1. Introduction

Surface phenomena such as surface tension of melt and adsorption of different components have very remarkable effect on the behavior of pyrometallurgical processes. For example, absorption and desorption of nitrogen during decarburization and secondary metallurgical treatments are related to the composition of gas–metal interphase. Surface tension also affects on the diameter of gas bubbles in liquid metal and slag. Then the reaction area as well as fluid flow dynamics of gas–liquid metal system is affected by surface tension. Although, the surface tension has an effect on fluid flows, it is generally assumed to be constant in CFD simulations.

Many studies of surface tension of binary iron alloys have been published in the literature. Surface tension of Fe–S system at 1 823 K was measured by Hajra and Divakar and Sahoo et al. studied Fe–S system as a function of temperature range of 1 823 to 1 923 K. Fe–O system was studied by Divakar and Hajra and Zhu and Mukai at 1 823 K. Takiuchi et al. measured the surface tension of Fe–O system temperature range of 1 823 to 2 023 K. Hajra and Divakar and Zhu and Mukai have also studied Fe–N system at 1 823 K.

Surface tensions of ternary iron alloy melts have been studied by several researchers during last years. Fe–O–N system was studied by Divakar and Hajra and Zhu and Mukai at 1 823 K. Gupt et al. studied Fe–S system as a function of temperature. Keene et al. as well as Hajra and Divakar researched Fe–S–O system temperature range of 1 873 to 1 923 K. There is also some published evaluations concerning quaternary systems like Fe–Ni–Cr–S in the temperature range of 1 800 to 3 000 K and Fe–C–S–O system at 1 823–1 923 K. However, it has not been found any evaluation of Fe–N–O–S system.

In the present work, the surface tension and the composition of gas–metal interphase of Fe–N–O–S system has been studied. Modified form of Butler’s equation and the derived values for the surface interaction parameters of the multi component system were used with the data available in the literature.

2. Derivation of the Surface Tension with Interaction Parameters for a Quaternary System

Model has been developed based on Butler’s equation. This equation uses the concepts of equating the chemical potential of a component of the interface to that of the bulk phase added with the value of the surface energy. It can be expressed as

\[ \sigma = \sigma_i^0 + \frac{RT}{S_i} \ln \left( \frac{a_i^n}{a_i} \right) \]  

where \( \sigma_i^0 \) is the surface tension of the pure component \( i \), \( a_i^n \) is the activity of the component \( i \) of the surface and \( a_i \) is the activity of the component \( i \) of the bulk phase, \( S_i \) is the molar surface area of the component \( i \), \( T \) is temperature and \( R \) is the molar gas constant.

Accordingly, Butler’s equation can be written for a quaternary system as

\[ \sigma = \sigma_i^0 + \frac{RT}{S_i} \ln \left( \frac{a_i^n}{a_i} \right) \]  

\[ = \sigma_1^0 + \frac{RT}{S_1} \ln \left( \frac{a_1^n}{a_1} \right) \]  

\[ = \sigma_2^0 + \frac{RT}{S_2} \ln \left( \frac{a_2^n}{a_2} \right) \]  

\[ = \sigma_3^0 + \frac{RT}{S_3} \ln \left( \frac{a_3^n}{a_3} \right) \]  

\[ = \sigma_4^0 + \frac{RT}{S_4} \ln \left( \frac{a_4^n}{a_4} \right) \]  

... (2)
Index 1 means the major component of the system, in this case Fe, and indexes 2–4 mean the minor components, such as S, O and N.

Using the infinitely dilute solution as standard state based on the Henrian law, these equations can be transformed as

\[
\sigma = \sigma_2^o + \frac{RT}{S_2} \ln \left( \frac{a_{m2}^{\infty}}{a_2} \right) = \sigma_2^o + \frac{RT}{S_2} \ln \left( \frac{a_{m2}^{\infty} \gamma_2^{m0}}{a_2^{\infty} \gamma_2^{m0}} \right) \quad (3)
\]

where \( \gamma_i^{\infty} \) is the activity coefficient of component \( i \) at infinitely dilution, \( a_i = x_i \gamma_i^\infty \) and \( a_{m}^m = x_{m} \gamma_{m}^\infty \).

From the latter form, the following formula is achieved

\[
\frac{a_{m2}^{\infty}}{a_2^{\infty}} = \exp \left( \sigma - \sigma_2^o \right) \frac{S_2}{RT} - \ln \left( \frac{\gamma_2^{m0}}{\gamma_2} \right) \quad (4)
\]

Moreover, it is known that \( a_i = x_i \gamma_i^\infty \) and \( a_{m}^m = x_{m} \gamma_{m}^\infty \), where \( x_i \) is the mole fraction of the component \( i \) of the bulk phase, \( x_{m} \) is the mole fraction of the component \( i \) of the surface phase, \( \gamma_i \) is the activity coefficient of the component \( i \) of the bulk phase based on the Henrian standard state and \( \gamma_{m}^m \) is the same coefficient for the surface phase.

So, from the above equations

\[
\frac{a_{m2}^{\infty}}{a_2^{\infty}} = \frac{x_{m} \gamma_m^{\infty}}{x_2 \gamma_2} \quad (5)
\]

This means

\[
\frac{x_{m2}^{m} \gamma_{m2}^{m0}}{x_2 \gamma_2} = \exp \left[ \left( \sigma - \sigma_2^o \right) \frac{S_2}{RT} - \ln \left( \frac{\gamma_2^{m0}}{\gamma_2} \right) \right] \exp \left[ \ln \left( \frac{\gamma_2^{m0}}{\gamma_2} \right) \right] \quad (6)
\]

Denote that

\[
\Phi_2^m = (\sigma_2^o - \sigma_2) \frac{S_2}{RT} - \ln \left( \frac{\gamma_2^{m0}}{\gamma_2} \right)
\]

when

\[
\frac{x_{m2}^{m} \gamma_{m2}^{m0}}{x_2 \gamma_2} = \exp (\Phi_2^m) \exp \left[ \left( \sigma - \sigma_2^o \right) \frac{S_2}{RT} + \ln \left( \frac{\gamma_2^{m0}}{\gamma_2} \right) \right] \quad (7)
\]

Since both \( \gamma_i^{m0} \) and \( \gamma_2 \) represent the value of the activity coefficient when the composition of component 2 (\( x_2 \)) and \( x_{m} \) approaches zero it can be concluded that \( \gamma_i^{m0} = \gamma_2^{m0} \) when the composition of the solvents in the bulk and on the surface are assumed to be nearly analogous. In that case, the Eq. (7) can be written on the following form.

\[
\frac{x_{m2}^{m} \gamma_{m2}^{m0}}{x_2 \gamma_2} = \exp (\Phi_2^m) \exp \left[ \left( \sigma - \sigma_2^o \right) \frac{S_2}{RT} \right] \quad (8)
\]

Similarly, can be transformed other part of Butler’s equation.

