Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 28(2018) 1256−1264
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Determination of thermodynamic properties in full composition range of Ti−Al binary melts based on atom and molecule coexistence theory

Sheng-chao DUAN[1,2], Xiao SHI[1,2], Wen-sheng YANG[1,2], Han-jie GUO[1,2], Jing GUO[1,2]

1. School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China;
2. Beijing Key Laboratory of Special Melting and Preparation of High-end Metal Materials, University of Science and Technology Beijing, Beijing 100083, China

Received 11 January 2017; accepted 16 May 2017

Abstract: The results of predicting thermodynamic properties in the full composition range of Ti−Al binary melts in a temperature range from 1973 to 2273 K were obtained by coupling with the developed thermodynamic model for calculating mass action concentration N_i of structural units in Ti−Al system based on the atom and molecule coexistence theory (AMCT). Temperature dependence of the activity coefficients of Ti and Al in natural logarithmic form in the infinitely dilute solution ($0<x_{Ti}<0.01$) of Ti−Al binary melts was also determined from the calculated activity coefficients of Ti and Al at temperatures of 1973, 2073, 2173, and 2273 K. The standard molar Gibbs free energy change of dissolving pure liquid element *i*(l) for forming 1% (mass fraction) element *i* in Ti−Al binary melts further was deduced. With the aid of this model, meanwhile, the determined excess thermodynamic properties, such as the excess molar mixing Gibbs free energy/entropy/enthalpy were also calculated.

Key words: Ti−Al binary system; Ti; Al; activity coefficient; thermodynamic model; mass action concentration; atom and molecule coexistence theory

1 Introduction

Titanium and its alloys have been the key materials used in various fields due to the attractive mechanical properties, including the lightweight, high specific strength, high ductility, and low thermal conductivity [1−4]. Therefore, it is necessary to ascertain the thermodynamic properties of the alloys, which are important database in order to know phase stabilities and the bonding forces of components and also to predict ternary and high order phase diagrams based on Ti−Al system [5−8]. For these reasons, many efforts have been made to study the thermodynamic properties of Ti−Al system in the past several decades [8−10]. Having in mind the presented literature survey, however, it is clear that many studies on the Ti−Al system concern the investigation on its alloys in the solid state, only few articles describe the thermodynamic behavior in the liquid phase [11]. The experimental techniques employed by the investigators are summarized in Table 1.

In order to overcome the limitation of these studies, investigations on the reaction abilities of elements, especially activity coefficient of Ti (γ_{Ti}) and activity coefficient of Al (γ_{Al}) in Ti−Al binary melts were also carried out. In the recent past, the activity of Al in molten Ti−Al alloy was measured by MAEDA et al [4] using free evaporation method at 2073 K in an electron beam vacuum furnace. They reported that γ_{Al} was about 0.03 under conditions of $x_{Al}\leq 0.1$, and it was about 0.1 at $x_{Al}\geq 0.2$. The experimental measurement of thermodynamic parameter is costly and difficult in the operation due to the systems containing highly reactive element such as titanium. It is therefore very necessary to develop a reliable model for predicting thermodynamic properties of Ti−Al binary melts. GUO et al [6] applied the Midema model to predict formation heat of Ti−Al binary system, which was used to calculate the activity of aluminum in molten Ti−Al alloy. On this basis, they studied the evaporation controlling mode of Al in the binary system during the cold crucible induction skull melting (ISM) process. KOSTOV et al [8] calculated the

Foundation item: Project (U1560203) supported by the Joint Funds of the National Natural Science Foundation of China; Project (51274031) supported by the National Natural Science Foundation of China
Corresponding author: Han-jie GUO; Tel/Fax: +86-10-62334964; E-mail: guohanjie@ustb.edu.cn
DOI: 10.1016/S1003-6326(18)64764-8

Table 1 Summary of previous investigations on thermodynamic activities in Ti−Al system

Temperature /K	Composition range	Experimental technique	Ref.
1780	$0<x_{Al}\leq0.4$	Thermodynamic activities of Ti and Al were measured in the β-Ti phase by the "three vapor pressure techniques"	[1]
890−1010	$0.05<x_{Al}\leq0.5$	Thermodynamic activities of Al were measured by electrochemical cell with a CaF_2 electrolyte	[2]
1113−1664	$0<x_{Al}<1$	The vaporization of solid alloy of Ti−Al system, 19 alloy samples of different composition ranges, has been studied by using Knudsen effusion mass spectrometry	[3]
2073	$0<x_{Al}<0.5$	The activities of Al in molten Ti−Al alloy were determined by "free evaporation method" that the specimen was melted and held at constant temperature in an electron beam vacuum furnace	[4]
1073−1674	Ti−45 Al and Ti−62 Al*	The activities of Ti and Al were measured by using a twin Knudsen-cell assembly with one cell acting as internal standard	[5]
2073	$0<x_{Al}<0.5$	The activities of Al in molten Ti−Al binary alloy were calculated by Midema model	[6]
820−900	31.3% Al, 47.9% Al, 64.7% Al, 73.6% Al, 99.0% Al	A solid reversible galvanic cell employing a CaF_2 solid electrolyte and an Al−CaF_2 reference electrode were used for solid Ti−Al alloy	[7]
1773−2273	$0<x_{Al}<1$	Thermodynamic activities in Ti−Al binary system predicted by FactSage™	[8]
1973−2273	$0<x_{Al}<1$	The thermodynamic properties in Ti−Al binary melts were determined by means of the AMCT	This study

* The alloy compositions were selected on the basis of interest range in understanding the oxidation of γ-TiAl based alloy

activity of titanium and aluminum in Ti−Al alloys using the FactSage™ thermochemical software and databases in a temperature range between 1773 and 2273 K. To the knowledge of the present authors, few prediction models were established to predict or evaluate the activity of Ti and Al in liquid Ti−Al alloys. Several prediction models were widely employed to describe thermodynamic properties of metallic melts with regressed artificial parameters obtained by experimental results [12], including but not limited to the regular solution model [13], Miedema model [14], molecular interaction volume model (MIVM) [15], non-random two-liquid (NRTL) equation [16], and Wilson equation [17]. Considering the fact that experimental difficulties and other factors, however, some parameters embodied in the foregoing theoretical models cannot be measured or estimated accurately so that the prediction models do not work well [18].

