



MODELING VISCOSITIES OF FERROMANGANESE SLAGS

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ABSTRACT

The primary aim of the present investigation is to develop a model which permits to calculate/predict the viscosities of ferromanganese slags, typically focus on the MnO-SiO₂-Al₂O₃-CaO-MgO-FeO multicomponent system. The present viscosity model emphasizes the ability of prediction, i.e. using the binary parameters to extrapolate the viscosities in ternary and higher order systems. To this end, a physical sound model is essential. Temperature dependence of viscosity is described by the Eyring's formalism. The well-known cell model is used to define the SiO₄⁺ tetrahedra in the silicate melts. Composition dependence is expressed in term of viscous activation energy, which is characterized by the binary structural units. The viscosities in ternary and higher order systems are hence predicted using the binary activation parameters. The model has been used to calculate the viscosities in the whole liquid composition range of ferromanganese slag.

1. INTRODUCTION

The ferroalloy industry is increasingly using physically based models to simulate production processes. The driving force for such modeling is to improve the productivity through lower energy costs, improved product quality and product consistency. Viscosities of ferromanganese metal and oxide melts are one of the important properties for the mathematical modeling and simulation. In addition to influencing the flow pattern in the furnace, slag viscosity has also a great impact on temperature distribution and reduction behaviour of MnO[1]. Changes in slag viscosity may affect the furnace operation by increasing the temperature at the coke bed boundary and thus affect the temperature distribution in the coke bed. Viscosity also plays an important role in determining the MnO content in addition to the MnO activity (given by the liquidus composition).

The primary goal of the present investigation is to develop a model that permits to calculate/predict the viscosity of ferromanganese slag, typically focus on the MnO-SiO₂-Al₂O₃-CaO-MgO-FeO multicomponent system. The present viscosity model emphasizes the ability of prediction, i.e. using only the binary parameters to extrapolate the viscosities in ternary and higher order systems. To this end, a physical sound model is essential. Furthermore, correlation exists between the structural units and thermal/electric conductivities of molten silicate melts[2]. It is expected to extend the structural model for the modeling of other thermophysical properties of ferromanganese slags.

2. THE MODEL

2.1 Previous studies

Over the past decades, a number of various models have been proposed for the calculation of viscosity of metallurgical melt. These models are based on one of the following theoretical equations: Eyring's equation[3], Bockris' equation[6] and Weymann-Frenkel's equation[7][8].

Experimental evidences have shown that the viscosity is a temperature-dependent property. In all theoretical equations, temperature dependence of viscosity is represented by the Arrhenius-type relationship:

$$\eta = \eta_0 \cdot \exp\left(\frac{G^*}{RT}\right) \quad (1)$$

where η_0 is the pre-exponential factor, G^* is the activation energy, R the gas constant and T the absolute temperature. The pre-exponential term varies in different theoretical expressions. In Eyring's equation[3], this term is expressed as $N_A h / V_m$ (h = Planck's constant; N_A = Avagadro's number; V_m = molar volume) while the Weymann-Frenkel formalism[7][8] relates the pre-exponential term to temperature:

$$\eta = A_w T \exp\left(\frac{G^*}{RT}\right) \quad (2)$$

Viscosity of silicate melt is also a composition dependent variable. Different models treat the composition dependence in different ways. It is widely accepted that the composition dependence of the viscosity of silicate melts is related to the degree of polymerization in the melts[10]. The models proposed by Riboud *et al.*[9] and by Urbain *et al.*[11] are among the typical examples which simplifies the effect of complex polymer on the viscosity of liquid silicate melt.

The Riboud's model[9] was primarily developed to estimate the viscosities of mould powders. It was later found that it could also be applied to the metallurgical slags. The Weymann-Frenkel equation is used to represent the temperature dependence. The slag constituents are classified as five different categories: (i) SiO_2 , $\text{PO}_{2.5}$, TiO_2 , ZrO_2 ; (ii) CaO , MgO , MnO , $\text{FeO}_{1.5}$, $\text{BO}_{1.5}$; (iii) Al_2O_3 ; (iv) CaF_2 and (v) Na_2O , K_2O . The pre-exponential factor A_w and activation energy G^* are then expressed as functions of the compositions of above five different components. The model proposed by Urbain *et al.*[11] is similar to the Riboud's model[9] which was developed based primarily on the experimental observation in the SiO_2 - Al_2O_3 - CaO ternary melt. The slag constituents are classified as three categories: glass former (SiO_2 and $\text{PO}_{2.5}$), modifiers (CaO , MgO , MnO , Na_2O , K_2O , $\text{FeO}_{1.5}$, $\text{BO}_{1.5}$, CaF_2 , TiO_2 , ZrO_2) and amphoteric (Al_2O_3). A modified version of the Urbain model has recently been proposed by Kondratiev and Jak[13]. The modification has been made by introducing more composition-dependence parameters to describe the viscosity of liquid SiO_2 - Al_2O_3 - CaO -“FeO” slag.

The viscosity model proposed by Du *et al.*[12] was developed based on the Eyring's formalism and the classical Temkin treatment. The liquid slag is described by a modified Temkin approach, which considers the mixing of cations and anions within each of their subgroups. The ionic solution is represented by the formula $(C_1, C_2, \dots, C_n)_P(A_1, A_2, \dots, A_m)_Q$, where P and Q are the coefficients determined by stoichiometric considerations; C_1, C_2, \dots, C_n represent different cations; and A_1, A_2, \dots, A_m represent different anions. Composition dependence of the viscosity is treated similarly as thermodynamic properties. Since both the binary and ternary parameters are necessary for the model to calculate the viscosities of ternary and higher-ordered silicate melts, this model has the less ability to predict the viscosities of multicomponent silicate melts.

Zhang and Jahanshahi[14][15] developed a structurally related model for the calculation of the viscosity of silicate melts based on the general behaviour of the viscosity of binary silicate melts. The cell model[4][5] is used to define the fractions of the bridging and free oxygen bonds in binary silicate melts. The model parameters for binary silicate melts are evaluated by fitting the experimental viscosities:

$$\eta = \exp(a' + b' E^w) T \exp\left(\frac{E^w}{RT}\right) \quad (3)$$

with

$$E^w = a + b(N_{o^0})^3 + c(N_{o^0})^2 + d(N_{o^-})^3 \quad (4)$$

where N_{O^0} and N_{O^-} are, respectively, the bridging and free oxygen bonds. a , b , c , d and a' , b' are the model parameters. For ternary and higher order systems, it is assumed that the model parameters are linear functions of the parameters of the binary silicate subsystems. The model was successfully applied to the SiO_2 -CaO-MgO-MnO-FeO- Fe_2O_3 - Al_2O_3 multicomponent system.

