Abstract

The present work is focused on the comparison of numerically and experimentally obtained values of surface tension of oxide systems forming base of the casting powders. The numerically obtained data were studied by several different types of models.

The ternary system of SiO$_2$-CaO-Al$_2$O$_3$ which presents a simplified base of the casting powders was submitted to the experiment. For mathematic calculation of the surface tension the semi empirical models including the modifications of Butler’s equation and Chou model were evaluated as suitable. Due to high rate of universality the model utilizing Butler’s equation can be extended in the poly-component systems. Two modifications of Butler’s equation were used for calculation of the surface tension in this work. These modifications use either ionic distance of components or ionic radii for evaluation. Chou model represents a semi empirical geometric model which enables the calculation of wide spectrum of ternary system physical-chemical properties. The input data for calculation per this model were obtained by experimental measurement. The results of simulation were compared with experimentally obtained values of the surface tension.

With regard to relatively higher temperatures of measurement and character of the ternary system the method of a sessile drop was chosen as an optimal method for obtaining experimental data. Using of this method the changes of temperature dependences of the concentration line surface tension with growing content of CaO was studied.

The very good accordance between experimental data and theoretical evaluations was found for semi empirical Chou model using experimental input data. The model based on the Butler’s equation for random ionic compounds is rather suitable for order estimation of the surface properties.

Key words: surface tension, oxidic melts, ternary system

1. INTRODUCTION

The surface tension of molten oxidic systems is one of important parameters for the control of interfacial phenomena in the continuos-casting process of steelmaking. Oxidic systems form the basis of the casting powders. During the production process the casting powder in contact with molten slag is being smelted and creates a protective film – molten slag. Among other things the created slag also has to absorb inclusions from the steel. Therefore these systems have to, besides of other required physical – chemical parameters, show appropriate surface tension [1].

Experimental research of these phenomena is technically demanding and largely limited by the necessity to operate at high temperatures. That is the reason why the model studies represent an important role in this research area. In recent years many models dealing with the numerical calculation of surface tension have been developed. Nevertheless, the models still face the problem of dissonance of experimentally obtained values and calculated values because of the complexity of process between slag and metal, character of slag systems and absence of thermodynamic data.
2. EXPERIMENT

The synthetic ternary system SiO₂ – CaO – Al₂O₃ was created. In this system the same fractions of majority components of oxidic system used as a base of casting powders was preserved. The chemical composition of ternary system is shown in Table 1.

<table>
<thead>
<tr>
<th>Component</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>47.20</td>
</tr>
<tr>
<td>CaO</td>
<td>36.90</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>15.90</td>
</tr>
</tbody>
</table>

To the ternary system in Table 1 the concentration line with additions of 3 wt% CaO was created (i.e. 39.9; 42.9; 45.9; 48.9; 51.9 wt% CaO).

4. 1 Experimental method

Considering the character of the measured system the method of sessile drop was chosen. This method is based on automatic recognition of geometric shape of drop, which is sessile on non-wettable plate. The recognition of the drop shape is divided in two steps. Firstly, it is estimated the approximate height of the drop in the image and secondly, the contour segments of the drop are found. For evaluation of the image it is used Laplace – Youg equation [2,3].

3. MATHEMATICAL MODELING

For mathematical modeling semi – empirical models operative with modifications of Butler’s equation and Chou model were used.

3. 1 Modified Butler’s equation using ionic radii of particular components


The following equations formulate used mathematic model:

\[
\sigma = \sigma_{SiO_2} + \frac{RT}{A_{SiO_2}} \cdot \ln \frac{M^{SiO_2}}{M^{SiO_2}} \\
\sigma = \sigma_{CaO} + \frac{RT}{A_{CaO}} \cdot \ln \frac{M^{CaO}}{M^{CaO}} \\
\sigma = \sigma_{Al_2O_3} + \frac{RT}{A_{Al_2O_3}} \cdot \ln \frac{M^{Al_2O_3}}{M^{Al_2O_3}}
\]

where

\[
M^{P_{SiO_2}} = \left\{ \frac{R_{Si^{4+}} \cdot N_{P_{SiO_2}}}{R_{SiO_4^{2-}}} \right\}
\]

\[
M^{P_{CaO}} = \left\{ \frac{R_{Ca^{2+}} \cdot N_{P_{CaO}}}{R_{O_2^{-}}} + \frac{R_{Al^{3+}} \cdot N_{P_{Al_2O_3}}}{R_{O_2^{-}}} \right\}
\]
Note: Superscripts P indicate the surface and bulk.

