CALCULATION MODEL OF SURFACE TENSION FOR ALLOY MELTS①

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ABSTRACT Based on the coexistence theory of metal melt involving compound formation and Butler's equation, a new model was proposed for the calculation of surface tension of alloy melt. This model established a specific correlation between the surface tension and mass action concentrations(activities) of bulk melt and surface melt on the basis of surface and bulk melt structures. It was shown that the calculated surface tensions for Fe-Si, Fe-Al alloy melt are in good agreement with the measured results. Furthermore, iso-surface tension lines for Fe-Si-Al alloy melt were also calculated.

Key words alloy melt surface tension activity mass action concentration

1 INTRODUCTION

It is of great importance for the estimation of surface tension for alloy melt. Many metallurgy phenomena, such as CO bubbles generation, inclusions formation in metal melt and its removing, the melt foaming, slag-metal emulsification, nitrogen absorption/desorption kinetics associated with surface active elements etc, are closely connected with surface tension of metallic melt. Until now, there have been many experimental results reported about surface tension[1-3] and some of them are closer. But as far as calculation model concerned, few works have been reported, especially the model based on the metal melt structure more little. This paper is to propose a new surface tension calculation model from the consideration of bulk and surface structure of metallic melt based on the Butler's equation. The calculated values by this model are in good agreement with experimental results.

2 SURFACE STRUCTURE MODEL

Since the coexistence theory of metallic melt involving compound formation was suggested by Zhang Jian[4], it had been successfully applied to many systems[4-7]. The distinguishing feature of this theory is to explore the thermodynamic properties from the structure characteristics of metallic melts. According to this theory, the type of structure unit of the melt, which only depends on the melt component and temperature, should be the same whether in bulk or in surface layer. Butler deduced a surface tension calculation equation based on the concept of chemical potential and surface energy[8]. Bulter's equation expressed as Eqn. (1) has been widely used[2, 3].

$$\sigma_{A-B} = \sigma_A + \frac{RT}{S_A}\ln\frac{a_A^s}{a_A^b} = \sigma_B + \frac{RT}{S_B}\ln\frac{a_B^s}{a_B^b} \quad (1)$$

where σ_A, σ_B and σ_{A-B} are the surface tensions of the pure component A, B and the system, respectively; R and T are the universal gas constant and temperature in Kelvin, respectively; S_A and S_B are the molar surface area of the pure component A and B, respectively; a_A^s and a_A^b are the activities of the component A of surface and bulk, respectively; a_B^s and a_B^b are the activities of the component B of surface and bulk, respectively.

On account of the fundamental considera-

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tion mentioned above, the viewpoints of this present model for surface tension calculation of metallic melt are summarized as follows:

(1) Surface structure units is the same as metal bulk, composed of atoms and moleculae.

(2) There are mobile equilibrium reactions between atoms and moleculae in surface layers, for example:

$$xA + yB = A_xB_y \quad (2)$$

(3) Chemical reactions in suface layer obey the mass action law. From Eqn. (2) we have

$$K = \frac{N^s_{A_xB_y}}{(N^s_A)^x (N^s_B)^y} \quad (3)$$

where N^s_A, N^s_B and $N^s_{A_xB_y}$ are the surface mass action concentration (surface activities) of A, B and A_xB_y component, respectively; K is the equilibrium constant of Eqn. (2).

(4) The relation of surface tension of melt system and mass action concentration of surface and bulk component conforms to the Butler's equation.

$$\sigma_{A\text{-}B} = \sigma_A + \frac{RT}{S_A}\ln\frac{N^s_A}{N^b_A} = \sigma_B + \frac{RT}{S_B}\ln\frac{N^s_B}{N^b_B} \quad (4)$$

where N^s_A and N^b_A are the surface and bulk mass action concentrations (activities) of component A, respectively; N^s_B and N^b_B are the surface and bulk mass action concentrations (activities) of component B, respectively.

3 APPLICATION TO ALLOY SYSTEMS

The above stated surface structure model has been successfully applied to Fe-Si, Fe-Al alloy melt systems for the calculation of surface tension. This model has also been used to predict the iso-surface tension lines of Fe-Si-Al ternary alloy melt.