Mills *et al.*[10] compared the model predictions with experimental data measured in different laboratories around world. It has finally been concluded that excellent results were obtained on the slag systems using the KTH[12] and Zhang[14][15] model. The KTH[12] and Zhang[14][15] models were limited for the slags with no fluorides present.

2.2 Temperature Dependence of Viscosity

As mentioned above, it is customary to correlate viscosity-temperature data in the form of Arrhenius-type relationship. The Weymann-Frenkel formalism[7][8] presumes a slight curvature between the logarithmic viscosity and reciprocal temperature, whereas the Eyring's equation[3] follows rigorously with the Arrhenius relationship, Eq.(1). A collection of the experimental viscosities on pure SiO_2 , five binary (SiO_2 - Al_2O_3 , SiO_2 -CaO, SiO_2 -MnO, SiO_2 -MgO and Al_2O_3 -CaO) and seven ternary (SiO_2 - Al_2O_3 -CaO, SiO_2 - Al_2O_3 -MnO, SiO_2 - Al_2O_3 -MgO, SiO_2 -CaO-MnO, SiO_2 -CaO-MgO, SiO_2 -CaO-FeO, SiO_2 -MnO-FeO) silicate melts has been used to analyse the temperature dependence of viscosity. It has been concluded that both the Weymann-Frenkel and Eyring formalisms describe the temperature dependence equally well (Figure 1). It is difficult to judge the curvature between logarithmic viscosity and reciprocal temperature within experimental uncertainties. A similar conclusion was obtained by Zhang and Jahanshahi[14] who tested temperature dependence in 12 different binary silicate melts. The Eyring's equation has thus been decided to apply for the temperature dependence of viscosity in the present investigation:

$$\eta = \frac{N_A \hbar}{V_m} \cdot \exp\left(\frac{G^*}{RT}\right) \quad (5)$$

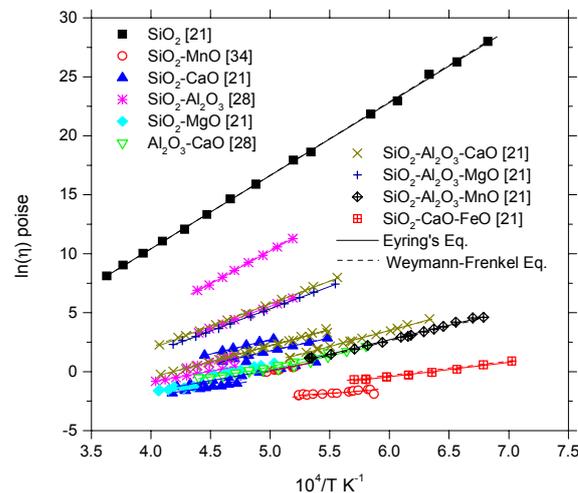


Figure 1: Temperature dependence of the viscosities in various silicate melts

2.3 Composition Dependence of Viscosity

Composition dependence of viscosity for the ferromanganese oxide melts is described as function of binary structure units. For binary SiO_2 -MO ($M = \text{Ca, Mn, Mg, Fe}$) silicate melts, based on the SiO_4^{4-} tetrahedra,

the following structural units are taken into account:

$$\begin{array}{cccc} \text{Si} & & \text{Si} & & \text{Si} & & \text{M} \\ | & & | & & | & & | \\ \text{Si}-\text{Si}-\text{Si} & , & \text{Si}-\text{Si}-\text{M} & , & \text{M}-\text{Si}-\text{Si} & , & \text{M}-\text{Si}-\text{Si} \\ | & & | & & | & & | \\ \text{Si} & & \text{Si} & & \text{M} & & \text{M} \end{array}$$

$\begin{array}{c} \text{M} \\ | \\ \text{M}-\text{Si}-\text{M} \\ | \\ \text{M} \end{array}$ and $M-M$. They are hereafter denoted as Si-Si_4 , $\text{Si-Si}_3\text{M}_1$, $\text{Si-Si}_2\text{M}_2$, $\text{Si-Si}_1\text{M}_3$, Si-M_4 and $M-M$, respectively, for the sake of brevity. Obviously, the Si-Si_4 and $M-M$ structural units are only related to the pure SiO_2 and MO .

In order to determine the structural units for a given binary SiO_2 - MO silicate melt, the cell model[4][5] is applied to define the equilibrium symmetric Si-O-Si and M-O-M cells and the asymmetric Si-O-M cells. The Si-O-Si , M-O-M and Si-O-M cells are hereafter abbreviated as Si-Si , $M-M$ and Si-M cells, respectively. The contents of tetrahedral $\text{Si-Si}_{(4-i)}\text{M}_i$ units in the melt are thus determined with respect to the asymmetric Si-M cells by the following relation:

$$\omega_i = \frac{4!}{i!(4-i)!} \left(\frac{N_{\text{Si-Si}_4}}{2N_{\text{SiO}_2}} \right)^i \left(1 - \frac{N_{\text{Si-Si}_4}}{2N_{\text{SiO}_2}} \right)^{(4-i)} \quad (i = 1,2,3,4) \tag{6}$$

$$N_{\text{Si-Si}_{(4-i)}\text{M}_i} = \omega_i \cdot N_{\text{Si-M}} \quad (i = 1,2,3,4) \tag{7}$$

where ω_i is the probability that a given Si is bridged to exactly i other silicon atoms; $N_{\text{Si-Si}_{(4-i)}\text{M}_i}$ and $N_{\text{Si-M}}$ are, respectively, the mole fractions of $\text{Si-Si}_{(4-i)}\text{M}_i$ tetrahedra and asymmetric Si-M cells.

It is then presumed that each silicate tetrahedra has its own activation energy, and the activation energy is only dependent on temperature. The “additive rule” is applied for the binary silicate melt:

$$G^* = N_{\text{Si-Si}_4} G_{\text{Si-Si}_4}^* + N_{M-M} G_{M-M}^* + N_{\text{Si-Si}_3\text{M}_1} G_{\text{Si-Si}_3\text{M}_1}^* + \dots + N_{\text{Si-M}_4} G_{\text{Si-M}_4}^* \tag{8}$$

where $G_{\text{Si-Si}_4}^*$ and G_{M-M}^* represent the activation energies of pure SiO_2 and MO , respectively. The $G_{\text{Si-Si}_{(4-i)}\text{M}_i}^*$ s are the activation energies of $\text{Si-Si}_{(4-i)}\text{M}_i$ tetrahedra. Temperature dependence of activation energy is expressed in term of activation enthalpy and entropy:

$$G^* = H^* - TS^* \tag{9}$$

Eq (9) inserted into Eq.(5) then gives:

$$\eta = \frac{N_A \hbar}{V_m} \cdot \exp \left[\frac{\sum_k (H_k^* - S_k^* T)}{RT} \right] \quad (k = 1,2,\dots) \tag{10}$$

Eq.(10) is used in the present investigation to calculate the viscosity of silicate melt.