\( \sigma \) is calculated the surface tension [mN/m],
\( \sigma_i \) is the surface tension of the pure molten component [mN/m],
\( R \) is the gas constant [J.K\(^{-1}\).mol\(^{-1}\)],
\( R_i \) are the radii of the cation and the anion [m],
\( T \) is the absolute temperature [K],
\( N_p^i \) is the mole fraction of the component \( i \) in phase \( P \) [1],
\( A_i \) is the molar surface area in monolayer of pure molten component \( i \) [m\(^3\).mol\(^{-2}\)].

\[
A_i = L \cdot N_a^{1/3} \cdot V_i^{2/3}
\]

where \( L \) is the correction factor resulting from the surface structure [1],
\( N_o \) is Avogadro number \([6.022045.10^{23} \text{ mol}^{-1}]\),
\( V_i \) is the molar volume of pure liquid \( i \) [m\(^3\).mol\(^{-1}\)].

Input values for \( V_i, \sigma_i, R_i \) were taken from the literature [6], [5].

### 3.2 Modified Butler’s equation using ionic distances of components

Authors of the work [7] created another thermodynamic model based on Butler’s equation. This model exchanged ionic radii of cation and anion for ionic distance of particular components.

To calculate the surface tension the equations were used as follows:

\[
\sigma = \sigma_{SiO_2} + \frac{RT}{A_{SiO_2}} \cdot \ln \frac{D_{SiO_2}^S}{D_{SiO_2}^B}
\]

\[
\sigma = \sigma_{CaO} + \frac{RT}{A_{CaO}} \cdot \ln \frac{D_{CaO}^S}{D_{CaO}^B}
\]

\[
\sigma = \sigma_{Al_2O_3} + \frac{RT}{A_{Al_2O_3}} \cdot \ln \frac{D_{Al_2O_3}^S}{D_{Al_2O_3}^B}
\]

where

\[
D_{SiO_2}^S = \frac{N_{SiO_2}^S \cdot A_{SiO_2}^S}{\sum N_i^S \cdot d_i^S}
\]

\[
D_{SiO_2}^B = \frac{N_{SiO_2}^B \cdot d_{SiO_2}^B}{\sum N_i^B \cdot d_i^B}
\]
In Eqs. (11) to (13) $d_i$ is ionic distance of component $i$ in the surface phase and in the bulk phase [m], and other parameters have the same meaning as the previous model.

The individual input values were taken from literature [7], [8].

3.3 Chou model

A new model developed by authors of the work [9], [10], is introduced to calculate the surface tension of ternary system with limited solubility, using the equilateral triangle.

This geometrical model comes out from the basic relation:

$$\sigma = W_A \cdot \sigma_A + W_B \cdot \sigma_B + W_C \cdot \sigma_C $$  \hspace{1cm} \text{(14)}

Where

$$W_A = \frac{S_{\Delta OB'C'}}{S_{\DeltaAB'C'}}$$ \hspace{1cm} \text{(15)}

$$W_B = \frac{S_{\DeltaOC'A'}}{S_{\DeltaAB'C'}}$$ \hspace{1cm} \text{(16)}

$$W_C = \frac{S_{\DeltaOA'B'}}{S_{\DeltaAB'C'}}$$ \hspace{1cm} \text{(17)}

$$S_{\DeltaAB'C'} = \frac{\sqrt{3}}{4} \begin{vmatrix} x_1^A & x_2^A & x_3^A \\ x_1^B & x_2^B & x_3^B \\ x_1^C & x_2^C & x_3^C \end{vmatrix}$$ \hspace{1cm} \text{(18)}

$$S_{\DeltaOC'A'} = \frac{\sqrt{3}}{4} \begin{vmatrix} x_1^O & x_2^O & x_3^O \\ x_1^A & x_2^A & x_3^A \\ x_1^C & x_2^C & x_3^C \end{vmatrix}$$ \hspace{1cm} \text{(19)}

$$S_{\DeltaOA'B'} = \frac{\sqrt{3}}{4} \begin{vmatrix} x_1^O & x_2^O & x_3^O \\ x_1^A & x_2^A & x_3^A \\ x_1^B & x_2^B & x_3^B \end{vmatrix}$$ \hspace{1cm} \text{(20)}

The basic process of solving the introduced equations (14) – (21) was following:
1. The miscible area of the ternary system in equilateral triangle was selected (Fig. 1).

