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Modelling viscosity of TiO_x containing silicate melts

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Experimental studies on viscosity of titanium bearing slags have been reviewed and the assessed data were used in extending the capability of the structurally related viscosity model for silicate melts, developed by the present authors. Experimental data on ternary and higher order systems containing CaO, MgO, MnO, FeO, Al_2O_3, TiO_2, Ti_2O_3, SiO_2 were assessed and used. The newly extended viscosity model represented the viscosity behaviour over broad temperature and composition ranges. The structural role played by TiO_2 and Ti_2O_3 in silicate network structure is discussed with respect to their effect on viscosity of melts.

Keywords: viscosity model, TiO_x containing silicate melts, silicate network structure.

Introduction

Titaniferous ore is sometimes used as a feed material for production of hot metal in electric arc and blast furnaces. The reducing conditions in these furnaces result in low FeO slags containing up to 35% TiO_x in a matrix of Al_2O_3-CaO-SiO_2-MgO-MnO. For improved operation of these ironmaking processes, modifications to the slags' chemistry could result in reducing the liquidus temperature and viscosity of the slag produced.

Previous studies by Holmes *et al.*[1] and Ratchev and Belton[2] have established the effects of slag chemistry and oxidation state on the liquidus region of titania rich slags. It was found that reduction of TiO_2 to Ti_2O_3 can have a pronounced effect on the liquidus temperature of such slags[2]. Similarly, there are published data on the viscosity of ternary and higher order systems containing varying concentrations of titanium oxides[3–14]. The influence of TiO_2 to Ti_2O_3 on viscosity of silicate slag has been studied in both homogeneous liquid and melts containing solid particles. It was found that for a given slag, additions of TiO_2 and Ti_2O_3 caused viscosity to decrease at a given temperature above the liquidus. However, the presence of the solid phase at temperatures below the liquidus resulted in a sharp rise in the viscosity.

It should be mentioned that the effect of a particular oxide component on viscosity should be considered in two aspects. The first is the effect on the homogeneous liquid, for example in silicate melts, additions of so called network modifiers, such as CaO and MnO, will in general reduce viscosity. Such an effect may be related to the bonding characteristic of the oxides concerned, as discussed previously by the present authors[15–17].

The second effect comes from the influence of the oxides on the liquidus temperature of the melts. If the addition of a certain amount of a particular oxide stabilizes a solid phase, the viscosity of the melt is expected to rise sharply with an increasing amount of the solid phases. The latter effect can very often override the effect on the homogeneous liquid phase.

The present work was part of ongoing development of a multi-phase reaction model at CSIRO[18]. The package enables metallurgists to simulate reactions in pyrometallurgical processes with respect to equilibrium between various phases, and to calculate slag viscosity at elevated temperatures. The viscosity model developed by the present authors during the past decade relates viscosity to the structural properties of the silicate melts[15–17]. The classification of oxide components as glass former, modifier and amphoteric as proposed by Urbain[21] was adopted to distinguish the structural role played by various oxides and analyse their contributions to viscosity. Such an approach has made it possible to describe viscosity behaviour of high order systems using binary model parameters only. The model has been validated using published data from binary to multi-component systems (silicate and calcium ferrite type), as well as various types of industrial slags[15–20]. The oxide components included in the model currently, are SiO_2, Al_2O_3, Fe_2O_3, TiO_2, Ti_2O_3 CaO, MgO, MnO, FeO, PbO, NiO, Cu_2O, ZnO and CoO. Details of the formulation of the model and most of the validation results can be found elsewhere[15–20].

In the present paper, application of the current modelling approach to multi-component silicate slags containing TiO_2 and Ti_2O_3 will be discussed. The extension of our viscosity model to TiO_2 and Ti_2O_3 containing silicate melts was based on analysis and review of the experimental data.

