RETRACTION

The following three articles were withdrawn upon request of their authors on October 3, 2014, because they were submitted without the consent of all the authors.

Retraction: Representation of Dephosphorization Ability for CaO–Containing Slags Based on the Ion and Molecule Coexistence Theory

Peng-cheng LI^{1,2)} and Jian-liang ZHANG¹⁾

1) State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing, 100083 P. R. China.

2) State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190 P. R. China.

This article was published in *ISIJ Int.*, **54** (2014), No. 3, 567–577.

Retraction: A Prediction Model of Phosphorus Distribution between CaO–SiO₂–MgO–FeO–Fe₂O₃–P₂O₅ Slags and Liquid Iron

Peng-cheng LI^{1,2,3)} and Jian-liang ZHANG^{1,2)}

1) State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing, 100083 P. R. China.

2) School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing, 100083 P. R. China.

3) State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190 P. R. China.

This article was published in *ISIJ Int.*, **54** (2014), No. 4, 756–765.

Retraction: Representation of Reaction Ability for Structural Units in Fe–Al Binary Melts

Peng-cheng LI^{1,2,3)} and Jian-liang ZHANG^{1,2)}

1) State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing, 100083 P. R. China.

2) School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing, 100083 P. R. China.

3) State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190 P. R. China.

This article was published in *ISIJ Int.*, **54** (2014), No. 6, 1185–1194.

Representation of Reaction Ability for Structural Units in Fe–Al Binary Melts

Peng-cheng LI^{1,2,3)*} and Jian-liang ZHANG^{1,2)}

1) State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing, 100083 P. R. China.

2) School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing, 100083 P. R. China.

3) State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190 P. R. China.

(Received on October 5, 2013; accepted on January 9, 2014)

A thermodynamic model for calculating the mass action concentrations of structural units in Fe–Al binary melts based on the atom–molecule coexistence theory, *i.e.*, AMCT– N_i model, has been developed and verified through comparing with the reported activities of both Al and Fe in Fe–Al binary melts in a temperature from 1573 K to 1873 K by different researchers. The calculated mass action concentration N_{Al} of Al or N_{Fe} of Fe can be applied to ideally substitute the measured activity $a_{\text{R, Al}}$ of Al or $a_{\text{R, Fe}}$ of Fe relative to pure liquid Al(l) or Fe(l) as standard state in Fe–Al binary melts. The following equations were derived for the activity coefficient of Al in natural logarithmic form $\ln \gamma_{\text{Al}}$ and the calculated activity coefficient of Fe in natural logarithmic form $\ln \gamma_{\text{Fe}}$ in the temperature range from 1573 K to 1873 K.

$$\ln \gamma_{\text{Al}} = -3.810 + 4.476x_{\text{Al}} \quad 0 < x_{\text{Al}} \leq 0.005, \quad T = 1573 \text{ K}$$

$$\ln \gamma_{\text{Al}} = -3.397 + 4.248x_{\text{Al}} \quad 0 < x_{\text{Al}} \leq 0.005, \quad T = 1673 \text{ K}$$

$$\ln \gamma_{\text{Al}} = -3.056 + 4.011x_{\text{Al}} \quad 0 < x_{\text{Al}} \leq 0.005, \quad T = 1773 \text{ K}$$

$$\ln \gamma_{\text{Al}} = -2.537 + 3.599x_{\text{Al}} \quad 0 < x_{\text{Al}} \leq 0.005, \quad T = 1873 \text{ K}$$

$$\ln \gamma_{\text{Fe}} = -3.837 + 6.701x_{\text{Fe}} \quad 0 < x_{\text{Fe}} \leq 0.005, \quad T = 1573 \text{ K}$$

$$\ln \gamma_{\text{Fe}} = -3.753 + 7.627x_{\text{Fe}} \quad 0 < x_{\text{Fe}} \leq 0.005, \quad T = 1673 \text{ K}$$

$$\ln \gamma_{\text{Fe}} = -3.701 + 8.066x_{\text{Fe}} \quad 0 < x_{\text{Fe}} \leq 0.005, \quad T = 1773 \text{ K}$$

$$\ln \gamma_{\text{Fe}} = -3.686 + 8.176x_{\text{Fe}} \quad 0 < x_{\text{Fe}} \leq 0.005, \quad T = 1873 \text{ K}$$

Temperature dependences of the activity coefficient of Al in natural logarithmic form $\ln \gamma_{\text{Al}}^0$ and the calculated activity coefficient of Fe in natural logarithmic form $\ln \gamma_{\text{Fe}}^0$ were given

$$\ln \gamma_{\text{Al}}^0 = 2.6917 - 10\,222.7/T \quad 1573 \text{ K} \leq T \leq 1873 \text{ K}$$

$$\ln \gamma_{\text{Fe}}^0 = -2.8573 - 1521.6816/T \quad 1573 \text{ K} \leq T \leq 1873 \text{ K}$$

The obtained values were compared with the results of the previous investigations.

KEY WORDS: Fe–Al binary melts; activity of aluminum; activity of iron; mass action concentration; reaction ability; thermodynamic model; structural units; atom and molecule coexistence theory (AMCT).

1. Introduction

The knowledge of the thermodynamics of Fe–Al binary melts is important both from a process metallurgy point of view and for an understanding of the thermochemical behavior of fiber–reinforced iron aluminized composites.¹⁾ For these reasons, the reaction abilities of elements, especially activity coefficient γ_{Al} of Al and γ_{Fe} of Fe in Fe–Al binary melts have attracted tremendous attention in the past several decades.^{2–10)} Chipman and Floridis²⁾ measured the distribution of aluminum between liquid iron and silver, and combined these data to extrapolate activity coefficient γ_{Al} of

Al in Fe–Al binary melts up to 9.66 mass% Al at 1873 K as $\gamma_{\text{Al}} = -3.477 + 6.0X_{\text{Al}}$. Wilder and Elliott³⁾ determined the activity of aluminum in liquid Al–Ag alloys between 973 K and 1173 K by a galvanic cell technique, and their results were extrapolated to 1873 K to reexamine Chipman *et al.*'s reported data. They reported γ_{Al}^0 , $\varepsilon_{\text{Al}}^{\text{Al}}$ and $e_{\text{Al}}^{\text{Al}}$ values in liquid iron as 0.063, 5.3 and 0.043 at 1873 K, respectively. Wooley and Elliott⁴⁾ measured the partial molar heats of solution of aluminum at 1873 K in the high–temperature solution calorimeter in the range of $0 < x_{\text{Al}} < 0.56$ for the Fe–Al system. They reported γ_{Al}^0 , $\varepsilon_{\text{Al}}^{\text{Al}}$ and $e_{\text{Al}}^{\text{Al}}$ values as 0.061, 5.6 and 0.045 at 1873 K, respectively. Coskun and Elliott⁵⁾ measured the activity of aluminum in liquid Fe–Al system by an improved version of the transportation method in which the metallic vapor was collected by its solution in

