THERMODYNAMIC DESCRIPTION OF
THE C-Ge AND C-Mg SYSTEMS

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Abstract

The thermodynamic modeling for the C-Ge and C-Mg systems is performed by the CALPHAD method. The enthalpy of formation for Mg_2C_3, the experimental value of which is not available in the literature, is obtained via first-principles calculation to refine the thermodynamic modeling of the C-Mg system. A comparison of the thermodynamic calculations with the available literature data shows that the presently obtained two sets of thermodynamic parameters for the C-Ge and C-Mg systems can well describe the these two systems.

Keywords*: C-Mg system; C-Ge system; Phase diagram; CALPHAD approach.*

1. Introduction

Olesinski and Abbaschian [1] reviewed the experimental data on the C-Ge system. Up to now, very limited information on the C-Ge system is available in the literature. By heating Ge in graphite containers in the temperature range from 2780 °C to 3170 °C and analyzing the phases, Scace and Slack [2] established a tentative phase diagram of the C-Ge system. According to them [2], a eutectic reaction occurs very close to pure Ge in the C-Ge system and mutual solid solubility of the elements is negligible. The experimental investigations performed by Barbier-Andrieux [3] and Taylor and Doyle [4] showed that there exists no intermediate phase in this system.

The phase diagram of the C-Mg system

over the entire compositions at 7.7 GPa was presented by Shu'zhenko et al. [5]. The C–Mg phase diagram at 1 atm. is not available in the literature though several experimental investigations on the C-Mg system were reported. Novak [6] reported the existence of two carbides, viz Mg_2C_3 and MgC_2, which was confirmed by the subsequent researchers [7-9]. It is indicated that MgC_2 is stable below 600 °C and decomposes through a reaction of $2MgC_2 \rightarrow Mg_2C_3 + (C)$ on heating up to about 600 °C [7-9]. Mg_2C_3, the stability range of which is expected to be between 600 °C and 660 °C, is dissociated into Mg vapor and graphite at about 660 °C [9, 10]. Though Shu'zhenko et al. [5] claimed the existence of MgC at 7.7 GPa, Hijek et al. [11] and Rueggeberg [12] revealed that MgC phase is thermally unstable under ambient pressure [11, 12]. In addition, the experimental data on the solubility of C in (Mg) is not available in the literature.

The C-Ge and C-Mg systems, which are two of the binary systems in multi-component Al alloys, have not been thermodynamically evaluated. The purpose of the present work is to obtain a self-consistent set of thermodynamic parameters for the two systems by CALPHAD approach and first-principles calculation.

2. Thermodynamic models

The Gibbs energy function $^{o}G_i^{\Phi}(T) = G_i^{\Phi}(T) - H_i^{SER}$ for the pure element i (i=C, Ge, Mg) in the phase Φ is expressed by an equation of the form [13]

$$^{o}G_i^{\Phi}(T) = a + b \cdot T + c \cdot T \cdot \ln(T) + d \cdot T^2 + e \cdot$$

$$\cdot T^3 + f \cdot T^{-1} + g \cdot T^7 + h \cdot T^{-9} \qquad ......(1)$$

where H_i^{SER} is the molar enthalpy of the element i at 298.15 K and 1 bar in its standard element reference (SER) state, and T is the absolute temperature. The last two terms in Eq.(1) are used only outside the ranges of stability [14], the term $g \cdot T^7$ is for a liquid below the melting point and $h \cdot T^{-9}$ is for solid phase above the melting point. In the present modeling, the Gibbs energies as a function of temperature are taken from the SGTE compilation by Dinsdale [13].

The Gibbs energy of liquid is described by the Redlich-Kister polynomial [15]:

$$G_m^L - H^{SER} = x_C \cdot {}^{o}G_C^L + x_i \cdot {}^{o}G_i^L + R \cdot T$$
$$\cdot [x_C \cdot \ln(x_C) + x_i \cdot \ln(x_i)] + x_C \cdot x_i \cdot [a_0 + b_0$$
$$\cdot T + (x_C - x_i) \cdot (a_1 + b_1 \cdot T) + ...] \qquad ...(2)$$

in which H^{SER} is the abbreviation of $x_C \cdot H_C^{SER} + x_i \cdot H_i^{SER}$, R is the gas constant, and x_c and x_i are the mole fractions of C and i (i=Ge, Mg), respectively. The coefficients a_j and b_j (j=0, 1) could be optimized from the experimental phase diagram and thermodynamic data. Similar equation can be written for the phases (C), (Ge) and (Mg).