Review of viscosity data

CaO-TiO_2-SiO_2 system

A number of groups[3,9–14] have measured the viscosity in the CaO-TiO_2-SiO_2 system and have shown that addition of TiO_2 reduces the viscosity of CaO-SiO_2 based melts. However, there is a large scatter among different studies and it was found that the data by Dingwell[9] are most accurate. Dingwell's measurements were carried out under well controlled conditions, i.e., in air and using Pt-20%Rh components. Under such conditions the slags can be considered free of Ti_2O_3 and other contaminants. Furthermore, only data in the liquid region were reported, which covered the targeted composition range of 10 to 80 mol% TiO_2 along the $CaSiO_3$-TiO_2 join, and the temperature range of 1400–1600°C. Figure 1 presents Dingwell's data, where the effect TiO_2 additions to the

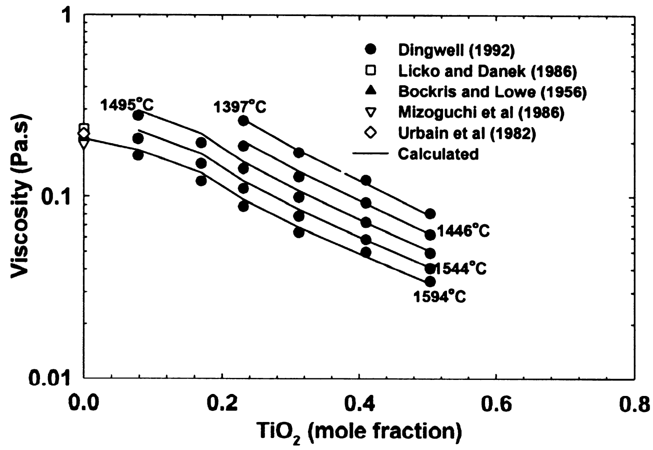

Figure 1. Comparison between the calculated viscosity and the experimental data[9] on the effect of TiO_2 addition along the $CaSiO_3$-TiO_2 join in the CaO-TiO_2-SiO_2 system

CaO-SiO_2 binary melt, with unit molar ratio CaO/SiO_2, is shown at different temperatures. It is apparent that at a given temperature, addition of TiO_2 causes viscosity to decrease. It is also noted that the measured viscosity for the CaO-SiO_2 binary melt at 1600ºC by Dingwell agree well with other published data[22–25] (Figure 1).

It should be mentioned that the compositions reported by Dingwell[9], which were obtained after the viscosity measurements, were used for the construction of Figure 1. These compositions for TiO_2 were generally lower than the targeted values and were not available for TiO_2 greater than 50 mol%. Furthermore, CaO/SiO_2 ratios were in a range of 0.94–0.98, rather than unity as targeted.

MnO-TiO_2-SiO_2 system

Viscosity behaviour in the MnO-TiO_2-SiO_2 system was investigated by Yagi *et al.*[13] over a temperature range of 1400–1600ºC with silica mole fractions varying from 0 to 0.5. Pt-Rh alloy components were used for these measurements, thus avoiding contamination of the melts. Figure 2 shows their results on the effect of substituting TiO_2 for MnO at given silica mole fractions at 1600ºC.

It is evident that for a given silica content (mole fraction), substitution of TiO_2 for MnO does not seem to cause significant change in the viscosity of these slags. This implies that TiO_2 and MnO have very similar effects on the viscosity of silicate melts.

MgO-TiO_2-SiO_2 system

In this ternary system only two experimental datum points by Nakamura *et al.*[11] were found. These measurements were on a 35%(mol)MgO-30%SiO_2-35% TiO_2 slag at 1500 and 1550 C. The results showed a viscosity decrease of 0.011 Pa.s as the temperature was increased from 1500 to 1550°C.

PbO-TiO_2-SiO_2 system

Nakamura *et al.* also investigated the effect of the addition of TiO_2 to the PbO-SiO_2 binary melts on viscosity[11]. Their study covered a temperature range of 800–1300ºC and TiO_2 content of 0 to 0.3 mole fraction at PbO/SiO_2 mole ratio of 1, 3/2 and 7/3. Their data showed that at the mole ratio of PbO/SiO_2 =1, TiO_2 addition resulted in a decrease in viscosity, while when PbO/SiO_2 =7/3, addition of TiO_2 had an opposite effect. Figure 3 shows the data at 1150ºC, for which more datum points are available.

