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Viscosity Of CaO-Cu_xO-MgO-SiO_2 Slags

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Viscosity measurements were carried out on slags in the CaO-Cu_2O-CuO-MgO-SiO_2 system containing ~ 63 wt% SiO_2 in air. The experimental work was carried out over a range of temperatures where the slags were completely liquid. Initial measurements were on a binary CaO-SiO_2 slag to which incremental additions of Cu_xO-MgO-SiO_2 slag with the same silica mole fraction were made. The viscosity-temperature relationship was measured for slags with 'Cu_2O'contents of 0.02, 0.19, 0.38, 0.79, 1.69, 2.47, 3.01, 5.31 and 10.0 wt%.

The proportions of Cu^+ and $Cu2^+$ in the slags were determined. The oxidation state of Cu shifted from predominantly Cu^+ to $Cu2^+$, with the $Cu^+/Cu2^+$ ratio of approximately 0.3 for slags with a Cu content above 2 wt%. This is equivalent to Cu1.13O. The trends observed for changes of $Cu2^+/Cu^+$ redox ratio with slag chemistry were consistent with the literature. Decreasing the CaO content by substituting copper oxide resulted in a decrease in the $Cu^+/Cu2^+$ redox ratio. The change in ratio corresponded to a shift of the value of x in Cu_xO from an initial value of 1.8 to 1.1, when the slags contained 10% 'Cu_2O'.

In this study, the SiO_2 content of the slags varied between 64 and 60 wt% as the Cu content increased. The viscosity of the slag containing 10 wt% Cu_xO was nearly 4.5 times lower than the binary CaO-SiO_2 slag. As the silica mole fraction ($xSiO_2$) actually stayed constant (0.61±0.009), the results show that Cu_xO acted as a network breaker. Comparison with other ternary slags with similar silica mole fractions suggest that that addition of CuxO to silicate slags has a stronger effect on lowering the viscosity than FeO or MnO has on a molar basis.

Keywords: viscosity, copper, silicate, slags

Introduction

While there is no shortage of thermodynamic data on copper containing slags, there is very little data on the viscosity of copper slags. Of the studies under copper smelting conditions[1,2], the focus has been on the viscosity of FeOx-SiO_2 melts and not on the effect of Cu_2O on the viscosity. There has been one study[3] on industrial slags containing around 0.3 wt.% Cu, with 4 experiments with the slags containing up to 15 wt.% Cu. There has also been a study of the viscosity of alumina saturated Al_2O_3-CaO-Cu_2O-SiO_2 slags containing between 0.6 and 15% Cu_2O[4].

With limited viscosity data available on copper slags it was decided to undertake an experimental programme to measure the viscosity of a suitable copper containing slag. Under copper smelting conditions, the oxygen partial pressure is low and the concentration of copper in the slags is also low and the thermodynamic activity with respect to liquid copper can be high. This makes container selection difficult as copper alloys with most metals. Ceramic containers such as alumina or magnesia would also not be suitable due to the temperature dependent solubility in the slag. Furthermore the uncertainty of viscosity measurements are quite high, typically 10 to 20 percent, and it is best to have the copper at quite high concentrations in the slag[5].

There is a narrow oxygen potential range under converting conditions where the copper content in the slag is quite significant, but the metallic Cu activity would still be high and any metallic crucible used may fail. Platinum and platinum-rhodium alloy crucibles can be stable enough in air (even though embrittlement occurs) for equilibrium and surface tension studies of Cu_2O-SiO_2 melts[6-8].

In order to quantify the effect of CuxO addition on the viscosity of CaO-SiO_2 based slags, in the present work use was made of Pt for the container and the viscometer bob. The metallic copper activity could be kept low by working in air, and there were potentially fewer problems with formation of solid phases. The advantages of starting with the CaO-SiO_2 binary were that the viscosity of the CaO-SiO_2 system was suited to the measuring range of the viscometer bob and the sensitivity of the viscosity measurement to the changes in the copper contents of the melt would be maximized. Comparison of the measurements on CaO-SiO_2 slags from the literature benchmark the accuracy of the measurements. The need for these measurements was solely driven by the need to develop a viscosity model for copper oxide containing slags.