3.1 Fe-Si melt

The mass action concentration calculation model of Fe-Si alloy melt has been deduced by Zhang Jian[5] and the structure units of this melt are determined as Fe, Si atoms and Fe_2Si, Fe_5Si_3, FeSi, $FeSi_2$ moleculae.

Assuming $N_1 = N_{Fe}$, $N_2 = N_{Si}$, $N_3 = N_{Fe_2Si}$, $N_4 = N_{Fe_5Si_3}$, $N_5 = N_{FeSi}$, $N_6 = N_{FeSi_2}$, and x_i represents the equilibrium mole fraction of component i; Σx_i represents the total mole fraction of component i, according to the chemical analysis; Σx represents the total equilibrium mole fraction of alloy system; N_i is the mass action concentration of component i, $N_i = x_i/\Sigma x$; superscripts "s" and "b" denote the "surface" and "bulk" of the alloy melt, respectively.

In the bulk of the melt, according to chemical equilibria (1420~1700 ℃)[5]:

$$2Fe(l) + Si(l) = Fe_2Si(l)$$
$$\Delta G^0_1/(J\cdot mol^{-1}) = -117630.84 + 21.13T$$
$$K_1 = \frac{N^b_3}{(N^b_1)^2(N^b_2)}, \quad N^b_3 = K_1(N^b_1)^2(N^b_2) \quad (5)$$

$$5Fe(l) + 3Si(l) = Fe_5Si_3(l)$$
$$\Delta G^0_2/(J\cdot mol^{-1}) = -295298.39 + 30.34T$$
$$K_2 = \frac{N^b_4}{(N^b_1)^5(N^b_2)^3}, \quad N^b_4 = K_2(N^b_1)^5(N^b_2)^3 \quad (6)$$

$$Fe(l) + Si(l) = FeSi(l)$$
$$\Delta G^0_3/(J\cdot mol^{-1}) = -158472.98 + 69.78T$$
$$K_3 = \frac{N^b_5}{(N^b_1)(N^b_2)}, \quad N^b_5 = K_3(N^b_1)(N^b_2) \quad (7)$$

$$Fe(l) + 2Si(l) = FeSi_2(l)$$
$$\Delta G^0_4/(J\cdot mol^{-1}) = -38163.07 - 5.47T$$
$$K_4 = \frac{N^b_6}{(N^b_1)(N^b_2)^2}, \quad N^b_6 = K_4(N^b_1)(N^b_2)^2 \quad (8)$$

The mass balances:

$$N^b_1 + N^b_2 + N^b_3 + N^b_4 + N^b_5 + N^b_6 = 1 \quad (9)$$
$$\Sigma x^b_{Fe} = \Sigma x^b(N^b_1 + 2N^b_3 + 5N^b_4 + N^b_5 + N^b_6) \quad (10)$$
$$\Sigma x^b_{Si} = \Sigma x^b(N^b_2 + N^b_3 + 3N^b_4 + N^b_5 + 2N^b_6) \quad (11)$$

In the surface layer of the molten melt, the similar equation forms to Eqns. (5) ~ (11) can be expressed as Eqns. (12) ~ (15).

$$\left.\begin{aligned} N^s_3 &= K_1(N^s_1)^2(N^s_2) \\ N^s_4 &= K_2(N^s_1)^5(N^s_2)^3 \\ N^s_5 &= K_3(N^s_1)(N^s_2) \\ N^s_6 &= K_4(N^s_1)(N^s_2)^2 \end{aligned}\right\} \quad (12)$$

$$N_1^s + N_2^s + N_3^s + N_4^s + N_5^s + N_6^s = 1 \quad (13)$$

$$\Sigma x_{Fe}^s = \Sigma x^s (N_1^s + 2N_3^s + 5N_4^s + N_5^s + N_6^s) \quad (14)$$

$$\Sigma x_{Si}^s = \Sigma x^s (N_2^s + N_3^s + 3N_4^s + N_5^s + 2N_6^s) \quad (15)$$