CaO-Al_2O_3-TiO_2-SiO_2 system

Ohno and Ross[3] studied viscosity in the CaO-TiO_2-Al_2O_3-SiO_2 system. Their measurements covered composition range of CaO/SiO_2 ratio=0.6, 1.0 and 1.16 and TiO_2 contents of 0 to 45 wt% between 1400–1500ºC. The Al_2O_3 levels were fixed at 10 and 20 wt%. Frohberg and Weber[14] also reported viscosity data in this quaternary system, with Al_2O_3 levels of 0 to 20 wt% (with 5 wt% interval) at 1600°C. Both sets of data showed that at a given temperature and CaO/SiO_2 ratio, viscosity decreased with TiO_2 addition. Figure 4 presents the data by Ohno and Ross[3] measured at 1500ºC. It can be seen that viscosity decreased as TiO_2 addition increased at a given CaO/SiO_2 ratio. It also showed that the higher level of Al_2O_3 corresponded to higher values of viscosity.

Blast furnace type slags

Measurements on blast furnace type slags containing CaO, MgO, TiO_2, Al_2O_3 and SiO_2 under neutral atmospheres have been reported by Xie *et al.*[4] and Van der Colf and Howat[5]. The composition and temperature ranges covered by the two studies are listed in Table I. Both sets of data covered similar composition range. Handfield *et al.* have

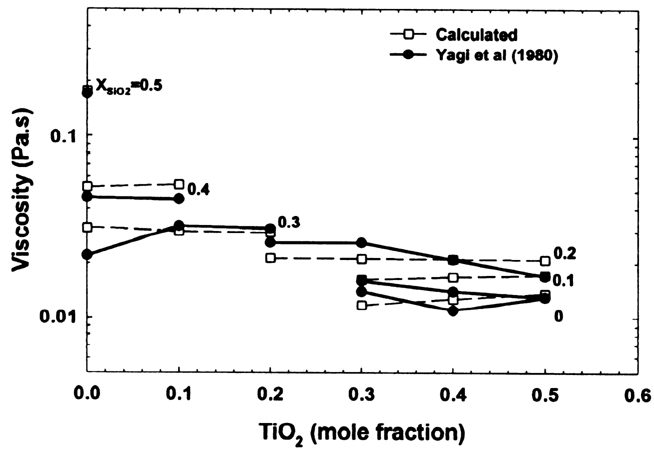

Figure 2. Comparison between the calculated viscosity and the experimental data[13] on the effect of substitution of TiO_2 for MnO in the MnO-TiO_2-SiO_2 system at 1600°C

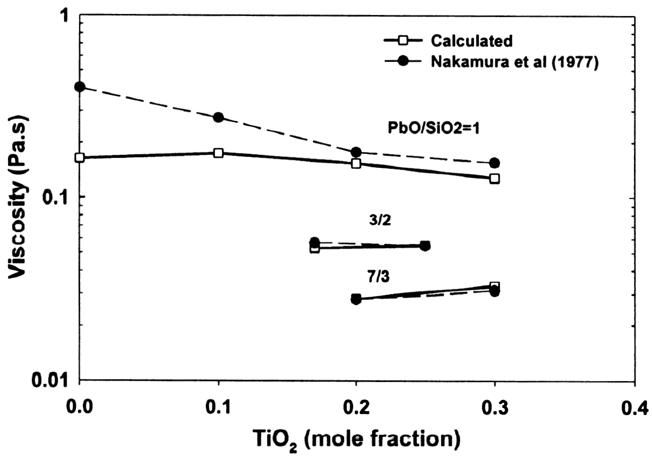

Figure 3. Comparison between the calculated viscosity and the experimental data[11] on the effect of addition of TiO_2 to the PbO-TiO_2-SiO_2 system at 1115°C