Experimental

The viscosity experiments were performed in a muffle with molybdenum disilicide heating elements. A schematic of the apparatus is shown in Figure 1. A Pt crucible with a 60 mm inner diameter contained the slag. Temperature measurements were made with a Pt-13%Rh/Pt thermocouple located on the back wall of the muffle. The

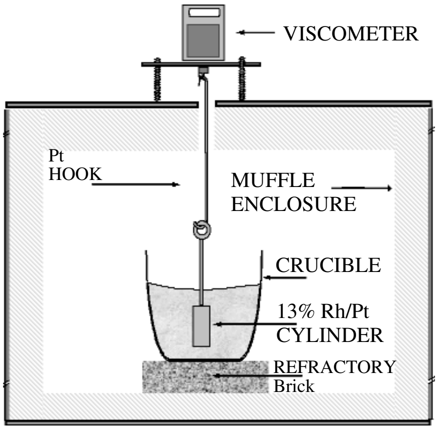

Figure 1. Schematic of experimental arrangement in the muffle to measure viscosity.

temperature difference between the control thermocouple and that of the melt was determined in a separate calibration of the enclosure by lowering a sheathed Pt/Pt-13%Rh thermocouple down the vent tube into the crucible full of $CaO-SiO_2$ slag. The thermal gradient in the stagnant melt was determined as ± 3°C. In the range of 1300 to 1550°C, the temperature of the melt was 20–23°C higher than the control thermocouple.

The viscometer bob was made from a Pt-13%Rh alloy, and was a 12 mm diameter, 25 mm high cylinder, with a concentric shaft 100 mm long and 3 mm in diameter. The shaft had a loop on the end to connect it to the extension rod that connected to the viscometer. A Brookfield DVII+ viscometer measuring head was located over the muffle vent hole and held in position by two brass plates. Around the circumference of the brass plates were three 150 mm long threaded studs positioned equidistantly, which enabled accurate height adjustment and levelling of the viscometer. The bottom brass flange had a central 40 mm diameter hole and was located over the muffle vent. The viscometer head was connected to the measuring bob by platinum extension rods with a total length of 250 mm. The height of the viscometer was adjusted so that there was a 10 mm gap between the bob and the crucible bottom.

Two master slags were used in this work. A $CaO-SiO_2$ master slag of composition close to the eutectic was prepared from a mixture of laboratory reagent grade $CaCO_3$ and SiO_2 which were milled in a ring mill and then melted in a Pt crucible at 1600°C in the muffle, quenched in a inclined steel launder, and milled. A Cu_xO-SiO_2 slag with the same silica content as the $CaO-SiO_2$ slag was prepared from a mixture of laboratory grade CuO and SiO_2. The master slag mix was milled and then melted in a magnesia crucible, and then cooled and crushed.

The $CaO-SiO_2$ slag mixture was placed in the crucible and loaded into the muffle and the viscometer positioned over the vent, and levelled. The bob was then suspended above the solid slag. The furnace was then heated up to temperature. After attaining temperature, the bob was immersed in the slag and the bob rotated to mix and homogenise the slag. The slag was then left for 1 hour to attain chemical and thermal equilibrium. After 1 hour the torque was then measured at several rotation speeds with 100–200 readings collected at each speed over a period of 5 minutes. When the measurements were completed, the muffle set temperature was increased and 30 minutes allowed for the system to equilibrate. After attaining the maximum temperature, the viscosity was re-measured at temperatures during a cooling cycle.

