THERMODYNAMIC CALCULATION OF INTERFACE REACTIONS BETWEEN TITANIUM MELT AND SPECIAL MOLD MATERIALS①

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ABSTRACT On the basis of the Miedema model of heat formation and Toop equation, the reactions between titanium melt and special mold materials have been analyzed and calculated thermodynamically. The refractory molding materials involved in the calculation include such materials as carbides, nitrides and borides that possess high chemical stability and high melting points. The results show that the changes of dissolved Gibbs energy(ΔG) of the reactions are all negative in the temperature range from titanium melting point to 2300 K. This means that the chemical stability of those kinds of molding materials decreases when they contact with titanium melt. Furthermore, considering the high chemical reactivity of titanium melt, the calculation will provide some instructions to choose mold materials for titanium castings.

Key words titanium interface reaction Gibbs free energy mold refractory materials

1 INTRODUCTION

Titanium castings have been widely applied in many regions such as aeronautics, aerospace and so forth. But the drawback of the high reactivity of molten titanium is easy to cause reactions between this metal and the mold materials, and produce a hardened layer on the titanium casting surface[1-3]. This will have bad effects on the properties and surface qualities of the titanium castings. Many authors have ever studied this problem by experimental method[4-6], but the theoretical analyses of such reactions have not yet been done by thermodynamic method. The special refractory materials such as carbides, nitrides and borides have been evaluated as crucible materials but their usage as mold materials has not been known for titanium casting. Miedema model[7-9] for heat formation of binary alloys has predicted the heat formation of nearly one hundred kinds of alloys successfully. By using this model and Toop equation for ternary solution, the activity coefficients of solutes in titanium melt can be calculated, then the changes of Gibbs free energy of solvent reactions between titanium melt and these materials are calculated in this paper.

2 THERMODYNAMIC MODEL

The interface reactions between titanium melt and mold materials can be defined as

$$A_xB_{y(s)} \rightarrow x\underline{A} + y\underline{B} \quad (1)$$

where $A_xB_{y(s)}$ represents the mold materials which will dissolve in titanium melt, x and y are stoichiometric coefficients, $\underline{A}$ and $\underline{B}$ are the constitution of mold materials dissolved in molten titanium(pure substance as standard state), respectively. Then, the changes of Gibbs energy (ΔG) of Eq.(1) is as follows:

$$\Delta G = \Delta G^0 + RT\ln J_a = \Delta G^0 + RT(x\ln a_A + y\ln a_B - \ln a_{A_xB_y}) \quad (2)$$

Assuming the pure substance as standard state

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for A_xB_y, and only one constitution of mold materials is put into reaction, then, the activity of A_xB_y ($a_{A_xB_y}$) is unit and can be expressed as $a = \gamma x$, therefore Eq.(2) can be rewritten as

$$\Delta G = \Delta G^0 + RT(x\ln \gamma_A x_A + y\ln \gamma_B x_B) \quad (3)$$

where ΔG^0 is standard changes of Gibbs free energy for Eq.(1), γ_A and γ_B are activity coefficient of *A* and *B*, and x_A and x_B are mole fractions of *A* and *B* in titanium solution, respectively.

According to the definition by Lupis and Elliott[10], the solute activity coefficient (γ_i) can be approximated in terms of first-order and second-order Gibbs energy interaction parameters by using Taylor's series expansion:

$$\ln \gamma_i = \ln \gamma_i^0 + \sum_{j=2}^{m} \varepsilon_i^j x_j + \sum_{j=2}^{m}\sum_{k=2}^{m} \rho^{j,k} x_j x_k + 0(x^3) \quad (4)$$

As *A*, *B* and titanium melt is considered as ternary solution, and among which Ti (supposed as *k*) is solvent, the other *A* and *B* (supposed as *i* and *j*) are solutes, as $x_{Ti} \to 1$, $x_A \to 0$, $x_B \to 0$, and only considering the interaction of *A* and *B*, then the coefficient items of Eq.(4) have the relationships with partial mole excess Gibbs energy of solute in the solution ($\overline{G}_i^E$)[11].