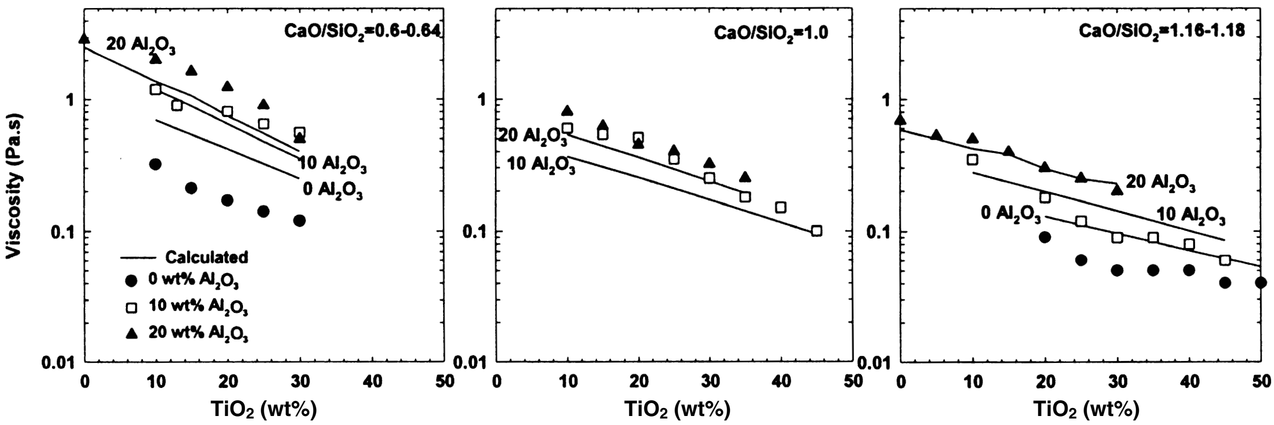

Figure 4. Comparison between the calculated viscosity and the experimental data at 1500°C[3] in the CaO- Al_2O_3-TiO_2-SiO_2 system

Table I
Experimental conditions used in the viscosity measurements by Xie *et al.*[4] and Van der Colf and Howat[5]

Ref	T (°C)	Composition wt%				
		SiO_2	TiO_2	Al_2O_3	CaO	MgO
[4]	1240–1540	21–29	17–33	9–19	24–31	7–16
[5]	1322–1492	21–31	25–30.2	11.2–13.8	8.3-24	8.3–23.5

investigated the influence of TiO_2, TiO and Ti_2O_3 additions and temperature (~1300–1600°C) on a blast furnace type slag from the Steel Company of Canada in both homogeneous liquid and melts containing solid particles[6–7]. The slag contained 37% SiO_2, 35 wt% CaO, 18% MgO, 1.2% TiO_2, 4% Al_2O_3, 1.2% S, 0.4% MnO, 0.2% Fe and 1.3% others. Molybdenum components were used in the viscosity measurements.

These measurements found that at a given temperature, addition of TiO_2 or Ti_2O_3 reduces the viscosity of the blast furnace type slags, for example the data by Xie *et al.*[4] and Van der Colf and Howat[5] as shown in Figure 5, and results by Handfield *et al.*[6–7] in Figures 6 and 7. It should be mentioned that only data in fully liquid region were shown in order to make comparison with the model. Three samples each with similar chemistry were chosen and shown in Figure 5. It is noted that the data by Van der Colf and Howat[5] are consistently lower than those by Xie *et al.*[4] though slag chemistry of samples chosen were close to each other.

Modelling results

As mentioned above, one of the objectives of the present work was to extend the capability of CSIRO's structurally related viscosity model for multi-component silicate melts to TiO_x containing slags. This model predicts viscosity of higher order systems using only binary parameters. For example, viscosity of the CaO-TiO_2-SiO_2 system can be predicted by using parameters determined for the two CaO-SiO_2 and TiO_2-SiO_2 binaries. Details of the formulation of the model and most of the validation results can be found in elsewhere[15–17].

Due to the lack of viscosity data for the binary TiO_2-SiO_2 and Ti_2O_3-SiO_2 systems, data on the CaO-TiO_2-SiO_2 ternary by Dingwell[9] were used in determination of the model parameters for the TiO_2-SiO_2 binary. The viscosity data of the CaO-TiO_2-SiO_2[9] and MnO-TiO_2-SiO_2[13] systems