After sufficient data on the $CaO-SiO_2$ slag had been collected, the muffle door was opened and a slag sample was carefully collected on a steel dip rod. The copper content of the slag was then adjusted by adding the Cu_xO-SiO_2 master slag to the crucible. In order to keep the melt depth nearly constant, the same mass of slag was collected from the crucible prior to adding the copper slag. The melt was then allowed to homogenize overnight and the same measurement protocol as for the $CaO-SiO_2$ slag was used. Slags dip samples were collected after each viscosity measurement was completed and prior to adding more Cu_xO-SiO_2 master slag. When the desired range of copper content had been covered, the bob was removed from the crucible, the crucible removed from the furnace, and the contents poured into a steel launder to quench.

Viscometer calibration and measurement uncertainties

The viscometer bob was calibrated against liquids (silicone oils) of known viscosity at 25°C (0.05–30.8 Pa•s). A 250 cm^3 beaker containing the known standard was placed in a water bath at a constant temperature of 25ºC. The equation for determining the spindle constant is given in Equation 1, where η is the viscosity of the standard oil, τ is the measured torque, S is the spindle constant, K is an instrument spring constant, and rpm is the rotation speed of the bob.

$$\eta(Pa \cdot s) = \frac{KxSx\tau}{rpm} \qquad [1]$$

Fully immersing the cylinder to a depth of 5 mm in the standard and then measuring the torque at several rotation speeds allowed determination of the spindle constant for the viscometer bob. The effect of thermal expansion of the Pt cylinder at 800–1400 °C on the spindle constant was considered negligible. The contribution of the shaft to the spindle constant is also small and a 5 mm displacement from the calibrated depth contributes only a 0.3% error.

The viscometer was also calibrated at high temperature with the SRM slag supplied by Hoogovens RL. The measurement protocol outlined by the authors of the SRM study was adopted[5]. The agreement between the measured viscosities and the recommended values were well within the quoted experimental uncertainties.

It was estimated that the uncertainties of temperature measurement in this work were ±10°C, the uncertainties of the viscosity standards were ±1% and the uncertainty of the bob/viscometer was ±5%. When combined with the uncertainty due to averaging and linear regressions, the overall uncertainty is around ±10%, which is typical of most viscosity measurement.

Chemical analysis

The slag samples collected during the viscosity measurements were analysed by an ICP-OES technique. The slag was analysed for Cu, Ca, Mg and Si using the ICP technique. The Cu^{2+}, Cu^{+} contents of the slag were determined using the method reported by Nakamura and Sano[6]. In this technique, the sample was dissolved in 0.5M H_2SO_4 with an aliquot of ferric sulphate solution under a nitrogen purge. The solution was then titrated with a 5 mg Fe per ml of potassium dichromate using a diphenylamine sodium sulfonic acid indicator. The experimental system was verified using four certified reference materials (CRM).

Table I.
Assays of the $CaO-SiO_2$ binary slags studied.

Experiment	CaO (wt%)	Cu_2O (wt%)	MgO (wt%)	SiO_2 (wt%)
Melt I	36.4	0.02	0.03	63.6
Melt II	36.0	0.03	0.11	63.8

Results and discussion

The $CaO-SiO_2$ binary

The viscosity of the binary $CaO-SiO_2$ slag was measured in two experiments with different batches of master slag. The composition of the melts studied was targeted to a lime content of 37.2 wt.% studied by Bockris and Lowe[9]. This composition is close to the eutectic composition[10] of 35.7 wt.% CaO. The compositions of the two melts studied in this work are reported in Table I. The copper and magnesia contents are at the impurity level. The average CaO content of the two batches was 36.2 wt.%. The measured viscosity data are shown in Figure 2, with the viscosity-temperature relationship shown in a simplified 'Weymann' type plot[11], the Weymann temperature dependence of viscosity is of the form:

$$1n(\eta) = a + bT^{-1} + 1n(T) \qquad [2]$$

where a and b are constants and T is in K.

