Phase stability determination of the Mg–B binary system using the CALPHAD method and ab initio calculations

Sungtae Kim*a, Donald S. Stonea, Jae-Ik Chob, Chang-Yeol Jeongb, Chang-Seog Kangb, Jung-Chan Baeb

aDepartment of Materials Science and Engineering, University of Wisconsin-Madison, Madison, WI 53706, USA
bKorea Institute of Industrial Technology, Gwangju Research Center, Gwangju, Republic of Korea

1. Introduction

Magnesium diboride (MgB2) is a superconductor whose critical temperature is the highest of any conventional superconductor, so its thermodynamic properties and stability are of interest ranging from low temperatures, where it is used, to high temperatures, where it is usually synthesized [1–5]. At the same time, MgB2 is being considered for introduction into magnesium alloys [6], the latter of which are attractive to the transportation industries because of the low density, abundance and relative environmental friendliness of magnesium [7]. To aid in the development of Mg–MgB2-based alloys it is necessary to develop a fluent database for describing the phase stability in the Mg–B binary and multicomponent systems so that alloy design can proceed without arbitrary selections of composition and solidification processing conditions.

The existing Mg–B phase diagram (Fig. 1) is not reliable [8]. Several decades ago, the Mg–B binary phase diagram was first tentatively constructed by guessing the decomposition temperatures of magnesium boride phases—MgB2, MgB4 and MgB7 [9]. There has been little theoretical or experimental underpinning for that diagram. Recent efforts [10,11] that improved the Mg–B phase diagram by means of a calculation of phase diagram (CALPHAD) method have referred the originally guessed phase diagram due to a deficient database of experimentally analyzed phase stability information. The literature decomposition temperatures of the MgB2, MgB4 and MgB7 phases in the existing Mg–B phase diagram are 1550 °C, 1830 °C and 2150 °C, respectively [8]. The reported decomposition reaction temperatures of boride phases:

\[ 2\text{MgB}_2 \rightarrow \text{MgB}_4 + \text{Mg}(g) \]

and

\[ 7\text{MgB}_4 \rightarrow 4\text{MgB}_7 + 3\text{Mg}(g) \]

are 850 °C ≤ \( T_{\text{decomp}}(\text{MgB}_2) \) ≤ 1550 °C and 1020 °C ≤ \( T_{\text{decomp}}(\text{MgB}_4) \) ≤ 1827 °C, respectively [8–17]. The literature decomposition temperatures exhibit big uncertainty. These issues require that the phase diagram of the Mg–B system be re-examined. Therefore, the present study estimates theoretically thermodynamic properties of magnesium boride phases, and subsequently the Mg–B phase diagram is assessed using the estimated thermodynamic data.

2. Computational methodologies

The high volatility of magnesium and strong tendency of boron to oxidize have made the synthesis of high-purity MgB2 a problem that remains to be solved. As a result of air exposure, the Mg and B element ingredients of magnesium borides contain MgO and B2O3 oxide impurity [18]. For this reason we forego for now an experimental effort to construct the phase diagram. Instead, we utilize ab initio calculations to compute the enthalpies of magnesium borides referenced against the enthalpies of elements in their standard reference state at 298.15 K (HSER). In addition, we employ additive entropy formulation [19] to estimate the entropy of mag-
nesium borides as functions of temperature and therefore the heat capacities of the magnesium borides. Based on the estimated thermodynamic database, the CALPHAD method can be used to assess the Mg–B binary phase diagram using PANDAT, a package for calculating multicomponent phase diagrams. A limited number of experimental data are available for the compounds in the Mg–B system, and these allow for independently checking the results of our theoretical analyses.

3. Results and discussions

Three magnesium boride phases in the Mg–B binary system are all considered as stoichiometric compounds due to their ordered crystal structure, which allows for assuming that all Mg atoms occupy the Mg sublattice sites and all B atoms occupy the B sublattice sites. Accordingly, there is no mixing entropy contribution to the entropy of a magnesium boride. It has been shown that the entropies of such phases can often be estimated from a simple rule of mixtures of the entropies of component elements. In this case, the entropy of a magnesium boride is described as:

$$S^{\circ}_{Mg_{1-x}B_x} = (1-x)S^{\circ}_{Mg} + xS^{\circ}_{B}$$  \hspace{1cm} (1)

