.337T$	This work
MgGa	$G_{\text{m}}^{\text{MgGa}} = 0.5G_{\text{Mg}}^{\text{hcp}} + 0.5G_{\text{Ga}}^{\text{Ort}} -$ $14\,539.49 + 0.200T$	This work
MgGa ₂	$G_{\text{m}}^{\text{MgGa}_2} = 0.333\,3G_{\text{Mg}}^{\text{hcp}} +$ $0.666\,7G_{\text{Ga}}^{\text{Ort}} - 12\,720.47 + 0.191T$	This work
Mg ₂ Ga ₅	$G_{\text{m}}^{\text{Mg}_2\text{Ga}_5} = 0.285\,7G_{\text{Mg}}^{\text{hcp}} +$ $0.714\,3G_{\text{Ga}}^{\text{Ort}} - 11\,463.53 + 0.158T$	This work

Table 3 Temperature and composition of invariant reactions in Mg-Ga binary system

Invariant reaction	Type	T/K	Composition (x_{Ga}^{L})	Reference
$L \leftrightarrow (\text{Mg}) + \text{Mg}_5\text{Ga}_2$	Eutectic	697	0.200	[23]
		696	0.191	[24]
		698	—	[29]
		698	0.195	[26]
		693	—	[27]
		688.1	0.187 3	[40]
		693	0.188	This work
$L \leftrightarrow \text{Mg}_5\text{Ga}_2$	Congruent	729	0.285 7	[23]
		743	—	[29]
		729	0.285 7	[32]
		743	0.285 7	[26]
		736	—	[27]
		732	0.286	[40]
		733	0.285 7	This work
$L + \text{Mg}_5\text{Ga}_2 \leftrightarrow \text{Mg}_2\text{Ga}$	Peritectic	714	0.333	[23]
		723	—	[29]
		714	0.333	[32]
		723	0.340	[26]
		718	—	[27]
		720.5	0.337 5	[40]
		720	0.342	This work
$L \leftrightarrow \text{MgGa}$	Congruent	646	—	[23]
		643	—	[25]
		646	—	[29]
		646	—	[32]
		643	0.500	[26]
		642	0.500	[27]
		646.6	0.500	[40]
$L \leftrightarrow \text{Mg}_2\text{Ga} + \text{MgGa}$	Eutectic	640	0.500	This work
		638	—	[29]
		638	0.460	[26]
		639	—	[27]
		641.8	0.464 5	[40]
		639	0.478	This work
$L + \text{MgGa} \leftrightarrow \text{MgGa}_2$	Peritectic	558	0.666	[23]
		553	0.705	[25]
		557	0.666	[31]
		558	0.666	[32]
		556	0.667	[26]
		556	0.690	[27]
		549.3	0.667 4	[40]
$L + \text{MgGa}_2 \leftrightarrow \text{Mg}_2\text{Ga}_5$	Peritectic	553	0.671	This work
		476	0.865	[25]
		478	—	[29]
		473	—	[33]
		475	0.850	[26]
		476	—	[27]
		471.5	0.833 4	[40]
$L \leftrightarrow \text{Mg}_2\text{Ga}_5 + (\text{Ga})$	Eutectic	476	0.866	This work
		301	~1.00	[23]
		301	~1.00	[25]
		303	~1.00	[26]
		301.5	~1.00	[40]
		303	0.999	This work