From Eqns. (14), (15), there are

$$\Sigma x_{Fe}^s = \frac{N_1^s + 2N_3^s + 5N_4^s + N_5^s + N_6^s}{N_1^s + N_2^s + 3N_3^s + 8N_4^s + 2N_5^s + 3N_6^s} \quad (16)$$

$$\Sigma x_{Si}^s = \frac{N_2^s + N_3^s + 3N_4^s + N_5^s + 2N_6^s}{N_1^s + N_2^s + 3N_3^s + 8N_4^s + 2N_5^s + 3N_6^s} \quad (17)$$

Butler's equation:

$$\sigma_{Fe} + \frac{RT}{S_{Fe}} \ln \frac{N_1^s}{N_1^b} = \sigma_{Si} + \frac{RT}{S_{Si}} \ln \frac{N_2^s}{N_2^b} \quad (18)$$

The combination of Eqns. (5) ~ (18) makes up the surface tension calculation model for Fe-Si alloy melt. The changes of bulk mass action concentrations with alloy compositions can be calculated by solving the Eqns. (5) ~ (11) and the detailed results are in Ref. [5]. On the above basis, the surface tension with alloy compositions will be evaluated by solving Eqns. (12), (13) and (18). The values of S_{Fe} and S_{Si} in Eqn. (18) are from Ref. [2]. Furthermore, the surface total mole fractions of components Fe and Si can be estimated from the Eqns. (16) and (17).

Fig. 1 shows the changes of bulk and surface mass action concentrations with the compositions of Fe in the melt bulk for Fe-Si system at 1 823 K. Both of N_{Fe}^b and N_{Si}^b exhibit negative deviations as a result of the formations of the four moleculae mentioned above in bulk melt. However, it is obvious that the surface mass action concentration of Si, N_{Si}^s, is higher than that of bulk, N_{Si}^b, which resulted from that component Si has lower surface tension and accumulates into surface layer from melt bulk. On the contrary, N_{Fe}^s is lower than N_{Fe}^b. Fig. 2 demonstrates the changes of surface mass action concentrations with surface concentrations and the changing tendency are similar to that of melt bulk[5].

The relationship between surface and bulk concentrations of Fe and Si is illustrated in Fig. 3. From this figure, Σx_{Si}^s is higher than Σx_{Si}^b, and Σx_{Fe}^s is lower than Σx_{Fe}^b, which are consistent with Fig. 1. The comparison of the calculated and the measured surface tensions shown in Fig. 4 is in good agreement, which verifies the

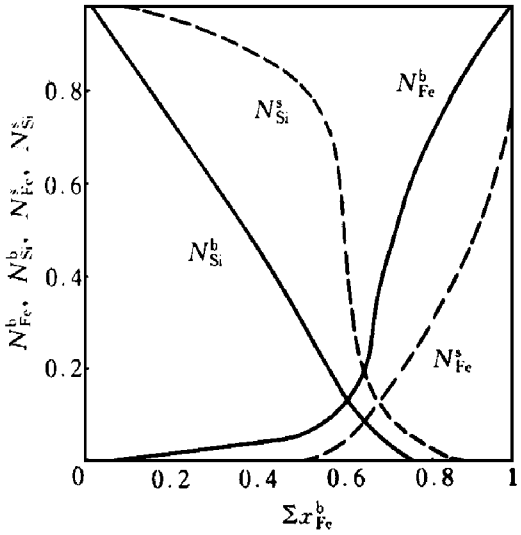

Fig. 1 Changes of surface and bulk mass action concentrations with Σx_{Fe}^b for Fe-Si alloy melt at 1 823 K