Finally, can be written as

\[
\sigma = \sigma_1^o + \frac{RT}{S_1} \ln \left( \frac{\gamma_1^{m0}}{\gamma_1} \right) + \frac{RT}{S_2} \ln \left( \frac{\gamma_2^{m0}}{\gamma_2} \right) \quad (9)
\]

where

\[
\Phi_1^o = (\sigma_1^o - \sigma_1) \frac{S_1}{RT} - \ln \left( \frac{\gamma_1^{m0}}{\gamma_1} \right)
\]

\[
\Phi_2^o = (\sigma_2^o - \sigma_2) \frac{S_2}{RT} - \ln \left( \frac{\gamma_2^{m0}}{\gamma_2} \right)
\]

\[
\Phi_3^o = (\sigma_3^o - \sigma_3) \frac{S_3}{RT} - \ln \left( \frac{\gamma_3^{m0}}{\gamma_3} \right)
\]

\[
\Phi_4^o = (\sigma_4^o - \sigma_4) \frac{S_4}{RT} - \ln \left( \frac{\gamma_4^{m0}}{\gamma_4} \right)
\]

The consistent relations\(^{13)}\) are used to represent the thermodynamic properties of the bulk phase of the quaternary system as

\[
\ln \gamma_1 = x_1 \epsilon_1^i(b) + x_3 \epsilon_3^i(b) + x_4 \epsilon_4^i(b) + \epsilon_1^i(b) \ln(1 - x_2) + \epsilon_3^i(b) \ln(1 - x_3) + \epsilon_4^i(b) \ln(1 - x_4)
\]

\[
+ \epsilon_1^i(b) \ln \left( \frac{(1 - x_1)(1 - x_2)}{1 - x_2} \right) + \epsilon_3^i(b) \ln \left( \frac{(1 - x_3)(1 - x_4)}{1 - x_4} \right) - \epsilon_4^i(b) \ln \left( \frac{(1 - x_4)(1 - x_3)}{1 - x_3} \right)
\]

\[
- \Psi(b) \ln \left( \frac{(1 - x_2)(1 - x_3)(1 - x_4)}{1 - x_2} \right) \quad (11)
\]

and other

\[
\ln \gamma_i = x_i \epsilon_i^j(b) + x_i \epsilon_i^j(b) + x_i \epsilon_i^j(b) + \epsilon_i^j(b) \ln(1 - x_i)
\]

\[
+ (\epsilon_i^j(b) - \epsilon_i^j(b)) \ln(1 - x_i) + \epsilon_i^j(b) \ln(1 - x_i)
\]

\[
+ \rho_{i}^{(j,k)}(b) \ln \left( \frac{(1 - x_i)(1 - x_k)}{1 - x_i} \right) \quad (12)
\]

where indexes \( i, j \) and \( k \) represent O, S and N.

Respectively, for the surface phase

\[
\ln \gamma_i = x_i \epsilon_i^j(m) + x_i \epsilon_i^j(m) + x_i \epsilon_i^j(m) + \epsilon_i^j(m) \ln(1 - x_i) + \epsilon_i^j(m) \ln(1 - x_i)
\]

\[
+ \epsilon_i^j(m) \ln(1 - x_i) + \epsilon_i^j(m) \ln(1 - x_i)
\]
\[-\epsilon_i^2(m) \ln \frac{(1-x_i^m)^2 (1-x_i^w)}{1-x_i^w x_i^m}\]
\[-\epsilon_i^2(m) \ln \frac{(1-x_i^w)^2 (1-x_i^m)}{1-x_i^w x_i^m}\]
\[-\epsilon_i^2(m) \ln \frac{(1-x_i^m)^2 (1-x_i^w)}{1-x_i^w x_i^m}\]
\[-\Psi(m) \ln \frac{(1-x_i^w)^2 (1-x_i^m)^2 (1-x_i^w-x_i^m)(1-x_i^w-x_i^m)}{(1-x_i^w)^2 (1-x_i^m)^2 (1-x_i^w-x_i^m)}\]

and other

\[\ln \gamma_i^m = x_i^m e_i^m(m) + x_i^n e_i^m(m) + x_i^u e_i^m(m)\]
\[+ (e_i^m(m) - e_i^m(m)) \ln (1-x_i^n)\]
\[+ (e_i^m(m) - e_i^m(m)) \ln (1-x_i^n)\]
\[+ \rho_i^{(3)}(m) \ln \frac{(1-x_i^n)(1-x_i^n)}{1-x_i^n - x_i^n}\]

In these equations the parameters \(e_i^m(m)\) and \(e_i^m(m)\) are the first order interaction parameters between different solute elements of the bulk and the surface phases, respectively. The parameters \(\rho_i^{(3)}(m)\) and \(\rho_i^{(3)}(m)\) are the second order ternary interaction parameters of the bulk and the surface phases, respectively and the parameters of the bulk and the surface phases, \(\Psi(b)\) and \(\Psi(m)\), are the consistent thermodynamic relation for the solvent component Fe of the quaternary system.

The part of the interaction parameters of the bulk phase is available in the literature and so the activity coefficients of the solute components are expressed according to the Henrian standard state. The parameters of the surface phase have been derived independently so that the thermodynamic properties of the surface phase of the system may be determined.