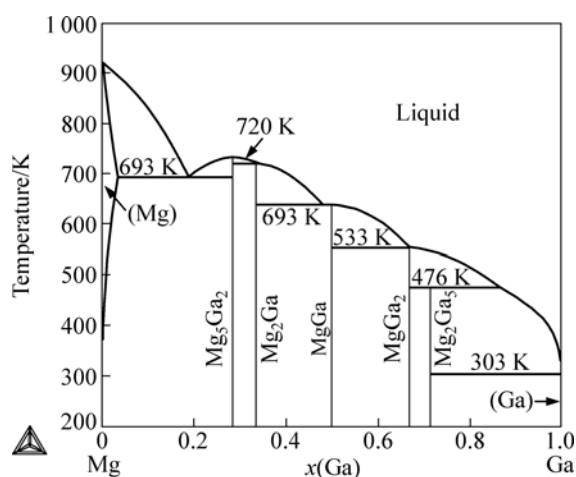


Fig.1 Calculated phase diagram of Mg-Ga binary system in present work

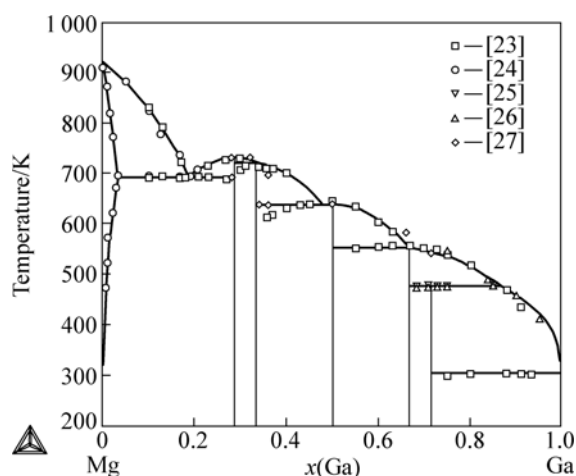


Fig.2 Calculated phase diagram of Mg-Ga binary system compared with experimental data[23–27]

data measured by PUSCHIN and MICIC[23], HUME-ROTHERY and RAYNOR[24], ELLNER et al[25], FESCHOTTE and YVON[26] and NOTIN et al[27]. The calculated liquidus in the present work is in good agreement with most experimental data[23–27]. Comparison of the present calculated phase diagram with the result assessed by FENG et al[40] is given in Fig.3. As can be seen, there is a large difference between the present calculated liquidus and the result assessed by FENG et al[40] in the Ga-rich part. Furthermore, it should be noticeable that the present calculated phase boundary of the Ga-rich part is better than the result assessed by FENG et al[40]. The present calculated phase boundary of hcp(Mg) is also consistent with the experimental data determined by HUME-ROTHERY and RAYNOR[24]. The calculated maximum solubility of Ga in hcp(Mg) (3.35% Ga, molar fraction) is in better agreement with the measured value (3.14% Ga, molar fraction) compared with the assessed value (4.4% Ga,

molar fraction) by FENG et al[40]. In combination with Table 3, the present calculated temperatures and compositions of all invariant reactions agree well with experimental data in Refs.[23–33] within experimental error. However, in Ref.[40], the calculated temperatures for three invariant reactions, $L \leftrightarrow \text{hcp}(\text{Mg}) + \text{Mg}_5\text{Ga}_2$, $L + \text{MgGa} \leftrightarrow \text{MgGa}_2$ and $L + \text{MgGa}_2 \leftrightarrow \text{Mg}_2\text{Ga}_5$, deviate much from the corresponding measured values. Therefore, the more reasonable agreement has been achieved between the calculated phase diagram in the present work and the experimental data reported.

Fig.4 compares the calculated enthalpies of mixing of the liquid Mg-Ga alloys at 973 K with the experimental data obtained by PREDEL and STEIN[29], SLABY and TERPILOWSKI[34] and MOSER et al[35]. The calculated enthalpies of mixing of the liquid Mg-Ga alloys agree excellently with the experimental data measured by MOSER et al[35], while they show obvious deviation from the experimental data reported by

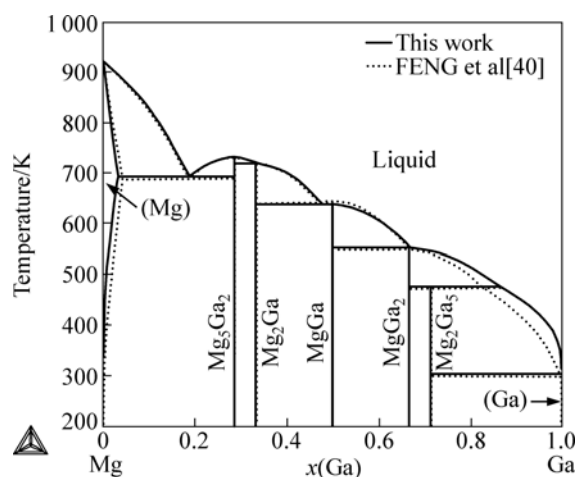


Fig.3 Comparison of present calculated phase diagram of Mg-Ga binary system with result assessed by FENG et al[40]