where $S^{\circ}_{Mg}$ and $S^{\circ}_{B}$ are the entropies of Mg and B elements. To check the validity of this analysis, Fig. 2 compares the entropies of magnesium boride phases at 298.15 K estimated by Eq. (1) with entropies from the literature. The estimated entropy of a magnesium boride agrees closely with the literature entropy. When Mg and B atoms are assumed to stay on their own sublattice sites up to the melting temperature of a magnesium boride intermetallic compound, Eq. (1) allows for establishing the entropy of the boride as a function of temperature. Based on definition of the heat capacity, $C_p$, the entropy and enthalpy with respect to HSER can be established:

$$S_T = S^{\circ}_{298.15} + \int_{298.15}^{T} \left( \frac{C_p}{T} \right) dT$$  \hspace{1cm} (2)

$$\Delta H_T = \Delta H^{\circ}_{298.15} + \int_{298.15}^{T} C_p dT$$  \hspace{1cm} (3)

By assuming the standard form $C_p = a + bT + cT^{-2} + dT^2$ and fitting Eq. (2) to the estimated entropy data the coefficients $S^{\circ}_{298.15}$, $a$, $b$, $c$ and $d$ were optimized.

In thermodynamics, the enthalpy for a closed system at constant pressure $P$ consists of the internal energy of the system and $P$–$V$ work, where $V$ is the volume change against the external pressure $P$. For solids at 1 atm the $P$–$V$ work is negligible compared to the internal energy, in which case the enthalpy of the system at 0 K becomes coincident with the internal energy, $E_{int}$, estimated from ab initio calculations. In this regard, the formation enthalpy of $Mg_{1-x}B_x$ at 0 K, $\Delta H^{\circ}_{f,0}(Mg_{1-x}B_x)$, can be re-written:

$$\Delta H^{\circ}_{f,0}(Mg_{1-x}B_x) = H^{\circ}_{f}(Mg_{1-x}B_x) - (1-x)H^{\circ}_{f}(Mg) - xH^{\circ}_{f}(B)$$

$$= E_{tot}(Mg_{1-x}B_x) - (1-x)E_{tot}(Mg) - xE_{tot}(B)$$  \hspace{1cm} (4)

Ab initio calculations were performed by means of ABINIT code, which is a Density Functional Theory (DFT) code that uses pseudopotentials and a planewave basis. The total internal energy, $E_{tot}$, is determined by finding the $k$ point grids and the kinetic energy cutoff that gives the total energy converged to within 1 meV/atom, where the kinetic energy cutoff controls the number of planewaves at given $k$ point grids. Atomic crystal structures of magnesium borides in Fig. 3 are employed to compute the total internal energy $E_{tot}$. In Fig. 3(a) the crystal structure of MgB$_2$ is hexagonal close packed with a space group of P6/mmm and the lattice param-
The enthalpy of \( \text{Mg}_1 \text{x}_B \) at 298.15 K with respect to HSER can be described as:

\[
\Delta H_{298.15}(\text{Mg}_{1-x}B_x) = \Delta H_0(\text{Mg}_{1-x}B_x) + \int_0^{298.15} C_p(\text{Mg}_{1-x}B_x) \, dT
\]

where \( \Delta H_{298.15}(\text{Mg}_{1-x}B_x) = H_{298.15}(\text{Mg}_{1-x}B_x) - (1 - x)H_{298.15}(\text{Mg}) - xH_{298.15}(\text{B}) \), which is equivalent to the formation enthalpy of \( \text{Mg}_{1-x}B_x \) at 298.15 K, \( \Delta H_{298.15}(\text{Mg}_{1-x}B_x) \). The enthalpy of \( \text{Mg}_{1-x}B_x \) at 0 K with respect to HSER can be described as:

\[
\Delta H_0(\text{Mg}_{1-x}B_x) = H_0(\text{Mg}_{1-x}B_x) - (1 - x)H_0(\text{Mg}) - xH_0(\text{B})
\]

where \( H_0(\text{Mg}_{1-x}B_x) = \Delta H_0(\text{Mg}_{1-x}B_x) \). Terms \( H_{298.15}(\text{Mg}) \) and \( H_{298.15}(\text{B}) \) are obtained from Eq. (3) and the literature heat capacity data [13] of Mg and B elements. The enthalpy of \( \text{Mg}_{1-x}B_x \) at 0 K with respect to HSER is \(-25.91 \text{ kJ/g-mol}\) for \( \text{MgB}_2 \), \(-27.64 \text{ kJ/g-mol}\) for \( \text{MgB}_4 \), and \(-27.68 \text{ kJ/g-mol}\) for \( \text{MgB}_7 \).

