MODELING VISCOSITY AND SURFACE TENSION OF CaO - Al₂O₃ - SiO₂ SYSTEM

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Abstract

The knowledge of physical-chemical properties of molten oxide systems is essential in view of the high-temperature metallurgical processes. Oxide systems form the basis of casting powders and metallurgical slags. The choice of an optimum slag mode influences not only the main metallurgical processes, but also the values of technical-economic indicators of the whole steelmaking process. One of the important characteristics are surface properties which influence properties of slags in metallurgy, the study of which contributes to the knowledge and the control of phenomena at the interface oxide system/metal. Viscosity is another important characteristic that affects useful properties of slags. It influences kinetic conditions in metallurgical processes. The presented paper is focused on the comparison between numerically and experimentally obtained values of surface tension and viscosity. The numerically obtained data were calculated using the Chou model. This model represents semi empirical geometric model, which allows the calculation of wide spectrum of the ternary systems physical-chemical properties. The ternary system of CaO-Al₂O₃-SiO₂, which presents a simplified base of the casting powders used for continuous casting of steel, was chosen for the experiment. Concentration series of SiO₂ was created to this ternary system. The experimental viscosity measurements were carried out by the rotating viscometer Anton Paar FRS 1600. The method of sessile drop was used for measurement of surface tension.

Keywords:
Viscosity, surface tension, geometrical model, slag

1. INTRODUCTION

Physical - chemical properties of molten oxide systems have a big influence on many phenomena in high-temperature metallurgical processes [1-5]. Oxide systems form the basis of casting powders and metallurgical slags. The viscosity of oxide melt is important physical property, in view of its direct effect on the kinetic conditions of the metallurgical processes. Viscosity depends mainly on temperature and chemical composition. Viscosity in metallurgical slags is determined by the silicate structure. Acid slag with large polymerised silicate ions is highly viscous, while basic slag with small de-polymerised silicates is less viscous [6]. The other important factor which influences the rate of chemical reaction at oxide system/metal interface is the surface tension. 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 [7, 8] dealing with the numerical calculation of various physical - chemical properties, such as surface tension and viscosity were developed. Nevertheless, the models still face the problem of dissonance of experimentally obtained values and calculated values because of the character of slag systems or absence of thermodynamic data.

The aim of this work was calculation of surface tension and viscosity of ternary system CaO-Al₂O₃-SiO₂ using geometrical Chou model and comparison of numerical results with experimentally obtained values.
2. EXPERIMENT

2.1 Materials
The ternary system CaO - Al₂O₃ - SiO₂ was selected for the experimental study. This system is the basis of casting powders used for continuous casting of steel. To this system the concentration line with the addition of 3; 6 and 9 of SiO₂ was created. Its chemical composition is shown in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂ (wt.%)</th>
<th>CaO (wt.%)</th>
<th>Al₂O₃ (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS</td>
<td>47.20</td>
<td>36.90</td>
<td>15.90</td>
</tr>
<tr>
<td>TS + 3 wt.% SiO₂</td>
<td>50.20</td>
<td>34.80</td>
<td>15.00</td>
</tr>
<tr>
<td>TS + 6 wt.% SiO₂</td>
<td>53.20</td>
<td>32.71</td>
<td>14.09</td>
</tr>
<tr>
<td>TS + 9 wt.% SiO₂</td>
<td>56.20</td>
<td>30.61</td>
<td>13.19</td>
</tr>
</tbody>
</table>

2.2 Viscosity measurements
The viscosity measurements were carried out by the rotating viscometer Anton Paar FRS 1600. The experimental instrument is shown in Figure 1. This instrument measures the torque of graphite spindle rotating in graphite crucible filled with oxide melt. The speed range of the spindle is 0 - 200 rpm. A high temperature furnace system with a maximum temperature limit of 1600°C that monitored by a Pt-13%Rh/Pt thermocouple was used in the instrument. The graphite crucible containing 55 g of the oxide system was placed into the furnace. In order to avoid the oxidation of graphite crucible and spindle, the nitrogen gas (purity > 99.999) was used at a flow rate of 250 l/h. The furnace was heated to 1400°C at the heating rate of 15.3°C/min and held for 30 min to stabilize the temperature and homogenize the oxide melt. The graphite spindle was then immersed into the oxide melt. The viscosity was measured during heating up to 1600°C at the heating rate of 3.3°C/min. The optimum shear rate of 85 rpm was chosen for viscosity measurements [9].