The first order interaction parameters between two solute elements, \(e_i^m(m)\) and \(e_i^m(m)\) (i, j = 2, 3, 4), can be derived from the differentials of the surface tension with respect to the experimental data.

The relation between \(x_i^m\) and \(x_i^m\) can be written from Butler’s equation as follow

\[(1-x_i^w-x_i^m-x_i^m) = (1-x_i^w-x_i^m-x_i^m)e_i^m\]
\[x_i^m = x_i^m e_i^m\]
\[x_i^m = x_i^m e_i^m\]
\[x_i^m = x_i^m e_i^m\]

\[\Phi_i = (\sigma - \sigma_i^0) \frac{S_i}{RT} - \ln \left(\frac{\gamma_i^w}{\gamma_i^m}\right)\]
\[\Phi_2 = (\sigma - \sigma_i^0) \frac{S_i}{RT} - \ln \left(\frac{\gamma_i^w}{\gamma_i^m}\right) + \Phi_0^0\]
\[\Phi_3 = (\sigma - \sigma_i^0) \frac{S_i}{RT} - \ln \left(\frac{\gamma_i^w}{\gamma_i^m}\right) + \Phi_0^0\] and

\[\Phi_i = (\sigma - \sigma_i^0) \frac{S_i}{RT} - \ln \left(\frac{\gamma_i^w}{\gamma_i^m}\right) + \Phi_0^0\]

From above equations, are obtained

\[1-x_i^w e_i^m-x_i^m e_i^m-x_i^m e_i^m = (1-x_i^w-x_i^m-x_i^m)\] (16)

The interaction parameters of the components of the surface can be derived from the second order differentials of the surface tension. This approach involves the repeated differentiation of Eq. (16) with respect to the composition of the solute components and the assumption of the boundary condition \(x_i^m \rightarrow 1\) (actually, \(x_i^m \rightarrow 1\), too) at each step of differentiation.

Now, can be note that

\[\ln \gamma_i^w = f(x_i^w, x_i^m, x_i^m), \quad \ln \gamma_i^w = f(x_i^w, x_i^m, x_i^m)\]
\[x_i^w = f(x_i^w, x_i^m, x_i^m), \quad x_i^m = f(x_i^w, x_i^m, x_i^m)\]

The complete differential of \(\gamma_i^m\) is expressed as

\[d \ln \gamma_i^m = \frac{\partial \ln \gamma_i^m}{\partial x_i^m} dx_i^m + \frac{\partial \ln \gamma_i^m}{\partial x_i^m} dx_i^m + \frac{\partial \ln \gamma_i^m}{\partial x_i^m} dx_i^m\]

Further

\[\frac{\partial \ln \gamma_i^m}{\partial x_i^m} = \frac{\partial \ln \gamma_i^m}{\partial x_i^m} + \frac{\partial \ln \gamma_i^m}{\partial x_i^m} + \frac{\partial \ln \gamma_i^m}{\partial x_i^m} + \frac{\partial \ln \gamma_i^m}{\partial x_i^m}\]

\[\frac{\partial \ln \gamma_i^m}{\partial x_i^m} = \frac{\partial \ln \gamma_i^m}{\partial x_i^m} + \frac{\partial \ln \gamma_i^m}{\partial x_i^m} + \frac{\partial \ln \gamma_i^m}{\partial x_i^m} + \frac{\partial \ln \gamma_i^m}{\partial x_i^m}\]

The equations of \(\ln \gamma_i^m\) and \(\ln \gamma_i^m\) are noted clearly that

\[\frac{\partial \ln \gamma_i^m}{\partial x_i^m} = \frac{\partial \ln \gamma_i^m}{\partial x_i^m} = \frac{\partial \ln \gamma_i^m}{\partial x_i^m} = 0\]

\[\frac{\partial \ln \gamma_i^m}{\partial x_i^m} = \frac{\partial \ln \gamma_i^m}{\partial x_i^m} = \frac{\partial \ln \gamma_i^m}{\partial x_i^m} = 0\]

Similarly, following relations can be shown to be valid

\[\frac{\partial \ln \gamma_i^m}{\partial x_i^m} = e_i^m(m), \quad \frac{\partial \ln \gamma_i^m}{\partial x_i^m} = e_i^m(m), \quad \frac{\partial \ln \gamma_i^m}{\partial x_i^m} = e_i^m(m)\]

\[\frac{\partial \ln \gamma_i^m}{\partial x_i^m} = e_i^m(m), \quad \frac{\partial \ln \gamma_i^m}{\partial x_i^m} = e_i^m(m), \quad \frac{\partial \ln \gamma_i^m}{\partial x_i^m} = e_i^m(m)\]

\[\frac{\partial \ln \gamma_i^m}{\partial x_i^m} = e_i^m(m), \quad \frac{\partial \ln \gamma_i^m}{\partial x_i^m} = e_i^m(m), \quad \frac{\partial \ln \gamma_i^m}{\partial x_i^m} = e_i^m(m)\]

\[\frac{\partial \ln \gamma_i^m}{\partial x_i^m} = e_i^m(b), \quad \frac{\partial \ln \gamma_i^m}{\partial x_i^m} = e_i^m(b), \quad \frac{\partial \ln \gamma_i^m}{\partial x_i^m} = e_i^m(b)\]

\[\frac{\partial \ln \gamma_i^m}{\partial x_i^m} = e_i^m(b), \quad \frac{\partial \ln \gamma_i^m}{\partial x_i^m} = e_i^m(b), \quad \frac{\partial \ln \gamma_i^m}{\partial x_i^m} = e_i^m(b)\]
It can be shown that \( \epsilon'(m) = \epsilon'(m) \) and \( \epsilon'(b) = \epsilon'(b) \).