In view of the negligible homogeneities for the compounds in the C-Mg system, Mg_2C_3 and MgC_2 are modeled as stoichiometric compounds. The Gibbs energy of Mg_2C_3 and MgC_2 per mole-formula is given by the following expression:

$$^{o}G_m^{Mg_2C_3} - 2 \cdot {}^{o}H_{Mg}^{SER} - 3 \cdot {}^{o}H_C^{SER} =$$
$$c_0 + d_0 \cdot T + 2 \cdot {}^{o}G_{Mg}^{Hcp} + 3 \cdot {}^{o}G_C^{Graphite} \qquad (3)$$

$$^{\circ}G_m^{MgC_2} - {^{\circ}H_{Mg}^{SER}} - 2 \cdot {^{\circ}H_C^{SER}} =$$

$$c_1 + d_1 \cdot T + {^{\circ}G_{Mg}^{Hcp}} + 2 \cdot {^{\circ}G_C^{Graphite}} \qquad (4)$$

where c_j and d_j ($j = 0,1$) are the parameters to be evaluated in the optimization.

The gas phase is described as an ideal gas mixture of the species C, C_2, C_3, C_4, C_5, C_{60}, Ge, Ge_2, and Mg, Mg_2, and its Gibbs energy per mol of species in the gas is given by the following expressions [16]:

$$G^{gas} - H^{gas} = \sum y_i[G_i^{gas} - H_i^{gas}$$

$$+ R \cdot T \cdot \ln(y_i)] + R \cdot T$$

$$\cdot \ln(0.98692 \cdot P / bar) \qquad .....(5a)$$

$$(n_C^{\circ} + n_{MgorGe}^{\circ}) / n = y_C + 2 \cdot y_{C_2}$$

$$+ 3 \cdot y_{C_3} + 4 \cdot y_{C_4} + 5 \cdot y_{C_5} + 60$$

$$\cdot y_{C_{60}} + y_{(MgorGe)} + 2 \cdot y_{(MgorGe)_2} \qquad .....(5b)$$

where n is the number of moles of the species in the gas in internal equilibrium, $(n_C^{\circ} + n_{MgorGe}^{\circ})$ the number of moles of atoms in the gas, $y_i = (n_i / n)$ is the mole fraction of the species i, $G^{gas} - H^{gas}$ the Gibbs energy of the species i, and P the pressure. The Gibbs energy functions of the individual gas species are taken from Ref. [17].

3. Results and discussion

The evaluation of the model parameters is attained by recurrent runs of the PARROT program [18] of Thermo-Calc software, which works by minimizing the square sum of the differences between experimental values and computed ones. The step-by-step optimization procedure carefully described

by Du et al. [16] was utilized in the present assessment. In the assessment procedure, each piece of experimental information is given a certain weight. The weights were changed systematically during the assessment until most of the experimental data were accounted for within the claimed uncertainty limits.

First-principles calculations within the generalized gradient approximation (GGA), as implemented in the highly efficient Vienna ab initio simulation package (VASP) [19], were carried out to obtain the enthalpy of formation ($\Delta_f H$) of Mg_2C_3 in the C-Mg system, due to the lack of the corresponding experimental data. The calculated ($\Delta_f H$) at 0 K for Mg_2C_3 is 3.499 kJ/mol. In view of the limited experimental message, it is assumed that Mg_2C_3 is stable at room temperature.

Considering that the solubilities of Ge in (C) and of C in (Ge) were reported to be negligible [2], the parameters of the excess Gibbs energies for these two phases were not introduced. Two coefficients a_0 and b_0 for liquid phase were appropriate to fit the liquidus L/(C) for the experimental data.

The optimization in the C-Mg system began with the liquid phase and Mg_2C_3. Only one interaction parameter for liquid phase was used. In order to remain Mg_2C_3 phase stable at room temperature, the optimized value of $\Delta_f H$ for Mg_2C_3 is less than that via first - principles calculation. The thermodynamic parameters for the C-Mg and C-Ge systems are listed in Table 1.

Figure 1 presents the calculated C-Ge phase diagram along with the experimental data. Figure 2 shows the calculated C-Ge phase diagram with gas phase, where the temperature of the invariant reaction

Table1. Presently optimized thermodynamic parameters in the C-Ge and C-Mg systems.