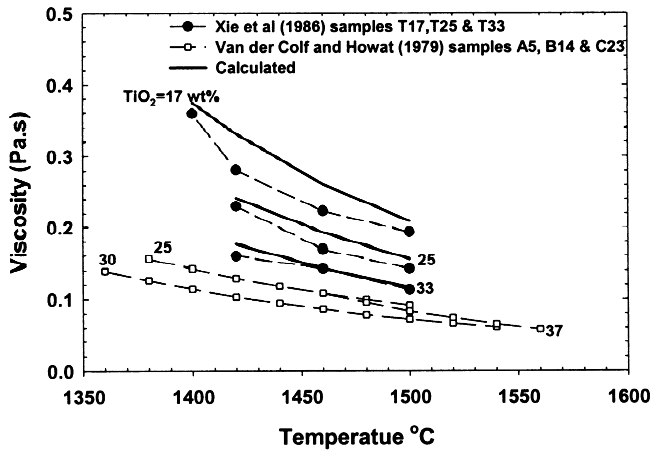

Figure 5. Comparison between the calculated viscosity and the experimental data[4,5] on the effect of TiO_2 addition to multi-component blast furnace type slags

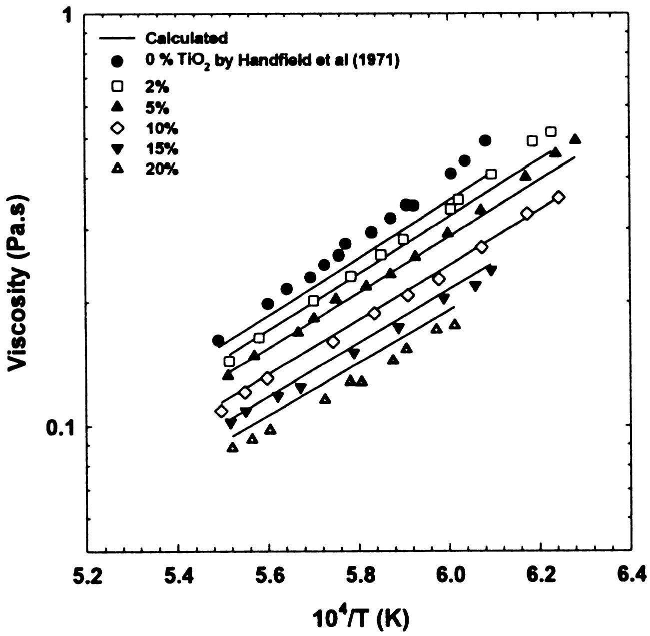

Figure 6. Comparison between the calculated viscosity and the experimental data by Handfield *et al.*[6] on the effect of TiO_2 addition to multi-component blast furnace type slags

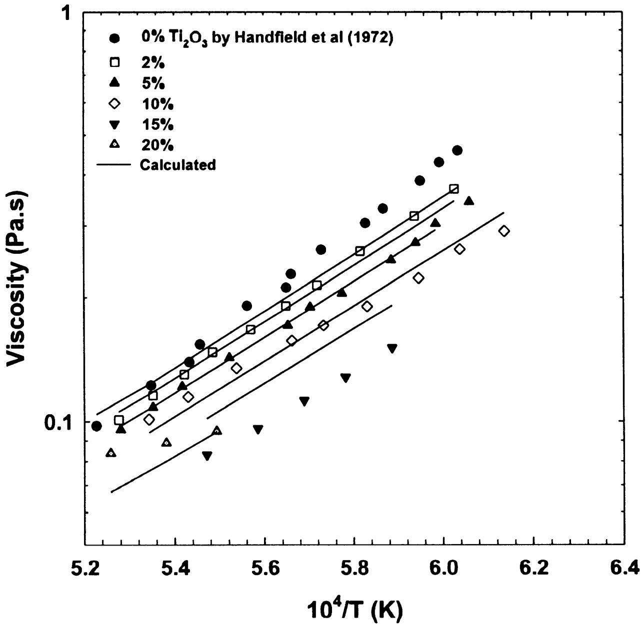

Figure 7. Comparison between the calculated viscosity and the experimental data by Handfield *et al.*[7] on the effect of Ti_2O_3 addition to multi-component blast furnace type slags

revealed that TiO_2 affects the viscosity in a similar manner to metal oxides, such as CaO and MnO, over a silica content of 0 to 0.5 mole fraction and TiO_2 up to 0.8. Based on this behaviour, TiO_2 and Ti_2O_3 were treated as network modifiers in the model. The model parameters for the TiO_2-SiO_2 binary were used for the Ti_2O_3-SiO_2 binary and $TiO_{1.5}$ was used as an oxide component in the model the same way as Fe_2O_3 was treated in the model[16].