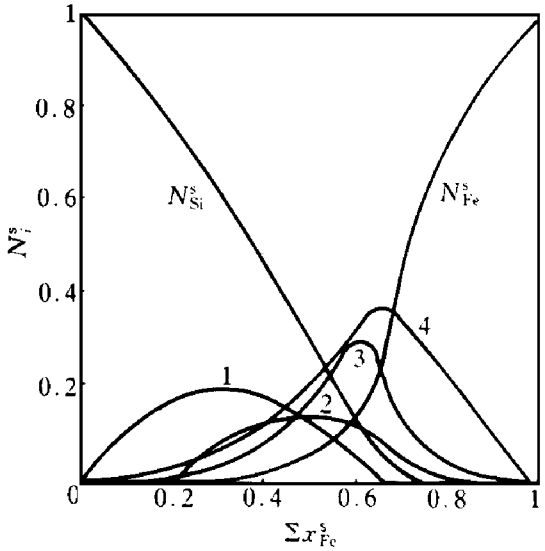

Fig. 2 Changes of surface mass action concentrations with Σx_{Fe}^s for Fe-Si alloy melt at 1 823 K

1 —$N_{FeSi_2}^s$; 2 —N_{FeSi}^s; 3 —$N_{Fe_5Si_3}^s$; 4 —$N_{Fe_2Si}^s$

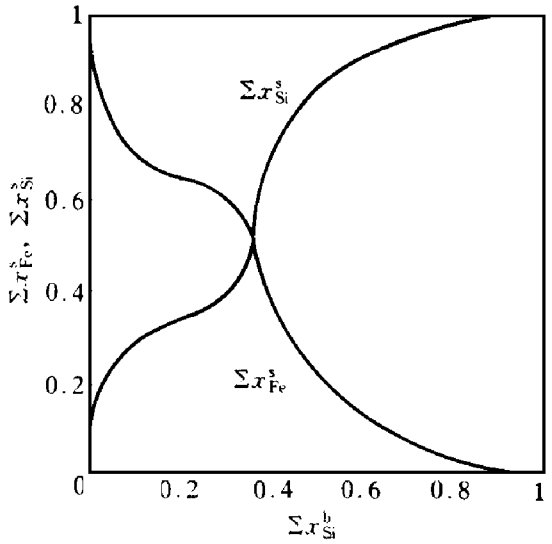

Fig. 3 Relationship of surface and bulk concentrations for Fe-Si alloy melt at 1 823 K

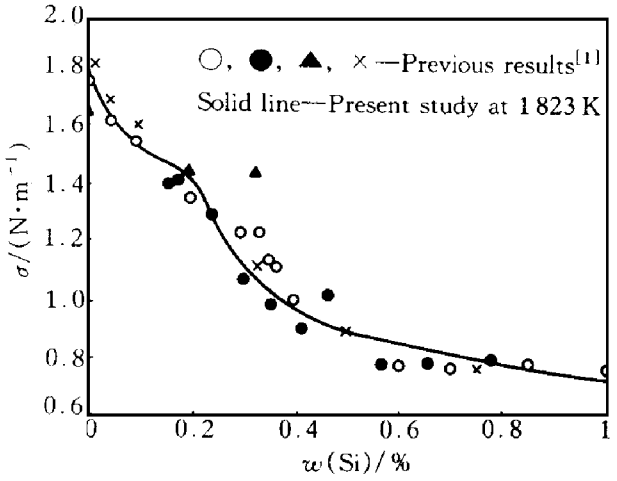

Fig. 4 Comparison of calculated surface tension with measured results for Fe-Si alloy melt at 1 823 K

above mentioned model is reasonable.

3.2 Fe-Al melt

The mass action concentration calculation model of Fe-Al alloy melt has been reported[9] and the structure units of this melt are determined as Fe, Al atoms and Fe_3Al, FeAl and $FeAl_2$ moleculae.

Assuming $N_1 = N_{Fe}$, $N_2 = N_{Al}$, $N_3 = N_{Fe_3Al}$, $N_4 = N_{FeAl}$, and $N_5 = N_{FeAl_2}$.