The atom and molecule coexistence theory (AMCT) has been reliably applied to predicting reaction abilities of multicomponent alloy system containing compound, eutecticum, metatectic, and solid solution [19,20]. In addition to this, investigators in Ref. [19,21−28] have proved that the calculated mass action concentration by means of AMCT-N_i model can be used for substituting the measured activities of corresponding elements in Fe−Si, Ge−Al, Au−Pb, Ag−Pd, Ca−Al−Si, and In−Sb−Cu systems relative to pure liquid matter as standard state. Also, it has been demonstrated in the authors' most recent study, based on the reported values of activity of Ti and Al in the full composition range of Ti−Al binary melts [9], that 1) atoms of Ti and Al and three molecules as $TiAl_3$, TiAl, and Ti_5Al_{11} could exist in Ti−Al binary melts; 2) the calculated mass action concentration of free Ti (N_{Ti}) or mass action concentration of free Al (N_{Al}) in the full composition range of Ti−Al binary melts by solving the nonlinear multivariable equations with Matlab™, which has good 1:1 corresponding relationship with the reported activity of Ti ($a_{R,Ti}$) or reported activity of Al ($a_{R,Al}$) relative to pure liquid Ti(l) or Al(l) as standard state (see Fig. 1); 3) a rod-type relationship between the calculated mass action concentration (N_i) and the calculated equilibrium mole number (n_i) of $TiAl_3$, and Ti_5Al_{11} in Ti−Al binary melts has been found. At the same time, a spindle-type relationship between the calculated mass action concentation (N_{TiAl}) and the calculated equilibrium mole number (n_{TiAl}) in this binary melt has also been investigated [9].

In consideration of the great practical significance, the aim of this paper is to give a contribution to thermodynamic study of Ti−Al binary melts by coupling with thermodynamic model, i.e., AMCT-N_i model, for calculating mass action concentration of structural units

(N_i) based on the atom and molecule coexistence theory (AMCT) in the full composition range of Ti−Al binary melts in the temperature range from 1973 to 2273 K, as well as to show the possibility of application of the used model in thermodynamic description of the system, such as the thermodynamic properties of Ti−Al binary melts: the Raoultian activity coefficient (γ_i^{Θ}), the standard molar Gibbs free energy change ($\Delta_{sol}G_{m,i}^{\Theta}$) of dissolving pure liquid i(l) for forming 1% (mass fraction) of element i in binary metallic melts, and excess molar mixing thermodynamic properties.

2 Hypotheses

It has been briefly demonstrated in Section 1 that atoms of Ti and Al, and molecules of $TiAl_3$, TiAl, and Ti_5Al_{11} can coexist in Ti−Al binary melts. The hypotheses of the developed AMCT-N_i model for Ti−Al binary melts can be summarized as follows [19]: 1) the Ti−Al binary melts at elevated temperature are composed of five structural units, including two atoms of Ti and Al and three molecules of $TiAl_3$, TiAl, and Ti_5Al_{11} according to the phase diagram of Ti−Al binary system; 2) each structural unit occupies its independent position in Ti−Al binary melts; 3) the elements of Ti and Al in Ti−Al binary melts will take part in reactions of forming three molecules $TiAl_3$, TiAl, and Ti_5Al_{11} in the form of atoms; 4) the reactions of forming molecules of $TiAl_3$, TiAl, and Ti_5Al_{11} are under the chemical dynamic equilibrium between the simple atoms of Ti and Al; 5) three structural units in Ti−Al binary melts as $TiAl_3$, TiAl, and Ti_5Al_{11} bear the structural continuity in the investigated composition range; 6) the chemical reactions of forming three molecules of $TiAl_3$, TiAl, and Ti_5Al_{11} from Ti and Al obey the mass action law.

3 Results and discussion

3.1 Results of AMCT-N_i thermodynamic model for Ti−Al binary melts

The establishment of AMCT-N_i thermodynamic model and determination of mass action concentration of structural units in Ti−Al binary melts at elevated temperatures have been given in detail elsewhere [9]. Figure 1 shows the comparison between model-calculated mass action concentration N_i and determined activities a_i of Ti and Al in Ti−Al melts, from which it can be observed that the calculated N_i can be applied to substituting the measured a_i relative to pure liquid matter as standard state in Ti−Al binary system. The standard molar Gibbs free energy change $\Delta_r G_{m,ci}^{\Theta}$ (1973 K≤T≤2273 K) of reactions for forming $TiAl_3$, TiAl, and Ti_5Al_{11} from Ti and Al relative to pure liquid matter as standard state is listed as follows.

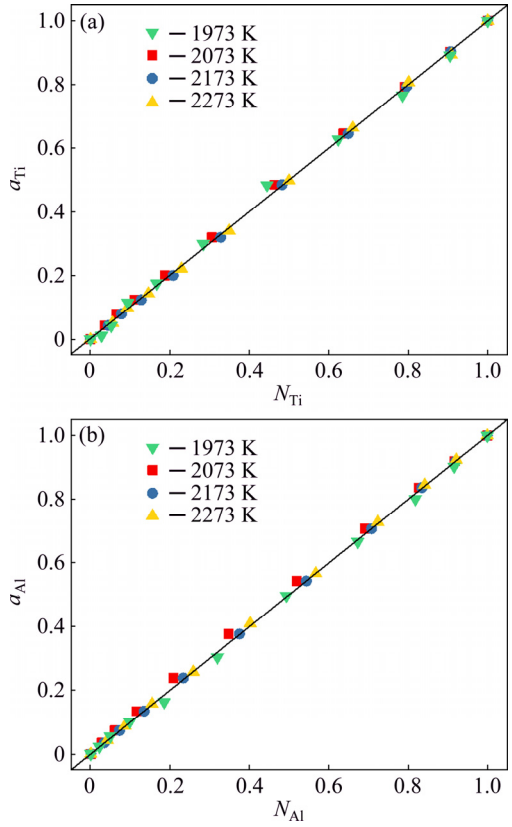

Fig. 1 Relationship between calculated mass action concentration N_i and activity a_i in full composition range of Ti−Al binary melts in temperature range from 1973 to 2273 K

$$[Ti]+3[Al]=[TiAl_3]$$

$$\Delta_r G_{m,TiAl_3}^{\Theta} = -RT\ln\left(\frac{a_{R,TiAl_3}}{a_{R,Ti}a_{R,Al}^3}\right) = -197906.62+81.45T \quad (1)$$

$$[Ti]+[Al]=[TiAl]$$

$$\Delta_r G_{m,TiAl}^{\Theta} = -RT\ln\left(\frac{a_{R,TiAl}}{a_{R,Ti}a_{R,Al}}\right) = -114990.08+46.47T \quad (2)$$

$$5[Ti]+11[Al]=[Ti_5Al_{11}]$$

$$\Delta_r G_{m,Ti_5Al_{11}}^{\Theta} = -RT\ln\left(\frac{a_{R,Ti_5Al_{11}}}{a_{R,Ti}^5 a_{R,Al}^{11}}\right) = -403082.46+93.67T \quad (3)$$

where R is the mole gas constant (8.314 J/(mol·K)), T is the temperature (K), and $a_{R,i}$ is the activity relative to pure liquid i as standard state (−).

As a representative, the relationship between mole fraction of Ti (x_{Ti}) and calculated mass action concentrations (N_i) of five structural units as Ti, Al, $TiAl_3$, TiAl, and Ti_5Al_{11} in the full composition range of Ti−Al binary melts in the temperature range from 1973 to 2273 K is shown in Fig. 2.