It should be mentioned that the following comparison between modelling results and the experimental data covers only the data in homogeneous liquid region. This is because the purpose of the present paper is to validate the liquid viscosity model, though the multi-phase reaction model mentioned earlier is able to produce estimated viscosity values for solid containing melts, which combines viscosity models with the thermodynamic models to calculate equilibrium among phases[18].

Ternary systems

Figures 1 and 2 show a comparison between the calculated viscosity and the experimental data in the CaO-TiO_2-SiO_2 and MnO-TiO_2-SiO_2 systems. Excellent agreement between the calculated viscosity and the experimental data were obtained. Figure 3 shows the agreement between the model prediction and the measurements to be close, except two compositions, i.e., at 0 and 10% TiO_2 additions and PbO/SiO_2 =1. The calculated viscosity for TiO_2 free binary PbO-SiO_2 is lower than the measured value.

The model parameters for the binary system were determined by fitting data of the PbO-SiO_2 system, which were measured in the temperature range of 800–1000°C[19]. The difference suggests the model may require refinement at higher temperatures. The experimental data showed that viscosity decreased continuously with TiO_2 addition at PbO/SiO_2 =1. However, the model predicted that initial addition of TiO_2 to the binary would cause viscosity to increase slightly, while further additions led to a reduction in viscosity. This can be explained as follows. When TiO_2 was added to the binary melts, there are two effects occurring. One is the dilution of SiO_2; the other is that PbO is expected to reduce viscosity more effectively than TiO_2 at a given SiO_2 mole fraction and temperature. Such an effect has been discussed previously by the present authors regarding the relative stability of oxide components[15–17]. In other words at a given SiO_2 mole fraction, substitution of TiO_2 for PbO is expected to result in a slight increase in viscosity. The model calculation showed the decrease in viscosity caused by SiO_2 dilution to be as effective as the tendency of TiO_2 to increase viscosity at 0.1 mole fraction TiO_2. However, the dilution effect dominates with further addition of TiO_2.

CaO-Al_2O_3-TiO_2-SiO_2 system

Comparison between the calculated viscosity and the experimental data by Ohno and Ross[3] and Frohberg and Weber[14] in the CaO-Al_2O_3-TiO_2-SiO_2 system was carried out. It was found that the fit to the data by Ohno and Ross was within ±50% uncertainty. However, there are large discrepancies between calculated values and the data by Frohberg and Weber[14]. The data by Frohberg and Weber[14] are systematically higher than model predictions. Due to limited space, only the comparison of modelling results with data by Ohno and Ross[3] at 1500ºC were presented in Figure 4. It can be seen that the model can represent the correct trend in regard to the effects of CaO/SiO_2 (wt%/wt%) ratio, Al_2O_3 level and TiO_2 additions on viscosity. The fit to the data in most cases is within 30% uncertainty. The poor fit to the data at 0 wt% Al_2O_3 implies disagreement between the data by Dingwell[9] and those by Ohno and Ross[3] for the ternary CaO-TiO_2-SiO_2 system.

Blast furnace type slags

The current viscosity model was used to predict viscosity of the blast furnace type slags. For convenience, the initial composition used in the model for the slags of Handfield *et al.*[6–7] was 37% SiO_2, 35wt % CaO, 18% MgO, 1.2% TiO_2, 4% Al_2O_3, and 4.8% FeO. The minor components, such as S, MnO and others were added in FeO. The overall fit of the predicted viscosity values to the measured data[4–8] for blast furnace type slag is shown in Figure 8.