* Corresponding author: E-mail: lipengcheng000@126.com
DOI: <http://dx.doi.org/10.2355/isijinternational.54.1185>

a metallic condenser, and proposed the equation $\log \gamma_{\text{Al}} = -3.0(1-x_{\text{Al}})^2$. Using Knudsen cell–mass spectrometry, Belton and Fruhan⁶⁾ directly measured the activity of aluminum in liquid Fe–Al alloys up to 20.29 mass% Al at 1 873 K. Ichise *et al.*⁷⁾ also used the same experimental technique to determine the activity of aluminum in liquid Fe–Al alloys up to 8.21 mass% Al in the temperature range from 1 673 K to 1 873 K. They reported the values of γ_{Al}^0 , $\varepsilon_{\text{Al}}^{\text{Al}}$, γ_{Fe}^0 and $\varepsilon_{\text{Fe}}^{\text{Fe}}$ in liquid iron as 0.049, 6.4, 0.017 and 8.2 at 1 873 K, respectively. Jacobson and Mehrotra⁸⁾ determined the activities of Fe and Al in Fe–Al alloys at 1 573 K using the ion–current–ratio technique in a high–temperature Knudsen cell–mass spectrometry, and reported the values of γ_{Al}^0 and γ_{Fe}^0 at 1 573 K as 0.016 and 0.019. In 2007, Kim *et al.*⁹⁾ investigated the thermodynamics of aluminum in liquid iron in the temperature range of 1 873 K–1 973 K and reported the values of γ_{Al}^0 as 0.066, 0.069 and 0.071 at 1 873 K, 1 923 K and 1 973 K. Recently, Zaitsev *et al.*¹⁰⁾ reported that three associative molecules as FeAl, FeAl₂, and Fe₂Al₅ could exist in Fe–Al binary melts based on the experimental results using Knudsen cell–mass spectrometer and an integral variant of the effusion method under the condition of super high oil–free vacuum. But after checking previous literatures and phase diagram of Fe–Al binary system, Zhang¹¹⁾ proposed that five molecules as Fe₃Al, FeAl, FeAl₂, Fe₂Al₅ and FeAl₆ could exist in Fe–Al binary melts. Other researchers^{12–17,24–26)} have reached the similar viewpoint for metallic melts that molecules can exist in metallic melts besides atoms. Several attempts^{24–26)} can well describe the thermodynamic properties of metallic melts on the concept of ionic or molecular constituents associated with artificial parameters, and most of the regressed artificial parameters were obtained by experimental results.²⁰⁾

Although various experimental technique were adopted to measure the activity of Al and Fe in liquid Fe–Al alloys, to the knowledge of the present authors, no prediction model was established to predict or evaluate the activity of Al and Fe in liquid Fe–Al alloys. In this study, the AMCT– N_i thermodynamic model for calculating the mass action concentrations N_i of structural units in Fe–Al binary melts in the temperature range from 1 573 K to 1 873 K has been developed without any regressed parameters. The reported activities of Al and Fe by different researchers in a temperature range from 1 573 K to 1 873 K were chosen as evaluation criteria to verify the accuracy of the developed AMCT– N_i thermodynamic model for Fe–Al binary melts. It should be emphasized that the reported activities of Al and Fe are relative to pure liquid Al(l) and Fe(l) as standard state, *i.e.*, $a_{\text{R, Al}}$ of Al and $a_{\text{R, Fe}}$ of Fe. The ultimate aim of this study is to pave the way for developing a universal AMCT– N_i thermodynamic model for representing the reaction abilities of structural units in any binary metallic melts by the calculated mass action concentrations N_i of structural units in the binary melts.

2. AMCT– N_i Thermodynamic Model for Fe–Al Binary Melts

2.1. Hypotheses

It has been briefly demonstrated in Section 1 that atoms of Fe and Al, and molecules as Fe₃Al, FeAl, FeAl₂, Fe₂Al₅ and FeAl₆ can coexist in Fe–Al binary melts. Therefore, the

atom–molecule coexistence theory, *i.e.*, AMCT, can be applied to describe the structural characteristics of Fe–Al binary melts. The hypotheses of the developed AMCT– N_i model for Fe–Al binary melts can be briefly summarized as follows: 1) the Fe–Al binary melts at elevated temperature are composed of seven structural units including two atoms as Fe and Al as well as five molecules as Fe₃Al, FeAl, FeAl₂, Fe₂Al₅ and FeAl₆ according to the phase diagram of Fe–Al binary melts^{18,21)} and viewpoints described in Section 1 from the literature;¹¹⁾ 2) each structural unit occupies its independent position in Fe–Al binary melts; 3) the elements of both Fe and Al in Fe–Al binary melts will take part in reactions of forming five molecules as Fe₃Al, FeAl, FeAl₂, Fe₂Al₅ and FeAl₆ in the form of atoms; 4) the reactions of forming five molecules as Fe₃Al, FeAl, FeAl₂, Fe₂Al₅ and FeAl₆ are under the chemical dynamic equilibrium between the simple atoms of both Fe and Al; 5) five structural units in Fe–Al binary melts as Fe₃Al, FeAl, FeAl₂, Fe₂Al₅ and FeAl₆ bear the structural continuity in the investigated composition range; 6) the chemical reactions of forming five molecules as Fe₃Al, FeAl, FeAl₂, Fe₂Al₅ and FeAl₆ from Fe and Al obey the mass action law.

2.2. Establishment of AMCT– N_i Thermodynamic Model for Fe–Al Binary Melts

The mole numbers of two atoms as Fe and Al before equilibrium or before forming five molecules as Fe₃Al, FeAl, FeAl₂, Fe₂Al₅ and FeAl₆ in 100–g Fe–Al binary melts were assigned as $b_1 = n_{\text{Fe}}^0$ and $b_2 = n_{\text{Al}}^0$ to represent the chemical composition of Fe–Al binary melts. Two atoms of Fe and Al as well as five molecules of Fe₃Al, FeAl, FeAl₂, Fe₂Al₅ and FeAl₆ in Fe–Al binary melts at the studied temperatures were summarized and assigned with exclusive numbers in **Table 1**. The defined equilibrium mole numbers n_i of all above–mentioned five structural units as Fe₃Al, FeAl, FeAl₂, Fe₂Al₅ and FeAl₆ in 100–g Fe–Al binary melts at the studied temperatures were also listed in Table 1. The total equilibrium mole number Σn_i of all seven structural units in

Table 1. Expressions of structural units as atoms or molecules, their equilibrium mole numbers n_i and mass action concentrations N_i in 100–g Fe–Al binary melts based on the AMCT.

Item	Structural units as atoms or molecules	No. of structural units	Mole numbers of structural units (mol)	Mass action concentrations of structural units N_i (–)
Atom (2)	Fe	1	$n_1 = n_{\text{Fe}}$	$N_1 = \frac{n_1}{\Sigma n_i} = N_{\text{Fe}}$
	Al	2	$n_2 = n_{\text{Al}}$	$N_2 = \frac{n_2}{\Sigma n_i} = N_{\text{Al}}$
Molecules (5)	Fe ₃ Al	c1	$n_{c1} = n_{\text{Fe}_3\text{Al}}$	$N_{c1} = \frac{n_{c1}}{\Sigma n_i} = N_{\text{Fe}_3\text{Al}}$
	FeAl	c2	$n_{c2} = n_{\text{FeAl}}$	$N_{c2} = \frac{n_{c2}}{\Sigma n_i} = N_{\text{FeAl}}$
	FeAl ₂	c3	$n_{c3} = n_{\text{FeAl}_2}$	$N_{c3} = \frac{n_{c3}}{\Sigma n_i} = N_{\text{FeAl}_2}$
	Fe ₂ Al ₅	c4	$n_{c4} = n_{\text{Fe}_2\text{Al}_5}$	$N_{c4} = \frac{n_{c4}}{\Sigma n_i} = N_{\text{Fe}_2\text{Al}_5}$
	FeAl ₆	c5	$n_{c5} = n_{\text{FeAl}_6}$	$N_{c5} = \frac{n_{c5}}{\Sigma n_i} = N_{\text{FeAl}_6}$

100-g Fe–Al binary melts can be expressed as

$$\begin{aligned}\Sigma n_i &= n_1 + n_2 + n_{c1} + n_{c2} + n_{c3} + n_{c4} + n_{c5} \\ &= n_{\text{Fe}} + n_{\text{Al}} + n_{\text{Fe}_3\text{Al}} + n_{\text{FeAl}} + n_{\text{FeAl}_2} + n_{\text{Fe}_2\text{Al}_5} + n_{\text{FeAl}_6} \\ &\quad (\text{mol}) \dots (1)\end{aligned}$$

According to the definition of mass action concentrations N_i for structural units based on the AMCT^{11,18–20} for metallic melts or the IMCT^{22,23} for metallurgical slags, the mass action concentrations N_i of structural units i in metallic melts can be calculated by

$$N_i = \frac{n_i}{\Sigma n_i} \quad (-) \dots (2)$$

The chemical reaction formulas of forming five molecules as Fe_3Al , FeAl , FeAl_2 , Fe_2Al_5 and FeAl_6 , the related standard reaction equilibrium constants $K_{ci}^{\Theta, R}$ relative to pure liquid matter as standard state, and the representations of mass action concentrations N_{ci} of five molecules as Fe_3Al , FeAl , FeAl_2 , Fe_2Al_5 and FeAl_6 using $K_{ci}^{\Theta, R}$, N_1 (N_{Fe}) and N_2 (N_{Al}) based on the mass action law were summarized in **Table 2**.