2.3 Surface tension measurements
The method of sessile drop was used for measurement of surface tension. This method is based on automatic recognition of geometric shape of drop, which is sessile on a non-wettable plate [10, 11]. Graphite plate was used as a non-wettable plate. The recognition of the drop shape is divided into 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 the Laplace – Young equation is used. Experimental research of surface tension was performed in horizontal resistance graphite Tamman’s furnace.

3. Mathematical modeling

For mathematical calculation of surface tension and viscosity Chou model was used [12]. This model represents a semi empirical geometric model which enables the calculation of wide spectrum of ternary system physical-chemical properties [13, 14]. According to this model the calculated physiochemical properties of 1-2-3 system (shown in figure 2) can be expressed in a combination of three binaries each with an assigned binary composition. Then the model comes out from the relation:

\[ \Delta G^E = W_{12} \Delta G_{12}^E + W_{31} \Delta G_{31}^E + W_{23} \Delta G_{23}^E \]  

where \( \Delta G^E \) and \( W_i \) represent the excess Gibbs free energy of mixing and probability weight of binary system at the selected composition point, respectively.

When the surface tension of the points A’, B’ and C’ is known then the equation (1) will become:

\[ \sigma = W_A \sigma_A + W_B \sigma_B + W_C \sigma_C \]  

where

\[
W_A' = \frac{S_{\Delta O B C'} \sigma_A}{S_{\Delta A B'C'}} \\
W_B' = \frac{S_{\Delta O C A'} \sigma_B}{S_{\Delta A B'C'}} \\
W_C' = \frac{S_{\Delta O A C'} \sigma_C}{S_{\Delta A B'C'}}
\]

\[
S_{\Delta A B'C'} = \frac{\sqrt{3}}{4} \begin{vmatrix} x_1^A & x_2^A & x_3^A \\ x_1^B & x_2^B & x_3^B \\ x_1^C & x_2^C & x_3^C \end{vmatrix} \\
S_{\Delta O B C'} = \frac{\sqrt{3}}{4} \begin{vmatrix} x_1^O & x_2^O & x_3^O \\ x_1^B & x_2^B & x_3^B \\ x_1^C & x_2^C & x_3^C \end{vmatrix} \\
S_{\Delta O C A'} = \frac{\sqrt{3}}{4} \begin{vmatrix} x_1^O & x_2^O & x_3^O \\ x_1^C & x_2^C & x_3^C \\ x_1^A & x_2^A & x_3^A \end{vmatrix} \\
S_{\Delta O A B'} = \frac{\sqrt{3}}{4} \begin{vmatrix} x_1^O & x_2^O & x_3^O \\ x_1^A & x_2^A & x_3^A \\ x_1^B & x_2^B & x_3^B \end{vmatrix}
\]

where \( \sigma \) is the surface tension of the ternary system solved in the point “O” (see below) [mN/m], \( \sigma_i \) is the surface tension of the point \( i \) [mN/m], \( W_i \) is the probability weight of points A’, B’, C’, \( x_i^j \) is mass fraction of the component \( i \).

In the case of viscosity calculation, the surface tension of points A’, B’ and C’ is replaced by viscosity of these points.

The basic process of solving the introduced equations (2) – (9) was following:

1. Themiscible area of the ternary system in equilateral triangle was selected.
2. On the borderline of this area three initial points (A’, B’ and C’) were selected.
3. To compare the calculated data, the experimentally measured points were recorded in the bordered area. These points are denoted individually as the points “O”.
4. By connecting each initial point with the point “O” three triangles \( \Delta O A' B' \), \( \Delta O A' C' \) and \( \Delta O C' B' \) are created. Using the coordinates of these triangles the equations (6) – (9) are calculated.

