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Computational Thermodynamic Modeling of the Mg-B System

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Abstract. It has been recently discovered that the compound MgB_2 possesses superconductivity at 39K. To better design and control the fabrication of the MgB_2 compound, a complete thermodynamic description of the system is desirable. In the present work, the phase equilibria and thermodynamic properties of the binary Mg-B system were analyzed and a complete thermodynamic description of the binary system was obtained by means of the CALPHAD technique using a computerized optimization procedure. The thermodynamic descriptions of pure Mg and B elements were taken from the literature. Based on the experimental data, three binary intermetallic compounds, MgB_2, MgB_4 and MgB_6, were considered. Good agreement was obtained between the calculated results and the available experimental data in the literature.

Introduction

The recent discovery of superconductivity in MgB_2 at 39 K has generated great interest in its potential high-current, high-field applications and in superconducting microelectronics[1, 2]. MgB_2 has the highest T_c known for non-oxide compounds and longer coherence length than those in high temperature cuprate superconductors. Its grain boundaries have a far less detrimental effect on superconducting current transport than other superconductors[3]. These properties hold tremendous promise for various large-scale and electronic applications of the compound. To better understand and control the processing of the MgB_2 compound, a complete thermodynamic description of the Mg-B system is needed. The present work aims to develop a consistent thermodynamic description of the Mg-B system by means of the CALPHAD technique. The Gibbs energy functions of the pure Mg and B were taken from the SGTE database compiled by Dinsdale[4].

Experimental Information

The experimental information for the Mg-B binary system is quite limited and was reviewed by Nayeb-Hashemi and Clark[5]. Following the suggestion by Spear[6], Nayeb-Hashemi and Clark included three intermediate compounds, i.e. MgB_2, MgB_4 and MgB_7 and drew most phase boundaries by dashed lines, indicating uncertainties in the phase equilibria of the system. More intermediate compounds have been reported in the literature such as Mg_3B_2[7, 8], MgB_6[9], MgB_{12}[9] and two undefined compounds[10], but they have not been confirmed and are considered either due to low-purity materials used in early experiments or as mixtures of stable borides and/or boron[11-14]. The most recent experimental work on the phase equilibria was conducted

by Naslain and co-workers[13-15]. The MgB_2 and MgB_4 crystals were prepared, in sealed molybdenum vessels, from mixtures of elements with excess amount of magnesium to generate a high pressure of magnesium to inhibit compounds decompositions. The MgB_7 crystals were prepared from the mixture of MgB_4 and 3B. The MgB_2 phase were also investigated by many other researchers[16, 17]. The crystal structures of the three compounds are shown in Table 1. No homogeneity information for any of the three compounds has been reported in the literature.

Table 1: The Binary Compounds in the Mg-B Binary System

Phase Name	Crystal Structure	Person Symbol	Reference
MgB_2	Hexagonal	hP3	[13, 16, 17]
MgB_4	Orthorhombic	oP20	[13]
MgB_7	Orthorhombic	oI64	[15]

The decomposition temperatures of the three intermediate compounds have not been well established. As the boiling temperature of Mg is considerably lower than the decomposition temperatures of the intermediate compounds, the experimental measurements of the decomposition temperatures of the intermediate compounds would depend very much on the magnesium vapor pressure. Based on the limited experimental data in the literature[9, 10, 13], the suggestion by Spear[6], and the thermodynamic data of MgB_2 and MgB_4 in the JANAF table and by SGTE[18], the decomposition temperatures of the three intermediate compounds are estimated to be 1545, 1735, and 2150 °C for MgB_2, MgB_4, and MgB_7, respectively. It should be pointed out that further experimental investigations are desirable to validate these temperatures.

Ariya et al.[19] measured the enthalpies of formation by means of calorimetry and vapor pressure, and Rybakova et al.[20] by means of calorimetry. Their results are shown in Table 2. It can be seen that two sets of data measured by means of calorimetry are very close to each other except, but less negative than the data measured by means of vapor pressure.