The physical picture of aluminosilicate melt is more complicated since both SiO_2 and Al_2O_3 can form the SiO_4^{4-} and AlO_4^{5-} tetrahedra. There are two ways to treat the composition dependence of viscosity on the aluminosilicate melt. The first treatment is to determine the contents of different AlO_4^{5-} tetrahedra similarly as SiO_4^{4-} . For example, a SiO_2 - Al_2O_3 melt contains five different SiO_4^{4-} and five different AlO_4^{5-} tetrahedra. Each tetrahedral unit has their own activation energy. The second treatment is rather simple: alumina is treated as metal oxide[15]. Eq.(6) and Eq.(7) still held for aluminosilicate melts. The present authors have preliminary tested the different treatments for the binary SiO_2 - Al_2O_3 and ternary SiO_2 -

Al₂O₃-CaO aluminosilicate melts. In the present paper, only the results of simplified treatment are presented due to limitation of space.

The treatments for ternary and higher order silicate melts are straightforward. For a given ternary SiO₂-MO-NO melt at fixed temperature, for instance, the cell model is first used to determine the equilibrium fractions of Si-Si, Si-M, Si-N, M-M, N-N and M-N cells. The asymmetric Si-M and Si-N cells are further used to determine the Si-Si_(4-i)M_i and Si-Si_(4-i)N_i tetrahedra with following relations:

$$N_{Si-Si_{(4-i)}M_i} = \omega_i \cdot N_{Si-M} \quad (i = 1,2,3,4) \quad (11)$$

$$N_{Si-Si_{(4-i)}N_i} = \omega_i \cdot N_{Si-N} \quad (i = 1,2,3,4) \quad (12)$$

here ω_i can be determined from Eq.(6). A ternary SiO₂-MO-NO silicate melt contains following twelve binary structural units: Si-Si₄, M-M, N-N, M-N, Si-Si₃M₁, Si-Si₂M₂, Si-Si₁M₃, Si-M₄, Si-Si₃N₁, Si-Si₂N₂, Si-Si₁N₃ and Si-N₄. The “additive rule” for the activation energy, Eq.(8), still applies to the ternary silicate melt. As all the binary structural units and their activation energies have been determined, the viscosity of a ternary SiO₂-MO-NO silicate melt is readily calculated from Eq.(10).

It is worth noting that the binary activation energies are the only parameters used to determine the viscosities of ternary, quaternary and multicomponent silicate melts. This provides the basis for the model to obtain reasonable extrapolations in a broad composition and temperature range of higher order systems. The current model has been implemented in an MS-Excel™ spreadsheet for the calculation of viscosity in the MnO-SiO₂-Al₂O₃-CaO-MgO-FeO multicomponent silicate melts.

3. RESULTS AND DISCUSSION

Since the activation energies (model parameters) are required to be determined from experimental data, the assessment of experimental data is the first important stage in the viscosity modelling. The experimental techniques, the errors of measurement (if available) and the consistence to higher order systems are the key criteria for the assessment of experimental data. An example is the viscosity modelling of pure “FeO”. Schenck *et al.*[18] carried out the measurements for the viscosities of pure “FeO” in equilibrium with metallic iron in the temperature region from 1380 to 1490°C. But the measured viscosities are not consistent with those in the SiO₂-FeO binary and FeO-containing ternary systems. Urbain *et al.*[19] and Mill[20] hence recommended the viscosities of pure “FeO” to be 50% lower than the values reported by Schenck[18]. Since the recommended values[19][20] are in good consistence with the other measurements for the binary SiO₂-FeO[21][43] and ternary SiO₂-CaO-FeO[21][35][43] melts, they are accepted in this study and used to fit the model parameters.

Experimental uncertainties in the viscosity measurements are also important to judge the reliability of experimental results. According to Mills[10][20], the primary sources of experimental uncertainties come from (i) changes in the composition of the melt due to reaction between the melt and graphite and (ii) the errors in temperature measurements of the melt. It was finally concluded by Mills[10][20] that most viscosity measurements were subject to experimental uncertainties of $\pm 25\%$, in some cases experimental uncertainties can be $>\pm 50\%$.

Another criterion for the judgement of experimental data is to examine whether the reported viscosity data are in the homogeneous liquid region. The FACT oxide thermochemical database[16] has been used to determine the liquid phase boundaries of a given system. A close examination of the measured data reported in the literature has found that many data were obtained in the heterogeneous liquid/solid region. These data should be carefully picked out before the evaluation of activation energy.

Several measurements for the viscosities of pure SiO₂[21]-[26] and pure Al₂O₃[27]-[31] can be found in the literature. Applying the above criteria to the experimental data, it has finally been confirmed that those reported by Urbain *et al.*[21] for pure SiO₂ and by Urbain[27] for pure Al₂O₃ are the most reliable. These experimental data have been used to fit the activation energies of pure SiO₂ and Al₂O₃ and the results are:

$$G_{Si-Si_4}^* = 515050 - 46.3 T (J/mol) \quad (13)$$

$$G_{Al-Al}^* = 78330 - 32.5 T (J/mol) \quad (14)$$

Figure 2:(a) shows the calculated viscosities of pure SiO₂ and Figure 2:(b) for Al₂O₃. In Figure 2:(a), a dash-dotted line divides the viscosity line into two parts: the left part is in the complete liquid state while right part is the one extrapolated into the undercooling of liquid silica. In Figure 2:(a) and (b), two dotted lines define the boundaries of $\pm 25\%$ measurement uncertainties.