Differentiating previous equations again with respect boundary condition \( x_i \rightarrow 1 \) gives

\[
\left( \frac{\partial^2 \ln \gamma_i^m}{\partial x_i^m} \right)_{x_i=1} = -\epsilon'_i(m)
\]

(21)

and

\[
\left( \frac{\partial^2 \ln \gamma_i}{\partial x_i^2} \right)_{x_i=1} = -\epsilon'_i(b), \quad \forall i, j, k = 2, 3, 4
\]

(22)

Moreover, have to be defined the differentials \( \partial x^m_i/\partial x_i \) and \( \partial x^m_i/\partial x_i \), (\( i, j \neq 1 \))

\[
\left( \frac{\partial x_i^m}{\partial x_i} \right)_{x_i=1} = \left( \frac{\partial x_i}{\partial x_i} e^{\Phi} + x_i \frac{\partial \Phi}{\partial x_i} \right)_{x_i=1} = e^{\Phi}
\]

\[
\left( \frac{\partial x_j^m}{\partial x_j} \right)_{x_j=1} = \left( \frac{\partial x_j}{\partial x_j} e^{\Phi} + x_j \frac{\partial \Phi}{\partial x_j} \right)_{x_j=1} = 0
\]

(23)

Using the all above differentials, one obtain to transmit the following differentials

\[
\frac{\partial \ln \gamma_i^m}{\partial x_i} = \epsilon'_i(m)e^{\Phi}, \quad \frac{\partial \ln \gamma_i^m}{\partial x_j} = \epsilon'_i(m)e^{\Phi}, \quad \frac{\partial \ln \gamma_i^m}{\partial x_k} = \epsilon'_i(m)e^{\Phi}
\]

\[
\frac{\partial \ln \gamma_i}{\partial x_i} = \epsilon'_i(b), \quad \frac{\partial \ln \gamma_i}{\partial x_j} = \epsilon'_i(b), \quad \frac{\partial \ln \gamma_i}{\partial x_k} = \epsilon'_i(b)
\]

(24)

Moreover,

\[
\frac{\partial \Phi_i}{\partial x_i} = \frac{S_1}{RT} \frac{\partial \sigma}{\partial x_i} - \frac{\partial \ln \gamma_i^m}{\partial x_i} + \frac{\partial \ln \gamma_i}{\partial x_i}
\]

\[
= \frac{S_1}{RT} \frac{\partial \sigma}{\partial x_i} - \frac{\partial \ln \gamma_i^m}{\partial x_i} + \frac{\partial \ln \gamma_i^m}{\partial x_j} + \frac{\partial \ln \gamma_i}{\partial x_j} + \frac{\partial \ln \gamma_i}{\partial x_k} + \frac{\partial \ln \gamma_i}{\partial x_l}
\]

\[
+ \frac{\partial \ln \gamma_i}{\partial x_i}, \quad (i, j, k = 2, 3, 4)
\]

(25)

\[
\frac{\partial^2 \Phi_i}{\partial x_i^2} = \frac{S_1}{RT} \frac{\partial^2 \sigma}{\partial x_i^2} - \frac{\partial^2 \ln \gamma_i^m}{\partial x_i^2} - \frac{\partial^2 \ln \gamma_i^m}{\partial x_j^2} - \frac{\partial^2 \ln \gamma_i^m}{\partial x_k^2} - \frac{\partial^2 \ln \gamma_i^m}{\partial x_l^2} + \frac{\partial^2 \ln \gamma_i}{\partial x_j^2} + \frac{\partial^2 \ln \gamma_i}{\partial x_k^2} + \frac{\partial^2 \ln \gamma_i}{\partial x_l^2}
\]

\[
= \frac{S_1}{RT} \frac{\partial^2 \sigma}{\partial x_i^2} - \frac{\partial^2 \ln \gamma_i^m}{\partial x_i^2} + \frac{\partial^2 \ln \gamma_i^m}{\partial x_i^2} + \frac{\partial^2 \ln \gamma_i}{\partial x_i^2}
\]

(26)

Differentiating both sides of the Eq. (16) with respect to \( x_2 \) gives
Imposing the boundary condition $x_1 \to 1$ to Eq. (31) yields rearrangement

$$
\left( \frac{\partial \Phi_1}{\partial x_2} \right)_{x_1=1} = 1 - e^{\Phi_1} \tag{32}
$$

Combining this result to Eq. (28) gives

$$
\left( \frac{\partial \sigma}{\partial x_2} \right)_{x_1=1} = \frac{RT}{S_1} (1 - e^{\Phi_1}) \tag{33}
$$

Similarly, can be transmitted equations of $(\partial \sigma/\partial x_3)_{x_1=1}$ and $(\partial \sigma/\partial x_3)_{x_1=1}$,

$$
\left( \frac{\partial \sigma}{\partial x_3} \right)_{x_1=1} = \frac{RT}{S_1} (1 - e^{\Phi_1}) \tag{34}
$$

$$
\left( \frac{\partial \sigma}{\partial x_3} \right)_{x_1=1} = \frac{RT}{S_1} (1 - e^{\Phi_1}) \tag{35}
$$

Now, differentiating both sides of the Eq. (31) again with respect to $x_1$ gives

$$
-2e^{\Phi_1} \frac{\partial^2 \Phi_1}{\partial x_2^2} - x_2 e^{\Phi_1} \left( \frac{\partial \Phi_1}{\partial x_2} \right)^2 - x_4 e^{\Phi_1} \left( \frac{\partial \Phi_2}{\partial x_2} \right)^2 - x_6 e^{\Phi_1} \left( \frac{\partial \Phi_3}{\partial x_2} \right)^2
$$

$$
= -2e^{\Phi_1} \frac{\partial \Phi_1}{\partial x_2} + (1 - x_2 - x_3 - x_4) e^{\Phi_1} \left( \frac{\partial^2 \Phi_1}{\partial x_2^2} + \left( \frac{\partial \Phi_1}{\partial x_2} \right)^2 \right)
$$

.......................(36)