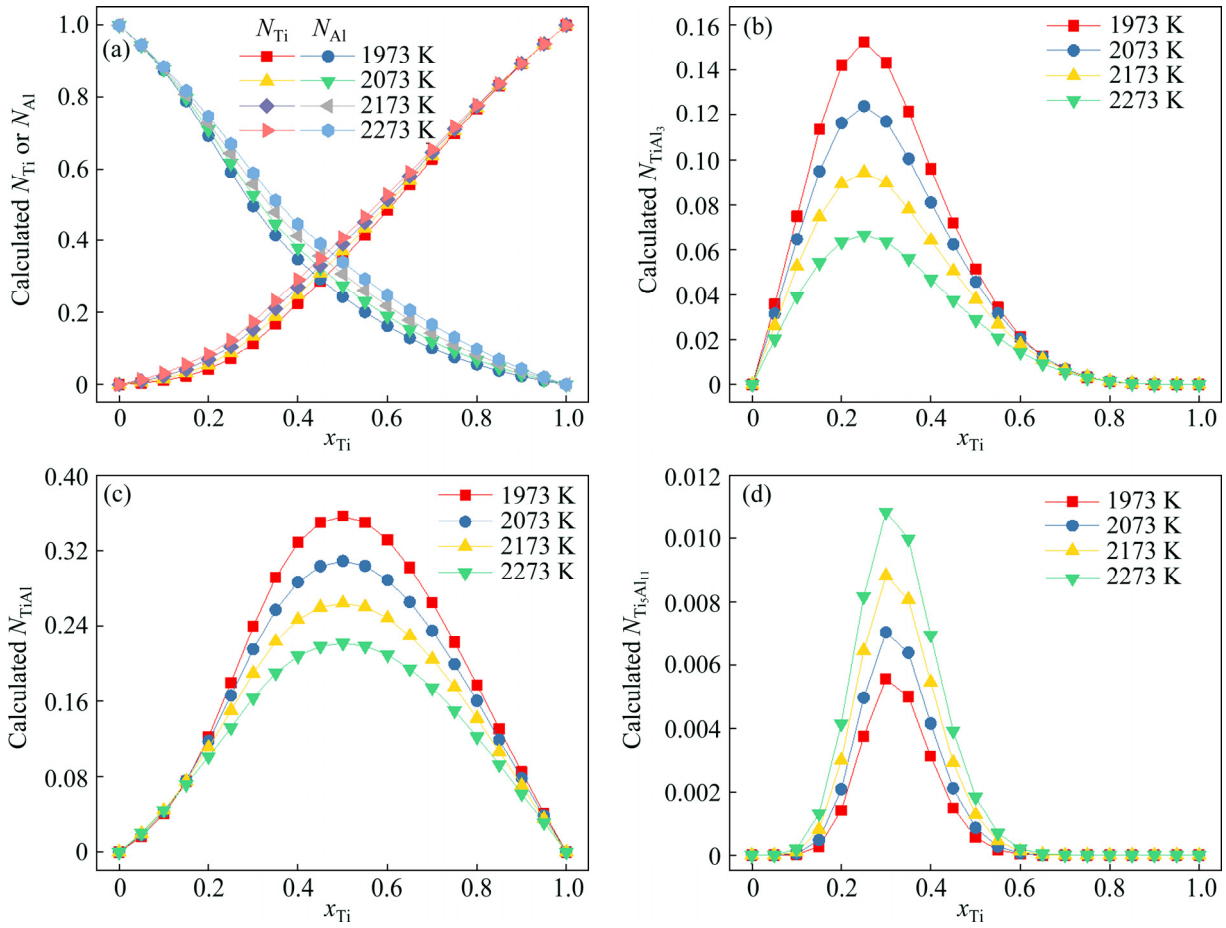

Fig. 2 Relationship between mole fraction of Ti (x_{Ti}) and calculated mass action concentrations (N_i) of structural units as Ti, Al, $TiAl_3$, TiAl, and Ti_5Al_{11} in full composition range of Ti−Al binary melts in temperature range from 1973 to 2273 K, respectively

Figure 2(a) shows the variation of the calculated mass action concentrations of Ti (N_{Ti}) and Al (N_{Al}) as a function of mole fraction of Ti (x_{Ti}) in the temperature range from 1973 to 2273 K. As can be observed in Fig. 2(a), at a given temperature, the calculated mass action concentration of Ti (N_{Ti}) shows a sluggish increase tendency with an increase of mole fraction of Ti (x_{Ti}) from 0 to 0.2, and then displays a drastic increase trend with an increase of mole fraction of Ti (x_{Ti}) from 0.2 to 1.0 at the above mentioned four temperatures. However, an opposite variation relationship of the calculated N_{Al} against x_{Ti} can be found at 1973, 2073, 2173, and 2273 K. Meanwhile, for a fixed concentration, as temperature increases, the activity of both components increases, which means that increasing temperature can promote the reaction ability.

The reverse V-type relationships between mole fraction x_{Ti} and calculated mass action concentrations of $TiAl_3$, TiAl, and Ti_5Al_{11} in the full composition range of Ti−Al binary melts at 1973, 2073, 2173, and 2273 K are shown in Figs. 2(b)−(d), respectively. As shown in Figs. 2(b) and (c), increasing temperature from 1973 to 2273 K can result in a decrease of the maximum value of calculated mass action concentration N_{TiAl_3} from 0.1525 to 0.0664 and N_{TiAl} from 0.3560 to 0.2215, respectively. However, the maximum value of calculated mass action concentration $N_{Ti_5Al_{11}}$ increases from 0.0056 to 0.0108 with an increase in the temperature range. It should be specially emphasized that the sum of the calculated mass action concentration N_i of five structural units as Ti, Al, $TiAl_3$, TiAl, and Ti_5Al_{11} in Ti−Al binary melts should be unity. Therefore, it can be deduced that the calculated mass action concentration N_i of five structural units in Ti−Al binary melts should be competitive or coupled each other [28].

3.2 Determination of standard molar Gibbs free energy change $\Delta_{sol}G^{\Theta}_{m,i}$ of dissolving pure liquid *i* for forming 1% element *i* in Ti−Al binary melts

According to the definition of N_i, the physical meaning of the N_i is equilibrium mole fraction of structural unit i in a closed system. The basic meaning of N_i is almost consistent with the traditionally applied activity a_i of component i in metallic melts, in which pure liquid matter is chosen as the standard state and mole faction is selected as a concentration unit [19]. Meanwhile, it has been pointed out by the present

authors [9] that the calculated mass action concentration of Ti (N_{Ti}) or that of Al (N_{Al}) had been validated to substitute the reported activity of Ti ($a_{R,Ti}$) or that of Al ($a_{R,Al}$) in Ti−Al binary melts in full composition range in a temperature range from 1973 to 2273 K.