The $C - Ge$ system :

Liquid : Model $(C, \ Ge)_1$

$^o L^L_{C,Ge} = +265617.18 - 68.12925 \cdot T$

Gas : Model $(C, \ C_2, \ C_3, \ C_4, \ C_5, \ C_{60}, \ Ge, \ Ge_2)$

$^o G^{gas}_C = R \cdot T \cdot \ln(0.98692 \cdot P) + GASC(T)$

$^o G^{gas}_{C_2} = R \cdot T \cdot \ln(0.98692 \cdot P) + GASC2(T)$

$^o G^{gas}_{C_3} = R \cdot T \cdot \ln(0.98692 \cdot P) + GASC3(T)$

$^o G^{gas}_{C_4} = R \cdot T \cdot \ln(0.98692 \cdot P) + GASC4(T)$

$^o G^{gas}_{C_5} = R \cdot T \cdot \ln(0.98692 \cdot P) + GASC5(T)$

$^o G^{gas}_{C_{60}} = R \cdot T \cdot \ln(0.98692 \cdot P) + GASC60(T)$

$^o G^{gas}_{G_e} = R \cdot T \cdot \ln(0.98692 \cdot P) + GASGE(T)$

$^o G^{gas}_{Ge_2} = R \cdot T \cdot \ln(0.98692 \cdot P) + GASGE2(T)$

The $C - Mg$ system :

Liquid : Model $(C, \ Mg)_1$

$^o L^L_{C,Mg} = -113771.49$

$Mg_2C_3 : Mg_{0.4}C_{0.6}$

$^o G^{MgC_2}_m - 0.4 \, ^o G^{Hcp-A3}_{Mg} - 0.6 \, ^o G^{Graphite}_C = +698.57 - 2.61126 \cdot T$

$MgC_2 : Mg_{1/3}C_{2/3}$

$^o G^{MgC_2}_m - 1/3 \, ^o G^{Hcp-A3}_{Mg} - 2/3 \, G^{Graphite}_C = +579.41 - 2.17291 \cdot T$

Gas : Model $(C, \ C_2, \ C_3, \ C_4, \ C_5, \ C_{60}, \ Mg, \ Mg_2)$

$^o G^{gas}_{Mg} = R \cdot T \cdot \ln(0.98692 \cdot P) + GASMG(T)$

$^o G^{gas}_{Mg_2} = R \cdot T \cdot \ln(0.98692 \cdot P) + GASMG2(T)$

In J/(mol of atom),and temperature(T) in Kelvin and pressure(P) in bar. The Gibbs energies for the pure elements are from the SGTE compilation [13], and the Gibbs energies for gas species are from Ref. [17].

Gas + (C) = Liquid was calculated to be 2722.9 ºC. As shown in Fig. 1, the experimental data from Scace and Slack [2] can be well described by the present set of thermodynamic parameters. The eutectic reaction, Liquid = (C) + (Ge), occurs at about pure Ge and 938.3 ºC.

Figure 3 presents the calculated C-Mg phase diagram together with the experimental data, while Figure 4 is the one

with gas phase. It can be seen that the present set of thermodynamic parameters can well describe the experimental data from Ehrlich [7] and Irmann [8]. According to the present calculation, three invariant reactions, viz Liquid + (C) = Mg_2C_3, Mg_2C_3 + (C) = MgC_2 and Liquid = (Mg) + Mg_2C_3, occur at 657 ^oC, 597 ^oC and 415.7 ^oC, respectively.

Knowledge of phase diagram and thermodynamic properties [20, 21] is of fundamental importance in many applications. High-throughput discovery of new materials
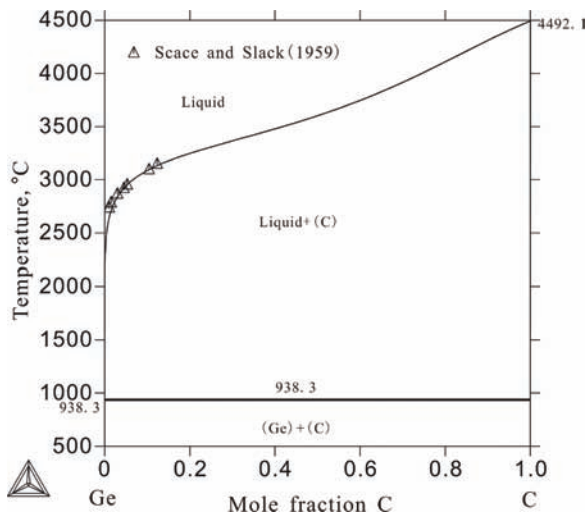