Imposing the boundary condition $x_1 \to 1$ to Eq. (36) yields rearrangement

$$
-2e^{\Phi_1} \left( \frac{\partial \Phi_1}{\partial x_2} \right)_{x_1=1} = \left( \frac{\partial^2 \Phi_1}{\partial x_2^2} \right)_{x_1=1} + \left( \frac{\partial \Phi_1}{\partial x_2} \right)_{x_1=1}
$$

$$
-2 \left( \frac{\partial \Phi_1}{\partial x_2} \right)_{x_1=1} \tag{37}\\n$$

Combining Eq. (37) with Eqs. (28), (29) and (30) as well as applying Eq. (33) to this, gives

$$
\left( \frac{\partial^2 \sigma}{\partial x^2 \partial x_2} \right)_{x_1=1} = -2 \frac{RT}{S_1} e^{\Phi_1} \left[ \frac{S_2}{S_1} (1 - e^{\Phi_1}) - \varepsilon_3^2 (m) e^{\Phi_1} + \varepsilon_3^4 (b) \right]
$$

$$
+ \frac{RT}{S_1} (1 - (e^{\Phi_1})^2)
$$

$$
- \frac{RT}{S_1} (\varepsilon_3^2 (m) (e^{\Phi_1})^2 - \varepsilon_3^4 (b)) \tag{38}
$$

Note, that $(e^{\Phi_1})_{x_1=1} = e^{\Phi_1}$.

In the same way, can be transmitted equations of $(\partial^2 \sigma/\partial x_3 \partial x_4)_{x_1=1}$ and $(\partial^2 \sigma/\partial x_3 \partial x_4)_{x_1=1}$,

$$
\left( \frac{\partial^2 \sigma}{\partial x^2 \partial x_4} \right)_{x_1=1} = -2 \frac{RT}{S_1} e^{\Phi_1} \left[ \frac{S_2}{S_1} (1 - e^{\Phi_1}) - \varepsilon_3^2 (m) e^{\Phi_1} + \varepsilon_3^4 (b) \right]
$$

$$
+ \frac{RT}{S_1} (1 - (e^{\Phi_1})^2)
$$

$$
- \frac{RT}{S_1} (\varepsilon_3^2 (m) (e^{\Phi_1})^2 - \varepsilon_3^4 (b)) \tag{39}
$$

Furthermore, have to transmitted equations for $(\partial^2 \sigma/\partial x_3 \partial x_4)_{x_1=1}$ and $(\partial^2 \sigma/\partial x_3 \partial x_4)_{x_1=1}$. Differnetiating both sides of the Eq. (30) with respect $x_3$ and imposing the boundary condition $x_1 \to 1$ give

$$
-2e^{\Phi_1} \left( \frac{\partial \Phi_2}{\partial x_2} \right)_{x_1=1} - \frac{\partial \Phi_1}{\partial x_2} \left( \frac{\partial \Phi_3}{\partial x_2} \right)_{x_1=1}
$$

$$
\left( \frac{\partial \Phi_1}{\partial x_2} \right)_{x_1=1}
$$

$$
\left( \frac{\partial \Phi_1}{\partial x_2} \right)_{x_1=1}
$$

$$
\left( \frac{\partial \Phi_1}{\partial x_2} \right)_{x_1=1}
$$

Applying Eqs. (26) and (27) as well as Eqs. (33), (34) and (35) for this gives

$$
\left( \frac{\partial^2 \sigma}{\partial x^2 \partial x_4} \right)_{x_1=1} = - \frac{RT}{S_1} e^{\Phi_1} \left[ \frac{S_2}{S_1} (1 - e^{\Phi_1}) - \varepsilon_3^2 (m) e^{\Phi_1} + \varepsilon_3^4 (b) \right]
$$

$$
- \frac{RT}{S_1} e^{\Phi_1} \left[ \frac{S_2}{S_1} (1 - e^{\Phi_1}) - \varepsilon_3^2 (m) e^{\Phi_1} + \varepsilon_3^4 (b) \right]
$$

$$
- \frac{RT}{S_1} (1 - (e^{\Phi_1})^2)
$$

$$
\left( \frac{\partial \sigma}{\partial x_3} \right)_{x_1=1}
$$

$$
\left( \frac{\partial \sigma}{\partial x_3} \right)_{x_1=1}
$$

$$
\left( \frac{\partial \sigma}{\partial x_3} \right)_{x_1=1}
$$

$$
\left( \frac{\partial \sigma}{\partial x_3} \right)_{x_1=1}
$$

In the same way, can be transmitted equations of $(\partial^2 \sigma/\partial x_3 \partial x_4)_{x_1=1}$ and $(\partial^2 \sigma/\partial x_3 \partial x_4)_{x_1=1}$,

$$
\left( \frac{\partial^2 \sigma}{\partial x^2 \partial x_4} \right)_{x_1=1} = - \frac{RT}{S_1} e^{\Phi_1} \left[ \frac{S_2}{S_1} (1 - e^{\Phi_1}) - \varepsilon_3^2 (m) e^{\Phi_1} + \varepsilon_3^4 (b) \right]
$$

$$
- \frac{RT}{S_1} e^{\Phi_1} \left[ \frac{S_2}{S_1} (1 - e^{\Phi_1}) - \varepsilon_3^2 (m) e^{\Phi_1} + \varepsilon_3^4 (b) \right]
$$

$$
- \frac{RT}{S_1} (1 - (e^{\Phi_1})^2)
$$

$$
\left( \frac{\partial \sigma}{\partial x_3} \right)_{x_1=1}
$$

$$
\left( \frac{\partial \sigma}{\partial x_3} \right)_{x_1=1}
$$

$$
\left( \frac{\partial \sigma}{\partial x_3} \right)_{x_1=1}
$$

$$
\left( \frac{\partial \sigma}{\partial x_3} \right)_{x_1=1}
$$

\[\text{Note: ISIJ International, Vol. 47 (2007), No. 11}\]

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The used interaction parameters are presented in Table 1. C. H. P. Lupis\textsuperscript{14} gives a generalized relation of the following temperature coefficients of the parameters

\[ e_{e_i} = e_{e_i} + \frac{\eta_e}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]  

where \( e \) is one of the interaction parameters like \( e_{e_2}(m), e_{e_3}(m) \), \( e_{e_6}(b) \) etc. and \( \eta_e \) is the temperature coefficient pertaining to the parameter \( e \).