The relationship of partial mole excess Gibbs energy and the system mole excess Gibbs energy in the ternary solutions is defined as follows[12]:

$$\overline{G}_i^E = G^E - x_j \frac{\partial G^E}{\partial x_j} + (1 - x_i) \frac{\partial G^E}{\partial x_i} \quad (5)$$

$$\overline{G}_j^E = G^E - x_i \frac{\partial G^E}{\partial x_i} + (1 - x_j) \frac{\partial G^E}{\partial x_j} \quad (6)$$

$$\overline{G}_k^E = G^E - x_i \frac{\partial G^E}{\partial x_i} - x_j \frac{\partial G^E}{\partial x_j} \quad (7)$$

Toop Equation has been widely used in forecasting the thermodynamic properties of ternary systems[11]. Supposing *i* is non-symmetrical component, then substituting $x_k = 1 - x_i - x_j$ in Toop equation, we have the relationship of ternary system excess mole Gibbs energy and that of binary alloy which can be consisted of two of the components of *i*, *j*, or *k*:

$$G^E = \frac{x_j}{1 - x_i} G_{ij}^E(x_i, 1 - x_i) + \frac{1 - x_i - x_j}{1 - x_i} G_{ik}^E(x_i, 1 - x_i) + (1 - x_i)^2 G_{jk}^E\left(\frac{x_j}{1 - x_i}, \frac{1 - x_i - x_j}{1 - x_i}\right) \quad (8)$$

where G^E is for the system excess mole Gibbs energy of ternary solution, G_{ij}^E, G_{ik}^E and G_{jk}^E are for the system excess mole Gibbs energies of binary system. In order to solve G_{ij}^E, G_{ik}^E and G_{jk}^E, the Miedema model of heat formation of binary alloys can be used. Although the Miedema model is empirical, it is widely used in predicting heat formation of binary alloys where the calculation results are identical to the experimental data of more than one hundred binary alloys[7,8]. According to the definition in Ref.[7] and deduction of Ref.[11], and assuming the binary solution is regular, so the excess entropy of binary system $S_{ik}^E = 0$, then, for the binary *i*-*k* solution (it is the same for *i*-*j* and *j*-*k*), we have:

$$G_{ik}^E = \Delta H_{ik} \quad (9)$$

$$\Delta H_{ik} = f_{ik} \frac{x_i[1 + u_i x_k(\varphi_i - \varphi_k)]\, x_k \cdot}{x_i[1 + u_i x_k(\varphi_i - \varphi_k)]\, V_i^{2/3} + \leftarrow \frac{[1 + u_k x_i(\varphi_k - \varphi_i)]}{x_k[1 + u_k x_i(\varphi_k - \varphi_i)]\, V_k^{2/3}}} \quad (10)$$

where $f_{ik} = \frac{2pV_i^{2/3}V_k^{2/3}\{q/p[(n_{ws}^{1/3})_i - (n_{ws}^{1/3})_k]^2 - (n_{ws}^{1/3})_i^{-1} + \leftarrow (\varphi_i - \varphi_k)^2 - b(r/p)\}}{(n_{ws}^{1/3})_k^{-1}}$, x_i, x_k are mole fractions; V_i, V_k are mole volumes; $(n_{ws})_i$ and $(n_{ws})_k$ are electronic densities; φ_i and φ_k are electronic charges for *i* and *k*, respectively; *p*, *q*, u_i, u_k, *b*, and *r*/*p* are constants, and *q*/*p* = 9.4, for liquid alloy *b* = 0.73. The values of the above parameters can be obtained from Refs. [7], [9] and [11]. For the same reason, the likely expression can be obtained for *i*-*j* and *j*-*k*. Combining the above equations, we have the expression of $\ln \gamma_i^0$, ε_i^i, ε_i^j, ρ^i, ρ^j and $\rho^{i,j}$ as follows:

$$\ln \gamma_i^0 = \frac{1}{RT} A \quad (11)$$

$$\varepsilon_i^i = \frac{1}{RT} D \quad (12)$$

$$\varepsilon_i^i = \varepsilon_j^i = \frac{1}{RT}(B - A - C) \quad (13)$$

$$\rho_i^i = \frac{1}{2RT}(-D + G) \quad (14)$$

$$\rho_i^j = \frac{1}{2RT}(-E) \quad (15)$$

$$\rho^{i,j} = \frac{1}{RT}(B - A + C + F - D) \quad (16)$$

Ordering $\Phi_{ij} = \varphi_i - \varphi_j$, $\Phi_{ji} = \varphi_j - \varphi_i$, $\Phi_{ik} = \varphi_i - \varphi_k$, $\Phi_{ki} = \varphi_k - \varphi_i$, $\Phi_{jk} = \varphi_j - \varphi_k$, $\Phi_{kj} = \varphi_k - \varphi_j$, $V_i^{2/3} = V_i$, $V_j^{2/3} = V_j$, $V_k^{2/3} = V_k$, and f_{ij} and f_{jk} having the same meanings of f_{ik}, then the expressions of A, B, C, D, E, F and G are:

$$A = f_{ik}[1 + \mu_i \Phi_{ik}] / V_k$$

$$B = f_{ij}[1 + \mu_i \Phi_{ij}] / V_j$$

$$C = f_{jk}[1 + \mu_j \Phi_{jk}] / V_k$$

$$D = f_{ik}\{2[(2\mu_i + \mu_k)\Phi_{ki} - 1 - \mu_k \mu_i \Phi_{ki}^2] / V_j - 2[1 + \mu_i \Phi_{ik}] \cdot [V_i(1 + \mu_i \Phi_{ik}) + V_k(-1 + \mu_k \Phi_{ki})] / (V_k)^2\}$$

$$E = f_{jk}\{2[(2\mu_j + \mu_k)\Phi_{kj} - 1 - \mu_k \mu_j \Phi_{kj}^2] / V_k - 2[1 + \mu_j \Phi_{jk}] \cdot [V_j(1 + \mu_j \Phi_{jk}) + V_k(-1 + \mu_k \Phi_{kj})] / (V_k)^2\}$$

$$F = f_{ij}\{2[(2\mu_i + \mu_j)\Phi_{ji} - 1 - \mu_i \mu_j \Phi_{ji}^2] / V_j - 2[1 + \mu_i \Phi_{ij}] \cdot [V_i(1 + \mu_i \Phi_{ij}) + V_j(-1 + \mu_j \Phi_{ji})] / (V_j)^2\}$$

$$G = f_{ik}\{6\mu_i \Phi_{ik} / V_k + 6\mu_i \mu_k \Phi_{ik}^2 / V_k + 6\mu_i \Phi_{ik}[V_i(1 + \mu_i \Phi_{ik}) + V_k \cdot (1 + \mu_k \Phi_{ki})] / V_k^2 + 6(1 + \mu_i \Phi_{ik}) \cdot \mu_k \Phi_{ik} / V_k + 6(1 + \mu_i \Phi_{ik})[V_i(1 + \mu_i \Phi_{ik}) + V_k(-1 + \mu_k \Phi_{ki})] / V_k^2 + 6(1 + \mu_i \Phi_{ik})\mu_k \Phi_{ik}[V_i(1 + \mu_i \Phi_{ik}) + V_k(-1 + \mu_k \Phi_{ki})] / V_k + 6(1 + \mu_i \Phi_{ik})[V_i(1 + \mu_i \Phi_{ik}) + V_k(-1 + \mu_k \Phi_{ki})]^2 / V_k^3 - 3(1 + \mu_i \Phi_{ik}) \cdot [V_i(-2\mu_i \Phi_{ik}) + V_k(-2\mu_k \Phi_{ki})] / V_k^2\}$$

The activity coefficients of A and B dissolving in titanium melt can be determined through the above equations, and the changes of Gibbs energy of reaction that A_xB_y dissolved in titanium melt can be calculated.

3 CALCULATIONS AND RESULTS

From the literatures, it is known that some refractory carbides, nitrides and borides possess high melting points and high chemical stability and can be selected as crucible or mold materials for titanium melting or casting. For the aim of quantitative calculation, some compounds including SiC, TiC, ZrC, CaC_2, Si_3N_4, AlN, TiN, ZrN, BN, TiB_2 and ZrB_2 are selected and the reactions of them with titanium melt are evaluated by the above thermodynamic method. The basic properties of some chemical elements and some parameters that will be used in the calculations are listed in Table 1 and Table 2. The calculating results of Gibbs free energy changes of the reactions interpreted as Eq. (1) are shown in Fig.1 to Fig.3.