The activity coefficient of Ti (γ_{Ti}) or that of Al (γ_{Al}) in Ti−Al binary melts with changing mole fraction of Ti (x_{Ti}) or that of Al (x_{Al}) from 0 to 0.01 at an interval of x_i as 0.0001 at temperatures of 1973, 2073, 2173, and 2273 K can be determined as $\gamma_i=N_i/x_i$ based on the developed AMCT-N_i model for Ti−Al binary melts [25,26,28]. The relationship between mole fraction of Ti (x_{Ti}) and the calculated activity coefficient of Ti in natural logarithmic form ($\ln\gamma_{Ti}$) in Ti−Al binary melts is illustrated in Fig. 3(a). The corresponding relationship at above mentioned four different temperatures can be expressed by the linear equations as follows:

$$\ln\gamma_{Ti,\ 1973\ K}=4.5891x_{Ti}-2.7138\ \ (0<x_{Ti}\leq 0.01) \quad (4)$$

$$\ln\gamma_{Ti,\ 2073\ K}=4.2404x_{Ti}-2.3021\ \ (0<x_{Ti}\leq 0.01) \quad (5)$$

$$\ln\gamma_{Ti,\ 2173\ K}=3.7810x_{Ti}-1.8822\ \ (0<x_{Ti}\leq 0.01) \quad (6)$$

$$\ln\gamma_{Ti,\ 2273\ K}=3.1988x_{Ti}-1.4786\ \ (0<x_{Ti}\leq 0.01) \quad (7)$$

The relationship between mole fraction of Al (x_{Al}) and the calculated activity coefficient of Al in natural logarithmic form ($\ln\gamma_{Al}$) in Ti−Al binary melts is illustrated in Fig. 3(b). The corresponding relationship at above mentioned four different temperatures can be expressed by the linear equations as follows:

$$\ln\gamma_{Al,1973\ K}=1.6241x_{Al}-1.6472\ \ (0<x_{Al}\leq 0.01) \quad (8)$$

$$\ln\gamma_{Al,2073\ K}=1.5116x_{Al}-1.3961\ \ (0<x_{Al}\leq 0.01) \quad (9)$$

$$\ln\gamma_{Al,2173\ K}=1.3810x_{Al}-1.1661\ \ (0<x_{Al}\leq 0.01) \quad (10)$$

$$\ln\gamma_{Al,2273\ K}=1.2319x_{Al}-0.9543\ \ (0<x_{Al}\leq 0.01) \quad (11)$$

In view of Wagner equation [29], activity coefficient of component i (γ_i) in binary metallic melts referring to pure matter as standard state can be expressed as follows:

$$\ln\gamma_i=\ln\gamma_i^{\Theta}+\varepsilon_i^i x_i \quad (12)$$

where γ_i^{Θ} is the activity coefficient of component i in the infinitely dilute solution (−), ε_i^i is the first-order activity interaction coefficient of element i (−), and x_i is the mole fraction of element i (−). Therefore, the intercepts of linear functions in Eq. (12) and in Fig. 3(a) can be treated as the values of the Raoultian activity coefficient of Ti (γ_{Ti}^{Θ}) in infinitely dilute Ti−Al binary melts at the above mentioned four temperatures. The dependence of the calculated Raoultian activity coefficient of Ti in natural logarithmic form ($\ln\gamma_{Ti}^{\Theta}$) in the infinitely dilute Ti−Al binary melts on the temperature range of interest is illustrated in Fig. 4(a) and regressed as

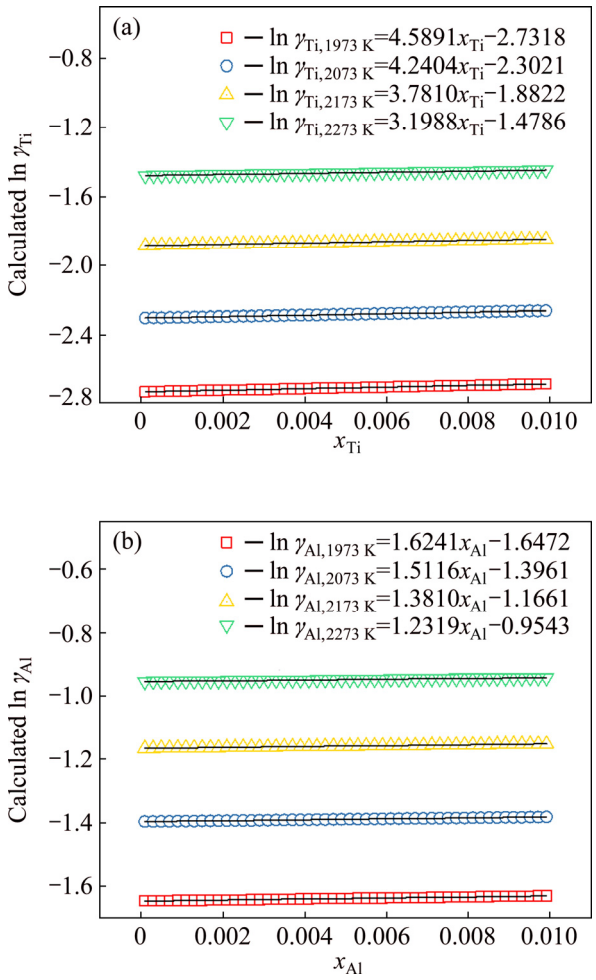

Fig. 3 Relationship between mole fraction of Ti (x_{Ti}) and calculated activity coefficient of Ti in logarithmic form ($\ln\gamma_{Ti}$) (a), and relationship between mole fraction of Al (x_{Al}) and calculated activity coefficient of Al in logarithmic form ($\ln\gamma_{Al}$) (b) in temperature range from 1973 to 2273 K

$$\ln\gamma_{Ti}^{\Theta}=6.6347-\frac{18479.9}{T}\ \ (1973\ K\leq T\leq 2273\ K) \quad (13)$$

Similarly, the temperature dependence of the calculated Raoultian activity coefficient of Al in natural logarithmic form ($\ln\gamma_{Al}^{\Theta}$) in the infinitely dilute Ti−Al binary melts is shown in Fig. 4(b) and regressed as

$$\ln\gamma_{Al}^{\Theta}=3.6009-\frac{10356.5}{T}\ \ (1973\ K\leq T\leq 2273\ K) \quad (14)$$

The standard molar Gibbs free energy change $\Delta_{sol}G_{m,i}^{\Theta}$ of dissolving liquid Ti or Al can be acquired by inserting the relationship between $a_{\%,i}$ and $a_{R,i}$ [29]:

Ti(l)=[Ti]$_{x_{Ti}=1\%}$

$$\Delta_{sol}G_{m,Ti}^{\Theta}=-RT\ln\frac{a_{\%,Ti}}{a_{R,Ti}}=RT\ln\left(\frac{M_{Al}}{100M_{Ti}}\gamma_{Ti}^{\Theta}\right) \quad (15)$$