Eq. (5) and ab initio calculations estimated the formation enthalpies for \( \text{MgB}_2 \), \( \text{MgB}_4 \), and \( \text{MgB}_7 \) at \(-23.44 \text{ kJ/g-mol}\), \(-25.67 \text{ kJ/g-mol}\), and \(-25.99 \text{ kJ/g-mol}\), respectively, at 298.15 K (Fig. 4). The literatures establish upper and lower bounds for the formation enthalpy at 298.15 K, \(-51.97 \text{ kJ/g-mol} \leq \Delta H_{298.15}(\text{MgB}_2) \leq -17.17 \text{ kJ/g-mol}\) and \(-21.00 \text{ kJ/g-mol} \leq \Delta H_{298.15}(\text{MgB}_4) \leq -14.39 \text{ kJ/g-mol}\) [13, 14, 31, 32]. The estimated formation enthalpy for the \( \text{MgB}_2 \) phase falls within the bounds for the literature \( \text{MgB}_2 \) formation enthalpy, while that for the \( \text{MgB}_4 \) phase lies near the literature bounds for \( \text{MgB}_4 \). This result indicates that the estimated formation enthalpies for \( \text{MgB}_2 \), \( \text{MgB}_4 \), and \( \text{MgB}_7 \) are reliable to use for a thermodynamic assessment of the Mg–B phase diagram.

Based on the estimated thermodynamic property data of magnesium boride phases as shown in Table 1 and Fig. 4, PANDAT software package [20] was utilized to thermodynamically re-assess the Mg–B binary phase diagram (Fig. 5), in which liquid and gas phases were assumed to be ideally mixed. The re-assessed Mg–B phase diagram (Fig. 5) reveals significant differences in the decomposition temperatures of the magnesium boride phases compared to the literature temperatures. The literature decomposition temperatures of the \( \text{MgB}_2 \), \( \text{MgB}_4 \), and \( \text{MgB}_7 \) phases that were originally guessed to construct the Mg–B phase diagram are 1550 °C, 1830 °C and 2150 °C, respectively [8]. For the decomposition reaction of boride phases: \( 2\text{MgB}_2 \Rightarrow \text{MgB}_4 + \text{Mg(g)} \) and \( 7\text{MgB}_4 \Rightarrow 4\text{MgB}_7 + 3\text{Mg(g)} \), upper and lower bounds for the literature decomposition temperatures are \( 850 \text{ °C} \leq T_{\text{decomp}}(\text{MgB}_2) \leq 1550 \text{ °C} \) and \( 1020 \text{ °C} \leq T_{\text{decomp}}(\text{MgB}_4) \leq 1827 \text{ °C} \), respectively [8, 10–17]. The present study estimated the decomposition temperatures at 1174 °C for \( \text{MgB}_2 \), 1273 °C for \( \text{MgB}_4 \) and 2509 °C for \( \text{MgB}_7 \) (Fig. 5).

For comparison, the Mg vapor pressures for the \( \text{MgB}_2/\text{MgB}_4 \) equilibrium reaction are plotted together with the literature data in Fig. 6. Our calculated Mg vapor pressures are approximately 0.5–2.7 orders of magnitude higher than the literature data. This indicates that at a given temperature pure \( \text{MgB}_2 \) can be more stable at higher temperatures.
Mg pressures than that would be suggested by the literature data. In thermodynamics a vapor pressure is the saturated pressure of a system at the temperature $T$ that equals to the external pressure (atmosphere pressure) acting on the system + system vapor. In this regard, Fig. 6 reveals that the decomposition temperature for the MgB$_2$/MgB$_4$ equilibrium reaction increases with the increasing atmosphere pressure. Fig. 5 is the Mg–B binary phase diagram at an external pressure of 101.325 kPa (1 atm). To examine the stability of the MgB$_2$/MgB$_4$ equilibrium reaction, the Mg–B binary phase diagram is assessed with the changing external pressures. In thermodynamics, the Gibbs free energy is dependent of pressure:

$$
\left( \frac{\partial G}{\partial P} \right)_T = V \tag{8}
$$

where $G$ is the Gibbs free energy, $V$ is the volume and $T$ is the temperature. For a solid substance, the volume compressibility is described [33]:

$$
\left( \frac{dP}{d\ln V} \right) = -B \tag{9}
$$

where $B$ is the bulk modulus. Based on an assumption of the bulk modulus independent of pressure, inserting Eq. (9) into Eq. (8) becomes:

$$
\Delta G_T = -B \Delta V \tag{10}
$$

where $\Delta V$ is the volume change due to the changing pressure $\Delta P$ and can be estimated from Eq. (9):

$$
\Delta V = V_1 \left\{ \exp \left( -\frac{P_2 - P_1}{B} \right) - 1 \right\} \tag{11}
$$

