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The oxidation state dependence of the electrical conductivity of high iron containing slags

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The oxidation state dependence of the electrical conductivity of a calcium ferrite slag with 25 wt% CaO was measured at 1300°C using a shallow slag layer and two-electrode technique. The experiments were started in air and the slag was sequentially reduced by means of a controlled gas atmosphere using CO_2 and CO. The electrical conductivity in air was approximately 300 S/m and increased with reduction to approximately 1900 S/m at a p_{O2} of 10^{-10} atm.

The interest in the oxidation state dependence of the conductivity of calcium ferrite slags was to provide a comparison with the conductivity of iron silicate slags and to establish the effect of slag basicity on the electrical conductivity and its oxidation state dependence. The results obtained are discussed in terms of the slag structural information available in the literature. The co-ordination of the ferric ions appears to play a large role in determining the electrical conductivity.

Keywords: calcium ferrite, slags, electrical conductivity.

Introduction

The major interest in the oxidation state dependence of the electrical conductivity of high iron (>50 wt% FeO_x) containing slags arose from earlier work carried out on lower iron containing slags by the present authors[1–2],. The aim of the earlier work was to identify the effect of slag basicity on the oxidation state dependence of the electrical conductivity. The oxidation state dependence of the conductivity relies on the electronic conduction, which occurs by charge exchange between ferric and ferrous cations. It was considered that by investigating the conductivity of slags at the extremes of basicity, one could gain further understanding of the factors affecting the conductivity of slags at intermediate basicities. Therefore, the electrical conductivity of iron silicate and calcium ferrite slags was investigated.

Data are available in the literature for the electrical conductivity of iron silicate slags under reducing conditions[3–7] i.e., at or near iron saturation, for slags with >50 mol% FeO_x. Conductivity values increase with increasing iron content, from ~100 S/m at 55 mol% FeO_x, to ~20000 S/m at 100 mol% FeOx at 1400°C.

The oxidation state dependence of the conductivity of several iron silicate slags was investigated by Fontana *et al.*[8] and Pastukhov *et al.*[9]. The findings are shown in Figure 1, where it is seen that conductivity increases with an increase in p_{O2} in the range 10^{-11} to 10^{-6} atm for all slags with > 60 mol% FeO_x. The magnitude of the conductivity and the increase in the conductivity is dependent on the total iron content of the slag. The increase in the conductivity with increasing p_{O2} is due to an increase in the ferric ion content in the slags and the corresponding increase in of electronic conduction that takes place.

Conductivity data for calcium ferrite slags at iron saturation were given by Inouye *et al.*[3] and Dancy and Derge[10]. The conductivity values rise from approximately 3000 S/m at 68 mol% FeO_x to around 20 000 S/m at 100 mol% FeO_x at 1400°C. Conductivity data for calcium ferrite slags in air were provided by Sumita *et al*[11]. and Adachi and Ogino[12]. The data of Adachi and Ogino suggests the conductivity at 1400°C in air increases from around 100 to 300 S/m for slags containing 65 to 76 mol% FeO_x, respectively. The data of Sumita *et al.*[11] suggest values around an order of magnitude higher at 1500°C (1000–2000 S/m for slags similar in composition to those of Adachi and Ogino).

There were no data for calcium ferrite slags, describing the oxidation state dependence of the electrical conductivity. Therefore, measurements were made to determine the oxidation state dependence and the results were interpreted along with the above data.

A greater understanding of the oxidation state dependence of the electrical conductivity of iron containing slags is relevant to smelter operations, where the slag oxidation state is controlled e.g during slag cleaning furnace operations.

Materials and methods

The experimental method employed was similar to that described by Hundermark *et al.*[1]. Briefly, the furnace used for the experiments was a vertical tube furnace, heated by $MoSi_2$ elements. Temperature was controlled by a Eurotherm controller (model 902). The experiments were carried out at 1300°C. Temperature in the tube was measured by a Pt/Pt-13%Rh (ASTM type R) thermocouple. The hot zone of the furnace was approximately 50 mm in height in which the temperature did not vary by more than ± 2°C at 1300°C. The crucible was supported by a pedestal at the top of a closed-end 5 mm x 3 mm alumina tube. The alumina tube passed through the bottom end cap through an O-ring system and connected to a programmable linear motion actuator. The actuator had a 500 mm stroke and could position and move the crucible vertically with a precision of 0.1 mm.