Fig.1 Calculated C-Ge phase diagram, compared with the experimental data from Scace and Slack [2].
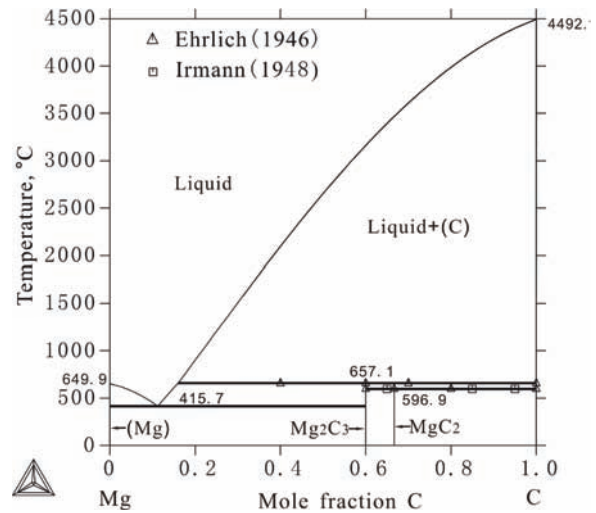

Fig.3 Calculated C-Mg phase diagram, compared with the experimental data from Ehrlich [7] and Irmann [8].
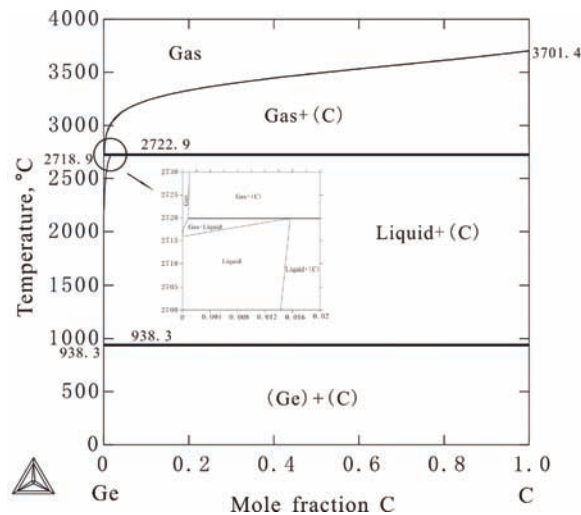

Fig.2 Calculated C-Ge phase diagram with solid phases, liquid and gas, and close up on the phase equilibrium in Ge-rich corner.
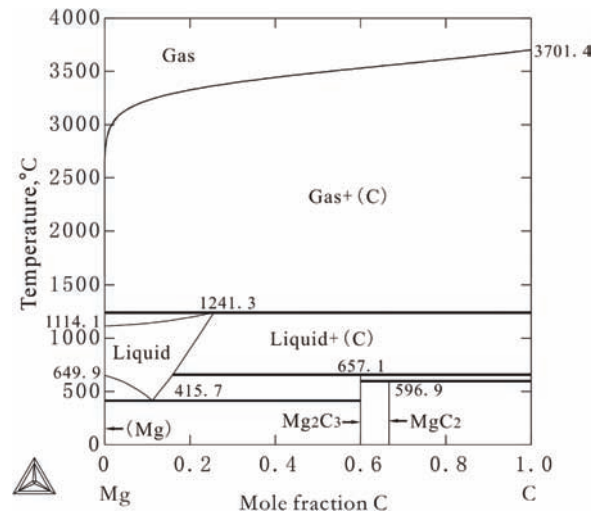

Fig.4 Calculated C-Mg phase diagram with solid phase, liquid and gas.

strongly depends on the establishment of an accurate thermodynamic database in a multi-component system.

The present work is a continuing effort of our previous attempts [22-26] to establish a thermodynamic database for Al alloys.

4. Conclusions

The literature on the C-Ge and C-Mg systems was critically reviewed. First-principles calculations were performed to obtain the enthalpy of formation of Mg_2C_3, refining the modeling of the C-Mg system. Two sets of self-consistent parameters corresponding respectively to the C-Ge and C-Mg systems were obtained by using the CALPHAD approach. The experimental data in the C-Ge and C-Mg systems can be well account for by using the presently obtained thermodynamic parameters.

Acknowledgements

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