In the bulk of the melt, ther are following chemical equilibria (1 600 ℃)[9]:

$3Fe(l) + Al(l) = Fe_3Al(l)$

$$\Delta G^0_5 = -49\,460.0\ \text{J/mol}$$

$$K_5 = \frac{N^b_3}{(N^b_1)^3(N^b_2)},\quad N^b_3 = K_5(N^b_1)^3(N^b_2) \tag{19}$$

$Fe(l) + Al(l) = FeAl(l)$

$$\Delta G^0_6 = -28\,189.0\ \text{J/mol}$$

$$K_6 = \frac{N^b_4}{(N^b_1)(N^b_2)},\quad N^b_4 = K_6(N^b_1)(N^b_2) \tag{20}$$

$Fe(l) + 2Al(l) = FeAl_2(l)$

$$\Delta G^0_7 = -17\,196.0\ \text{J/mol}$$

$$K_7 = \frac{N^b_5}{(N^b_1)(N^b_2)^2},\quad N^b_5 = K_7(N^b_1)(N^b_2)^2 \tag{21}$$

and the mass balances:

$$N^b_1 + N^b_2 + N^b_3 + N^b_4 + N^b_5 = 1 \tag{22}$$

$$\Sigma x^b_{Fe} = \Sigma x^b(N^b_1 + 3N^b_3 + N^b_4 + N^b_5) \tag{23}$$

$$\Sigma x^b_{Al} = \Sigma x^b(N^b_2 + N^b_3 + N^b_4 + 2N^b_5) \tag{24}$$

In the surface layer of the alloy melt, the similar equation forms to Eqns. (19) ~ (24) can be expressed as Eqns. (25) ~ (28).

$$\left.\begin{aligned} N^s_3 &= K_5(N^s_1)^3(N^s_2)\\ N^s_4 &= K_6(N^s_1)(N^s_2)\\ N^s_5 &= K_7(N^s_1)(N^s_2)^2 \end{aligned}\right\} \tag{25}$$

$$N^s_1 + N^s_2 + N^s_3 + N^s_4 + N^s_5 = 1 \tag{26}$$

$$\Sigma x^s_{Fe} = \Sigma x^s(N^s_1 + 3N^s_3 + N^s_4 + N^s_5) \tag{27}$$

$$\Sigma x^s_{Al} = \Sigma x^s(N^s_2 + N^s_3 + N^s_4 + 2N^s_5) \tag{28}$$

From Eqns. (27), (28), there are

$$\Sigma x^s_{Fe} = \frac{N^s_1 + 3N^s_3 + N^s_4 + N^s_5}{N^s_1 + N^s_2 + 4N^s_3 + 2N^s_4 + 3N^s_5} \tag{29}$$

$$\Sigma x^s_{Al} = \frac{N^s_2 + N^s_3 + N^s_4 + 2N^s_5}{N^s_1 + N^s_2 + 4N^s_3 + 2N^s_4 + 3N^s_5} \tag{30}$$

Butler's equation:

$$\sigma_{Fe} + \frac{RT}{S_{Fe}}\ln\frac{N^s_1}{N^b_1} = \sigma_{Al} + \frac{RT}{S_{Al}}\ln\frac{N^s_2}{N^b_2} \tag{31}$$

The combination of Eqns. (19) ~ (26), (29) ~ (31) is the surface tension calculation model for Fe-Al alloy melt. The values of S_{Fe} and S_{Al} in Eqn. (31) are from Ref. [2]. The process of solving above model is similar to that of Fe-Si alloy model discussed before.

The comparison of the calculated and the measured surface tensions shown in Fig. 5 is in good agreement, which verifies the above mentioned model is reasonable.

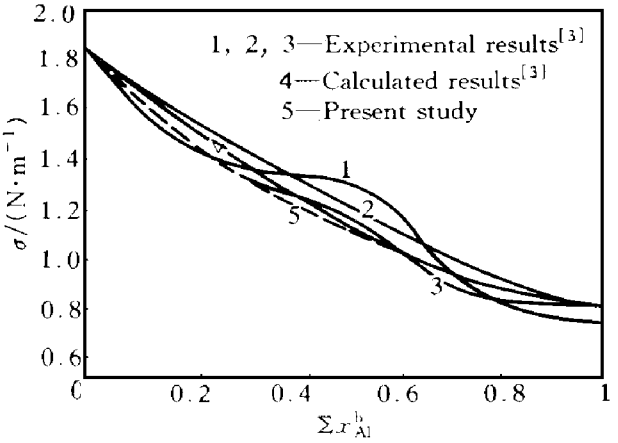

Fig. 5 Comparison of calculated values with reference's results for Fe-Al alloy melt at 1 873 K