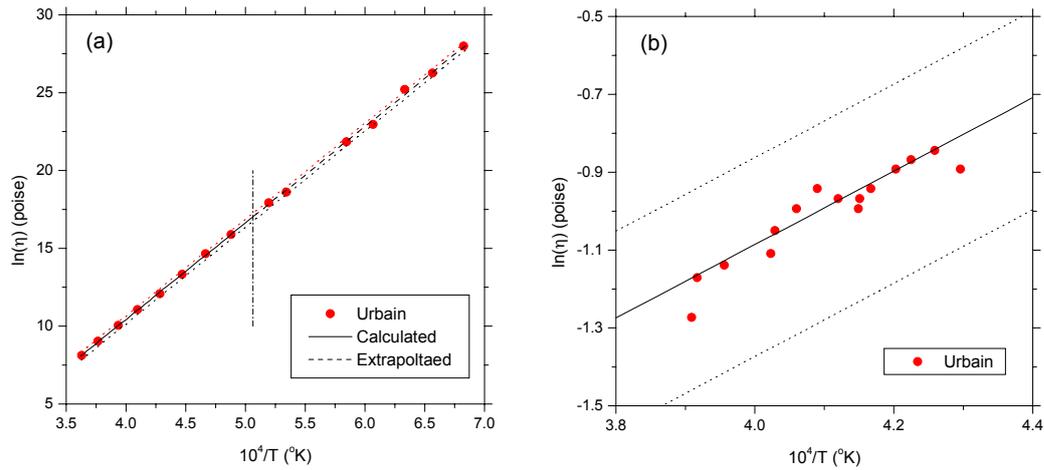


Figure 2: Comparison of the calculated and measured viscosities for (a) pure SiO₂ and (b) pure Al₂O₃ melts

Measurement for the viscosity of pure CaO, MnO and MgO was not reported in the literature. The activation energies of these pure components are required to be extrapolated from the assessed binary and ternary experimental data.

A number of researchers conducted the measurements for the viscosities of various binary silicate and aluminosilicate melts using different experimental techniques[21]-[28][33]-[35][40][43]. The experimental data used in this work are summarized in 0.

Table 1: Summary of the measured viscosities in binary melts used in present study

System	Source	Temperature range (K)
SiO ₂ -Al ₂ O ₃	Urbain <i>et al.</i> [21]	1926-2477
	Kozakevitch[28]	2123-2373
SiO ₂ -CaO	Urbain <i>et al.</i> [21]	1825-2393
	Hofmaier <i>et al.</i> [22]	1833-2393
	Kozakevitch[28]	1773-2273
	Bockris <i>et al.</i> [24]	1723-2073
	Ji <i>et al.</i> [35]	1713-1773
	Machin & Yee[33]	1773
SiO ₂ -MnO	Urbain <i>et al.</i> [21]	1705-2020
	Seeger <i>et al.</i> [34]	1533-1573
	Ji <i>et al.</i> [35]	1538-1758
SiO ₂ -MgO	Urbain <i>et al.</i> [21]	1714-2188
	Bockris <i>et al.</i> [24]	1723-2073
SiO ₂ -FeO	Urbain <i>et al.</i> [21]	1439-1773
	Kozakevitch[43]	1473-1723
Al ₂ O ₃ -CaO	Urbain <i>et al.</i> [21]	1926-2477

System	Source	Temperature range (K)
	Kozakevitch[28]	2123-2373
Al ₂ O ₃ -FeO	Lopatin <i>et al.</i> [40]	1673-1823

The calculation results for the SiO₂-Al₂O₃ melt are shown in Figure 3:(a) and (b), respectively. Figure 3:(a) compares the modelled viscosities with the selected experimental data. This figure can be used to judge the accuracy of the model calculations. The calculated values fall into the recommended uncertainty range ($\pm 25\%$) limited by two dotted lines. Figure 3:(b) shows the calculated composition dependence of the viscosity in this binary melt. The solid lines represent the calculated viscosities of homogeneous liquid melt while the dashed lines the extrapolated values in the liquid/solid coexistence region.

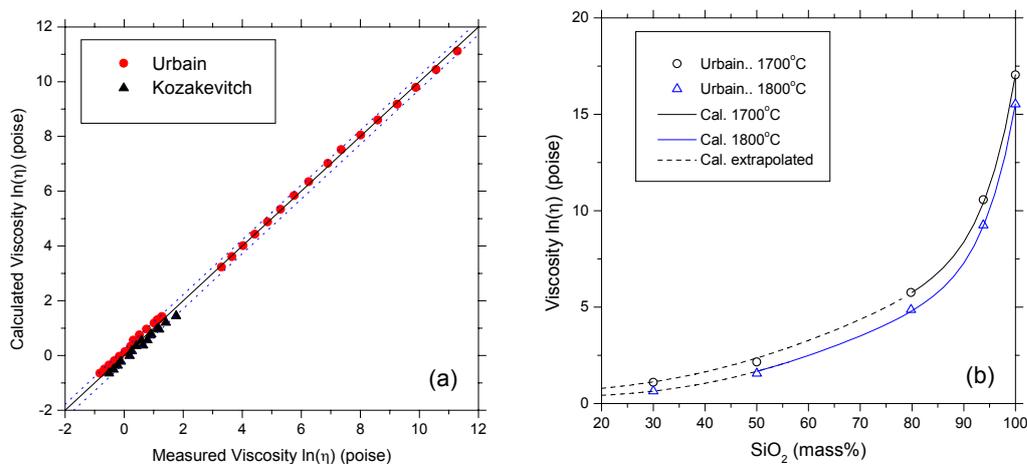


Figure 3: Viscosities of the SiO₂-Al₂O₃ melt (a) comparison of calculated with measured values (b) compositional dependence of viscosity

Similarly, comparisons for the calculated and measured viscosities in the binary SiO₂-CaO and SiO₂-MnO melts are shown in Figure 4 and Figure 5, respectively. The model is able to reproduce most of the assessed experimental data within the recommended uncertainties.

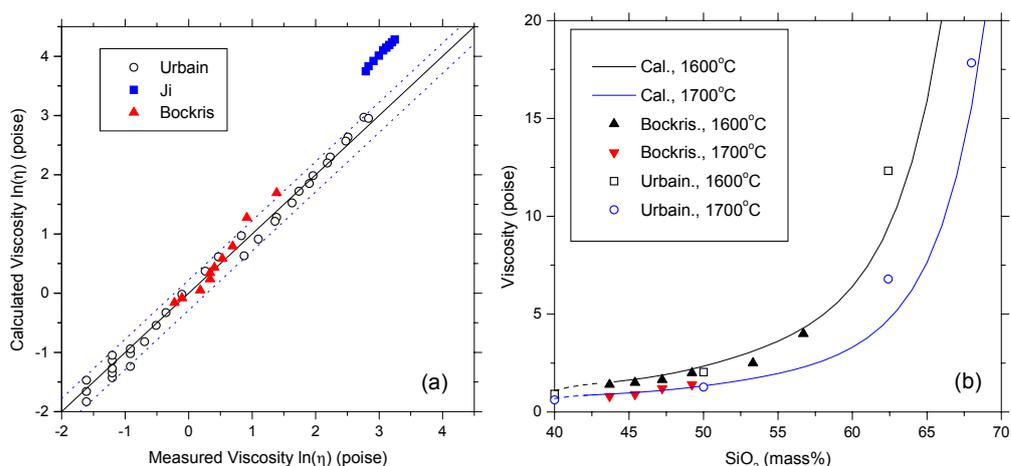


Figure 4: Viscosities of the SiO₂-CaO melt (a) comparison of calculated with measured values (b) compositional dependence of viscosity