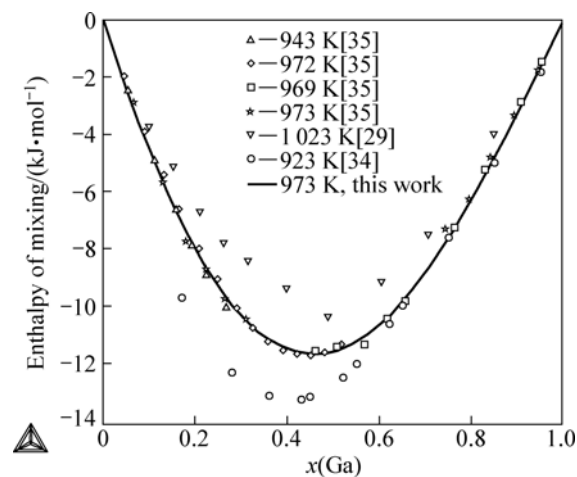


Fig.4 Calculated enthalpies of mixing of liquid alloys in comparison with experimental data[29, 34–35]

PREDEL and STEIN[29] and SLABY and TERPILOWSKI[34]. The discrepancy between the calculated values and experiment data in Ref.[29, 34] is not avoided because they were not used in the present optimization. The experimental data obtained by PREDEL and STEIN[29] are less believable due to the oxidation of the bath or samples. On the other hand, the experimental data in Ref.[34] are deduced from the partial molar quantities of the liquid alloys measured using the EMF method. It should be pointed out that larger error may exist in such deduced values of the enthalpy of mixing in comparison with the data obtained by using calorimetry directly. Therefore, the calculated enthalpies of mixing of the liquid Mg-Ga alloys are reasonable and acceptable in the present work.

Figs.5(a), (b) and (c) present comparisons of the calculated activities of Mg in the liquid Mg-Ga alloys with the experimental data[34–36] at 800 K, 873 K and 923 K, respectively. It can be seen that the calculated activities of Mg in liquid Mg-Ga alloys are in good agreement with the experimental data measured by MOSER et al[35] at 800 K, 873 K and 923 K, but show only a small discrepancy in the composition range from 35% to 65% Ga (molar fraction) compared with the experimental data reported by SLABY and TERPILOWSKI[34]. In Fig.5(c), the activities of Mg in liquid Mg-Ga alloys measured by NEBELL[36] are very scattered in the Mg-rich part and more positive than the experimental data by SLABY and TERPILOWSKI[34] and MOSER et al[35]. Considering that the experimental data of mixing enthalpies of the liquid alloys in Ref.[34] are more negative near 40% Ga (molar fraction) than the results in Ref.[35], the experimental data by NEBELL[36] is less reliable especially in the Mg-rich part. Thus, the calculated activities of Mg in Mg-Ga liquid alloys are accepted in the present work.

The enthalpies of formation of solid alloys and intermetallic compounds in the Mg-Ga binary system at 298.15 K were calculated, as presented in Fig.6. As can be seen, the present calculated values show some deviation from the experimental data reported by MOSER et al[35] and PREDEL and HÜLSE[37] and the assessed values by FENG et al[40]. The calculated enthalpies of formation of all intermetallic compounds are more negative than the experimental data obtained by PREDEL and HÜLSE[37] and MOSER et al[35] and the assessed values by FENG et al[40]. During the present optimization, care and great attention were paid to fix well the enthalpies of formation of intermetallic compounds measured by PREDEL and HÜLSE[37] and MOSER et al[35]. However, in the case that the difference between the calculated and experimental data for intermetallic compounds was limited within

experimental error (about 10%, molar fraction), the agreement between the temperatures and compositions of invariant reactions with the corresponding measured values might be worse. Nevertheless, the present work suggests further experimental investigations to measure directly and accurately the standard enthalpies of formation of intermetallic compounds in this binary system.