The mass conservation equations of two atoms as Fe and Al in 100-g Fe–Al binary melts can be established based on the above-mentioned definitions^{11,18–20,22,23} of n_i , N_i , and Σn_i as follows

$$\begin{aligned}b_1 &= (N_1 + 3N_{c1} + N_{c2} + N_{c3} + 2N_{c4} + N_{c5}) \Sigma n_i \\ &= (N_1 + 3K_{c1}^{\Theta, R} N_1^3 N_2 + K_{c2}^{\Theta, R} N_1 N_2 \\ &\quad + K_{c3}^{\Theta, R} N_1 N_2^2 + 2K_{c4}^{\Theta, R} N_1^2 N_2^5 + K_{c5}^{\Theta, R} N_1 N_2^6) \Sigma n_i \\ &= (N_{\text{Fe}} + 3K_{c1}^{\Theta, R} N_{\text{Fe}}^3 N_{\text{Al}} + K_{c2}^{\Theta, R} N_{\text{Fe}} N_{\text{Al}} + K_{c3}^{\Theta, R} N_{\text{Fe}} N_{\text{Al}}^2 \\ &\quad + 2K_{c4}^{\Theta, R} N_{\text{Fe}}^2 N_{\text{Al}}^5 + K_{c5}^{\Theta, R} N_{\text{Fe}} N_{\text{Al}}^6) \Sigma n_i = n_{\text{Fe}}^0 \quad (\text{mol}) \\ &\quad \dots (3a)\end{aligned}$$

$$\begin{aligned}b_2 &= (N_2 + N_{c1} + N_{c2} + 2N_{c3} + 5N_{c4} + 6N_{c5}) \Sigma n_i \\ &= (N_2 + K_{c1}^{\Theta, R} N_1^3 N_2 + K_{c2}^{\Theta, R} N_1 N_2 + 2K_{c3}^{\Theta, R} N_1 N_2^2 \\ &\quad + 5K_{c4}^{\Theta, R} N_1^2 N_2^5 + 6K_{c5}^{\Theta, R} N_1 N_2^6) \Sigma n_i \\ &= (N_{\text{Al}} + K_{c1}^{\Theta, R} N_{\text{Fe}}^3 N_{\text{Al}} + K_{c2}^{\Theta, R} N_{\text{Fe}} N_{\text{Al}} + 2K_{c3}^{\Theta, R} N_{\text{Fe}} N_{\text{Al}}^2 \\ &\quad + 5K_{c4}^{\Theta, R} N_{\text{Fe}}^2 N_{\text{Al}}^5 + 6K_{c5}^{\Theta, R} N_{\text{Fe}} N_{\text{Al}}^6) \Sigma n_i = n_{\text{Al}}^0 \quad (\text{mol}) \\ &\quad \dots (3b)\end{aligned}$$

According to the principle that the sum of mole fraction of all structural units in a fixed amount of metallic melts

under equilibrium condition is equal to unity as 1, the following equation can be established

$$\begin{aligned}N_1 + N_2 + N_{c1} + N_{c2} + N_{c3} + N_{c4} + N_{c5} \\ = N_{\text{Fe}} + N_{\text{Al}} + N_{\text{Fe}_3\text{Al}} + N_{\text{FeAl}} + N_{\text{FeAl}_2} + N_{\text{Fe}_2\text{Al}_5} + N_{\text{FeAl}_6} = 1.0 \\ (-) \dots (4)\end{aligned}$$

The governing equations of the developed AMCT– N_i thermodynamic model for calculating the mass action concentrations N_i of structural units in Fe–Al binary melts are comprised by the equation group of Eqs. (3) and (4). Obviously, there are three unknown parameters as N_1 (N_{Fe}), N_2 (N_{Al}), and Σn_i with three independent equations in the established equation group of Eqs. (3) and (4). The unique solution of N_i , Σn_i , and n_i can be calculated by solving the algebraic equation group of Eqs. (3) and (4) through combining with the definition of N_i in Eq. (2) after knowing the values of $K_{c1}^{\Theta, R}$ ($K_{\text{Fe}_3\text{Al}}^{\Theta, R}$), $K_{c2}^{\Theta, R}$ ($K_{\text{FeAl}}^{\Theta, R}$), $K_{c3}^{\Theta, R}$ ($K_{\text{FeAl}_2}^{\Theta, R}$), $K_{c4}^{\Theta, R}$ ($K_{\text{Fe}_2\text{Al}_5}^{\Theta, R}$), and $K_{c5}^{\Theta, R}$ ($K_{\text{FeAl}_6}^{\Theta, R}$).

The standard equilibrium constant $K_{ci}^{\Theta, R}$ of reactions for five molecules as Fe_3Al , FeAl , FeAl_2 , Fe_2Al_5 and FeAl_6 in Fe–Al binary melts at a fixed temperature can be calculated based on the obtained standard molar Gibbs free energy change $\Delta_r G_{m, ci}^{\Theta, R}$ of the same reaction from the mass action law as $\Delta_r G_{m, ci}^{\Theta, R} = -RT \ln K_{ci}^{\Theta, R}$ based on $K_{ci}^{\Theta, R} = a_{\text{Fe}_3\text{Al}} / (a_{\text{Fe}}^3 a_{\text{Al}})$. Meanwhile, the standard molar Gibbs free energy changes $\Delta_r G_{m, ci}^{\Theta, R}$ of reactions for forming Fe_3Al , FeAl , FeAl_2 , Fe_2Al_5 and FeAl_6 from Fe and Al have been reported by Zhang^{11,18} relative to pure liquid matter as standard states as follows

$$\begin{aligned}3[\text{Fe}] + [\text{Al}] &= [\text{Fe}_3\text{Al}] \\ \Delta_r G_{m, \text{Fe}_3\text{Al}}^{\Theta, R} &= -RT \ln \left(\frac{a_{\text{Fe}_3\text{Al}}}{a_{\text{Fe}}^3 a_{\text{Al}}} \right) = -120\,586.85 + 48.61T \\ &\quad (\text{J/mol}) \dots (5)\end{aligned}$$

$$\begin{aligned}[\text{Fe}] + [\text{Al}] &= [\text{FeAl}] \\ \Delta_r G_{m, \text{FeAl}}^{\Theta, R} &= -RT \ln \left(\frac{a_{\text{FeAl}}}{a_{\text{Fe}} a_{\text{Al}}} \right) = -47\,813.257 + 7.893T \\ &\quad (\text{J/mol}) \dots (6)\end{aligned}$$

$$\begin{aligned}[\text{Fe}] + 2[\text{Al}] &= [\text{FeAl}_2] \\ \Delta_r G_{m, \text{FeAl}_2}^{\Theta, R} &= -RT \ln \left(\frac{a_{\text{FeAl}_2}}{a_{\text{Fe}} a_{\text{Al}}^2} \right) = 130\,186.64 - 84.582T \\ &\quad (\text{J/mol}) \dots (7)\end{aligned}$$

Table 2. Chemical reaction formulas of formed molecules, their standard equilibrium constants $K_{ci}^{\Theta, R}$, and mass action concentrations N_{ci} of formed molecules in Fe–Al binary melts based on the AMCT.