The results shown in Fig.1 to Fig.3 illustrate the trend of chemical stability of those calculated materials within the temperature range from 1 900 K to 2 300 K. The changes of Gibbs free energy denoted as ΔG for the solvent reac-

Table 1 Basic properties of some chemical elements

Elements	Electronic charge, φ/V	Electronic density, $n_{ws}^{1/3}$/(d.u.)$^{1/3}$	Mole volume, $V_m^{2/3}$/cm^2
Ti	3.65	1.47	4.8
Si	4.70	1.50	4.2
Al	4.20	1.39	4.6
Ca	2.55	0.91	8.8
Zr	3.40	1.39	5.8
C	6.20	1.90	1.8
N	7.00	1.60	2.2
B	4.75	1.55	2.8

Table 2 Parameters of r/p^* and μ

Elements	Ti	Si	Al	Ca	Zr	C	N	B
r/p	1.0	2.1	1.9	1.9	1.0	2.1	2.3	1.9
μ	0.04	0.04	0.07	0.14	0.04	0.10	0.04	0.10

* The values of r/p are the products of elements for solid alloys, and for liquid alloys are 0.73 r/p. The values of p are 14.1, 10.6 and 12.3 for alloys of two transition metals, two non-transition metals and a transition metal with a non-transition metal, respectively.

tions are all negative for carbides, nitrides and borides. This means, namely, that all the materials involved in the calculation would react with liquid titanium. And the values of ΔG are more negative as the temperature rises, i.e. the reaction tendency is enhanced. Fig.1 to Fig.3 show that the changes of Gibbs energy are several hundred kJ lower than zero. This illustrates that the solvent reaction would occur to some extent. By comparing the values of free energy changes in Fig.1, the value of ΔG for ZrC is the largest. In view of this, ZrC is the most stable material as it contacts with the titanium melt, and SiC is the most unstable for its ΔG is the most negative. Thus, the sequence of chemical stability for carbides can be graded in decreasing order as ZrC, TiC, CaC_2 and SiC. The calculation results shown in Fig.2 and Fig.3 also illustrate the same situations for nitrides and borides. Meanwhile, by contrasting the results of ΔG for these kinds of materials, it can be concluded that the carbide is the most stable material for its value of the changes of Gibbs free energy is the greatest, and the nitride is the most unstable material.

The calculated results can be supported by experimental data introduced from the melting experience by using ceramic crucibles made of carbides, nitrides or borides. But, when the dynamic factors are being considered, some reactions would be significantly retarded, it is said that the thermophysical characteristics of titanium such as smaller heat capability, lower heat conductivity and relatively lower density will cause the temperature of metal to drop rapidly and make it solidify fast. The relative stability of refractory used for casting titanium is dependent on both thermodynamics and dynamics. Furthermore, it could be pointed out that it is possible to use less chemically stable refractories as mold materials for titanium castings when the dynamic factors are taken into account.

Fig.1 Gibbs free energy changes of interface reactions of carbides with titanium melt

Fig.2 Gibbs free energy changes of interface reactions of nitrides with titanium melt

Fig.3 Gibbs free energy changes of interface reactions of borides with titanium melt

4 CONCLUSIONS

Based on the results of thermodynamic calculations about the values of changes of Gibbs free energy for the interactions of carbides, nitrides or borides with titanium melt, the relative

chemical stability can be determined. Above the temperature of the melting point of titanium, all the three kinds of materials react with the molten titanium, and the tendency is increasing with increasing temperature. According to the calculated values of ΔG, the carbides are more stable than nitrides and borides, and the nitrides have relatively lower stability. For carbides, the sequence of chemical stability in the order of decreasing is ZrC, TiC, CaC_2 and SiC, and it is likely the same for nitrides and borides. The dynamic factors have effects on the reactivity of them with molten titanium, and retard the process of such interactions.

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