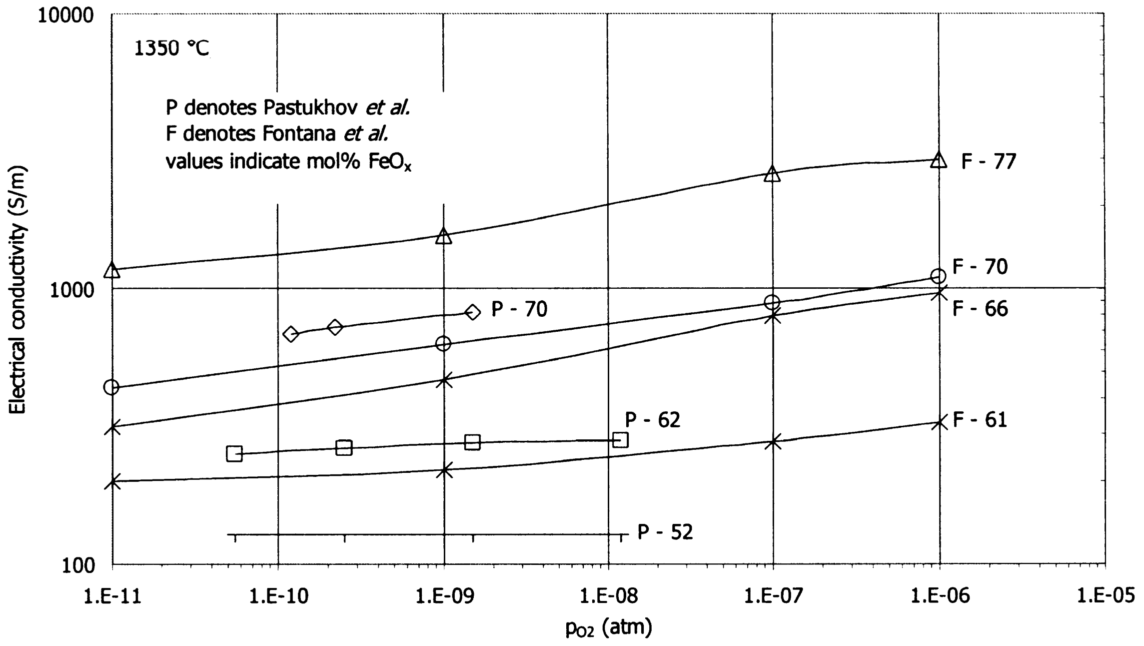

Figure 1: The oxidation state dependence of the electrical conductivity of iron silicate slags at 1350°C based on the data of Fontana *et al.*[8] and Pastukhov *et al.*[9]

Table I
Initial and final compositions of the calcium ferrite slags tested

Componrnts	Initial composition		Final composition-run 1		Final composition-run 2	
	wt%	mol%	wt%	mol%	wt%	mol%
Al_2O_3	0.2	0.2	0.4	0.4	0.4	0.4
CaO	23.5	45.9	26.3	47.2	26.5	47.0
Fe_2O_3	73.6	50.6	72.2	45.6	75.5	47.0
Mg.O	0.9	2.4	2.2	5.4	1.8	4.5
SiO_2	0.5	0.9	0.8	1.4	0.7	1.2
Total	98.6	100.0	101.8	100.0	105.0	100.0

The calcium ferrite slag was prepared using dried calcium carbonate and haematite powders (both Aldrich Chemical Company > 99% purity). The components were mixed in the desired proportions and the mixture was then premelted in a Pt crucible at 1350°C in air and quenched on a steel launder. The slag was crushed in a ring mill, assayed, sampled and was ready for use. The initial and post-experimental slag analyses are given in Table I. The use of magnesia boat crucibles gave rise to the increase in the MgO contents in the final compositions.

In the two experiments the atmosphere in the furnace needed to be controlled to obtain the desired partial pressure of oxygen (p_{O2}) and therefore the specified oxidation state of the slag. This was done by passing gas mixtures of fixed p_{CO2}/pCO ratios through the furnace. High purity CO_2 (99.8%), CO (99.5%), N_2 (99.99%) gases were cleaned, dried, measured and mixed before being delivered to the tube furnace.

Electrical conductivity measurements

A two-electrode technique was used for the electrical conductivity measurements. The electrodes were made up from two platinum wires of 0.5 mm diameter with 1 mm diameter Pt wire tips. The electrode tips were held rigidly in place by a spacer, ensuring an electrode spacing of 25 mm (centre to centre).

The conductivity cell consisted of a boat crucible made from MgO. The boat dimensions were 50 mm long, 8 mm wide and 6 mm high. Two grams of slag was used in each experiment, which gave rise to a liquid depth of approximately 2.5 mm. The amount of MgO that dissolved into the slag was from 1 to 2% (see Table I). The electrodes were immersed in the slag to a depth of 2 mm. A non-metallic crucible had to be used to prevent a parallel current path through the crucible. Magnesia was selected as reaction of the slag and crucible was limited. A small amount of slag was used to ensure that equilibration with the gases occurred relatively quickly, and that a high cell constant was obtained. It took approximately 45–60 minutes for the slag to reach equilibrium at the desired oxygen partial pressure.