Reactions	$K_{ci}^{\Theta, R} (-)$	$N_{ci} (-)$
$3[\text{Fe}] + [\text{Al}] = [\text{Fe}_3\text{Al}]$	$K_{c1}^{\Theta, R} = \frac{N_{c1}}{N_1^3 N_2} = \frac{N_{\text{Fe}_3\text{Al}}}{N_{\text{Fe}}^3 N_{\text{Al}}}$	$N_{c1} = K_{c1}^{\Theta, R} N_1^3 N_2 = K_{\text{Fe}_3\text{Al}}^{\Theta, R} N_{\text{Fe}}^3 N_{\text{Al}}$
$[\text{Fe}] + [\text{Al}] = [\text{FeAl}]$	$K_{c2}^{\Theta, R} = \frac{N_{c2}}{N_1 N_2} = \frac{N_{\text{FeAl}}}{N_{\text{Fe}} N_{\text{Al}}}$	$N_{c2} = K_{c2}^{\Theta, R} N_1 N_2 = K_{\text{FeAl}}^{\Theta, R} N_{\text{Fe}} N_{\text{Al}}$
$[\text{Fe}] + 2[\text{Al}] = [\text{FeAl}_2]$	$K_{c3}^{\Theta, R} = \frac{N_{c3}}{N_1 N_2^2} = \frac{N_{\text{FeAl}_2}}{N_{\text{Fe}} N_{\text{Al}}^2}$	$N_{c3} = K_{c3}^{\Theta, R} N_1 N_2^2 = K_{\text{FeAl}_2}^{\Theta, R} N_{\text{Fe}} N_{\text{Al}}^2$
$[\text{Fe}] + [\text{Al}] = [\text{Fe}_2\text{Al}_5]$	$K_{c4}^{\Theta, R} = \frac{N_{c4}}{N_1^2 N_2^5} = \frac{N_{\text{Fe}_2\text{Al}_5}}{N_{\text{Fe}}^2 N_{\text{Al}}^5}$	$N_{c4} = K_{c4}^{\Theta, R} N_1^2 N_2^5 = K_{\text{Fe}_2\text{Al}_5}^{\Theta, R} N_{\text{Fe}}^2 N_{\text{Al}}^5$
$[\text{Fe}] + 6[\text{Al}] = [\text{FeAl}_6]$	$K_{c5}^{\Theta, R} = \frac{N_{c5}}{N_1 N_2^6} = \frac{N_{\text{FeAl}_6}}{N_{\text{Fe}} N_{\text{Al}}^6}$	$N_{c5} = K_{c5}^{\Theta, R} N_1 N_2^6 = K_{\text{FeAl}_6}^{\Theta, R} N_{\text{Fe}} N_{\text{Al}}^6$

$$\Delta_r G_{\text{m, Fe}_2\text{Al}_5}^{\ominus, \text{R}} = -RT \ln \left(\frac{a_{\text{R, Fe}_2\text{Al}_5}}{a_{\text{R, Fe}}^2 a_{\text{R, Al}}^5} \right) = -165\,372.213 + 43.05T \quad (\text{J/mol}) \dots (8)$$

$$\Delta_r G_{\text{m, FeAl}_6}^{\ominus, \text{R}} = -RT \ln \left(\frac{a_{\text{R, FeAl}_6}}{a_{\text{R, Fe}} a_{\text{R, Al}}^6} \right) = -14\,710.17 - 18.712T \quad (\text{J/mol}) \dots (9)$$

3. Results and Discussion for Calculated Mass Action Concentrations N_i of Structural Units in Fe–Al Binary Melts

3.1. Comparison between Calculated Mass Action Concentration N_{Al} of Al or N_{Fe} of Fe and Reported Activity $a_{\text{R, Al}}$ of Al or $a_{\text{R, Fe}}$ of Fe by Different Researchers

To improve the readability of this article, chemical composition of Fe–Al binary melts, reported activity $a_{\text{R, Fe}}$ of Fe or $a_{\text{R, Al}}$ of Al in a temperature range from 1 573 K to 1 873 K by different investigators,^{5–8,21)} calculated mass action concentrations N_i of seven structural units including Fe, Al, Fe_3Al , FeAl , FeAl_2 , Fe_2Al_5 and FeAl_6 , and calculated total equilibrium mole number Σn_i of structural units in 100–g Fe–Al binary melts were summarized in Table 3.

The comparison between the calculated mass action concentration N_{Al} of Al and the reported activity $a_{\text{R, Al}}$ of Al by different researchers^{5–8,21)} relative to pure liquid Al(l) as standard state in Fe–Al binary melts with changing mole fraction x_{Al} of Al from 0 to 1 in a temperature range from 1 573 K to 1 873 K was illustrated in Fig. 1(a). The comparison between the calculated mass action concentration N_{Fe} of Fe and the reported activity $a_{\text{R, Fe}}$ of Fe by different researchers^{6–8,21)} relative to pure liquid Fe(l) as standard state in Fe–Al binary melts with changing mole fraction x_{Fe} of Fe from 0 to 1 in the same temperature range was also shown in Fig. 1(b). The calculated mass action concentration N_{Al} of Al has a very excellent agreement with the reported activity $a_{\text{R, Al}}$ of Al by different researchers^{5–8,21)} in Fe–Al binary melts as shown in Fig. 1(a). Meanwhile, the calculated mass action concentration N_{Fe} of Fe in the full composition has a very good 1:1 corresponding relationship with the reported activity $a_{\text{R, Fe}}$ of Fe by different researchers^{6–8,21)} in Fe–Al binary melts as shown in Fig. 1(b). Obviously, the calculated mass action concentration N_{Al} of Al or N_{Fe} of Fe can be successfully applied to substitute the reported activity $a_{\text{R, Al}}$ of Al or $a_{\text{R, Fe}}$ of Fe by different researchers^{5–8,21)} in Fe–Al binary melts in the full composition range in a temperature range from 1 573 K to 1 873 K.

3.2. Determination of Raoultian Activity Coefficient γ_{Al}^0 of Al and γ_{Fe}^0 of Fe from Calculated Mass Action Concentration N_{Al} of Al and N_{Fe} of Fe in Fe–Al Binary Melts

The good 1:1 corresponding relationship between the calculated mass action concentration N_{Al} of Al and the reported

activity $a_{\text{R, Al}}$ of Al by previous researchers^{5–8,21)} in Fe–Al binary melts as described in Fig. 1(a) shows that the calculated mass action concentration N_{Al} of Al, like the measured activity $a_{\text{R, Al}}$ of Al, can be applied to determine the activity coefficient γ_{Al} of Al in Fe–Al binary melts as $\gamma_{\text{Al}} = N_{\text{Al}}/x_{\text{Al}}$.

The mass action concentrations N_i of seven structural units in Fe–Al binary melts with changing mole fraction x_{Al} of Al from 0 to 0.005 at an interval of x_{Al} as 0.00005 at temperatures of 1 573 K, 1 673 K, 1 773 K, and 1 873 K have been calculated based on the developed AMCT– N_i model for Fe–Al binary melts.