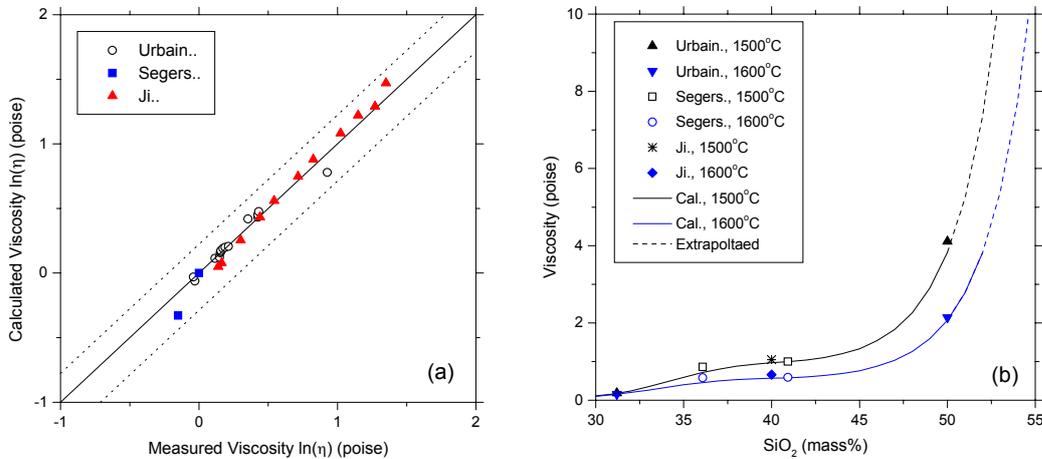


Figure 5: Viscosities of the $\text{SiO}_2\text{-MnO}$ melt (a) comparison of calculated with measured values (b) compositional dependence of viscosity

Less experimental data were available in the literature for the viscosities of binary aluminate melts. Urbain *et al*[21] and Kozakevitch[28] measured the viscosities of the $\text{Al}_2\text{O}_3\text{-CaO}$ melt in the temperature region from 1653 to 2204°C. Lopatin *et al.*[40] reported their measurement on the viscosity of $\text{Al}_2\text{O}_3\text{-"FeO"}$ melt in the temperature region from 1400 to 1550°C. The activation energies of the binary $\text{Al}_2\text{O}_3\text{-CaO}$, $\text{Al}_2\text{O}_3\text{-MnO}$, $\text{Al}_2\text{O}_3\text{-MgO}$ and $\text{Al}_2\text{O}_3\text{-FeO}$ melts have been evaluated using the binary and the relevant ternary experimental data.

The experimental data for the viscosities of metal oxide melts are very limited. This is due to the fact that the binary MnO-CaO , CaO-MgO and MnO-MgO systems are all in solid state in the temperature region from 1200 to 1700°C. A close examination to the measured viscosities for the ternary $\text{SiO}_2\text{-MO-NO}$ ($M, N = \text{Mn, Ca, Mg, Fe}$) melts has revealed that the influence of binary MO-NO activation energies on the ternary viscosities is not significant. In the present model, the activation energies of binary metal oxide melts are all set to be zero.

Viscosities of the $\text{MnO-SiO}_2\text{-CaO}$ ternary melts were measured by Seger *et al.*[34] The measurements cover a composition range of MnO from 10 to 60 wt% at 1210-1410°C. The authors also extrapolated the viscosities at 1500°C using an empirical formula. These experimental data have been used to verify the model predictions. Figure 6 shows the calculated iso-viscosity contours at 1500°C. Liquid phase boundaries have been calculated using the FactSage commercial software package[17]. The viscosity behaviour in this ternary melt is clear. Increase of SiO_2 content leads to a continuous rise the viscosity. Substitution of MnO for CaO results in the reduction of viscosity assuming the same SiO_2 content. The calculation results are able to well represent the viscosity behaviour in the $\text{MnO-SiO}_2\text{-CaO}$ melt.

Similarly, experimental viscosities in ternary $\text{MnO-SiO}_2\text{-FeO}$ [21][35][43], $\text{SiO}_2\text{-CaO-MgO}$ [21][36][42], $\text{SiO}_2\text{-CaO-FeO}$ [21][35][39] and $\text{SiO}_2\text{-MgO-FeO}$ [21][35] have been employed to test the predictive ability of the present model. Only the results for $\text{MnO-SiO}_2\text{-FeO}$ ternary melt are presented in Figure 7 due to paucity of space. The present model provides good representation for most of the experimental data in these ternary systems. As can be seen from Figure 7, the model calculations give better descriptions for the measurements by Kozakevitch[43].

As mentioned above, the activation energies for the binary $\text{MnO-Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3\text{-MgO}$ aluminate mixtures require to be extrapolated from ternary experimental data in $\text{MnO-SiO}_2\text{-Al}_2\text{O}_3$ [21] and $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ [21][44] melts. The activation energies for binary $\text{Al}_2\text{O}_3\text{-CaO}$ are obtained using the experimental viscosities in binary $\text{Al}_2\text{O}_3\text{-CaO}$ [21][28] and ternary $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ [21][28][36] melts. The measured viscosities of binary $\text{Al}_2\text{O}_3\text{-FeO}$ [40] and ternary $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-FeO}$ [21] melts are simultaneously used to evaluate the activation energies of $\text{Al}_2\text{O}_3\text{-FeO}$ system.