The surface tension or viscosity of initial points A’, B’ and C’ for the equation (2) was obtained by experimental measurements.
4. RESULTS

4.1 Viscosity

The viscosity data of concentration series were calculated using the geometrical Chou model. The input parameters for calculation per this model were obtained by experimental measurements. The results of mathematical modeling are shown in figure 3 and results of experimental measurements in figure 4.

![Fig. 3](image1.png) **Fig. 3** The calculated temperature dependences of viscosity of concentration line of SiO\(_2\).

![Fig. 4](image2.png) **Fig. 4** The measured temperature dependences of viscosity of concentration line of SiO\(_2\).

4.2 Surface tension

The calculation of the surface tension for concentration series of ternary system SiO\(_2\) – CaO – Al\(_2\)O\(_3\) was realized using the Chou model too. The results of mathematical modeling are shown in figure 5 and results of experimental measurements obtained by the method of sessile drop are presented in figure 6.

![Fig. 5](image3.png) **Fig. 5** The calculated temperature dependences of surface tension of concentration line of SiO\(_2\).

![Fig. 6](image4.png) **Fig. 6** The measured temperature dependences of surface tension of concentration line of SiO\(_2\).
5. DISCUSSION AND CONCLUSIONS

The viscosity and surface tension temperature dependences of laboratory prepared SiO$_2$ concentration series of ternary system CaO - Al$_2$O$_3$ - SiO$_2$ were obtained using the geometrical Chou model. This model enables calculation of wide spectrum of ternary system physical-chemical properties. The calculated values were compared with the experimentally measured values.

At first the input data for calculation of viscosity were measured experimentally. Subsequently, these data were used in calculation of viscosity using the equations (2) - (9). It can be seen from figures 3 and 4 that viscosity exponentially decreases with temperature and increases with additional SiO$_2$ in both calculated values and experimentally measured values. Comparison between the calculated values and experimental values is shown in figure 7. This figure shows that the deviation is significant. While experimentally measured viscosity values of basic ternary system (without addition of SiO$_2$) are in the interval of 1.01 Pa.s - 0.34 Pa.s, the calculated values are in the interval of 7.79 Pa.s - 1.91 Pa.s. In case of concentration series the tendency of increase of calculated viscosity values is analogous. In slag systems, viscosity is dominated by the silicate structure; an acid slag with large polymerized silicate ions is highly viscous whereas a basic slag with small de-polymerized silicates is much more fluid. Except the presence of net-forming and non-net-forming oxides in the slag, complicated interactions between the cations and anions make the predicting and modeling of slag viscosity often quite problematic. For this reason, the functionality of many mathematical models for viscosity calculation is limited by concentration range of some components, such as SiO$_2$, Al$_2$O$_3$ [15, 16].

Surface tension values were calculated as viscosity using the Chou model. Figures 5 and 6 show, that surface tension decreases with addition of SiO$_2$ in both calculated values and experimentally measured values. Increase of surface tension with temperature is more evident in experimental data, while in the calculated data this increase is very slight. Figure 8 shows comparison of the experimentally obtained surface tension values with the calculated data. From this figure it is evident, that Chou model is suitable for calculation of surface tension. For example the surface tension experimental values of basic ternary system are in the range of 515 mN/m - 535 mN/m and the calculated values are in the range of 507 mN/m - 515 mN/m. Average deviation of the calculated values from the experimental values is 5%.

The obtained results can be summarized as follows. Although the Chou model enables the calculation of wide spectrum of ternary system physical-chemical properties, it is unsuitable for calculation of viscosity of the ternary system CaO - Al$_2$O$_3$ - SiO$_2$ with concentration range of 47.20 wt. % - 56.20 wt. % of SiO$_2$. On the other hand this model is suitable for calculation of surface tension of the ternary system CaO - Al$_2$O$_3$ - SiO$_2$.

![Graph comparison of viscosity values](image1.png)  
*Fig. 7* Comparison of experimentally obtained viscosity values with the calculated data.

![Graph comparison of surface tension values](image2.png)  
*Fig. 8* Comparison of experimentally obtained surface tension values with the calculated data.
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LITERATURE