The relationship between mole fraction x_{Al} of Al and the calculated activity coefficient of Al in natural logarithmic form $\ln \gamma_{\text{Al}}$ in Fe–Al binary melts with changing mole fraction x_{Al} of Al from 0 to 0.005 at an interval of x_{Al} as 0.00005 at temperatures of 1 573 K, 1 673 K, 1 773 K, and 1 873 K was illustrated in Fig. 2(a), respectively. The corresponding relationships at the above-mentioned four temperatures can be expressed by the linear equations as follows

$$\ln \gamma_{\text{Al}} = -3.810 + 4.476x_{\text{Al}} \quad 0 < x_{\text{Al}} \leq 0.005, T = 1\,573\text{ K } (-) \dots (10a)$$

$$\ln \gamma_{\text{Al}} = -3.397 + 4.248x_{\text{Al}} \quad 0 < x_{\text{Al}} \leq 0.005, T = 1\,673\text{ K } (-) \dots (10b)$$

$$\ln \gamma_{\text{Al}} = -3.056 + 4.011x_{\text{Al}} \quad 0 < x_{\text{Al}} \leq 0.005, T = 1\,773\text{ K } (-) \dots (10c)$$

$$\ln \gamma_{\text{Al}} = -2.537 + 3.599x_{\text{Al}} \quad 0 < x_{\text{Al}} \leq 0.005, T = 1\,873\text{ K } (-) \dots (10d)$$

The relationship between mole fraction x_{Fe} of Fe and the calculated activity coefficient of Fe in natural logarithmic form $\ln \gamma_{\text{Fe}}$ in Fe–Al binary melts with changing mole fraction x_{Fe} of Fe from 0 to 0.005 at an interval of x_{Fe} as 0.00005 at temperatures of 1 573 K, 1 673 K, 1 773 K, and 1 873 K was illustrated in Fig. 2(b), respectively. The corresponding relationship at the above-mentioned four temperatures can be expressed by the linear equations as follows

$$\ln \gamma_{\text{Fe}} = -3.837 + 6.701x_{\text{Fe}} \quad 0 < x_{\text{Fe}} \leq 0.005, T = 1\,573\text{ K } (-) \dots (11a)$$

$$\ln \gamma_{\text{Fe}} = -3.753 + 7.627x_{\text{Fe}} \quad 0 < x_{\text{Fe}} \leq 0.005, T = 1\,673\text{ K } (-) \dots (11b)$$

$$\ln \gamma_{\text{Fe}} = -3.701 + 8.066x_{\text{Fe}} \quad 0 < x_{\text{Fe}} \leq 0.005, T = 1\,773\text{ K } (-) \dots (11c)$$

$$\ln \gamma_{\text{Fe}} = -3.686 + 8.176x_{\text{Fe}} \quad 0 < x_{\text{Fe}} \leq 0.005, T = 1\,873\text{ K } (-) \dots (11d)$$

The Raoultian activity coefficient γ_{Al}^0 of Al in the infinitely dilute Fe–Al binary melts related with activity $a_{\text{R, Al}}$ of Al can be defined as the value of $\gamma_{\text{Al}, x_{\text{Al}} \rightarrow 0.0}$. Therefore, the intercepts of the linear functions in Eq. (10) and in Fig. 2(a) can be treated as the values of the Raoultian activity coefficient $\ln \gamma_{\text{Al}}^0$ of Al in the infinitely dilute Fe–Al binary melts at the above-mentioned four temperatures. The effect of temperature from 1 573 K to 1 873 K on the determined Raoultian activity coefficient in natural logarithmic form $\ln \gamma_{\text{Al}}^0$ of Al in the infinitely dilute Fe–Al binary melts was

Table 3. Chemical composition of Fe–Al binary melts, reported activity $a_{\text{R, Fe}}$ of Fe or $a_{\text{R, Al}}$ of Al in a temperature range from 1 573 K to 1 873 K by different investigators, calculated mass action concentrations N_i of seven structural units including Fe, Al, Fe_3Al , FeAl , FeAl_2 , Fe_2Al_5 and FeAl_6 , and calculated total equilibrium mole number Σn_i of structural units in 100–g Fe–Al binary melts based on the developed AMCT– N_i thermodynamic model for Fe–Al binary melts.

Investigator	Chemical composition				Activity of Fe and Al (–)		Temperature [K]	Calculated mass action concentrations of structural units N_i (–)							Σn_i (mol)
	Mass percentage		Mole fraction					N_{Fe}	N_{Al}	$N_{\text{Fe}_3\text{Al}}$	N_{FeAl}	N_{FeAl_2}	$N_{\text{Fe}_2\text{Al}_5}$	N_{FeAl_6}	
	[% Fe]	[% Al]	x_{Fe}	x_{Al}	$a_{\text{R, Fe}}$	$a_{\text{R, Al}}$									
Desai <i>et al.</i>	100	0	1	0	1.000	0.000	1 873	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.79050
	94.90588	5.094122	0.9	0.1	0.877	0.009	1 873	0.88106	0.00918	0.04185	0.06745	0.00046	0.00000	0.00000	1.58140
	87.82482	12.17518	0.8	0.2	0.719	0.028	1 873	0.68519	0.03496	0.07496	0.19976	0.00513	0.00001	0.00000	1.41040
	82.8477	17.1523	0.7	0.3	0.550	0.064	1 873	0.55157	0.06463	0.07229	0.29730	0.01412	0.00008	0.00000	1.37350
	73.00972	26.99028	0.6	0.4	0.388	0.122	1 873	0.34116	0.14858	0.03933	0.42276	0.04617	0.00195	0.00009	1.40260
	67.42726	32.57274	0.5	0.5	0.250	0.209	1 873	0.25264	0.20937	0.02250	0.44115	0.06789	0.00593	0.00052	1.43460
	54.59166	45.40834	0.4	0.6	0.142	0.331	1 873	0.11601	0.37883	0.00394	0.36653	0.10206	0.02424	0.00837	1.49620
	47.01047	52.98953	0.3	0.7	0.069	0.488	1 873	0.06989	0.48810	0.00111	0.28452	0.10207	0.03124	0.02308	1.54340
	31.07439	68.92561	0.2	0.8	0.026	0.673	1 873	0.02136	0.70525	0.00005	0.12565	0.06513	0.01838	0.06418	1.77630
	18.69957	81.30043	0.1	0.9	0.006	0.859	1 873	0.00634	0.85514	0.00000	0.04525	0.02844	0.00425	0.06058	2.24550
	0	100	0	1	0.000	1.000	1 873	0.00000	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	3.70640
Belton <i>et al.</i>	100	0	1	0	1.000	0.000	1 873	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.79050
	94.90588	5.094122	0.9	0.1	0.862	0.006	1 873	0.88106	0.00918	0.04185	0.06745	0.00046	0.00000	0.00000	1.58140
	87.82482	12.17518	0.8	0.2	0.654	0.030	1 873	0.68519	0.03496	0.07496	0.19976	0.00513	0.00001	0.00000	1.41040
	82.8477	17.1523	0.7	0.3	0.445	0.095	1 873	0.55157	0.06463	0.07229	0.29730	0.01412	0.00008	0.00000	1.37350
	73.00972	26.99028	0.6	0.4	0.328	0.178	1 873	0.34116	0.14858	0.03933	0.42276	0.04617	0.00195	0.00009	1.40260
	67.42726	32.57274	0.5	0.5	0.220	0.286	1 873	0.25264	0.20937	0.02250	0.44115	0.06789	0.00593	0.00052	1.43460
	54.59166	45.40834	0.4	0.6	0.136	0.419	1 873	0.11601	0.37883	0.00394	0.36653	0.10206	0.02424	0.00837	1.49620
	47.01047	52.98953	0.3	0.7	0.075	0.572	1 873	0.06989	0.48810	0.00111	0.28452	0.10207	0.03124	0.02308	1.54340
	31.07439	68.92561	0.2	0.8	0.037	0.730	1 873	0.02136	0.70525	0.00005	0.12565	0.06513	0.01838	0.06418	1.77630
	18.69957	81.30043	0.1	0.9	0.013	0.885	1 873	0.00634	0.85514	0.00000	0.04525	0.02844	0.00425	0.06058	2.24550
	0	100	0	1	0.000	1.000	1 873	0.00000	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	3.70640
Jacobson <i>et al.</i>	100	0	1	0	1.000	0.000	1 573	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.79050
	94.90588	5.094122	0.9	0.1	0.860	0.004	1 573	0.87296	0.003792	0.07364	0.04959	0.00002	0.00000	0.00000	1.48610
	87.82482	12.17518	0.8	0.2	0.668	0.016	1 573	0.63211	0.020601	0.15189	0.19506	0.00033	0.00000	0.00000	1.22550
	82.8477	17.1523	0.7	0.3	0.466	0.047	1 573	0.46964	0.047828	0.14462	0.33646	0.00134	0.00010	0.00000	1.19480
	73.00972	26.99028	0.6	0.4	0.292	0.110	1 573	0.25811	0.13607	0.06830	0.52609	0.00595	0.00544	0.00005	1.29950
	66.14345	33.85655	0.52	0.48	0.184	0.197	1 573	0.17363	0.21151	0.03232	0.55011	0.00967	0.02233	0.00045	1.35280
	65.64539	34.35461	0.48	0.52	0.184	0.197	1 573	0.16874	0.21722	0.03047	0.54905	0.00991	0.02409	0.00052	1.35440
	54.59166	45.40834	0.4	0.6	0.102	0.312	1 573	0.084844	0.35885	0.00640	0.45606	0.01360	0.07494	0.00530	1.34100
	47.01047	52.98953	0.3	0.7	0.045	0.486	1 573	0.04719	0.48078	0.00147	0.33985	0.01358	0.10008	0.01704	1.35270
	31.07439	68.92561	0.2	0.8	0.016	0.680	1 573	0.012505	0.73018	0.00004	0.13677	0.00830	0.05679	0.05541	1.70310
	18.69957	81.30043	0.1	0.9	0.004	0.865	1 573	0.004348	0.86736	0.00000	0.05650	0.00407	0.01624	0.05413	2.26790
0	100	0	1	0.000	1.000	1 573	0.00000	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	3.70640	
Ichise <i>et al.</i>	100	0	1	0	1.000	0.000	1 673	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.79050
	94.90588	5.094122	0.9	0.1	0.868	0.005	1 673	0.87591	0.005428	0.06136	0.05724	0.00006	0.00000	0.00000	1.52090
	89.22438	10.77562	0.8	0.2	0.689	0.021	1 673	0.69864	0.019854	0.11390	0.16699	0.00062	0.00000	0.00000	1.32260
	82.8477	17.1523	0.7	0.3	0.501	0.054	1 673	0.50027	0.054366	0.11451	0.32743	0.00334	0.00010	0.00000	1.26270
	78.04653	21.95347	0.632	0.368	0.382	0.093	1 673	0.38117	0.093617	0.08722	0.42959	0.00754	0.00086	0.00001	1.29190
	75.17747	24.82253	0.594	0.406	0.382	0.093	1 673	0.32344	0.12145	0.06913	0.47291	0.01076	0.00227	0.00003	1.32080
	67.42726	32.57274	0.5	0.5	0.226	0.176	1 673	0.20793	0.20736	0.03136	0.51907	0.02017	0.01362	0.00045	1.38930
	57.9838	42.0162	0.4	0.6	0.114	0.308	1 673	0.11918	0.32668	0.00930	0.46872	0.02870	0.04342	0.00396	1.41190
	47.01047	52.98953	0.3	0.7	0.050	0.481	1 673	0.056083	0.48894	0.00145	0.33012	0.03025	0.07221	0.02095	1.43600
	34.10271	65.89729	0.2	0.8	0.018	0.676	1 673	0.020771	0.67988	0.00010	0.17001	0.02166	0.05149	0.05608	1.64220
	18.69957	81.30043	0.1	0.9	0.004	0.863	1 673	0.005254	0.8618	0.00000	0.05451	0.00881	0.01078	0.05884	2.24730
0	100	0	1	0.000	1.000	1 673	0.00000	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	3.70640	
Coskun <i>et al.</i>	57.37199	42.62801	0.394	0.606	–	0.2121	1 588	0.10428	0.32241	0.00978	0.48652	0.01482	0.05882	0.00339	1.35890
	48.76844	51.23156	0.315	0.685	–	0.3494	1 588	0.055934	0.45298	0.00212	0.36665	0.01569	0.09264	0.01398	1.35610
	32.25563	67.74437	0.187	0.813	–	0.6423	1 588	0.014402	0.71294	0.00006	0.14858	0.01001	0.05932	0.05471	1.66680
	18.86833	81.13167	0.101	0.899	–	0.8001	1 588	0.004476	0.86541	0.00000	0.05605	0.00458	0.01510	0.05439	2.25680
	0	100	0	1	–	1.0000	1 588	0	1	0.00000	0.00000	0.00000	0.00000	0.00000	3.70640

