MODELLING OF SURFACE PROPERTIES OF OXIDE MELTS WITH VARIABLE BASICITY

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Abstract

The subject of this work is the comparison of numerically obtained values of surface tension using different types of models and experimentally measured data of surface tension of oxide systems.

The ternary system of CaO-Al₂O₃-SiO₂, which presents simplified base of the casting powders used in technological process, was submitted to the experiment. For mathematic calculation of surface tension the semi empirical models resulting from Butler’s equation and Chou model were evaluated as suitable. Further the functionality of empiric model based on theory of regular ionic solution was tested. Due to high rate of universality the model utilizing the Butler’s equation can be extended in the poly-component systems. Chou model represents model that enables the calculation of wide spectrum of the ternary systems physical-chemical properties. The results of simulation were compared with experimentally obtained values of surface tension.

With regard to relatively higher temperatures of measurement and character of ternary system a sessile drop method was chosen as optimal method for obtaining experimental data. The changes of temperature dependences of surface tension of concentration line with growing content of the component SiO₂ were studied by using this method.

Keywords: surface tension, molten slag, mathematical modelling

1. INTRODUCTION

Surface tension of molten slag systems is important physical-chemical property, which is directly related to technological processes in steelmaking [1, 2, 3]. It is not always possible to find the relevant data on surface tension of molten slag systems, since these are poly-component oxidic-fluoride systems and experimental research is highly demanding and limited in great extent by the necessity to work under high temperatures. That’s why modelling studies play in this area such an important role. In spite of the fact that lately numerous models dealing with numeric calculations of surface tension have been developed, they steel struggle with the problem of disagreement of experimentally obtained data with calculated values due to complexity of processes running between slag and metal, and also due to character of slag systems.

The submitted work deals with verification of functionality of three mathematical models for calculation of surface tension in the system CaO-Al₂O₃-SiO₂ with various degrees of basicity.

2. EXPERIMENT

Ternary system CaO-Al₂O₃-SiO₂, which represents a simplified basis of casting powders used in technological practice, was chosen for presentation of results. A concentration line with increments of 3wt. % of SiO₂ was created for this system. Its chemical composition is given in table 1.

Verification of functionality of mathematical models an experimental measurement of surface tension by sessile drop technique was realised [4].
3. MATHEMATICAL MODELLING

3.1 Modified Butler’s equation using ionic distances of components

Tanaka et al. [5], developed a model for determination of surface tension of molten oxidic systems, based on the Butler's equation and on the procedure proposed by Speiser et al. [6]. They expressed the modified Butler’s equation by ion distances of pure oxides participating in the system in the following manner:

\[
\sigma = \sigma_{SiO_2} + \frac{RT}{A_{SiO_2}} \ln \frac{D_{SiO_2}^S}{D_{SiO_2}^B} \\
\sigma = \sigma_{CaO} + \frac{RT}{A_{CaO}} \ln \frac{D_{CaO}^S}{D_{CaO}^B} \\
\sigma = \sigma_{Al_2O_3} + \frac{RT}{A_{Al_2O_3}} \ln \frac{D_{Al_2O_3}^S}{D_{Al_2O_3}^B}
\]

where

\[
D_{SiO_2}^S = \frac{N_{SiO_2}^S \cdot d_{SiO_2}^S}{\sum N_i^S \cdot d_i^S}, \quad D_{SiO_2}^B = \frac{N_{SiO_2}^B \cdot d_{SiO_2}^B}{\sum N_i^B \cdot d_i^B}
\]

\[
D_{CaO}^S = \frac{N_{CaO}^S \cdot d_{CaO}^S}{\sum N_i^S \cdot d_i^S}, \quad D_{CaO}^B = \frac{N_{CaO}^B \cdot d_{CaO}^B}{\sum N_i^B \cdot d_i^B}
\]