Table 2: Heat of formation of the compounds (kJ/mole of atoms)

Reference	MgB_2	MgB_4	MgB_6	MgB_{12}	Mg_2B	Mg_4B
Ariya et al. [19] by vapor pressure	-26.66±10.0	-17.57±3.85	-15.54±2.09	N/A	N/A	N/A
Ariya et al. [19] by calorimetry	-17.17±1.39	-14.39±0.75	-13.39±0.60	N/A	N/A	N/A
Rybakova et al. [20] by calorimetry	-18.55±1.12	-14.73±0.50	-13.39±0.30	-10.07±0.90	-14.23±0.84	-19.53±1.39

Thermodynamic Models

There are three types of phases in the system, i.e., the gas phase, the solution phases and the intermetallic compounds. The thermodynamic property of the gas phase is taken from the SGTE substance database[18] with the species of B, B_2, Mg, Mg_2. Ideal mixing of species is assumed for the gas phase. The Gibbs energy of the gas phase is thus written as

$$G_m = \sum_i y_i \, {}^{\circ}G_i + RT \sum_i y_i \ln y_i \qquad (1)$$

where y_i and ${}^{\circ}G_i$ are the mole fraction and Gibbs energy of species i in the gas phase.

The solution phases in the Mg-B system include liquid, hcp (magnesium side) and β-rhombohedral (boron side) phases and are treated as substitutional solutions, (Mg, B), with the Gibbs energy expressed as

$$G_m^\Phi = x_{Mg} \, {}^\circ G_{Mg}^\Phi + x_B \, {}^\circ G_B^\Phi + RT(x_{Mg} \ln x_{Mg} + x_B \ln x_B) \tag{2}$$

where ${}^\circ G_i^\Phi$ is the molar Gibbs energy of the pure element with the structure Φ from Dinsdale [4]. All the solution phases are treated as ideal solutions due to very limited solubility in the solutions.

The three intermetallic compounds in the Mg-B system (see Table 1) are all modeled as stoichiometric compounds, and their Gibbs energy functions are written as

$$G_m^{MgBx} = {}^\circ G_{Mg}^{hcp} + x {}^\circ G_B^{\beta-rho} + (1+x)(a^{MgBx} + b^{MgBx} T) \tag{3}$$

where ${}^\circ G_{Mg}^{hcp}$ and ${}^\circ G_B^{\beta-rho}$ are the molar Gibbs energy of the hcp Mg and the β-rhombohedral B, respectively. a^{MgBx} and b^{MgBx} are the parameters to be evaluated, and $\Delta G_m^{MgBx} = a^{MgBx} + b^{MgBx} T$ represents the Gibbs energy of formation of the compound *MgBx* with *x* being 2, 4, and 7, respectively, expressed in per mole of atoms.

Evaluation of the Thermodynamic Parameters and Discussions

The model parameters were evaluated using the Parrot module[21] in Thermo-Calc [22]. This program is able to take various kinds of experimental data in one operation. It works by minimizing an error sum with each of the selected data values given a certain weight. The weight is chosen and adjusted based upon the data uncertainties given in the original publications and upon the modeler's judgment when examining all experimental data simultaneously. All thermodynamic calculations are carried out using Thermo-Calc. The reference state of the Gibbs energy of individual phases is the so-called Standard Element Reference (SER) i.e. the enthalpy of the pure elements in their stable state at 298.15 K.

The enthalpy of formation and the estimated decomposition temperatures of the three intermediate phases were used to evaluate the parameters *a* and *b* in Eq.3 simultaneously for all the three compounds. Constraints on phase stability were introduced to ensure that all the three intermediate phases are stable down to 100 degree below the room temperature. The Gibbs energy of formation is thus obtained for the three compounds and listed in Table 3. As mentioned previously, the gas phase and solution phases were assumed to be ideal.

The calculated binary phase diagram is shown in Figure 1. The calculated invariant phase equilibria are listed in Table 4 with the phases on the left of the reactions being stable at high temperatures. The calculated enthalpy of formation is compared with the experimental data in Figure 2. The large scattering between the data obtained by vapor pressure and by calorimetry is clearly shown, which can be due to the volatility of magnesium.