Fig. 1. Relationship between calculated mass action concentration N_{Al} of Al and reported activity $a_{R, Al}$ of Al by different researchers relative to pure liquid Al(l) as standard state (a), and relationship between calculated mass action concentration N_{Fe} of Fe and reported activity $a_{R, Fe}$ of Fe by different researchers relative to pure liquid Fe(l) as standard state (b) in Fe–Al binary melts in the temperature range from 1 573 K to 1 873 K, respectively.

Fig. 2. Relationship between mole fraction x_{Al} of Al and calculated activity coefficient of Al in logarithmic form $\ln \gamma_{Al}$ (a), and relationship between mole fraction x_{Fe} of Fe and calculated activity coefficient of Fe in logarithmic form $\ln \gamma_{Fe}$ in Fe–Al binary melt at temperatures of 1 573 K, 1 673 K, 1 773 K, and 1 873 K, respectively.

Fig. 3. Relationship between reciprocal of temperature $1/T$ and calculated Raoultian activity coefficient of Al in logarithmic form $\ln \gamma_{Al}^0$ (a), and relationship between reciprocal of temperature $1/T$ and calculated Raoultian activity coefficient of Fe in logarithmic form $\ln \gamma_{Fe}^0$ (b) in the infinitely dilute Fe–Al binary melts in a temperature range from 1 573 K to 1 873 K.

illustrated in **Fig. 3** and can be regressed as

$$\ln \gamma_{Al}^0 = 2.6917 - 10\,222.7/T \quad (12)$$

1 573 K $\leq T \leq$ 1 873 K (–)

Similarly, the Raoultian activity coefficient γ_{Fe}^0 of Fe in Fe–Al binary melts related with activity $a_{R, Fe}$ of Fe can be defined as the value of $\gamma_{Fe, x_{Fe} \rightarrow 0.0}$. Therefore, the intercepts

of the linear functions in Eq. (11) and in Fig. 2(b) can be considered as the values of the Raoultian activity coefficient $\ln \gamma_{Fe}^0$ of Fe in Fe–Al binary melts at the above-mentioned four temperatures. The effect of temperature from 1 573 K to 1 873 K on the determined Raoultian activity coefficient in natural logarithmic form $\ln \gamma_{Fe}^0$ of Fe in Fe–Al binary melts was illustrated in Fig. 3(b) and can be regressed as

Table 4. Comparison of reported activity coefficient γ_{Al}^0 and γ_{Fe}^0 in Fe–Al binary melts from different researchers.

No.	Investigator	T(K)	$\gamma_{\text{Al}}^0(-)$	$\gamma_{\text{Fe}}^0(-)$	Method	Ref
1	Jacobson	1 573	0.016	0.019	Ion–current–ratio technique	8)
2	Ichise	1 673	0.027	0.02	Knudsen Cell Mass Spectrometry	7)
4	Wilder	1 873	0.063	–	Fe–Al/Ag–Al(estimated from Chipman’s data)	3)
5	Woolley	1 873	0.061	–	Heats of solution in Fe–Al	4)
7	Ichise	1 873	0.049	0.017	Knudsen Cell Mass Spectrometry	7)
8	KIM	1 873	0.066	–	Meta–gas equilibration	9)
9	Present study	1 573	0.022	0.021	AMCT– N_i model	–
10	Present study	1 673	0.033	0.023	AMCT– N_i model	–
11	Present study	1 773	0.047	0.0247	AMCT– N_i model	–
12	Present study	1 873	0.062	0.025	AMCT– N_i model	–

$$\ln \gamma_{\text{Fe}}^0 = -2.8573 - 1521.6816/T \quad (13)$$

$$1\,573\text{ K} \leq T \leq 1\,873\text{ K} \quad (-)$$

To evaluate the reliability of Eqs. (12) and (13) in this study, several reported Raoultian activity coefficient $\ln \gamma_{\text{Al}}^0$ of Al and $\ln \gamma_{\text{Fe}}^0$ of Fe by previous researchers^{3,4,7–9)} were summarized in **Table 4** and displayed in Fig. 3 for comparison. Obviously, the reported $\ln \gamma_{\text{Al}}^0$ of Al by previous researchers have good agreement with the determined Raoultian activity coefficient $\ln \gamma_{\text{Al}}^0$ of Al in the infinitely dilute Fe–Al binary melts. This suggests that the determined Raoultian activity coefficient $\ln \gamma_{\text{Al}}^0$ of Al in the infinitely dilute Fe–Al binary melts in a temperature range from 1 573 K to 1 873 K has an ideal accuracy. Meanwhile, the accuracy of the predicted Raoultian activity coefficient $\ln \gamma_{\text{Fe}}^0$ of Fe in Fe–Al binary melts in a temperature range from 1 573 K to 1 873 K can be verified from Fig. 3(b).