Measurements of the impedance were made using a Fluke Programmable Automatic RCL meter (model PM6304). There was a four-wire measurement up to the connection with the electrodes. The RCL meter was connected via an RS232 interface to a computer, which allowed for frequency scans or continuous data measurement at specified frequency settings.

The calibration of the conductivity cell was carried out with 0.01, 0.1 and 1.0N KCl solutions. For the given cell geometry, the cell constant was approximately 1700 m^{-1}. The measurements on the slags were made at an applied frequency of 100 kHz, where the measured impedance was independent of the frequency.

The experiments were commenced at 1300°C and in an air atmosphere. Once the system had come to thermal equilibrium the electrodes were immersed in the slag, and remained there for the duration of the experiment. By leaving the electrodes in the slag one could obtain continuous measurements of the impedance, and hence determine when equilibrium was achieved. The gas atmosphere was then changed to a more reducing atmosphere by controlling the p_{CO2}/p_{CO} ratio at a given value. Once the system had again established equilibrium, the atmosphere was changed to a lower ratio. In this way, the conductivity of the slag was determined in air and at p_{CO2}/p_{CO} ratios of 70, 22.5, 7, 2.25 and 0.7. At 1300°C these ratios equate to oxygen partial pressures in the range of 1×10^{-10} to 0.21 atm.

The errors in the absolute values of the measured conductivity were estimated to be approximately 25%. This relatively large error was due to the small margin for error in the immersion depth of the slag, the small amount of slag being used and interactions between the slag and the crucible. However, the dependence of the slag conductivity on oxidation state was the main objective of the investigation. For a given experiment on a slag, it was likely that the relative change in the conductivity with varying oxidation state was considerably more accurate than 25%.

Results

The conductivity measurements were made at defined p_{CO2}/p_{CO} ratios. However, the equivalent pO_2 values have been calculated at 1300°C. These results are shown in Figure 2. It should be noted that in the duplicate run, the slag was exposed to a CO and N_2 gas mixture at the end of the run, and a sharp increase in the conductivity was observed (not shown in graph). This was ascribed to the precipitation of metallic iron.

It was considered more meaningful for the conductivity values to be plotted against the ferric and ferrous fractions. The ferric/total Fe fraction was estimated using a correlation given by Takeda et al.[13] relating the Fe^{3+}/Fe^{2+} ratio to a function of the wt% CaO and pO_2 for calcium ferrite slags. The conductivity (average of two runs) for the calcium ferrite slag is, therefore, presented as a function of the ferric / total iron fraction in Figure 3.

Figures 2 and 3 show that, as the slag becomes more reduced, the conductivity increases. The value of the conductivity in air (370 S/m) is higher than the values reported in the literature (Adachi and Ogino[12]: ~200 S/m at 1300°C). The conductivity value at the reduced conditions (~1900 S/m at $p_{O2} = 10^{-10}$) is lower than values reported in the literature for calcium ferrite slags in iron crucibles (Dancy and Derge[10]: ~3000 S/m). A possible reason for this is that the slags contained in iron crucibles were closer to iron saturation and some precipitation of iron occurred due to surface heat losses. It was noted in the repeat run that the precipitation of iron significantly increased the conductivity.

Discussion

As already mentioned, calcium ferrite and iron silicate slags were studied, as these systems provide extremes in terms of slag basicity. The explanation of the trends determined at intermediate basicities should follow from examination of trends for the extremes. Initially, the conductivity was examined at the extremes of oxidation state, therefore at very reduced and very oxidised conditions. Thereafter the conductivity was examined in situations where the oxidation state was varied.

In the case of solid wüstite and magnetite at high temperature, it has been shown that the electronic conduction was dependent on the fraction of octahedrally co-ordinated ferric and ferrous ions and not tetrahedrally co-ordinated ferric ions (see Wu and Mason[14] and Nell and Wood[15]). It was considered that the electronic conduction mechanism in liquid slags was likely to be similar to that of solid wüstite and magnetite, i.e. charge movement among ferric and ferrous ions of similar co-ordination.