A least squares fit to the viscosity data of this study using Equation 2 was extrapolated 1800°C to compare with the measurements of Bockris and Lowe[9]. The line drawn in Figure 2 shows that agreement is excellent even when extrapolated to 1800°C.

The $CaO-Cu_xO-MgO-SiO_2$ system

The aim of the study was to examine substitution of Cu_2O for lime in the $CaO-Cu_2O-SiO_2$ ternary system. This was achieved by mixing the $CaO-SiO_2$ slag with a copper silicate slag with a silica mole fraction of 0.622. The compositions of the slags studied are given in Table II. There is a small but significant increase in the MgO content as the Cu_2O-SiO_2 slag is added. The Cu_2O-SiO_2 master slag was prepared in a magnesia crucible and, although the time the slag was liquid was probably not long enough to completely saturate the melt, the master slag contained 16.4% MgO. The oxidation state of Cu shifted from initially Cu^+ to Cu^{2+}, with the Cu^+/Cu^{2+} ratio of approximately 0.3 for melts with a Cu content above 2%. This is equivalent to $Cu_{1.13}O$. The observed changes of Cu^+/Cu^{2+} redox ratio were consistent with the literature[6]. Decreasing the basic oxide content (CaO) by substituting copper oxide resulted in a decrease in the Cu^+/Cu^{2+} redox ratio.

A review of viscosity measurements on $CaO-MgO-SiO_2$ slags[12] has shown that MgO substitution for CaO increases the viscosity only very slightly and the iso-viscosity lines lie almost parallel to the lines of constant SiO_2 mole fraction on a $CaO-MgO-SiO_2$ ternary diagram. The effect of MgO on the viscosity of $CaO-Cu_xO-MgO-SiO_2$ slags can be considered as small compared to the effect of Cu. The effect of substituting Cu_2O for CaO on the viscosity is shown in Figure 3. At a constant temperature, there was a fourfold decrease in the viscosity when 10 wt% $Cu_{1.13}O$ (X_{CuxO} = 0.074) was substituted for CaO. This is consistent with the behaviour in $Al_2O_3-CaO-SiO_2$ slags as reported by Nowakowski and Ptak[4].

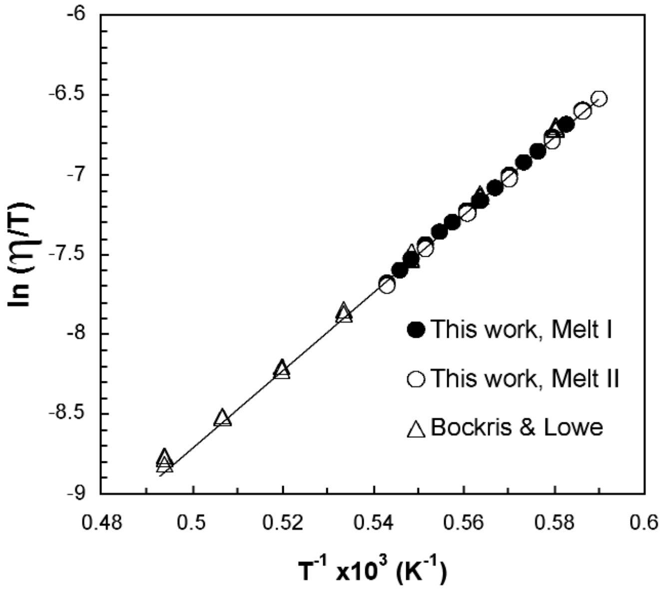

Figure 2. Measured viscosity of the $CaO-SiO_2$ binary of this work and the line of best fit extrapolated to 1800°C to compare with the high temperature data of Bockris and Lowe[9]