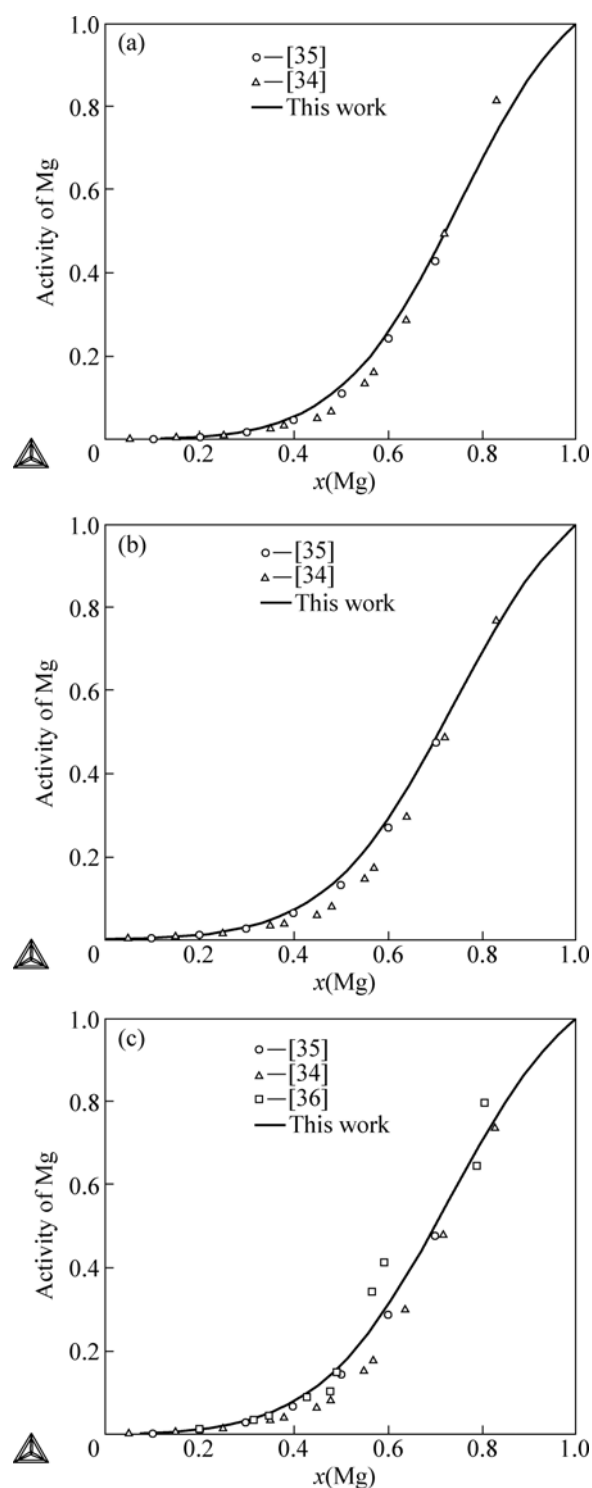


Fig.5 Calculated activity of Mg with experimental data[34–36] at different temperatures: (a) 800 K; (b) 873 K; (c) 923 K

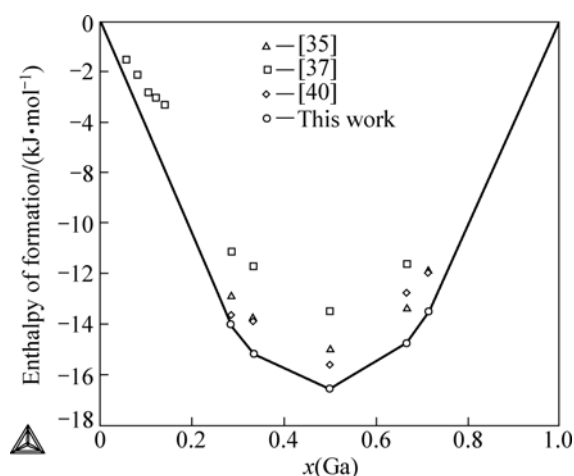


Fig.6 Calculated enthalpies of formation of solid alloys and intermetallic compounds in comparison with experimental data[35, 37, 40] at 298.15 K

5 Conclusions

1) The present work review critically all the experimental information on phase diagram and thermodynamic properties of the Mg-Ga binary system published in literature.