It is noted that due to the high volatility of magnesium, the gas phase comes into play at relatively low temperatures as shown in Figure 1, which can make the fabrication of MgB$_2$ thin films by *in-situ* deposition difficult. From the point of view of MgB$_2$ fabrication, the Mg:B atomic ratio (x_{Mg}/x_B) should be higher than 1/2 to avoid the formation of MgB$_4$. As shown in Figure 1, the phase relationships do not change for a wide range of the Mg:B atomic ratio from 1/2 and up, except the relative amount of the phases. In our recent publication[23], we presented several calculations specifically for design of fabricating MgB$_2$, especially the effect of pressure on phase equilibria to show the thermodynamic stability window for MgB$_2$ film deposition.

Table 3: Optimized Thermodynamic Data of the Mg-B System (J/mole of atoms)

	MgB$_2$	**MgB$_4$**	**MgB$_7$**
ΔG_m^{MgBx}	−24025−0.343 T	−18429−0.655 T	−15375+0.100 T

Table 4: Calculated Invariant Phase Equilibria in the Mg-B Binary Systems

Invariant Phase Equilibria	Temperature, °C	B content, mole fraction
Gas+Liquid=MgB$_7$	2150	$x^{gas} \approx 10^{-5}$, x^{liq}=0.991
Liquid=MgB$_7$+β-rho	2071	x^{liq}=0.996, $x^{\beta-rho}$=1
Gas+MgB$_7$=MgB$_4$	1735	$x^{gas} \approx 10^{-7}$
Gas+MgB$_4$=MgB$_2$	1545	x^{gas}=0
Gas+MgB$_2$=Liquid	1094	x^{gas}=0, x^{liq}=0.01
Liquid=hcp+MgB$_2$	650	x^{liq}=0.0002, x^{hcp}=0

Summary

A self-consistent thermodynamic description for the Mg-B system is obtained with the available thermochemical and phase diagram data well reproduced. Three binary intermediate phases are considered and their individual Gibbs energies are evaluated. The evaluated thermodynamic description of the Mg-B binary system has been used to make useful calculations to predict the conditions for fabricating the MgB$_2$ compound, which was recently found to be a superconductor with the highest critical temperature among non-oxide superconductors.

Acknowledgment

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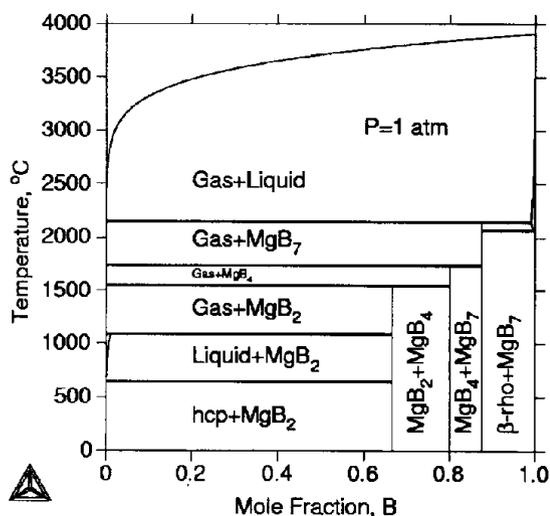
Figure 1: Calculated Mg-B binary phase diagram using the present thermodynamic description shown in Table 3.
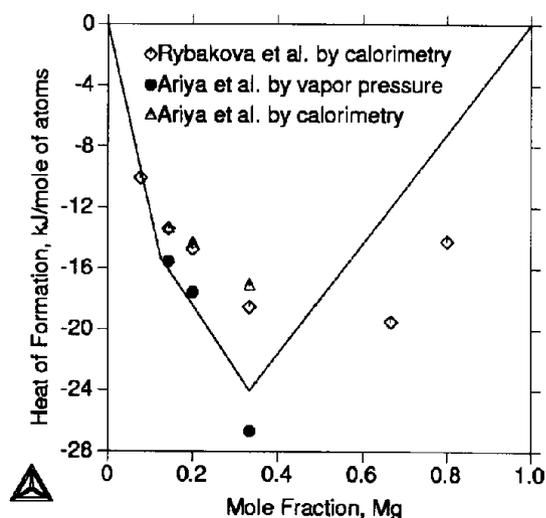
Figure 2: Calculated enthalpy of formation in comparison with the experimental data in the literature by Ariya et al.[19] and Rybakova et al.[20].