2. On the borderline of this area three initial points were selected. (In this solution, the peaks of inside triangle.)

3. To compare the calculated data, the experimentally measured points were recorded into the bordered area. These points are denoted individually as points “O”.

4. Connecting each initial point with point “O” three triangles ΔOA’B’, ΔOA’C’ and ΔOC’B’ originate. Using the coordinates of these triangles the equations (18) – (21) are calculated.

5. The surface tension of initial points A’, B’ and C’ for the equation (14) was obtained by experimental measurement.

4. RESULTS

4.1 Modified Butler’s equation using ionic radii of particular components

The calculation of the surface tension for ternary system SiO₂ – CaO – Al₂O₃ was realized using modified Butler’s equation (Eqs. (1) – (7)). The surface tension temperature dependences of concentration range were observed (Fig. 2). System of equations of this model was solved using mathematical software MATHCAD. For the calculation the modified Newton’s method was chosen.

![Fig. 2](image.jpg)

Fig. 2: The temperature dependence of surface tension of concentration line with addition of CaO calculated using a modified Butler’s model using ionic radii of components.

4.2 Modified Butler’s equation using ionic distances of components

Figure 3 shows the temperature dependence of surface tension of the ternary system with addition of CaO. The data were obtained from numerical calculation using modified Butler’s equation (Eqs.(8)-(13)). As with previous model, the calculations were performed using modified Newton’s method in sphere of software MATHCAD.
Fig. 3: The temperature dependence of surface tension of concentration line with addition of CaO calculated using a modified Butler’s model with ionic distances of components.

4.3 Chou model

Also the calculation of surface tension using Chou model was performed. The calculation was realized according to formulas (14) – (21). The results are shown in figure 4.

Fig. 4: The temperature dependence of surface tension of concentration line with addition of CaO calculated using Chou model.

5. DISCUSSION

The surface tension temperature dependences of laboratory prepared ternary system SiO₂ – CaO – Al₂O₃ were obtained using selected mathematical models. The calculated values were compared with experimentally measured values.

The first of the presented models is the modified Butler’s model. For calculation of the surface tension two modifications of Butler’s equation were used in this work; Butler’s model working with ionic radii and ionic distances of components. Figures 2 and 3 show the surface tension increasing tendency in connection with temperature and with increasing content of CaO.

When the numerical calculated values of surface tension using Butler’s equation with ionic radii were compared with experimentally gained data the average deviation 21 % was obtained (Fig 5).
The Butler’s equation using ionic distances of components in comparison with experimentally data showed the smaller average deviation 16% (Fig. 6). It follows, that this model works with higher accuracy and it better reflects the real behavior of system.

Nevertheless, because of high deviations, both modifications of Butler’s equation may be used for estimation of orientation and ordinal values of surface tension only.

On the basis of the work of Chou [9], [10] another thermodynamic model was used. The input parameters for the evaluation of surface tension using this model were obtained by experimentally measurement. The surface tension of input points A’, B’, C’ was obtained using the method of a sessile drop.

The increasing tendency of the surface tension with increasing content of CaO (Fig. 4) is observed as with previous models. The trend of temperature dependence shows the moderate decrease of surface tension with temperature. Figure 7 shows the comparison of numerically calculated values using Chou model with experimentally measured data. This model provides very good results with the average error 5%.

The advantage of both models base of modified Butler’s equation consists in higher universality and applicability to any systems, but in the calculation it can not include to the possible phase or chemical transformations resulting from the surface tension experimental measurement. In the case of Chou model with experimentally measured input data this deficiency is possible to some extent eliminate.
6. CONCLUSION

In the presented work the selected thermodynamic models for calculation of the surface tension of studied system were tested. The functionality of these models was tested by comparison of surface tension experimental results with theoretically calculated values.

The obtained results can be summarized as follows:

- The Butler’s equation using ionic radii and ionic distances of components is partly usable for calculation of the ternary systems surface tension. The results may be used as orientation values only.
- For the tested SiO₂ – CaO – Al₂O₃ ternary system Chou model was found as suitable. When the calculated data and experimentally obtained values were compared, the deviation not exceeding 5% was found.

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LITERATURE