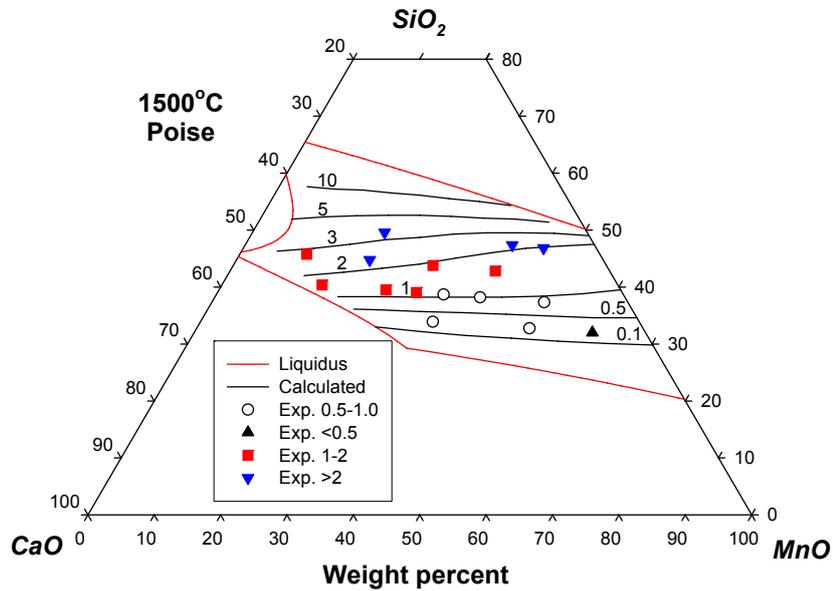


Figure 6: Comparison between the calculated iso-viscosity curves with the measured points for the MnO-SiO₂-CaO system at 1500°C

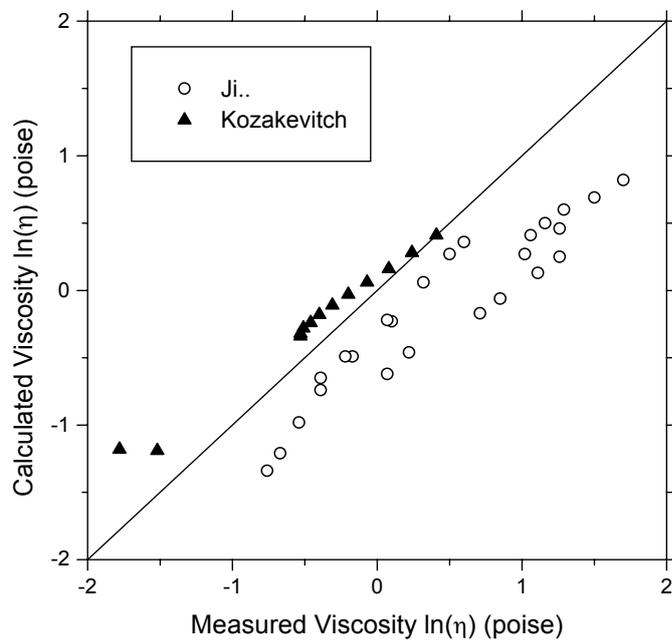


Figure 7: Comparison of the calculated and measured viscosities in ternary MnO-SiO₂-FeO melt

Figure 8 shows a comparison between the calculated and measured viscosities in ternary MnO-SiO₂-Al₂O₃ melts. The experimental data cover a composition range of MnO from 12 to 48 wt% in the temperature region from 1200 to 1993°C. Two dotted lines define the experimental uncertainty range. As can be seen from the figure, most of the calculation results fall in the experimental uncertainties.

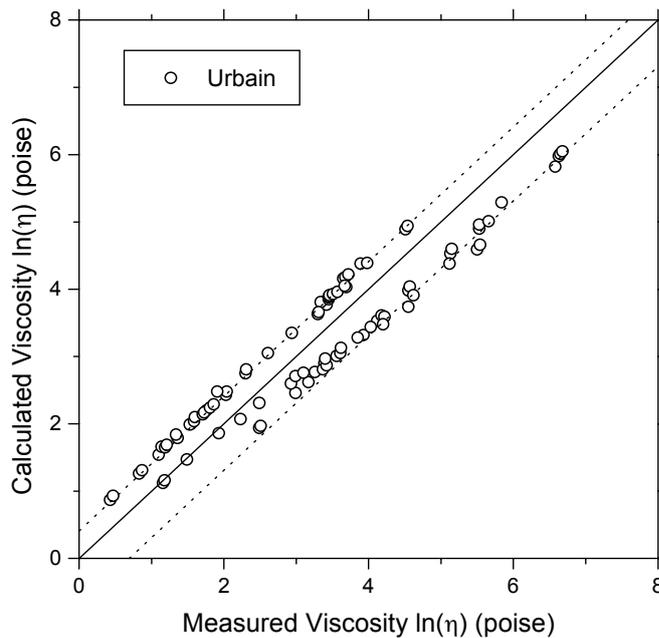


Figure 8: Comparison of the calculated and measured viscosities in ternary MnO-SiO₂-Al₂O₃ melt

Viscosities in the quaternary MnO-SiO₂-Al₂O₃-CaO melt were measured at 1400°C by Tanabu and Honda[38]. The measurements were carried out isothermally at constant MnO (10 wt%) and Al₂O₃ (6 wt%) contents, respectively. Comparing with the same isothermal sections calculated by FactSage package[17], some measured points are located outside of the fully liquid region. According to the criteria mentioned above, only the measured viscosities in the homogenous liquid area have been chosen to verify the model calculations. Figure 9 shows the calculated viscosities in comparison with the experimental data. The error bar for each point is estimated from the iso-viscosity contours given in the original figures. A rather good agreement exists between the calculated and measured viscosities in this quaternary system.

The experimental iso-viscosity curves show a “valley” at SiO₂ around 40 wt% in both the 10 wt% MnO and 6 wt% Al₂O₃ isothermal sections. However, the model calculations clearly indicate that viscosities in this quaternary system increase monotonously with the increase of SiO₂ content. Addition of basic oxide (CaO, MnO) leads to the decrease in viscosity at 1400°C. A close examination to the experimental data has revealed that this “valley” is due to the heterogeneous effect on the viscosity. Viscosity of partial crystallized slag is not only dependent on temperature and composition, but also dependent strongly on the amount of solids in suspension. As shown in Figure 11, as an example, viscosity increases dramatically as the solid particles continuously precipitate.

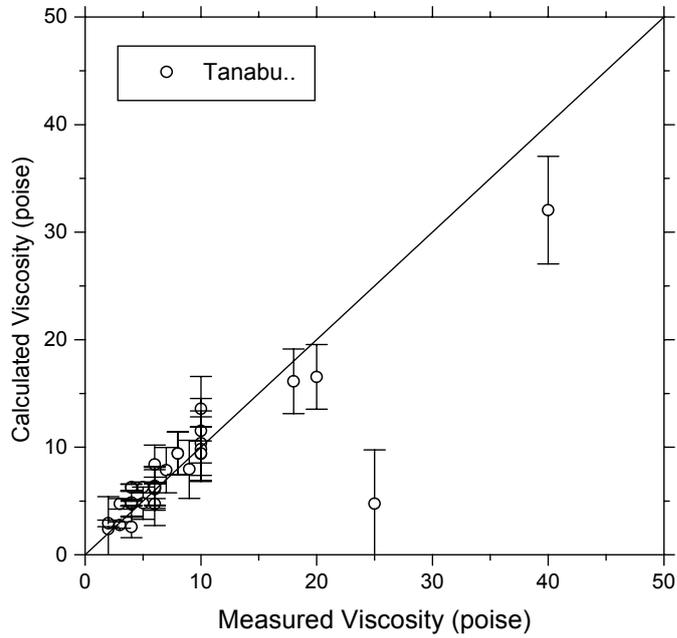


Figure 9: Comparison of the calculated and measured viscosities in quaternary $\text{MnO-SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ melt at 1400°C