3.3 Fe-Si-Al melt

On the basis of the mass action concentrations of both Fe-Si and Fe-Al alloy melts, the structural units of Fe-Si-Al ternary melt are determined as Fe, Si, Al atoms and Fe_3Si, Fe_2Si, Fe_5Si_3, FeSi, $FeSi_2$, Fe_3Al, FeAl, $FeAl_2$ moleculae, while the ternary compounds including Fe, Si and Al are not embraced in these structural units because the detailed reports about their existing in this melt are not enough.

Let $N_1 = N_{Fe}$, $N_2 = N_{Si}$, $N_3 = N_{Al}$, $N_4 = N_{Fe_2Si}$, $N_5 = N_{Fe_5Si_3}$, $N_6 = N_{FeSi}$, $N_7 = N_{FeSi_2}$, $N_8 = N_{Fe_3Al}$, $N_9 = N_{FeAl}$, $N_{10} = N_{FeAl_2}$.

In the melt bulk, the chemical equilibria are written as Eqn. (32) from Eqns. (5) ~ (8), (19) ~ (21).

$$\left.\begin{aligned} N^{b}_4 &= K_1 (N^{b}_1)^2 (N^{b}_2) \\ N^{b}_5 &= K_2 (N^{b}_1)^5 (N^{b}_2)^3 \\ N^{b}_6 &= K_3 (N^{b}_1)(N^{b}_2) \\ N^{b}_7 &= K_4 (N^{b}_1)(N^{b}_2)^2 \\ N^{b}_8 &= K_5 (N^{b}_1)^3 (N^{b}_3) \\ N^{b}_9 &= K_6 (N^{b}_1)(N^{b}_3) \\ N^{b}_{10} &= K_7 (N^{b}_1)(N^{b}_3)^3 \end{aligned}\right\} \quad (32)$$

The mass balances:

$$\sum_{i=1}^{10} N^{b}_i = 1 \quad (33)$$

$$\Sigma x^{b}_{Fe} = \Sigma x^{b} (N^{b}_1 + 2N^{b}_4 + 5N^{b}_5 + N^{b}_6 + N^{b}_7 + 3N^{b}_8 + N^{b}_9 + N^{b}_{10}) \quad (34)$$

$$\Sigma x^{b}_{Si} = \Sigma x^{b} (N^{b}_2 + N^{b}_4 + 3N^{b}_5 + N^{b}_6 + 2N^{b}_7) \quad (35)$$

$$\Sigma x^{b}_{Al} = \Sigma x^{b} (N^{b}_3 + N^{b}_8 + N^{b}_9 + 2N^{b}_{10}) \quad (36)$$

In the surface layer of the alloy melt, the similar equation forms to Eqns. (32) ~ (36) can be expressed as Eqns. (37) ~ (41).

$$\left.\begin{aligned} N^{s}_4 &= K_1 (N^{s}_1)^2 (N^{s}_2) \\ N^{s}_5 &= K_2 (N^{s}_1)^5 (N^{s}_2)^3 \\ N^{s}_6 &= K_3 (N^{s}_1)(N^{s}_2) \\ N^{s}_7 &= K_4 (N^{s}_1)(N^{s}_2)^2 \\ N^{s}_8 &= K_5 (N^{s}_1)^3 (N^{s}_3) \\ N^{s}_9 &= K_6 (N^{s}_1)(N^{s}_3) \\ N^{s}_{10} &= K_7 (N^{s}_1)(N^{s}_3)^2 \end{aligned}\right\} \quad (37)$$

$$\sum_{i=1}^{10} N^{s}_i = 1 \quad (38)$$

$$\Sigma x^{s}_{Fe} = \Sigma x^{s} (N^{s}_1 + 2N^{s}_4 + 5N^{s}_5 + N^{s}_6 + N^{s}_7 + 3N^{s}_8 + N^{s}_9 + N^{s}_{10}) \quad (39)$$

$$\Sigma x^{s}_{Si} = \Sigma x^{s} (N^{s}_2 + N^{s}_4 + 3N^{s}_5 + N^{s}_6 + 2N^{s}_7) \quad (40)$$

$$\Sigma x^{s}_{Al} = \Sigma x^{s} (N^{s}_3 + N^{s}_8 + N^{s}_9 + 2N^{s}_{10}) \quad (41)$$