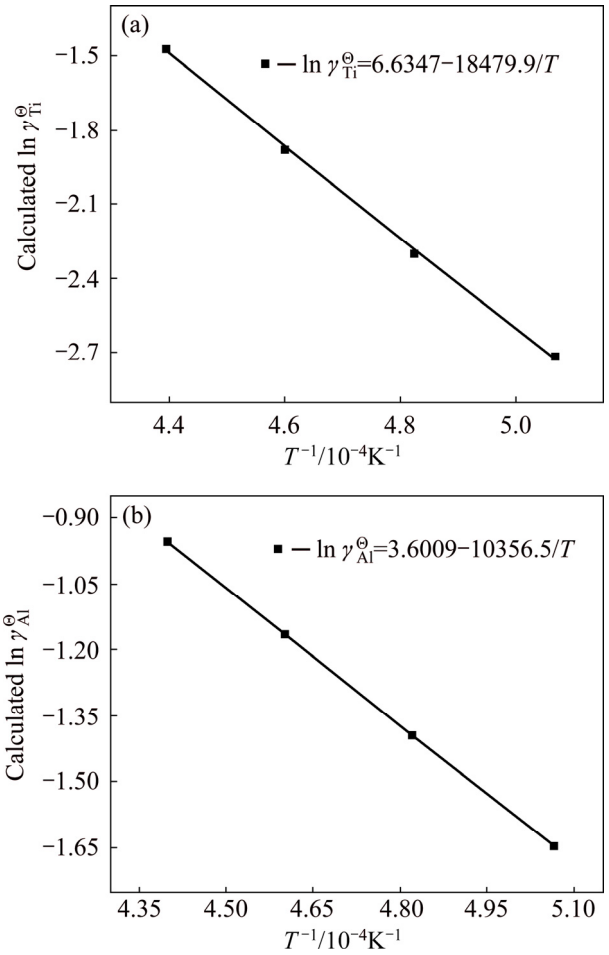

Fig. 4 Relationship between reciprocal of temperature and calculated activity coefficient of Ti in logarithmic form ($\ln \gamma_{Ti}$) (a), and calculated activity coefficient of Al in logarithmic form ($\ln \gamma_{Al}$) (b) in full composition range of Ti−Al binary melts in temperature range from 1973 to 2273 K

$$\mathrm{Al(l)}=[\mathrm{Al}]_{x_{\mathrm{Al}}=1\%}$$

$$\Delta_{\mathrm{sol}}G_{\mathrm{m,Al}}^{\Theta}=-RT\ln\frac{a_{\%,\mathrm{Al}}}{a_{\mathrm{R,Al}}}=RT\ln\left(\frac{M_{\mathrm{Ti}}}{100M_{\mathrm{Al}}}\gamma_{\mathrm{Al}}^{\Theta}\right) \tag{16}$$

where $a_{\%,i}$ or $a_{\mathrm{R},i}$ is activity relative to 1% (mass fraction) of element i as standard state or pure liquid i as standard state (−), and M_i is relative molecular mass (kg/mol). Accordingly, the influence of changing temperature from 1973 to 2273 K on the determined standard molar dissolve Gibbs free energy $\Delta_{\mathrm{sol}}G_{\mathrm{m},i}^{\Theta}$ can be obtained by inserting the determined Raoultian activity coefficient γ_i^{Θ} in Eqs. (13) and (14) into Eqs. (15) and (16) as

$$\Delta_{\mathrm{sol}}G_{\mathrm{m,Ti}}^{\Theta}=-153641.89+12.11T$$
$$(1973\ \mathrm{K}\le T\le 2273\ \mathrm{K}) \tag{17}$$

$$\Delta_{\mathrm{sol}}G_{\mathrm{m,Al}}^{\Theta}=-86103.94-3.58T$$
$$(1973\ \mathrm{K}\le T\le 2273\ \mathrm{K}) \tag{18}$$

3.3 Determination of excess molar mixing thermodynamic properties

The excess molar mixing Gibbs free energy change of Ti−Al binary melts can be defined as [29]

$$\Delta_{\mathrm{mix}}G_{\mathrm{m,Ti-Al}}^{\mathrm{E}}=\Delta_{\mathrm{mix}}G_{\mathrm{m,Ti-Al}}-\Delta_{\mathrm{mix}}G_{\mathrm{m,Ti-Al}}^{\mathrm{id}}=$$
$$RT(x_{\mathrm{Ti}}\ln a_{\mathrm{Ti}}+x_{\mathrm{Al}}\ln a_{\mathrm{Al}})-$$
$$RT(x_{\mathrm{Ti}}\ln x_{\mathrm{Ti}}+x_{\mathrm{Al}}\ln x_{\mathrm{Al}})=$$
$$RT(x_{\mathrm{Ti}}\ln \gamma_{\mathrm{Ti}}+x_{\mathrm{Al}}\ln \gamma_{\mathrm{Al}}) \tag{19}$$

where $\Delta_{\mathrm{mix}}G_{\mathrm{m,Ti-Al}}^{\mathrm{E}}$ is the excess molar Gibbs free energy change of Ti−Al binary melts as a real solution comparing with ideal solution as a basis (J/mol), $\Delta_{\mathrm{mix}}G_{\mathrm{m,Ti-Al}}$ is the molar mixing Gibbs free energy change of Ti−Al binary melts as a real solution (J/mol), $\Delta_{\mathrm{mix}}G_{\mathrm{m,Ti-Al}}^{\mathrm{id}}$ is the molar mixing Gibbs free energy change of Ti−Al binary melts as an ideal solution (J/mol). The excess molar mixing entropy change $\Delta_{\mathrm{mix}}S_{\mathrm{m,Ti-Al}}^{\mathrm{E}}$ of Ti−Al binary melts can be derived from Eq. (19) as

$$\Delta_{\mathrm{mix}}S_{\mathrm{m,Ti-Al}}^{\mathrm{E}}=\Delta_{\mathrm{mix}}S_{\mathrm{m,Ti-Al}}-\Delta_{\mathrm{mix}}S_{\mathrm{m,Ti-Al}}^{\mathrm{id}}=$$
$$\frac{\partial\Delta_{\mathrm{mix}}G_{\mathrm{m,Ti-Al}}^{\mathrm{E}}}{\partial T}=-R(x_{\mathrm{Ti}}\ln\gamma_{\mathrm{Ti}}+x_{\mathrm{Al}}\ln\gamma_{\mathrm{Al}})-$$
$$RT(x_{\mathrm{Ti}}\frac{\partial\ln\gamma_{\mathrm{Ti}}}{\partial T}+x_{\mathrm{Al}}\frac{\partial\ln\gamma_{\mathrm{Al}}}{\partial T}) \tag{20}$$

The excess molar mixing enthalpy change $\Delta_{\mathrm{mix}}H_{\mathrm{m,Ti-Al}}^{\mathrm{E}}$ of Ti−Al binary melts can be derived from Eq. (19) and Eq. (20) as

$$\Delta_{\mathrm{mix}}H_{\mathrm{m,Ti-Al}}^{\mathrm{E}}=\Delta_{\mathrm{mix}}G_{\mathrm{m,Ti-Al}}^{\mathrm{E}}+T\Delta_{\mathrm{mix}}S_{\mathrm{m,Ti-Al}}^{\mathrm{E}}=$$
$$-RT^2(x_{\mathrm{Ti}}\frac{\partial\ln\gamma_{\mathrm{Ti}}}{\partial T}+x_{\mathrm{Al}}\frac{\partial\ln\gamma_{\mathrm{Al}}}{\partial T}) \tag{21}$$

The quantity of $\partial\ln\gamma_i/\partial T$ shown in Eqs. (20) and (21) can be calculated by means of the method reported by YANG et al [28] in the study of Fe−Si binary system.