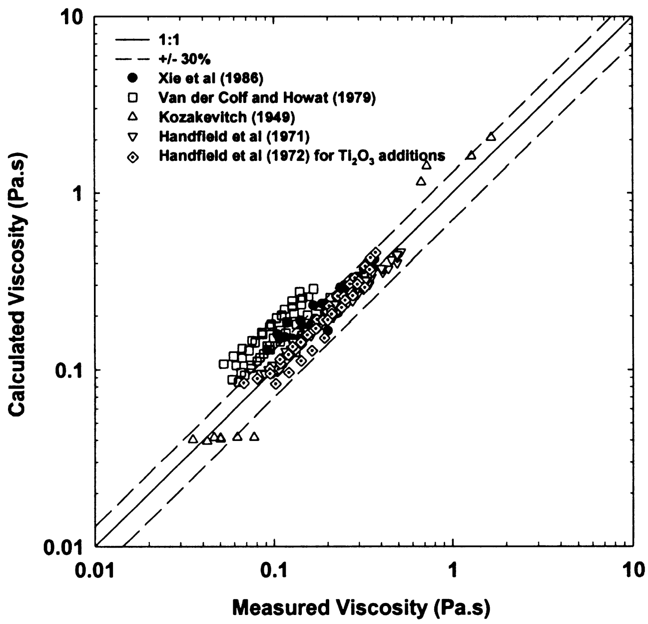

Figure 8. Comparison between the calculated viscosity and the experimental data[4–8] blast furnace type slags

This figure shows that the fit to most of the data is within 30% uncertainty except the data by Van der Colf and Howat[5]. As mentioned earlier, their data were consistently lower than those by Xie *et al.*[4] for slags with similar compositions. In order to examine the accuracy of the model for different variables, the calculated viscosity are compared with the data by Xie *et al.*[4] and Handfield *et al.*[6–7] directly with respect to variations in temperature and TiO_2 and Ti_2O_3 additions. It should be mentioned that the model predicts continuous reduction of viscosity with addition of Ti_2O_3 as shown in Figure 7. However, Handfield *et al*'s data[7] showed that 15% Ti_2O_3 addition caused viscosity to decrease more so than for 20% Ti_2O_3. Further investigations may be required to clarify the behaviour in this region. The results shown in Figures 4 to 6 demonstrated the close fit to the data. Furthermore the model provides correct representation of changes in viscosity with variations in temperature and slag chemistry.

Structural role/behaviour of TiO_x

The above review of experimental and modelling studies has shown that in general, additions of TiO_2 and Ti_2O_3 to silicate melts will result in decreased viscosity. It is thus reasonable to consider that TiO_2 and Ti_2O_3 predominantly act as network modifiers. There have been numerous studies on the structural role of titanium in melts and glasses, and the literature does show inconsistencies in findings. Mysen[26] reviewed the spectroscopic data on titania bearing glasses and noted the findings from various spectroscopic measurements tended to indicate that more than one structural position of Ti^{4+} might be possible.

It has been also proposed[27] that, since the Ti^{4+} cation is larger than the Si^{4+} cation, then Ti-O-Ti and Ti-O-Al bonds are expected to be weaker than Si-O-Si and Si-O-Al bonds; thus addition of TiO_2 to highly polymerized aluminosilicate melts will decrease their viscosity. In the case of non-silicate TiO_2 containing slags, i.e., high titania slags, the viscosity measurements on the CaO(30 wt%)-TiO_2(70%) binary melt and Soreslag (FeO-TiO_2 rich slags) by Handfield and Charrette[28] have shown that when the slags are completely molten, viscosity was as low as 0.03 Pa.s. Furthermore, the viscosity value is independent of temperature and the variation of FeO from 3.3 to 15 wt% did not seem to influence the viscosity of the Soreslag. The effect of TiO_2 on viscosity of slags as discussed suggests that TiO_2 acts in a similar way to other metal oxides, such as CaO or FeO. The possible variation to the coordination, namely, tetrahedral, when TiO_2 is low in silicate melts[26], or octahedra, in TiO_2 rich slags, does not seem to alter the bonding characteristic of TiO_2. The strength of the Ti-O bonds seems to be much weaker than that of the Si-O or Al-O bonds in the melts.

Conclusions

The review of the published viscosity data for TiO_x containing silicate melts showed that the addition of TiO_2 and Ti_2O_3 resulted in a decrease in viscosity. The CSIRO's viscosity model was extended to TiO_x containing silicate melts by treating TiO_2 and Ti_2O_3 as network modifiers. Good agreement between the predicted and measured viscosity of ternary systems was obtained. The predictive power of the model has been demonstrated by a good fit to the measured viscosity of the blast furnace type slags. The model was able to represent effects of temperature and variations in slag compositions with respect to each component accurately.

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