Butler's equation:

$$\sigma_{Fe} + \frac{RT}{S_{Fe}} \ln \frac{N^{s}_1}{N^{b}_1} = \sigma_{Si} + \frac{RT}{S_{Si}} \ln \frac{N^{s}_2}{N^{b}_2} = \sigma_{Al} + \frac{RT}{S_{Al}} \ln \frac{N^{s}_3}{N^{b}_3} \quad (42)$$

The above Eqns. (32) ~ (42) are the calculation model of surface tension for Fe-Si-Al ternary alloy melt. The iso-surface tension lines calculated by solving these equations for Fe-Si-Al ternary alloy system are shown in Fig. 6. However, the validity of this model's result should be verified by reliably measured surface tensions which are not enough at present.

4 CONCLUSIONS

(1) Based on the coexistence theory of metallic melt involving compound and Butler's equation, a new model for the calculation of sur-

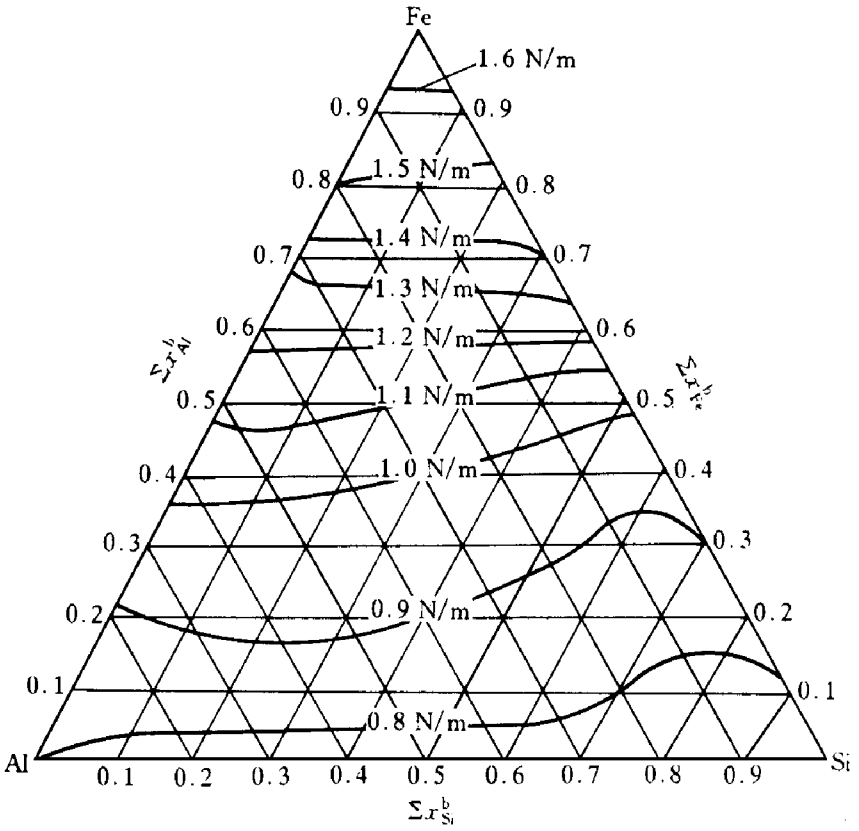

Fig. 6 Iso-surface tension lines for Fe-Si-Al alloy melt at 1 873 K

face tension of alloy melt is proposed.

(2) It is shown that the calculated surface tensions for Fe-Si and Fe-Al alloy melt are consistent with the measured results.

(3) Iso-surface tension lines for Fe-Si-Al alloy melt have been calculated.

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