When the external pressure increases from 1 atm ($P_1 = 101.325$ kPa) to 100 MPa ($P_2$), the volume change of MgB$_2$ is $-0.00082V_1$. Using the known lattice parameters ($a=b=3.084$ Å, $c=3.522$ Å [3,21,25]) of MgB$_2$ and its bulk modulus of $B = 122$ GPa [34], the free energy change becomes 0.52 kJ/g-mol (Table 2). For Mg and B, their free energy changes due to the external pressure increase are 1.40 kJ/g-mol and 0.60 kJ/g-mol, respectively. However, the free energy change of the ideally mixed gas phase is $RT \ln(P_2/P_1) = 17.20$ kJ/g-mol at 25 °C [13]. Based on these estimations, the free energy change of solid substance under the external pressure in ranges of 0.1–100 MPa is small enough to be ignorable, compared to the free energy change of the ideally mixed gas phase. Therefore, the gas phase is the only phase affected by the external pressure change:

$$
G_{\text{gas}} = \sum_i X_i G_{i}^\circ + RT \sum_i X_i \ln(X_i) + RT \ln \left( \frac{P}{P_1} \right) \tag{12}
$$

**Table 2**

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>B</th>
<th>MgB$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk modulus (GPa)</td>
<td>45</td>
<td>320</td>
<td>122</td>
</tr>
<tr>
<td>Free energy change (kJ/g-mol)</td>
<td>1.40</td>
<td>0.60</td>
<td>0.52</td>
</tr>
</tbody>
</table>

The bulk modulus is obtained from Refs. [34,35].
where \( x_i \) is the mole fraction of \( i \) \((i=\text{Mg, B})\), \( C_i^\circ \) is the standard free energy of \( i \) at 1 atm, \( P \) is the external pressure and \( P_i \) is 101.325 kPa.

Fig. 7 shows the assessed Mg–B phase diagrams at the external pressures of 1 MPa, 10 MPa and 100 MPa, respectively. When the external pressure is 1 MPa (Fig. 7(a)), Mg(l) phase exhibits a B solubility of 4.8% at 1017 °C. The decomposition temperature of the MgB\(_2\)/MgB\(_4\) reaction increases from 1174 °C at 101.325 kPa to 1519 °C at 1 MPa. When the external pressure is 10 MPa (Fig. 7(b)), the gas phase appears at \( T > 2121.5 \) °C. In addition, two peritectic reactions, \( L + \text{MgB4} \iff \text{MgB2} \) and \( L + \text{MgB7} \iff \text{MgB4} \), arise at 1740.5 °C and 2201.1 °C, respectively. The Mg-rich liquid phase has the highest B solubility of 41.7% at 2374.5 °C. Further increase in the external pressure increases the boiling temperature of Mg. In the Mg–B binary phase diagram at the external pressure of 100 MPa (Fig. 7(c)), gas phase does not exist below 3000 °C. There are two peritectic reactions, \( L + \text{MgB4} \iff \text{MgB2} \) and \( L + \text{MgB7} \iff \text{MgB4} \), at 1740.5 °C and 2201.1 °C as well as the congruent melting of MgB\(_7\) at 2810.2 °C.

Based on the Mg–B binary phase diagrams shown in Fig. 7, it is worthy to note that at high ambient pressure magnesium boride phases can be solidified from liquid without loss of Mg through evaporation. Since Mg evaporation can be suppressed, the high ambient pressure limits loss of Mg during syntheses of magnesium boride alloys, indicating that the alloy composition becomes controllable. In practical, the high ambient pressure allows for casting magnesium boride alloys.

4. Conclusion

The Mg–B binary phase diagram is thermodynamically reconstructed by means of ab initio calculations and CALPHAD methods. The estimated formation enthalpies of magnesium boride phases by ab initio calculations reveal that they are reliable to use for thermodynamic assessments of the Mg–B phase diagram and their decomposition temperatures. The Mg–B phase diagrams at higher external pressure illustrate that Mg loss in the form of gas phase can be avoided during the syntheses of the Mg–B alloys.

Acknowledgement

The financial support of Korea Institute of Industrial Technology (KITECH) is gratefully acknowledged.

References