\[
D_{Al_2O_3}^S = \frac{N_{Al_2O_3}^S \cdot d_{Al_2O_3}^S}{\sum N_i^S \cdot d_i^S}, \quad D_{Al_2O_3}^B = \frac{N_{Al_2O_3}^B \cdot d_{Al_2O_3}^B}{\sum N_i^B \cdot d_i^B}
\]

\[
\sigma \text{ is calculated the surface tension [mN/m],} \\
\sigma_i \text{ is the surface tension of the pure molten component [mN/m],} \\
R \text{ is the gas constant [J.K^{-1}.mol^{-1}],} \\
d_i \text{ is ionic distance of the component } i \text{ in the surface phase and in the bulk phase [m],} \\
T \text{ is the absolute temperature [K],} \\
N_i^{P,S} \text{ is the mole fraction of the component } i \text{ in phase } P, \\
A_i \text{ is the molar surface area in monolayer of pure molten component } i \text{ [m}^3\text{.mol}^{-2}].
\]

Individual input data were taken from the works [5] and [7].
3.2 Chou model

This geometric model [8, 9] enables calculation of surface tension of liquid phase of ternary system with limited area of solubility, with use of equilateral triangle.

It is based on the following basic relation:

$$\sigma = W'_A \cdot \sigma_A' + W'_B \cdot \sigma_B' + W'_C \cdot \sigma_C'$$  \hspace{1cm} (7)

where

$$W'_A = \frac{S_{\Delta OB'C'}}{S_{\Delta AB'C'}}$$  \hspace{1cm} (8)
$$W'_B = \frac{S_{\Delta OC'A'}}{S_{\Delta AB'C'}}$$  \hspace{1cm} (9)
$$W'_C = \frac{S_{\Delta OA'B'}}{S_{\Delta AB'C'}}$$  \hspace{1cm} (10)

$$S_{\Delta AB'C'} = \frac{\sqrt{3}}{4} \begin{vmatrix}
    x_1^A' & x_2^A' & x_3^A' \\
    x_1^B' & x_2^B' & x_3^B' \\
    x_1^C' & x_2^C' & x_3^C'
\end{vmatrix}$$  \hspace{1cm} (11)

$$S_{\Delta OB'C'} = \frac{\sqrt{3}}{4} \begin{vmatrix}
    x_1^O & x_2^O & x_3^O \\
    x_1^B' & x_2^B' & x_3^B' \\
    x_1^C' & x_2^C' & x_3^C'
\end{vmatrix}$$  \hspace{1cm} (12)

$$S_{\Delta OC'A'} = \frac{\sqrt{3}}{4} \begin{vmatrix}
    x_1^O & x_2^O & x_3^O \\
    x_1^C' & x_2^C' & x_3^C' \\
    x_1^A' & x_2^A' & x_3^A'
\end{vmatrix}$$  \hspace{1cm} (13)

$$S_{\Delta OA'B'} = \frac{\sqrt{3}}{4} \begin{vmatrix}
    x_1^O & x_2^O & x_3^O \\
    x_1^A' & x_2^A' & x_3^A' \\
    x_1^B' & x_2^B' & x_3^B'
\end{vmatrix}$$  \hspace{1cm} (14)

where $\sigma$ is the surface tension of the ternary system solved in the point “O” [mNm$^{-1}$],

$\sigma_i$ is the surface tension of the point $i$ [mNm$^{-1}$],

$W_i$ is the probability weight of the points A’, B’, C’,

$x_i^j$ is mass fraction of the component $i$.

Basic procedure of solution of equations (7) to (14) was described in detail in the previous work [10]:

3.3 Model of regular solution

Author Kozheurov has introduced the theory of regular ion solutions. He deduced with use of methods of statistic thermodynamics a model of regular ion solution first for the systems with a single common ion [11], and later also for the systems with general number of ions [12] with application for metallurgical slags.