At the temperatures and high silica mole fractions (X_{SiO2}~ 0.6) of the present study, comparison viscosity data on the effect of other oxides are limited to a few measurements from the $CaO-MnO-SiO_2$[13,14], $CaO-FeO_x-SiO_2$[15,16] and $CaO-MgO-SiO_2$ [17,18] systems, which are shown in Figure 4. At a constant SiO_2 mole fraction, substitution of lime with Cu_xO has brought about a significant decrease in the viscosity. Considering that the copper slags also had a substantial concentration of MgO, which increases the viscosity slightly when substituted for CaO in $CaO-MgO-SiO_2$ slags[18], Cu_xO is very effective in breaking up the network to decrease viscosity and slightly

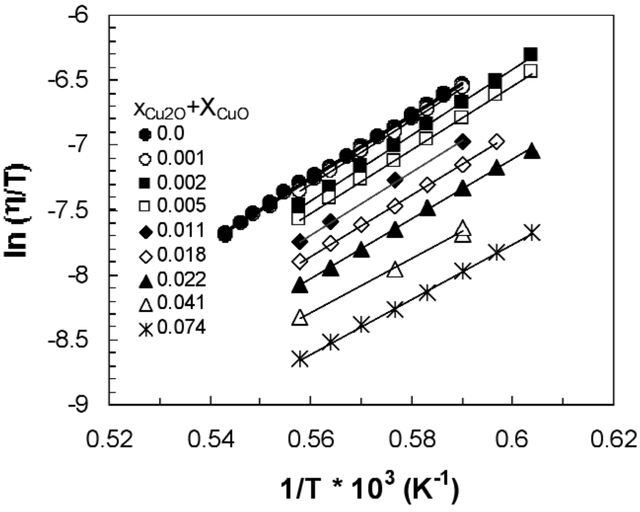

Figure 3. Observed Weymann behaviour of $CaO-Cu_2O-CuO-MgO-SiO_2$ slags with an average SiO_2 mole fraction of 0.610 (± 0.009)

Table II.
Composition of the slags targeted to a constant mole fraction of SiO_2

CaO (wt.%)	Cu_2O (wt.%)	MgO (wt.%)	SiO_2 (wt.%)	Cu^+/Cu^{2+}	x_{CaO}	x_{Cu_2O}	x_{CuO}	x_{MgO}	x_{SiO_2}
36	0.19	0.23	63.6	7.7	0.376	0.001	0	0.003	0.62
36.7	0.38	0.3	62.6	2.08	0.383	0.001	0.001	0.004	0.61
36	0.79	0.45	62.8	0.91	0.376	0.002	0.003	0.007	0.612
34.7	1.69	0.68	62.9	0.66	0.364	0.003	0.008	0.01	0.615
33.7	2.47	0.96	62.9	0.3	0.353	0.002	0.016	0.014	0.615
33.2	3.01	1.13	62.7	0.4	0.348	0.004	0.018	0.017	0.614
32.2	5.31	1.82	60.7	0.16	0.338	0.003	0.038	0.027	0.595
26.6	10.01	3.3	60.1	0.29	0.282	0.009	0.065	0.049	0.595

more effective in reducing the viscosity of silica containing slags than FeO or MnO. Zhang and Jahanshahi[19-20] have proposed that the effectiveness of oxides in reducing viscosity is related to the melting points of the oxides. From the thermochemical compilation by Barin [21], solid CuO is not stable above 1124°C and decomposes to Cu_2O, which has a melting point of 1243°C. FeO has a melting point of 1377°C and MnO and MgO have melting points of 1842°C and 2832°C respectively. The decrease in viscosity shown in Figure 4 is consistent with the model of Zhang and Jahanshahi.

The effect that the valence state of a transition metal has on the viscosity is virtually unknown except for iron where there have now been a few experimental studies where the results are ambiguous. Bodnar *et al.*[22] reported that the Fe_2O_3 content can have a large effect on viscosity and increasing Fe_2O_3 concentration increases the viscosity. Kaiura *et al.*[23] studied the viscosity of iron silicate melts at oxygen partial pressures of 10^{-11} to 10^{-7} atm., and their results show that the Fe^{3+}/Fe^{2+} ratio has only a very small effect on viscosity and decreases the viscosity slightly as the Fe^{3+}/Fe^{2+} ratio increases. This trend is also supported by Vartainen[2] and the author[24].