Figure 5 represents the calculated activity coefficient of Ti in natural logarithmic form ($\ln\gamma_{\mathrm{Ti}}$) or that of Al ($\ln\gamma_{\mathrm{Al}}$) in the full composition range of Ti−Al binary melts as a function of temperature under the fixed mole fraction of Ti (x_{Ti}) from 0.05 to 0.95 at an interval of 0.05, respectively. By plotting $\partial\ln\gamma_i/\partial T$ versus T at different mole fractions x_{Ti}, a straight line should be obtained. From the slope of straight line, the values of $\partial\ln\gamma_{\mathrm{Ti}}/\partial T$ or $\partial\ln\gamma_{\mathrm{Al}}/\partial T$ at different mole fractions x_{Ti} can be determined. The relationship between the calculated $\partial\ln\gamma_i/\partial T$ and mole fraction of Ti (x_{Ti}) in full composition range in a temperature range from 1973 to 2273 K is

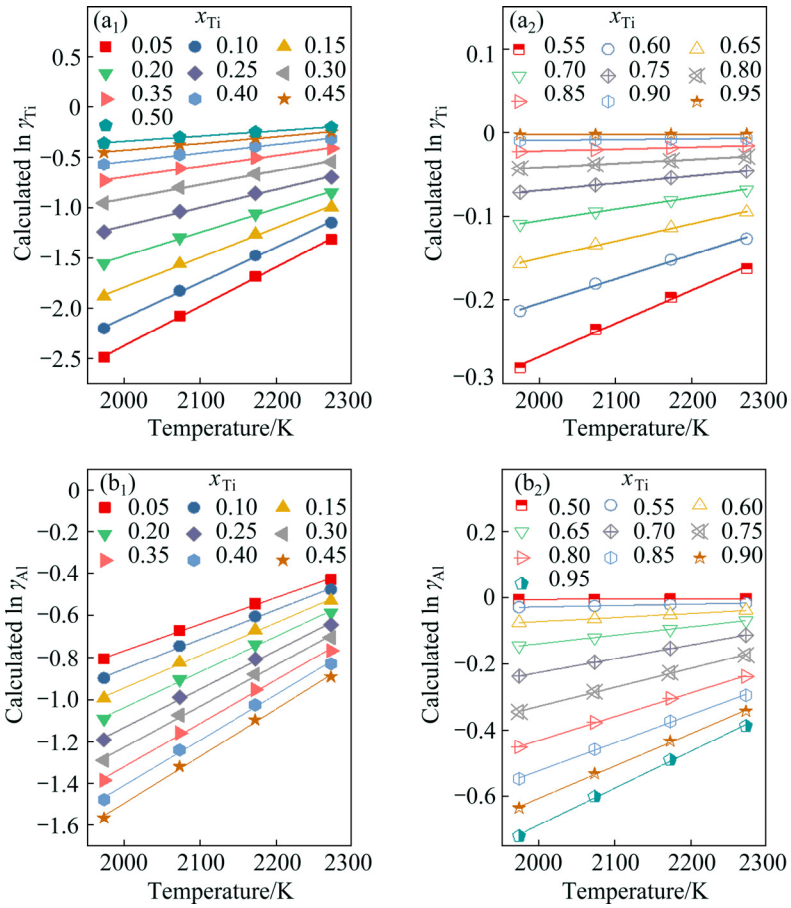

Fig. 5 Calculated activity coefficient of Ti in logarithmic form (ln γ_{Ti}) (a_1, a_2) or that of Al in logarithmic form (ln γ_{Al}) (b_1, b_2) in full composition range of Ti−Al binary melts as function of temperature under fixed mole fraction of Ti (x_{Ti}) from 0.05 to 0.95 at interval of 0.05

illustrated in Fig. 6. The regressed formula of $\partial\ln\gamma_{Ti}/\partial T$ or $\partial\ln\gamma_{Al}/\partial T$ against mole fraction of Ti (x_{Ti}) can be expressed as

$$\frac{\partial\ln\gamma_{Ti}}{\partial T}=-2.3303\times10^{-6}+\frac{6.9023\times10^{-3}}{1+\exp\left(\dfrac{x_{Ti}-0.0957}{0.1540}\right)} \quad (22)$$

$$\frac{\partial\ln\gamma_{Al}}{\partial T}=0.0029-\frac{3.7047\times10^{-3}}{1+\exp\left(\dfrac{x_{Ti}-0.4851}{0.3186}\right)} \quad (23)$$

To describe the excess thermodynamic properties of Ti−Al binary melts, the excess molar mixing Gibbs free energy $\Delta_{mix}G^{E}_{m,Ti-Al}$, the excess molar mixing entropy $\Delta_{mix}S^{E}_{m,Ti-Al}$, and the excess molar mixing enthalpy $\Delta_{mix}H^{E}_{m,Ti-Al}$ were estimated by inserting the obtained values of $\partial\ln\gamma_i/\partial T$ into Eqs. (19)−(21), respectively. The relationships between the excess thermodynamic properties and mole fraction of Ti (x_{Ti}) at temperatures of 1973, 2073, 2173 and 2273 K are well presented in Fig. 7,

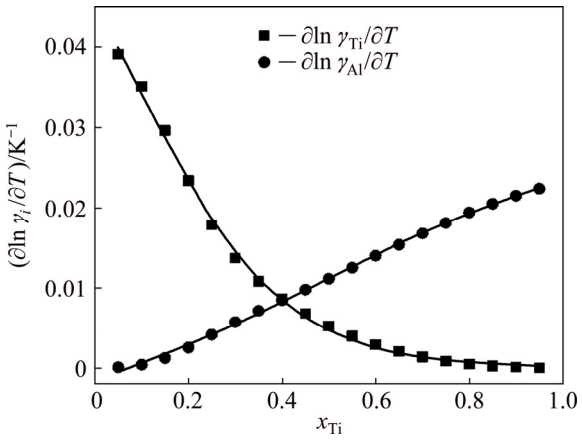

Fig. 6 Calculated $\partial\ln\gamma_{Ti}/\partial T$ or $\partial\ln\gamma_{Al}/\partial T$ in Ti−Al binary melts as function of mole fraction of Ti (x_{Ti}) from 0.05 to 0.95 at interval of 0.05 in temperature range from 1973 to 2273 K

from which a V-type relationship between the determined $\Delta_{mix}G^{E}_{m,Ti-Al}$, $\Delta_{mix}S^{E}_{m,Ti-Al}$ or $\Delta_{mix}H^{E}_{m,Ti-Al}$ of Ti−Al binary melts and x_{Ti} can be seen. Meanwhile, it can be observed that changing temperature from 1973 to 2273 K can give rise to a visible decrease tendency of the

determined $\Delta_{mix}S^{E}_{m,Ti-Al}$ and $\Delta_{mix}H^{E}_{m,Ti-Al}$, while the increasing temperature has a little effect on $\Delta_{mix}G^{E}_{m,Ti-Al}$ at a fixed mole fraction of Ti.