This empiric model is based on the following equation:

$$\sigma = \sigma_c \cdot x_c + \sigma_A \cdot x_A + \sigma_S \cdot x_S + \sigma_{Q_{C-A}} \cdot x_c \sigma_A Q_{C-A} + \sigma_{Q_{S-C-S}} \cdot x_c \sigma_S Q_{S-C-S} + \sigma_{Q_{A-S}} \cdot x_A \sigma_S Q_{A-S}$$  \hspace{1cm} (15)

where $\sigma_i$ is surface tension of pure oxides [mNm$^{-1}$] [8],

$X_i$ is molar fraction,

$Q_{ij}$ is surface interaction parameter [mNm$^{-1}$],

Values of surface interactions parameters were taken from the literature [13].
4. RESULTS

4.1 Modified Butler’s equation using ionic distances of components

In the first phase of modelling a calculation of surface tension for the ternary system CaO – Al₂O₃ – SiO₂ was made with use of the modified Butler’s equation (1) - (6). Temperature dependencies of surface tension of the given addition of with SiO₂ increments of 3wt.% and with the maximum addition of 15wt.% were investigated – see Fig. 1. The system of equations of this mathematical model was solved in mathematical program MATHCAD. Calculation itself was made by modified Newton’s method.

![Fig. 1](image)

Fig. 1: The temperature dependence of surface tension of concentration line with addition of SiO₂ calculated using a modified Butler’s model with ionic distances of components.

4.2 Chou model

Figure 2 presents temperature dependencies of surface tension obtained by Chou model. Calculation of surface tension was made according to the relations (7) – (14).

![Fig. 2](image)

Fig. 2: The temperature dependence of surface tension of concentration line with addition of SiO₂ calculated using Chou model.

4.3 Model of regular solution

In the last phase of modelling a calculation of surface tension of the concentration line of the ternary system CaO–Al₂O₃–SiO₂ was made with use of empiric model of regular solution. Figure 3 shows the obtained temperature dependencies.

![Fig. 3](image)
5. DISCUSSION AND CONCLUSIONS

Surface tension of the concentration line of SiO$_2$ prepared in laboratory was calculated with use of three selected mathematical models. These values were afterwards compared with the surface tension data experimentally measured by sessile drop technique.

This work presents Butler’s modified equation with use of ion distances of individual components, Chou model and model of regular solution. Figure 1 shows evident decreasing tendency of surface tension with an increasing content of silicon dioxide in the Butler’s modified equation. The same tendency of concentration dependence of surface tension was repeated also in the Chou model (Fig. 2), as well as in empiric model of regular solution (Fig. 3). What concerns behaviour of surface tension with temperature, the situation is quite opposite. While in the Butler’s equation the surface tension increases with temperature, in the Chou model and in the model of regular solution the tendency of temperature dependence is decreasing.

Figure 4 presents comparison of the values of surface tension calculated numerically by mathematical models with the results obtained from experiments. The best concordance rate was found in the Chou model. This model provides very good results with a mean deviation from the measured values of 3%. In case of the Butler’s modified equation the mean deviation was 15%. Model of regular solution had the biggest mean deviation from the experimental values, i.e. approx. 20%.
It is therefore possible to summarise the obtained results in the following manner:

- Butler’s modified equation with use of ion distances and model of regular solution can be used, due to comparatively big deviations from the measured values, only for an estimation of indicative, values of surface tension of the order of magnitude.
- The Chou model was found to be suitable for calculation of surface tension of the ternary system CaO-Al$_2$O$_3$-SiO$_2$. A mean deviation of 3% was determined at comparison of calculated and experimentally obtained values.

ACKNOWLEDGEMENTS

The work was carried out in the scope of the project of the Czech Science Foundation (106/09/0370) and of the student’s project entitled „Selected studies of heterogeneous systems”, and it was financed from the specific research resources of the Faculty of Metallurgy and Materials Engineering, VSB-Technical University of Ostrava, Czech Republic.

LITERATURE