The parameters of the bulk and the surface phases, \( \Psi(b) \) and \( \Psi(m) \), are the consistent thermodynamic relation for the solvent component Fe of the quaternary system. Since there is no experimental data available on the Fe–S–O–N system to evaluate the quaternary parameters, these have been estimated using the Central Atoms Model proposed by Foo and Lupis.\textsuperscript{15} These parameters are related to the other quaternary parameters of the bulk and the surface phases \( e_i \) and \( \rho_i^{(b)} \) as follows

\[ \Psi(b) = \rho_i^{(2,3)}(b) + e_i^b(m) = \rho_i^{(2,3)}(b) + e_i^b(m) \]

\[ \Psi(m) = \rho_i^{(1,4)}(m) + e_i^m(m) = \rho_i^{(1,4)}(m) + e_i^m(m) \]

Now, when one of these parameters of the both phases is known, the other quaternary parameters are easily calculated using above relation. E. Foo and C. H. P. Lupis\textsuperscript{15} have derived the equation for the parameter \( \rho_N^{(b)} \). It gives that

\[ \rho_N^{(b)} = \frac{1}{12} \rho_{N}^{O} \]  

Now, there are all necessary interaction parameters for the calculation of surface tension and surface composition.

### 4. Calculation of Surface Tension and Surface Composition of Fe–N–O–S System

Based on the Eq. (9) the surface tension and the compositions of the surface can be calculated for each bulk compositions at the given temperature by Newton–Raphson root-finding technique. So can be finding the surface compositions, which is satisfying Butler’s equation in this condition. All used interaction parameters are presented in Table 1.

Moreover, the molar surface areas of iron, oxygen, sulphur and nitrogen as well as the surface tension of pure iron must be determined. The molar surface area of iron at any given temperature can be calculated using the following equation

\[ S_F = kN_0^{1/3} \rho^{2/3} \] 

where \( k \) is a geometric factor with a value of 1.091 for a closed packed lattice, \( N_0 \) is the Avogadro’s number and \( \rho \) is the molar volume of iron. Value of the molar surface areas of iron, oxygen, sulphur and nitrogen are represented in Table 2.

### Table 1. The used values of parameters.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( e_{e_2}(m) )</th>
<th>( e_{e_3}(m) )</th>
<th>( e_{e_6}(m) )</th>
<th>( e_{e_6}(b) )</th>
<th>( e_{e_6}(b) )</th>
<th>( e_{e_6}(b) )</th>
<th>( e_{e_6}(b) )</th>
<th>( e_{e_6}(b) )</th>
<th>( e_{e_6}(b) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1823 K</td>
<td>-0.95</td>
<td>-0.491</td>
<td>0.127</td>
<td>-0.498</td>
<td>2.555</td>
<td>-0.132</td>
<td>-0.264</td>
<td>-14.194</td>
<td>-10.901</td>
</tr>
<tr>
<td>1923 K</td>
<td>-0.491</td>
<td>-0.621</td>
<td>0.127</td>
<td>-0.498</td>
<td>2.555</td>
<td>-0.132</td>
<td>-0.264</td>
<td>-14.194</td>
<td>-10.901</td>
</tr>
</tbody>
</table>

\* at \( T = 1873 \) K

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_N^{(b)} )</td>
<td>12 ( \rho_N^{O} )</td>
</tr>
</tbody>
</table>

### Table 2. Molar surface areas.\textsuperscript{13,19}

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (m(^2)/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_F )</td>
<td>3724.28</td>
</tr>
<tr>
<td>( S_O )</td>
<td>4296.01</td>
</tr>
<tr>
<td>( S_S )</td>
<td>7692.0</td>
</tr>
<tr>
<td>( S_N )</td>
<td>10526.3</td>
</tr>
</tbody>
</table>

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The surface tension of pure iron depend temperature as follows:  
\[ \sigma_F^0(T) = \sigma_F^0(T_m) + \frac{d\sigma}{dT} (T - T_m) \quad \ldots(50) \]
where \( T_m \) is the melting point of pure iron with a value of 1,809 K, \( (d\sigma/dT) \) is the surface tension of pure iron at its melting point with value of 1.943 N/m.

Although in the present investigation the numerical algorithm for calculating of the surface tension is developed based on Newton–Raphson root-finding technique, it isn’t stable in all studied cases. The procedure can be unstable e.g. near a horizontal asymptote and a local extremum as well as it can oscillate with a bad initial choice of the root’s position. Part of this kind of problems can be avoided a good initial choice, but, in that case, the efficiency of the procedure can be lost. Newton–Raphson requires that the evaluation of both the function and its derivative at each iteration. This may be difficult, time-consuming even impossible if e.g. the function isn’t defined or its derivative doesn’t exist at all points. In cases of this study, these kinds of problems are very common.

5. Validation of Calculations

Validation of the calculations was made based on the measured surface tension data available in the published literature. Validation was started by binary systems (Fe–O, Fe–S and Fe–N) and then continued by ternary systems (Fe–S–O, Fe–O–N). According to the validation, agreement between the measured surface tension data and the developed surface tension model is very good. Generally mean deviation varies between 0.008–0.062 N/m depending on the studied system. Comparing the experimental data of Borodulin et al. of the Fe–S and Fe–N–S systems gives little bit larger mean deviations.

Comparison of calculated surface tension and measured values for Fe–S–O system at \( T = 1,923 \) K and Fe–O–N system at \( T = 1,823 \) K are presented in Table 3 and Table 4. Details of binary systems (Fe–O, Fe–S and Fe–N) and ternary systems (Fe–N–S and Fe–S–O) are presented in Tables 5–12.

### Table 3. 
Comparison of calculated and measured surface tension of Fe–S–O system at \( T = 1,923 \) K. (B. J. Keene et al.)