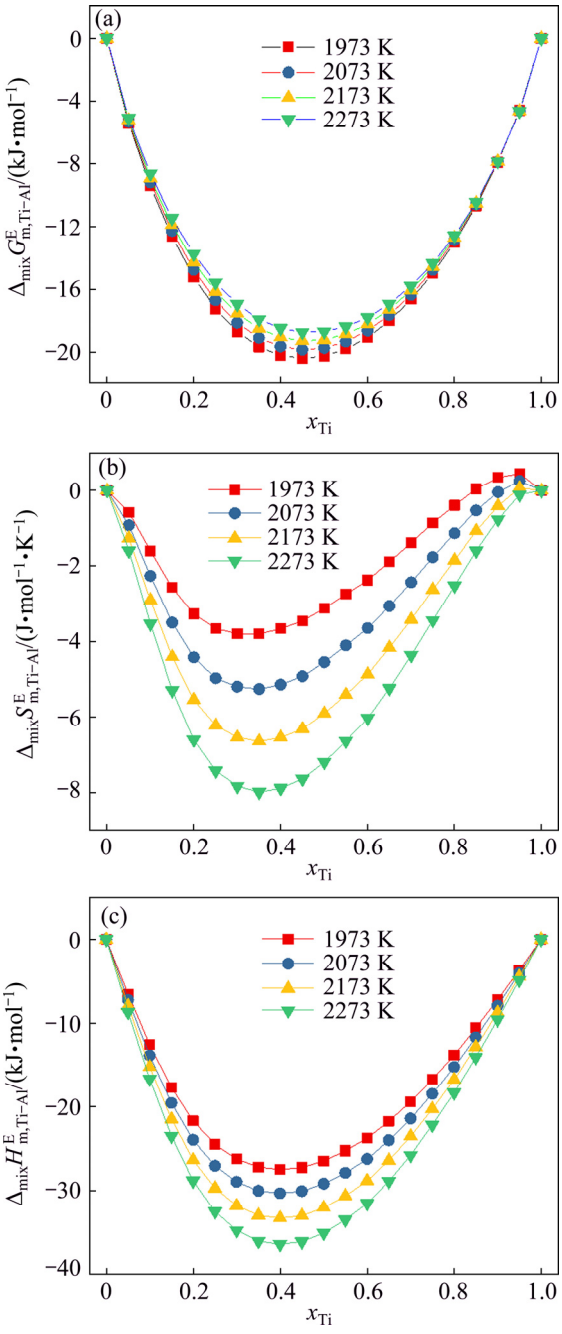

Fig. 7 Relationship between mole fraction of Ti (x_{Ti}) and calculated excess molar mixing Gibbs free energy change $\Delta_{mix}G^{E}_{m,Ti-Al}$ (a), excess molar mixing entropy change $\Delta_{mix}S^{E}_{m,Ti-Al}$ (b), and excess molar mixing enthalpy change $\Delta_{mix}H^{E}_{m,Ti-Al}$ (c) in temperature range from 1973 to 2273 K

4 Conclusions

1) A thermodynamic prediction model for determining the thermodynamic properties of Ti−Al binary melts based on the atom and molecule coexistence theory (AMCT) was developed in a temperature range from 1973 to 2273 K.

2) The determined $\ln\gamma_i^{\Theta}$ by AMCT model has a good linear relationship with temperature, and the values of the Raoultain activity coefficient of Ti (γ_{Ti}^{Θ}) and that of Al (γ_{Al}^{Θ}) in the infinitely dilute solution of Ti−Al binary melts in the temperature range from 1973 to 2273 K can be expressed as $\ln\gamma_{Ti}^{\Theta}=6.6347-18479.9/T$ and $\ln\gamma_{Al}^{\Theta}=3.6009-10356.5/T$.

3) The standard molar Gibbs free energy change $\Delta_{sol}G^{\Theta}_{m,i}$ of dissolving pure liquid i(l) for forming 1% element i in Ti−Al binary melts in a temperature range from 1973 to 2273 K can be presented as $\Delta_{sol}G^{\Theta}_{m,Ti}=-153641.89+12.11T$ and $\Delta_{sol}G^{\Theta}_{m,Al}=-86103.94-3.58T$.

4) The plot of $\ln\gamma_i^{\Theta}$ versus T at fixed mole fraction of Ti x_{Ti} from 0.05 to 0.95 at an interval 0.05 should give a straight line, and the $\partial\ln\gamma_i/\partial T$ values of Ti or Al in Ti−Al binary melts can be obtained from its slope. The regressed formula of $\partial\ln\gamma_i/\partial T$ of Ti or Al against mole fraction of Ti (x_{Ti}) can be further obtained.

5) The excess thermodynamic properties, such as $\Delta_{mix}G^{E}_{m,Ti-Al}$, $\Delta_{mix}S^{E}_{m,Ti-Al}$, and $\Delta_{mix}H^{E}_{m,Ti-Al}$ can be accurately predicted by developed AMCT model. Changing temperature from 1973 to 2273 K can give rise to a visible decrease tendency of the determined $\Delta_{mix}S^{E}_{m,Ti-Al}$ and $\Delta_{mix}H^{E}_{m,Ti-Al}$, while the increase of temperature has a little effect on $\Delta_{mix}G^{E}_{m,Ti-Al}$ at a fixed mole fraction of Ti (x_{Ti}).

References

[1] HOCH M, USELL R J. Thermodynamics of titanium alloys: II. Titanium and aluminum activities in the BCC β phase of the Ti−Al system [J]. Metallurgical Transactions, 1971, 2(9): 2627−2632.

[2] SAMOKHVAL V V, POLESHCHUK P A, VECHER A A. Thermodynamic property of aluminum−titanium and aluminum−vanadium alloys [J]. Russian Journal of Physical Chemistry, 1971, 45(8): 1174−1176.

[3] ECKERT M, BENCZE L, KATH D, NICKEL H, HILPERT K. Thermodynamic activities in the alloys of the Ti−A1 system [J]. Berichte der Bunsengesellschaft für Physikalische Chemie, 1996, 100(4): 418−424.

[4] MAEDA M, KIWAKE T, SHIBUYA K, IKEDA T. Activity of aluminum in molten Ti−Al alloys [J]. Materials Science and Engineering A, 1997, 239−240: 276−280.

[5] JACOBSON N S, BRADY M P, MEHROTRA G M. Thermodynamics of selected Ti−Al and Ti−Al−Cr alloys [J]. Oxidation of Metals, 1999, 52(5−6): 537−556.