2) Based on the CALPHAD method, thermodynamic description of the Mg-Ga binary system has been performed using the Thermo-calc[®] software package.

3) A set of self-consistent thermodynamic parameters formulating the Gibbs energies of various phases in the Mg-Ga binary system has been obtained, which can reproduce well most of the experimental data on thermodynamic properties and phase diagram.

4) The present thermodynamic description of the Mg-Ga binary system is much better than the previous assessment.

References

- [1] LUO A A. Magnesium: Current and potential automotive applications [J]. Journal of the Minerals, Metals and Materials Society, 2002, 54: 42–48.
- [2] LUO A A. Recent magnesium alloy development for elevated temperature applications [J]. Int Mater Rev, 2004, 49: 13–30.
- [3] BAMBERGER M, DEHM G. Trends in the development of new Mg alloys [J]. Annu Rev Mater Res, 2008, 38: 505–533.
- [4] TSUSHIO Y, AKIBA E. Hydrogenation properties of Mg-based Laves phase alloys [J]. J Alloys Compd, 1998, 269: 219–223.
- [5] WU W H, XIA C Q. Microstructures and mechanical properties of Mg-Ce-Zn-Zr wrought alloy [J]. Journal of Central South University of Technology, 2004, 11: 367–370.
- [6] XIONG C X, ZHANG X M, DENG Y L, XIAO Y, DENG Z Z, CHEN B X. Effects of cryogenic treatment on mechanical properties of extruded Mg-Gd-Y-Zr(Mn) alloys [J]. Journal of Central South University of Technology, 2007, 14: 305–309.
- [7] YIN D S, ZHANG E L, ZENG S Y. Effect of Zn on mechanical property and corrosion property of extruded Mg-Zn-Mn alloy [J]. Transactions of Nonferrous Metals Society of China, 2008, 18: 763–768.
- [8] YANG M B, MA Y L, PAN F S. Effects of little Ce addition on as-cast microstructure and creep properties of Mg-3Sn-2Ca magnesium alloy [J]. Transactions of Nonferrous Metals Society of China, 2009, 19: 1087–1092.
- [9] KING J F, UNSWORTH W. Magnesium in seawater batteries [J]. Light Metal Age, 1978, 36: 22–24.
- [10] WILCOCK W S D, KAUFFMAN P C. Development of a seawater battery for deep-water applications [J]. J Power Sources, 1997, 66: 71–75.
- [11] KIM J G, JOO J H, KOO S J. Development of high-driving potential and high-efficiency Mg-based sacrificial anodes for cathodic protection [J]. J Mater Sci Lett, 2000, 19: 477–479.
- [12] HIROI M. Pressure effects on the performance and the e.m.f. of the Mg-AgCl seawater battery [J]. J Appl Electrochem, 1980, 10: 203–211.
- [13] RENUKA R. AgCl and Ag₂S as additives to CuI in Mg-CuI seawater activated batteries [J]. J Appl Electrochem, 1997, 27: 1394–1397.
- [14] RENUKA R. Influence of allotropic modifications of sulphur on the cell voltage in Mg-CuI(S) seawater activated battery [J]. Mater Chem Phys, 1999, 59: 42–48.
- [15] PINASCO M R, ANGELINI E, CORDANO E, ROSALBINO F. Structural characterisation and corrosion resistance of Ga-precious metal alloys formed by liquid-solid reaction at room temperature [J]. J Alloys Compd, 2001, 317/318: 411–418.
- [16] FENG Y, WANG R C, YU K, PENG C Q, LI W X. Influence of Ga and Hg on microstructure and electrochemical corrosion behavior of Mg alloy anode materials [J]. Transactions of Nonferrous Metals Society of China, 2007, 17: 1363–1366.
- [17] FENG Y, WANG R C, YU K, PENG C Q, WANG N G. Influence of Mg₂₁Ga₅Hg₃ compound on electrochemical properties of Mg-5%Hg-5%Ga alloy [J]. Transactions of Nonferrous Metals Society of China, 2009, 19: 154–159.
- [18] FENG Y, WANG R C, YU K, PENG C Q, ZHANG J P, ZHANG C. Activation of Mg-Hg anodes by Ga in NaCl solution [J]. J Alloys Compd, 2009, 473: 215–219.
- [19] KAUFMAN L, BERNSTEIN H. Computer calculation of phase diagrams [M]. New York: Academic Press, 1970.
- [20] SAUNDERS N, MODWNIK A P. CALPHAD—A comprehensive guide [M]. Switzerland: Pergamon, Lausanne, 1998.
- [21] SUNDMAN B, JANSSON B, ANDERSON J O. Thermo-calc databank system [J]. CALPHAD, 1985, 9: 153–190.
- [22] NAYEB-HASHEMI A A, CLARK J B. The Ga-Mg (gallium-magnesium) system [J]. Bull Alloy Phase Diagrams, 1985, 6: 434–439.
- [23] PUSCHIN N A, MICIC O K. On the alloys of gallium with magnesium [J]. Z Anorg Chem, 1937, 234: 229–232.
- [24] HUME-ROTHERY W, RAYNOR G V. The constitution of the magnesium-rich alloys in the systems aluminum-magnesium, gallium-magnesium, indium-magnesium, and thallium-magnesium [J]. J Int Met, 1938, 63: 201–226.
- [25] ELLNER M, GOEDECKE T, DUDDEK G, PREDEL B. Structure and constitutional studies in the gallium-rich part of the magnesium-gallium system [J]. Z Anorg Chem, 1980, 463: 170–178.
- [26] FESCHOTTE P, YVON K. Stoichiometric study of intermediate phases in the gallium-magnesium systems (Etude stoechiometrique des composés intermédiaires dans le système gallium-magnesium) [J]. J Less-Common Met, 1990, 158: 89–97.
- [27] NOTIN M, BELBACHA E, CHARLES J, HERTZ J. New experimental results and improvement of the modelization of the (Ga,Mg) system [J]. J Alloys Compd, 1991, 176: 25–38.