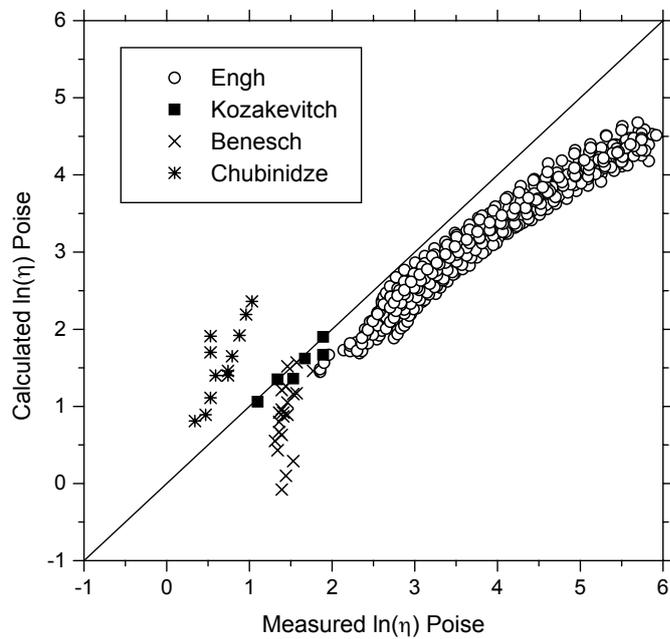


Figure 10: Comparison of the calculated and measured viscosities in quinary $\text{MnO-SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO}$ melt

Viscosities in the MnO-SiO₂-Al₂O₃-CaO-MgO quinary system were measured by Engh[41], Kozakevitch[43], Benesch *et al.*[46] and Chubinidze[47]. The experimental data have first been checked by the homogeneity criterion using the FactSage thermochemical software[16][17]. The valid experimental data are used to verify the model predictions. As shown in Figure 10, the modelled viscosities are in good agreement with the experimental data reported by Kozakevitch[43], which contain very low MnO (0.7-1.2 wt%). A fair agreement exists between the calculated and measured viscosities reported by Engh[41], who measured the viscosities of silicomanganese slags. The measurements covered a composition range of MnO from 8-26 wt% and of SiO₂ from 35-50 wt% in the temperature region from 1250 to 1540°C. The calculated viscosities are in general lower than those reported by Benesch *et al.*[46], but higher than those measured by Chubinidze[47]. The Urbain model[11] has also been used to test the correlation between the calculated and measured values reported by Benesch[46] and Chubinidze[47]. The same conclusion has been obtained for the Benesch's and Chubinidze's data. This suggests that the experimental data reported by Benesch[46] and Chubinidze[47] are not reliable.

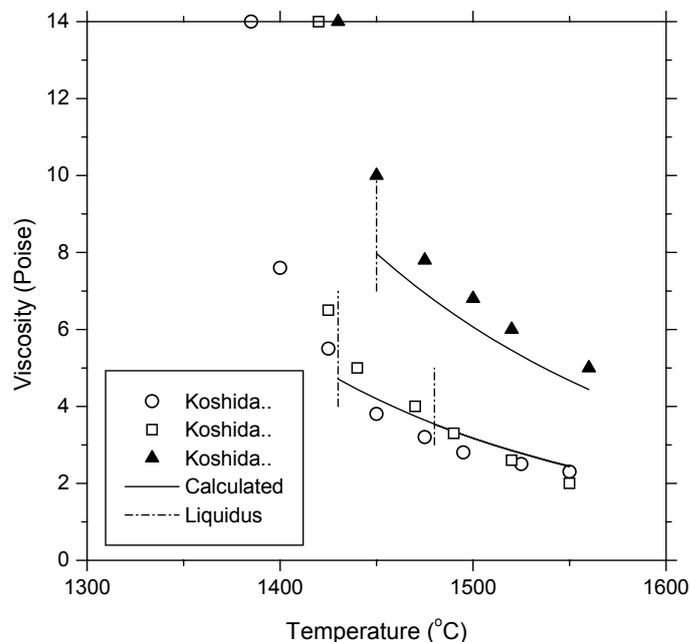


Figure 11: Comparison of the calculated and measured viscosities in the MnO-SiO₂-Al₂O₃-CaO-MgO-FeO melt

Finally, the predictive ability of the present model has been examined using the experimental viscosities in the MnO-SiO₂-Al₂O₃-CaO-MgO-FeO system. Owing to lack of data for ferromanganese melts, the experimental data for the blast furnace type slags[48] are used to verify the calculated results. Figure 11 shows three sets of experimental data as a function of temperature. The liquidus boundaries given by Koshida *et al.*[48] are also plotted as the dash-dotted lines in the diagram. Agreement for the liquid blast furnace slags is satisfactory. Viscosities of the heterogeneous melts increase dramatically as temperature decreases. To model the viscosity of partial crystallized slag, the Einstein-Roscoe equation[45] must be applied in order to estimate the effect of solid precipitation. But this is not the subject of the present investigation.

4. CONCLUSIONS

A structural viscosity model designed for the liquid ferromanganese slags has recently been developed. Temperature dependence of viscosity is described by the Eyring's formalism. Composition dependence of viscosity is expressed in term of the activation energies of binary structural units. The well-known cell model is used to define the SiO_4^{4-} tetrahedra in the silicate melts. Treatments for the aluminosilicate melts have been proposed. The results of simplified treatment are presented in the paper.

The assessed experimental viscosities of several unary and binary systems have been used to fit the model parameters. As the cell model for the thermodynamic properties, the viscosity behaviours of several liquid ternary, quaternary and higher order silicate melts are able to be predicted within their experimental uncertainties. Only the binary activation energies are required to represent the viscosities of multicomponent systems. The present approach is readily to be extended to the sulphide-, fluoride- and chloride-containing melts.