<table>
<thead>
<tr>
<th>Wt pct O</th>
<th>Wt pct S</th>
<th>( \sigma ) calc. (N/m)</th>
<th>( \sigma ) exp. (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.013</td>
<td>0.06</td>
<td>1.5005</td>
<td>1.510</td>
</tr>
<tr>
<td>0.058</td>
<td>0.046</td>
<td>1.9467</td>
<td>1.300</td>
</tr>
<tr>
<td>0.005</td>
<td>0.003</td>
<td>1.7445</td>
<td>1.756</td>
</tr>
<tr>
<td>0.007</td>
<td>0.007</td>
<td>1.6983</td>
<td>1.720</td>
</tr>
<tr>
<td>0.0057</td>
<td>0.0089</td>
<td>1.7045</td>
<td>1.752</td>
</tr>
<tr>
<td>0.0022</td>
<td>0.015</td>
<td>1.6975</td>
<td>1.721</td>
</tr>
<tr>
<td>0.0054</td>
<td>0.021</td>
<td>1.6524</td>
<td>1.650</td>
</tr>
<tr>
<td>0.021</td>
<td>0.094</td>
<td>1.5750</td>
<td>1.474</td>
</tr>
<tr>
<td>0.0069</td>
<td>0.021</td>
<td>1.6404</td>
<td>1.688</td>
</tr>
<tr>
<td>0.0097</td>
<td>0.02</td>
<td>1.6278</td>
<td>1.600</td>
</tr>
<tr>
<td>0.0048</td>
<td>0.028</td>
<td>1.6168</td>
<td>1.605</td>
</tr>
<tr>
<td>0.0068</td>
<td>0.013</td>
<td>1.6534</td>
<td>1.705</td>
</tr>
<tr>
<td>0.0045</td>
<td>0.064</td>
<td>1.5765</td>
<td>1.512</td>
</tr>
<tr>
<td>0.047</td>
<td>0.0052</td>
<td>1.4306</td>
<td>1.302</td>
</tr>
<tr>
<td>0.0044</td>
<td>0.002</td>
<td>1.7603</td>
<td>1.769</td>
</tr>
<tr>
<td>0.0043</td>
<td>0.046</td>
<td>1.5464</td>
<td>1.561</td>
</tr>
<tr>
<td>0.005</td>
<td>0.008</td>
<td>1.7170</td>
<td>1.790</td>
</tr>
<tr>
<td>0.005</td>
<td>0.003</td>
<td>1.7445</td>
<td>1.805</td>
</tr>
<tr>
<td>0.007</td>
<td>0.0037</td>
<td>1.7120</td>
<td>1.796</td>
</tr>
<tr>
<td>0.006</td>
<td>0.011</td>
<td>1.4917</td>
<td>1.379</td>
</tr>
<tr>
<td>0.042</td>
<td>0.018</td>
<td>1.4518</td>
<td>1.452</td>
</tr>
</tbody>
</table>

Mean Deviation 0.040

### Table 4. 
Comparison of calculated and measured surface tension of Fe–O–N ([S] 5 ppm) system at \( T = 1,823 \) K. (J. Zhu and K. Mukai)

<table>
<thead>
<tr>
<th>Wt pct O</th>
<th>( \sigma ) calc. (N/m)</th>
<th>( \sigma ) exp. (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0225</td>
<td>1.794</td>
<td>1.723</td>
</tr>
<tr>
<td>0.0225</td>
<td>1.009</td>
<td>1.410</td>
</tr>
<tr>
<td>0.0425</td>
<td>1.373</td>
<td>1.395</td>
</tr>
<tr>
<td>0.0475</td>
<td>1.246</td>
<td>1.240</td>
</tr>
<tr>
<td>0.0475</td>
<td>1.220</td>
<td>1.216</td>
</tr>
</tbody>
</table>

Mean Deviation 0.020

### Table 5. 
Comparison of calculated and measured surface tension of Fe–N system at \( T = 1,823 \) K. (Kozakevitch and Urban)

<table>
<thead>
<tr>
<th>Wt pct N</th>
<th>( \sigma ) calc. (N/m)</th>
<th>( \sigma ) exp. (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.021</td>
<td>1.794</td>
<td>1.723</td>
</tr>
<tr>
<td>0.031</td>
<td>1.724</td>
<td>1.709</td>
</tr>
<tr>
<td>0.043</td>
<td>1.637</td>
<td>1.651</td>
</tr>
<tr>
<td>0.045</td>
<td>1.622</td>
<td>1.625</td>
</tr>
</tbody>
</table>

Mean Deviation 0.028

### Table 6. 
Comparison of calculated and measured surface tension of Fe–N ([S] 5 ppm, [O] 20–30 ppm) system at \( T = 1,823 \) K. (J. Zhu and K. Mukai)

<table>
<thead>
<tr>
<th>Wt pct O</th>
<th>Wt pct N</th>
<th>( \sigma ) calc. (N/m)</th>
<th>( \sigma ) exp. (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00001</td>
<td>1.934</td>
<td>1.930</td>
<td></td>
</tr>
<tr>
<td>0.0250</td>
<td>1.769</td>
<td>1.753</td>
<td></td>
</tr>
<tr>
<td>0.0356</td>
<td>1.693</td>
<td>1.702</td>
<td></td>
</tr>
<tr>
<td>0.0432</td>
<td>1.636</td>
<td>1.634</td>
<td></td>
</tr>
</tbody>
</table>

Mean Deviation 0.008

### Table 7. 
Comparison of calculated and measured surface tension of Fe–O ([S] 5 ppm) system at \( T = 1,823 \) K. (J. Zhu and K. Mukai)

<table>
<thead>
<tr>
<th>Wt pct O</th>
<th>( \sigma ) calc. (N/m)</th>
<th>( \sigma ) exp. (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.019</td>
<td>1.886</td>
<td>1.860</td>
</tr>
<tr>
<td>0.0047</td>
<td>1.821</td>
<td>1.803</td>
</tr>
<tr>
<td>0.0056</td>
<td>1.802</td>
<td>1.767</td>
</tr>
<tr>
<td>0.0255</td>
<td>1.454</td>
<td>1.535</td>
</tr>
<tr>
<td>0.0264</td>
<td>1.443</td>
<td>1.488</td>
</tr>
<tr>
<td>0.0283</td>
<td>1.422</td>
<td>1.465</td>
</tr>
<tr>
<td>0.0500</td>
<td>1.248</td>
<td>1.337</td>
</tr>
<tr>
<td>0.0556</td>
<td>1.213</td>
<td>1.314</td>
</tr>
<tr>
<td>0.0604</td>
<td>1.184</td>
<td>1.290</td>
</tr>
<tr>
<td>0.0623</td>
<td>1.174</td>
<td>1.244</td>
</tr>
</tbody>
</table>

Mean Deviation 0.061

### Table 8. 
Comparison of calculated and measured surface tension of Fe–O system at \( T = 1,823 \) K. (Takiuchi et al.)