3.3. Prediction of Mass Action Concentrations N_i of Structural Units in Full Composition Range of Fe–Al Binary Melts

As a representative, the relationship between mole fraction x_{Al} of Al and the calculated mass action concentrations N_i of seven structural units as Fe, Al, Fe_3Al , FeAl, FeAl_2 , Fe_2Al_5 and FeAl_6 in the full composition range of Fe–Al binary melts at 1 873 K was illustrated in **Fig. 4**. The effect of changing temperature from 1 573 K to 1 873 K on the relationship of the calculated mass action concentrations N_i of seven structural units as Fe, Al, Fe_3Al , FeAl, FeAl_2 , Fe_2Al_5 and FeAl_6 against mole fraction x_{Al} of Al in the full composition range of Fe–Al binary melts was shown in **Fig. 5**, respectively.

It can be observed from Figs. 4 and 5(a) that the calculated mass action concentration N_{Al} of Al shows a slow increase tendency with an increase of mole fraction x_{Al} of Al from 0 to 0.40, and then displays a sharp increase trend with an increase of mole fraction x_{Al} of Al from 0.40 to 1.0 at the above–mentioned four temperatures. Meanwhile, an opposite variation trend of the calculated mass action concentration N_{Fe} of Fe against mole fraction x_{Fe} of Fe can be found at the above–mentioned four temperatures. Changing

Fig. 4. Relationship between mole fraction x_{Al} of Al and calculated mass action concentration N_i of seven structural units as Fe, Al, Fe_3Al , FeAl, FeAl_2 , Fe_2Al_5 and FeAl_6 in the full composition range of Fe–Al binary melts at an interval of mole fraction x_{Al} of Al as 0.05, respectively.

temperature from 1 573 K to 1 873 K cannot cause an obvious variation on the calculated mass action concentration N_{Al} of Al as well as N_{Fe} of Fe as shown in Figs. 4 and 5(a), respectively.

The reverse V–type relationship between mole fraction x_{Al} of Al and the calculated mass action concentration Fe_3Al , FeAl, FeAl_2 , Fe_2Al_5 and FeAl_6 in the full composition range of Fe–Al binary melts at temperatures of 1 573 K, 1 673 K, 1 773 K, and 1 873 K can be found in Figs. 5(b)–5(f). As shown in Figs. 5(c) and 5(f), changing temperature from 1 573 K to 1 873 K cannot cause an obvious variation on the calculated mass action concentration N_{FeAl} of FeAl or N_{FeAl_6} of FeAl_6 in Fe–Al binary melts. The greatest value of the calculated mass action concentration N_{FeAl} of FeAl is 0.75 corresponds to mole fraction x_{Al} of Al as 0.5; the largest value of the calculated mass action concentration N_{FeAl_6} of FeAl_6 is 0.064 corresponds to mole fraction x_{Al} of Al as 0.9. This implies that the magnitude of the calculated mass action concentration N_{ci} of molecule ci as Fe_xAl_y has a close relationship with the ratio of atom Fe to atom Al.

As shown in Fig. 5(b), the maximum value of the calculated mass action concentration $N_{\text{Fe}_3\text{Al}}$ of Fe_3Al is 0.152 corresponds to mole fraction x_{Al} of Al as 0.2 at 1 573 K; the greatest value of the calculated mass action concentration $N_{\text{Fe}_3\text{Al}}$ of Fe_3Al as 0.08 meets mole fraction x_{Al} of Al as 0.3 at 1 873 K. Increasing temperature from 1 573 K to 1 873 K can lead to a decrease of the maximum value of the calculated mass action concentration $N_{\text{Fe}_3\text{Al}}$ of Fe_3Al from 0.152 to 0.08. As illustrated in Fig. 5(d), the largest value of the calculated mass action concentration N_{FeAl_2} of FeAl_2 is 0.102 corresponds to mole fraction x_{Al} of Al as 0.6 at 1 873 K; the greatest value of the calculated mass action concentration N_{FeAl_2} of FeAl_2 is 0.0136 corresponds to mole fraction x_{Al} of Al as 0.6 at 1 573 K. Increasing temperature from 1 573 K to 1 873 K can cause an increase of the largest value of the calculated mass action concentration N_{FeAl_2} of FeAl_2 from 0.102 to 0.0136. As described in Fig. 5(e), the largest value of the calculated mass action concentration $N_{\text{Fe}_2\text{Al}_5}$ of Fe_2Al_5 as 0.1 corresponds to mole fraction x_{Al} of Al as 0.7 at 1 573 K; the greatest value of the calculated mass action concentration $N_{\text{Fe}_2\text{Al}_5}$ of Fe_2Al_5 is 0.0312 corresponds to

Fig. 5. Relationship between mole fraction x_{Al} of Al and calculated mass action concentration N_i of seven structural units as Fe, Al, Fe_3Al , $FeAl$, $FeAl_2$, Fe_2Al_3 and $FeAl_6$ in the full composition range of Fe–Al binary melts at temperatures of 1 573 K, 1 588 K, 1 673 K, and 1 873 K, respectively.

mole fraction x_{Al} of Al as 0.037 at 1 873 K. Increasing temperature from 1 573 K to 1 873 K can cause a decrease of the largest value of the calculated mass action concentration $N_{Fe_2Al_3}$ of Fe_2Al_3 from 0.1 to 0.0312.

It should be specially emphasized that the sum of the calculated mass action concentrations N_i of seven structural units as Fe, Al, Fe_3Al , $FeAl$, $FeAl_2$, Fe_2Al_3 and $FeAl_6$ in Fe–Al binary melts should be unity as 1 as expressed in Eq. (4) in Section 2.1. Therefore, the calculated mass action concentration N_i of seven structural units in Fe–Al binary melts should be competitive or coupled each other. The competitive or coupled effect of the calculated mass action concentrations N_i of seven structural units in Fe–Al binary melts is also valid in the cases changing temperature from 1 573 K to 1 873 K.

3.4. Relationship between Calculated Equilibrium Mole Number n_i and Mole Fraction of x_i of Structural Units in Fe–Al Binary Melts

It has been described in Section 2.2 that the calculated equilibrium mole numbers n_i is an important parameter to represent mass content of structural units in Fe–Al binary melts under equilibrium, like mole fraction x_{Al} of Al or mole fraction x_{Fe} of Fe, according to the AMCT^{11,18–20)} or the IMCT.^{22,23)}

The relationship of the calculated equilibrium mole number n_i of each structural unit against mole fraction x_{Al} of Al shown in Fig. 6 is similar with that of the calculated mass action concentration N_i of each structural unit against mole fraction x_{Al} of Al in Fe–Al binary melts at the above-mentioned four temperatures as shown in Fig. 5. Changing temperature from 1 573 K to 1 873 K cannot bring an obvious variation on the calculated equilibrium mole number n_{Fe}

Fig. 6. Relationship between mole fraction x_{Al} of Al and calculated equilibrium mole numbers n_i of seven structural units as Fe, Al, Fe_3Al , $FeAl$, $FeAl_2$, Fe_2Al_5 and $FeAl_6$ in the full composition range of Fe–Al binary melts at temperatures of 1 573 K, 1 588 K, 1 673 K, and 1 873 K, respectively.

of Fe as well as n_{Al} of Al, respectively. It can be observed from Fig. 6(a) that the calculated equilibrium mole number n_{Al} of Al shows a slow increase tendency with an increase of mole fraction x_{Al} of Al from 0.0 to 0.4, and then displays a sharp increase trend with an increase of mole fraction x_{Al} of Al from 0.4 to 1.0. An opposite variation trend of the calculated equilibrium mole number n_{Fe} of Fe against mole fraction x_{Al} of Al can also be found from Fig. 6(a).