REFERENCES

- [1] M. Tangstad: "Slag viscosity in the ferromanganese submerged arc furnace process", SINTEF report STF80MK F05066, Feb. 2005, Norway.
- [2] K.C. Mills: ISIJ International, vol.33(1993), pp148-155.
- [3] S. Glasstone, K.J. Laidler and H. Eyring: Theory of Rate Processes, McGraw-Hill, New York, NY, 1941.
- [4] H. Gaye and J. Welfringer: 2nd International Symposium on Metallurgical Slags and Fluxes, Warrendale, PA., Met. Soc. of AIME, Ed. Fine H.A. and Gaskell D.R., 1983, pp.357-375.
- [5] H. Gaye, J. Lehmann, T. Matsumiya. and W. Tamada: "A Statistical Thermodynamic Model of Slags: Applications to Systems Containing S, F, P₂O₅ and Cr Oxides", 4th International Conference on Molten Slags and Fluxes, ISIJ, 1992, Sendi, Japan, pp. 103-108.
- [6] J. O' M. Bockris and A. K. N. Reddy: Modern Electrochemistry, Plenum Press, New York, NY, 1970.
- [7] H. D. Weymann: Kolloid Z. Polymer, 1962, vol. 181, pp. 131-37.
- [8] J. Frenkel: Kinetic Theory of Liquids, Clarendon Press, Oxford, United Kingdom, 1946.
- [9] P. V. Riboud, Y. Roux, L. D. Lucas and H. Gaye: Fachber. Huttenprax. Metallweiterverarb, 1981, vol.19, pp. 859-69.
- [10] K. C. Mills, L. Champman, A. B. Fox and S. Sridhar: The 6th Intern. Conf on Molten slags, fluxes and salts, Stockholm, Sweden -Helsinki, Finland, 12-15 June 2000 (CD-ROM).
- [11] G. Urbain, F. Cambicr, M. Dcletter and M.R Anseau: Trans. Brit. Ceram. Soc. vol.80 , 1981, pp.139.
- [12] Du Sichen, J. Bygden and S. Scetharaman: Metall. Mater. Trans. vol.25B, 1994, pp.519-25.
- [13] A. Kondratiev and E. Jak: Metall. Mater. Trans., vol.32B, 2001, pp.1015-1025.
- [14] L. Zhang and S. Jahanshahi: Metall. Mater. Trans. vol.29B, 1998, pp. 177-186. and 187-195.
- [15] L. Zhang and S. Jahanshahi: Scan. J. Metall., vol.30, 2001, pp. 364-369.
- [16] Fact oxide database: <http://www.crct.polymtl.ca/fact/>.
- [17] FactSage software: <http://www.factsage.com/>.
- [18] H. Schenck, M. G. Frohberg and W. Rohde: Arch. Eiserhutteiawes., vol. 32, 1961, pp.521-523.
- [19] G. Urbain, F. Cambier, M. Deletter and M.R. Anseau: Trans. J. Brit. Ceram. Soc., vol. 80, 1981, pp.139-41.
- [20] K. C. Mills: Slag Atlas, 2nd Edition, Verlag Stahleisen GmbH, Germany, 1995.
- [21] G. Urbain, Y. Bottinga, and P. Richet: Geochim. Cosmochim. Acta, vol.46, 1982, pp.1061-72.
- [22] G. Hofmaier and G. Urbain: Sci. Ceram., vol. 4, 1968, pp.25-32.
- [23] R. Rossin, J. Bersan, and G. Urbain: Rev. Int. Haut. Temp. Refract., vol. 1, 1964, pp.159-70.
- [24] J.O'M. Bockris, J. D. MacKenzie and J. A. Kitchener: Trans. Faraday Soc., vol. 51, 1955, pp. 1734-48.
- [25] D.W. Bowen and R.W. Taylor: Ceram. Bull., vol. 57, 1978, pp.818-819.
- [26] R. Bruckner: Glastechn. Ber., vol. 37, 1964, pp.413-425.
- [27] G. Urbain: Rev. Int. Haut. Temp. Refract., vol. 19, 1982, pp. 55-57.
- [28] P. Kozakevitch: Rev. Metall., vol. 57, 1960, pp.149-160.

- [29] G. Hofmaier: Berg und Hutterun. Monatsh. Montcur. Hochschule in Loeben, vol. 113, pp. 1968, pp.270-281.
- [30] V. P. Elioutin, B. C. Mitin and Y.A. Nagibin: Fiz. Aerodispersuykh Sist., vol. 7, 1972, pp.129-135.
- [31] R. A. Blomquist, J. K. Fink and L. Leibowitz: Ceram. Bull., vol.5, 1978, p.522.
- [32] J. O'M. Bockris and D. C. Lowe: Proc. Royal Soc., vol. 1954, A226, pp.423-435.
- [33] J. S. Machin and T. B. Yee: J. Am. Ceram. Soc., vol. 31, 1948, pp.200-204.
- [34] L. Segers, A. Fontana and R. Winand: Trans. Inst. Min. Metall. Sec. C, vol. 88, 1979, pp.c53-c56.
- [35] F-Z Ji, Du Sichen and S. Seetharaman: Ironmaking & Steelmaking, vol.25, 1998, pp.309-316.
- [36] J. S. Machin and T. B. Yee: J. Am. Ceram. Soc., vol. 37, 1954, pp.177-186.
- [37] G. Urbain: Compc Rendus, vol. 232, 1951, pp.330-332.
- [38] Y. Tanabu, O. Honda: Electrochem. Vol.28, 1960, pp. 9-14 .
- [39] M. Kucharski, N.M. Stubina and J.M. Toguri: Can. Metall. Q., vol. 28, 1989, pp.7-11.
- [40] V. M. Lopatin, Y. P. Nikitin, L. N. Barmin and L. B. Bobylev: Fiz Khim.Issled. Metall. Protsessov, vol. 3, 1975, pp.63-66.
- [41] T.A. Engh: "Viskositetsmålinger I Slagger", Metallurgisk Institutt, NTH, Norway, 1975.
- [42] T. Licko and V. Danek: Phys. Chem. Glasses, vol. 27, 1986, pp.22-26.
- [43] P. Kozakevitch: Rev. Metall., vol. 46, 1949, pp.572-582.
- [44] E.F. Riebling: Canad. J. Chem. vol.42, 1964, pp.2811.
- [45] R. Roscoe: Br. J. Appl. Phys., vol.3, 1952, pp267-289.
- [46] B. Benesch, R. Kuthnicki and M. Jaworski: Archiv Hutnick, vol.29, 1984, pp.277-283.
- [47] T. A. Chubinidze: Teoriya i praktika poluch i primeneniya kompleks ferrosplavov. (1974). 31-35.
- [48] T. Koshida, T. Ogasawara and H. Kitihidaka: Tetsu-to-Hagane vol.67, 1981, pp.1491-1497.