<table>
<thead>
<tr>
<th>Wt pct O</th>
<th>( \sigma ) calc. (N/m)</th>
<th>( \sigma ) exp. (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003</td>
<td>1.859</td>
<td>1.875</td>
</tr>
<tr>
<td>0.007</td>
<td>1.773</td>
<td>1.875</td>
</tr>
<tr>
<td>0.012</td>
<td>1.680</td>
<td>1.662</td>
</tr>
<tr>
<td>0.015</td>
<td>1.621</td>
<td>1.612</td>
</tr>
<tr>
<td>0.018</td>
<td>1.561</td>
<td>1.523</td>
</tr>
<tr>
<td>0.030</td>
<td>1.404</td>
<td>1.387</td>
</tr>
<tr>
<td>0.034</td>
<td>1.366</td>
<td>1.400</td>
</tr>
<tr>
<td>0.043</td>
<td>1.296</td>
<td>1.250</td>
</tr>
<tr>
<td>0.047</td>
<td>1.269</td>
<td>1.300</td>
</tr>
<tr>
<td>0.052</td>
<td>1.235</td>
<td>1.225</td>
</tr>
<tr>
<td>0.083</td>
<td>1.073</td>
<td>1.012</td>
</tr>
<tr>
<td>0.108</td>
<td>0.993</td>
<td>0.975</td>
</tr>
</tbody>
</table>

Mean Deviation 0.033

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6. Results and Discussion

Surface tension of Fe–O–S–N system at 1923 K temperature is presented in Fig. 1. With low oxygen (1 ppm), nitrogen (50 ppm) and sulphur (100 ppm) contents the surface tension of melt is about 1.73 N/m. If sulphur content is increased to 500 ppm or to 700 ppm surface tension of melt decreases to 1.52 N/m and 1.47 N/m respectively. Increase of oxygen content of melt decreases the surface tension of melt so that at the near oxygen solution limit [O] / H11005 2000 ppm surface tension is about 1.1 N/m. When oxygen content is higher than 800 ppm, nitrogen or sulphur contents have no any effects on the surface tension of system at the given temperature.

Traditional BOF process with large content range of sulphur can be presented by Fig. 1. Nitrogen content of melt is assumed to be 50 ppm although it can vary during carburization period between 10–100 ppm depending on the injected gases and the composition of steel melt. Calculations show that surface tension of melt decreases from 1.73 to 1.1 N/m during the decarburization period. This shows that surface tension can not be treated by a constant value when BOF process is studied.

Figure 2 shows that at the beginning of decarburization period the surface of the Fe–O–S–N melt is mainly covered by sulphur (about 80% of surface positions) if sulphur content of melt is 500 ppm. The relative fraction of oxygen and nitrogen on the surface phase is only 1–2%. Rest 20% of surface of melt droplet is covered by Fe. At the end of decarburization period, sulphur is replaced by oxygen and the surface phase of melt droplet is covered by oxygen (about 75% surface is covered by oxygen).

Surface tension of Fe–O–S–N melt with different nitrogen contents as a function of sulphur is presented in Fig. 3. Figure 3 shows clearly that nitrogen also works as a surface active elements and decreases surface tension of melt. Effect of nitrogen on the surface tension is higher with low contents of strong surface active elements such as sulphur and oxygen. Surface tension of semi-killed steel ([O] / H11005 20 ppm) with [N] / H11005 50 ppm content and very low sulphur content is about 1.80 N/m. If sulphur is alloyed up to the level of 500 ppm, the surface tension is lowered from 1.80 to 1.52 N/m when the nitrogen content of the melt is 50 ppm. The decrease in the surface tension due to similar sulphur addition is from 1.71 to 1.48 N/m and from 1.60 to 1.40 N/m for the melts with the nitrogen content of
200 ppm and 500 ppm respectively.

The relative fractions of the oxygen, sulphur and nitrogen in the metal/gas-interface as a function of the sulphur content in the bulk phase are presented in the Fig. 4. As a surface active element, the oxygen covers approximately 15% of the surface when the sulphur content of the melt is close to zero. The amount of oxygen on the surface decreases with the increasing sulphur content and is approximately 1% with sulphur content of 0.05%. Inverse behavior is observed when the sulphur content of the melt is held constant and the amount of oxygen in the melt is increased. With high sulphur contents the metal/gas-interface is mostly covered with sulphur so that its content on the surface being over 1000 times higher than the amount in the bulk phase. The fraction of nitrogen on the interface is lowered from 6 to 3% when the sulphur content is increased from 0 to 0.05%.

Figure 3 demonstrates that surface tension decreases because of high alloying of nitrogen and sulphur also during secondary metallurgical treatments although decrease is not as remarkable as during decarburization. Furthermore, the composition of gas–metal interphase changes dramatically (Fig. 4). It can be assumed that this effects also on reactions during treatments in ladle.

7. Conclusion

In the present work, surface tension and surface composition of gas–iron alloy interphase were calculated for Fe–N–S–O system based on Butler’s equations. The calcu-
lated values are found to be in very good agreement with published experimental data in literature.

Simulations showed that if the contents of strong surface active elements such as sulphur and oxygen are low, nitrogen also works as a surface active element and decreases surface tension of melt. According to the calculations, the surface tension of steel in traditional BOF process changes from 1.73 to 1.1 N/m. Furthermore, it decreases due to high alloying of nitrogen and sulphur also during secondary metallurgical treatments although decrease is not as remarkable as during decarburization. Hence the surface tension can’t be assumed to be constant especially when fluid flows of BOF were studied. The compositions of the surface phases are totally different than bulk phases because of the differences in surface activity of solute elements. This difference affects significantly properties of the interphase.

Acknowledgement

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