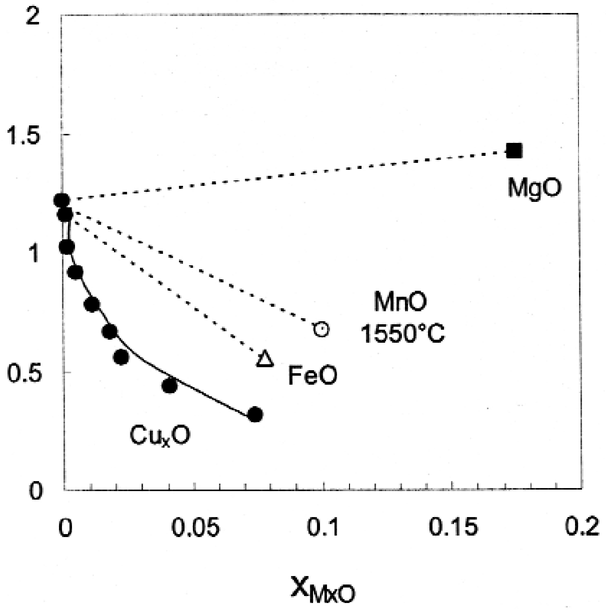

Figure 4. Comparison of the effect of substitution of CaO with Cu_xO in the pseudo-ternary (CaO+MgO)-(Cu_2O-CuO)-SiO_2 slag (x_{SiO_2}= 0.61) on the measured viscosity at 1520°C compared with other experimental results for FeO[15], MnO[13] and MgO[17] (X_{SiO_2}~ 0.6).

The influence that the oxidation state of other transition metal oxides has on viscosity has not been established. Collecting viscosity measurements at lower oxygen potential may establish the effect of the Cu^{2+}/Cu^+ redox couple might has on viscosity. However, this could be very difficult to do experimentally. Even at 1450°C and under the relatively oxidizing conditions where the oxygen partial pressure is 10^{-2} atm., the equilibrium the Cu^{2+}/Cu^+ redox ratio would be halved. A thermodynamic calculation of the equilibrium between the slag and the Pt-Cu alloy suggests the Cu concentration in the alloy would nearly double. Of course an atmosphere of pure oxygen could be also used. The Cu^{2+}/Cu^+ ratio would be larger and the Cu losses to the Pt would be lower, but the worth of doing so, in terms of developing a description of the effect of copper on viscosity for a copper containing industrial slag, would have to be clearly established.

Conclusions

The viscosity of CaO-SiO_2 and CaO-Cu_xO-MgO-SiO_2 slags has been measured at a constant SiO_2 mole fraction of 0.61 and with Cu_xO mole fractions of up to 0.074 (10 wt.%) at temperatures between 1380°and 1520°C in air with the following findings:

- The measured viscosity at the CaO-SiO_2 binary composition was in good agreement with other experimental work at the same composition.
- Under the conditions of this study, copper was found in the Cu^+ and Cu^{2+} valence states. The trends observed for changes of Cu^{2+}/Cu^+ redox ratio with slag chemistry were consistent with the literature. Under conditions where the SiO_2 content of the melt was nearly constant, decreasing the basic oxide content (CaO) by substituting copper oxide resulted in a decrease in the Cu^+/Cu^{2+} redox ratio. The change in ratio corresponded to a shift of the value of x in Cu_xO from an initial value of 1.8 to 1.1, when the Cu_xO mole fraction was 0.074.
- From the limited data available to compare with other oxides, Cu_xO is slightly better in reducing the viscosity than FeO or MnO.

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