[6] GUO Jin-jie, JIA Jun, LIU Yuan, LIU Gui-zhong, SU Yan-qing, DING Hong-sheng. Evaporation behavior of aluminum during the cold crucible induction skull melting of titanium aluminum alloys [J]. Metallurgical and Materials Transactions B, 2000, 31(4): 837−844.

[7] REDDY R G, YAHYA A M, BREWER L. Thermodynamic properties of Ti−Al intermetallics [J]. Journal of Alloys and

Compounds, 2001, 321(2): 223−227.
[8] KOSTOV A, FRIEDRICH B, ZIVKOVIC D. Predicting thermodynamic properties in Ti−Al binary system by FactSage [J]. Computational Materials Science, 2006, 37(3): 355−360.
[9] DUAN Sheng-chao, CHEN Hun-bin, GUO Han-jie, LIAN Yun-fei. Representation of reaction abilities for Al−Ti binary melts based on the atom−molecule coexistence theory [J]. Chinese Journal of Engineering, 2016, 38(10): 1377−1385. (in Chinese)
[10] CUI Ren-jie, TANG Xiao-xia, GAO Ming, ZHANG Hu, GONG Sheng-kai. Thermodynamic analysis of interactions between Ti−Al alloys and oxide ceramics [J]. Transactions of Nonferrous Metals Society of China, 2012, 22(4): 887−894.
[11] NOVAKOVIC R, GIURANNO D, RICCI E, TUISSI A, WUNDERLICH R, FECHT H, EGRY I. Surface, dynamic and structural properties of liquid Al−Ti alloys [J]. Applied Surface Science, 2012, 258(7): 3269−3275.
[12] XU Shuai, SONG Bin-yi, JIANG Wen-long, YANG Bin. Modeling and calculation of activities of constituent elements in binary alloys [J]. Chinese Journal of Vacuum Science and Technology, 2015(8): 919−925. (in Chinese)
[13] HILDEBRAND J H. A quantitative treatment of deviations from Raoult's law [J]. Proceedings of the National Academy of Sciences of the United States of America, 1927, 13(5): 267−272.
[14] MIEDEMA A R, de CHATEL P F, de BOER F R. Cohesion in alloys-fundamentals of a semi-empirical model [J]. Physica B+C, 1980, 100(1): 1−28.
[15] TAO Dong-ping. A new model of thermodynamics of liquid mixtures and its application to liquid alloys [J]. Thermochimica Acta, 2000, 363(1−2): 105−113.
[16] RENON H, PRAUSNITZ J M. Local compositions in thermodynamic excess functions for liquid mixtures [J]. AIChE Journal, 1968, 14(1): 135−144.
[17] WILSON G M. Vapor−liquid equilibrium. XI: A new expression for the excess free energy of mixing [J]. Journal of the American Chemical Society, 1964, 86(2): 127−130.
[18] YANG Xue-min, ZHANG Meng, LI Peng-cheng, LI Jin-yan, ZHANG Jian. A thermodynamic model for representation reaction abilities of structural units in full composition range of Fe−Si binary melts based on the atom–molecule coexistence theory [J]. Steel Research International, 2013, 84(8): 784−811.
[19] ZHANG Jian. Computational thermodynamics of metallurgical melts and solutions [M]. Beijing: Metallurgical Industry Press, 2007. (in Chinese)
[20] ZHANG Jian. Classification of thermodynamic properties of binary metallic melts according to their phase diagrams [J]. Acta Metallurgica Sinica, 1998, 34(1): 75−85. (in Chinese)
[21] ZHANG Jian. Thermodynamic properties and mixing thermodynamic parameters of Ba−Al, Mg−Al, Sr−Al and Cu−Al metallic melts [J]. Transactions of Nonferrous Metals Society of China, 2004, 14(2): 345−350.
[22] ZHANG Jian. Calculating model of mass action concentrations for Fe−Si melts [J]. Journal of Iron and Steel Research, 1991, 3(2): 7−12. (in Chinese)
[23] ZHANG Jian. On the coexistence theory of metallic structure involving compound formation [J]. Journal of University of Science and Technology Beijing, 1990, 12(3): 201−211. (in Chinese)
[24] ZHANG Jian, WANG Ping. The widespread applicability of the mass action law to metallurgical melts and organic solutions [J]. Calphad, 2001, 25(3): 343−354.
[25] YANG Xue-min, LI Peng-cheng, LI Jin-yan, ZHANG Meng, ZHANG Jian-liang, ZHANG Jian. Representation reaction abilities of structural units and related thermodynamic properties in Fe−P binary melts based on the atom–molecule coexistence theory [J]. Steel Research International, 2014, 85(3): 426−460.
[26] YANG Xue-min, LI Jin-yan, WEI Meng-fang, ZHANG Jian. Thermodynamic evaluation of reaction abilities of structural units in Fe−O binary melts based on the atom–molecule coexistence theory [J]. Metallurgical and Materials Transactions B, 2016, 47(1): 174−206.
[27] YANG Xue-min, ZHANG Meng, LI Peng-cheng, LI Jin-yan, ZHANG Jian-liang, ZHANG Jian. A thermodynamic model for representation reaction abilities of structural units in Fe−S binary melts based on the atom−molecule coexistence theory [J]. Metallurgical and Materials Transactions B, 2012, 43(6): 1358−1387.
[28] YANG Xue-min, LI Jin-yan, LI Peng-cheng, ZHANG Meng, ZHANG Jian. Determination of activity coefficients of elements and related thermodynamic properties of Fe−Si binary melts based on the atom–molecule coexistence theory [J]. Steel Research International, 2014, 85(2): 164−206.
[29] GUO Han-jie. Metallurgical physical chemistry [M]. 2nd ed. Beijing: Metallurgical Industry Press, 2007. (in Chinese)

基于原子−分子共存理论的全浓度 Ti−Al 二元熔体热力学性质计算

段生朝[1,2]，石 骁[1,2]，杨文晟[1,2]，郭汉杰[1,2]，郭 靖[1,2]

1. 北京科技大学 冶金与生态工程学院，北京 100083；
2. 北京科技大学 高端金属材料特种熔炼与制备北京市重点实验室，北京 100083

摘 要：基于原子−分子共存理论建立计算温度为 1973~2273 K 及全浓度范围 Ti−Al 二元熔体质量作用浓度 N_i 的热力学模型。利用不同温度(1973、2073、2173 和 2273 K)下的模型计算结果，得到在无限稀溶液($0<x_{Ti}<0.01$)中铝、钛活度因子的对数与温度的关系式。根据该表达式，进一步得到组元 *i* 溶解于 Ti−Al 二元熔体形成浓度为 1%(质量分数)溶液为标准态的溶解 Gibbs 自由能。与此同时，对 Ti−Al 二元熔体的过剩 Gibbs 自由能、过剩熵、过剩焓也进行了计算。

关键词：Ti−Al 二元系；Ti；Al；活度因子；热力学模型；质量作用浓度；原子−分子共存理论

(Edited by Wei-ping CHEN)