As shown in Figs. 6(c) and 6(f), changing temperature from 1 573 K to 1 873 K cannot cause an obvious variation of the calculated equilibrium mole number n_{FeAl} of $FeAl$ and n_{FeAl_6} of $FeAl_6$ in Fe–Al binary melts. The greatest value of the calculated equilibrium mole number n_{FeAl} is 0.75 corresponds to mole fraction x_{Al} of Al as 0.5; the largest value of the calculated equilibrium mole number n_{FeAl_6} of $FeAl_6$ is 0.136 corresponds to mole fraction x_{Al} of Al as 0.9.

As described in Fig. 6(b), increasing temperature from

1 573 K to 1 873 K can lead to a decrease tendency of the maximum value of the calculated equilibrium mole number n_{Fe_3Al} of Fe_3Al from 0.186 to 0.106. The maximum value of the calculated equilibrium mole number n_{Fe_3Al} of Fe_3Al is 0.186 corresponds to mole fraction x_{Al} of Al as 0.2 at 1 573 K; the greatest value of the calculated equilibrium mole number n_{Fe_3Al} of Fe_3Al as 0.106 meets mole fraction x_{Al} of Al as 0.2 at 1 873 K. As illustrated in Fig. 6(d), increasing temperature from 1 573 K to 1 873 K can lead to an increase tendency of the maximum value of the calculated equilibrium mole number n_{FeAl_2} of $FeAl_2$ from 0.0184 to 0.158 corresponds to mole fraction x_{Al} of Al as 0.7. As shown in Fig. 6(e), increasing temperature from 1 573 K to 1 873 K can cause a decrease tendency of the maximum value of the calculated equilibrium mole number $n_{Fe_2Al_5}$ of Fe_2Al_5 from 0.135 to 0.482 meets mole fraction x_{Al} of Al as 0.7.

4. Conclusions

A thermodynamic model for calculating the mass action concentrations of structural units in Fe–Al binary melts based on the atom–molecule coexistence theory, *i.e.*, AMCT– N_i model, has been developed and verified through comparing with the reported activities of both Al and Fe in Fe–Al binary melts in a temperature from 1 573 K to 1 873 K from the literature. The main summary remarks can be obtained as follows.

(1) The calculated mass action concentration N_{Al} of Al or N_{Fe} of Fe in Fe–Al binary melts has a good 1:1 corresponding relationship with the reported activity $a_{\text{R, Al}}$ of Al or $a_{\text{R, Fe}}$ of Fe relative to pure liquid Al(l) or Fe(l) as standard state in a temperature range from 1 573 K to 1 873 K from different researchers. The calculated mass action concentration N_{Al} of Al or N_{Fe} of Fe can be applied to ideally substitute the measured activity $a_{\text{R, Al}}$ of Al or $a_{\text{R, Fe}}$ of Fe relative to pure liquid Al(l) or Fe(l) as standard state in Fe–Al binary melts. Therefore, the developed AMCT– N_i model for Fe–Al binary melts can be successfully applied to represent the reaction ability of structural units in Fe–Al binary melts in a temperature from 1 573 K to 1 873 K.

(2) The values of the Raoultian activity coefficient γ_{Al}^0 of Al and γ_{Fe}^0 of Fe in the infinitely dilute solution of Fe–Al binary melts in a temperature range from 1 573 K to 1 873 K can be expressed as $\ln \gamma_{\text{Al}}^0 = 2.6917 - 10\,222.7/T$ and $\ln \gamma_{\text{Fe}}^0 = -2.8573 - 1\,521.6816/T$, respectively. The calculated values of the Raoultian activity coefficient γ_{Al}^0 of Al or γ_{Fe}^0 of Fe has good agreement with the reported γ_{Al}^0 of Al or γ_{Fe}^0 of Fe by previous researchers.

(3) The reaction abilities of structure units Fe, Al, Fe_3Al , FeAl , FeAl_2 , Fe_2Al_5 and FeAl_6 show a competitive or coupling relationship in the investigated temperature range.

REFERENCES

- 1) A. K. Misra: *Metall. Mater. Trans. A*, **21A** (1990), 441.
- 2) J. Chipman and T. P. Floridis: *Acta Metall.*, **3** (1955), 456.
- 3) T. C. Wilder and J. F. Elliott: *J. Electro. Chem. Soc.*, **107** (1960), 628.
- 4) F. Wooley and J. F. Elliott: *Trans. Met. Soc. AIME*, **239** (1967), 1872.
- 5) A. Coskun and J. F. Elliott: *Trans. Met. Soc. AIME*, **242** (1968), 253.
- 6) G. R. Belton and R. J. R. Fruehan: *Trans. Met. Soc. AIME*, **245** (1969), 113.
- 7) E. Ichise, T. Yamauchi and T. Mori: *Tetsu-to-Hagane*, **63** (1977), 417.
- 8) N. S. Jacobson and G. M. Mehrotra: *Metall. Mater. Trans. B*, **24B** (1993), 481.
- 9) W. Y. Kim, J. G. Kang, C. H. Park, J. B. Lee and J. J. Pak: *ISIJ Int.*, **47** (2007), 945.
- 10) A. I. Zaitsev, N. E. Zaitseva, R. Y. Shimko, N. A. Arutyunyan, S. F. Dunaev, V. S. Kraposhin and H. T. Lam: *J. Phys.: Condens. Matter.*, **20** (2008), 114121.
- 11) J. Zhang: *J. Iron Steel Res., Int.*, **12** (2005), 11.
- 12) A. D. Pelton, S. A. Degterov, G. Eriksson, C. Robelin and Y. Dessureault: *Metall. Mater. Trans. B*, **31B** (2000), 651.
- 13) D. W. Hoffman: *Metall. Trans.*, **3** (1972), 3231.
- 14) Y. E. Lee: *Metall. Mater. Trans. B*, **29B** (1998), 397.
- 15) M. Le Bouteiller, A. M. Martre, R. Farhi and C. Petot: *Metall. Mater. Trans. B*, **1B** (1977), 339.
- 16) P. Chartrand and A. D. Pelton: *Metall. Mater. Trans. A*, **32A** (2001), 1397.
- 17) F. Sommer: *Z. Metallkd.*, **73** (1982), 72.
- 18) J. Zhang: *Computational Thermodynamics of Metallurgical Melts and Solutions*, Metallurgical Industry Press, Beijing, China, (2007), 40.
- 19) X. M. Yang, M. Zhang, P. C. Li, J. Y. Li, J. L. Zhang and J. Zhang: *Metall. Mater. Trans. B*, **43B** (2012), 1358.
- 20) X. M. Yang, M. Zhang, P. C. Li, J. Y. Li, J. L. Zhang and J. Zhang: *Steel Res. Int.*, **84** (2013), 784.
- 21) P. D. Desai: *J. Phys. Chem. Ref. Data*, **16** (1987), 109.
- 22) X. M. Yang, J. S. Jiao, R. C. Ding, C. B. Shi and H. J. Guo: *ISIJ Int.*, **49** (2009) 1828.
- 23) C. B. Shi, X. M. Yang, J. S. Jiao, C. Li and H. J. Guo: *ISIJ Int.*, **50** (2010), 1362.
- 24) J. H. Hildebrand and E. D. Eastman: *J. Am. Chem. Soc.*, **37** (1915), 2452.
- 25) R. C. Sharma and Y. A. Chang: *Metall. Mater. Trans. B*, **10B** (1979), 103.
- 26) Y. Y. Chuang, K. C. Hsieh and Y. A. Chang: *Metall. Mater. Trans. B*, **16B** (1985), 277.