- [28] WECHERLE K. Germany: Dissertation, Freiburg, 1935.
- [29] PREDEL B, STEIN D W. Thermodynamic investigation of the gallium-magnesium system [J]. J Less-Common Met, 1969, 18: 202–213.
- [30] SMITH G S, JOHNSON Q, WOOD D H. Crystal structure of Ga_5Mg_2 [J]. Acta Crystallogr B, 1969, 25: 554–557.
- [31] SMITH G S, MUCKER K F, JOHNSON Q, WOOD D H. Crystal structure of Ga_2Mg [J]. Acta Crystallogr B, 1969, 25: 549–553.
- [32] PREDEL B. Thermodynamic investigations on the formation and decomposition of metallic glasses [J]. Physica B, 1981, 103: 113–122.
- [33] STAHLIN W. Binary diagram of gallium-magnesium [J]. J Less-Common Met, 1973, 32: 395–397.
- [34] SLABY H, TERPILOWSKI J. Thermodynamic properties of liquid magnesium-gallium solutions [J]. Bull Acad Pol Sci, 1964, 9: 581–585.
- [35] MOSER Z, KAWECKA E, SOMMER F, PREDEL B. Thermodynamic studies on the Mg-Ga system [J]. Met Trans B, 1982, 13: 71–76.
- [36] NEBELL H. Thermodynamic properties of liquid magnesium-lead, magnesium-indium, and magnesium-gallium alloys [J]. Revue Roumaine de Chimie, 1970, 15: 59–65.
- [37] PREDEL B, HÜLSE K. Thermodynamic properties of solid magnesium-gallium alloys [J]. J Less-Common Met, 1979, 63: 159–170.
- [38] DINSDALE A T. SGTE data for pure elements [J]. CALPHAD, 1991, 15: 317–425.
- [39] REDLICH O, KISTER A T. Algebraic representation of thermodynamic properties and the classification of solution [J]. Indust Eng Chem, 1948, 40: 345–348.
- [40] FENG Y, WANG R C, LIU H S, JJIN Z P. Thermodynamic reassessment of the magnesium-gallium system [J]. J Alloys Compd, 2009, 486: 581–585.

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