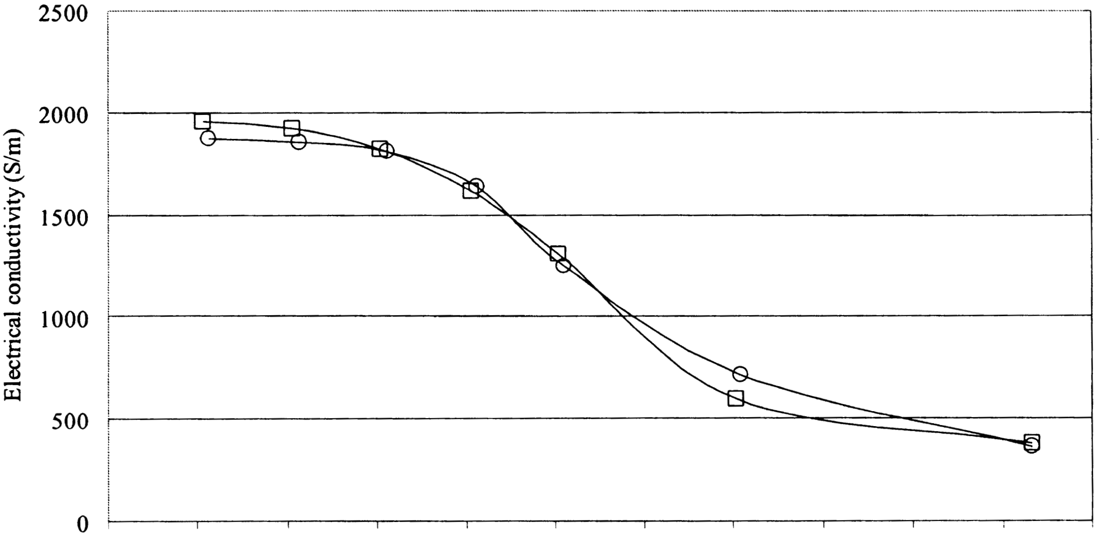

Figure 2: Oxidation state dependence of the electrical conductivity of a calcium ferrite slag at 1300°C (25 wt% CaO, 75 wt% FeO_x). Obtained in two runs

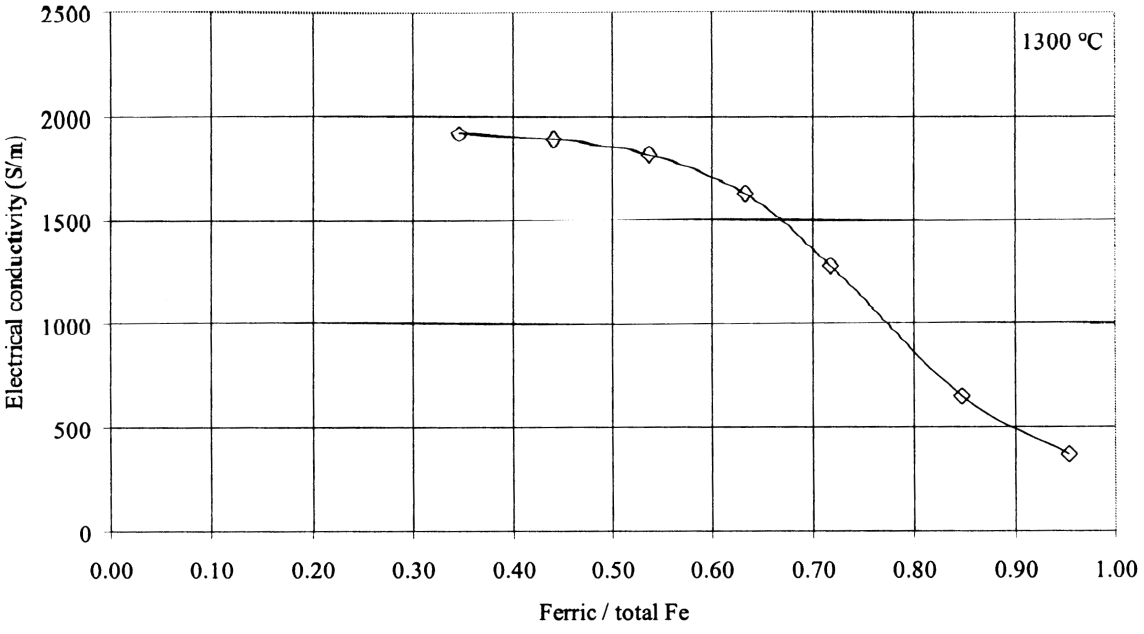

Figure 3. Variation of electrical conductivity at 1300°C of calcium ferrite slag (25 wt% CaO) with ferric fraction

Conductivity at reduced conditions

At reduced conditions the majority of the iron in a slag will be present as ferrous ions. In the case of iron silicate slags, almost all the iron is ferrous, while in calcium ferrites, at reduced conditions, it is likely that around 70–90% of iron will be ferrous (depending on total iron content).

Conductivity and current efficiency measurements in iron crucibles for calcium ferrite and iron silicate slags are shown in Figure 4. Briefly, current efficiency measurements give an indication of the proportion of current carried electronically or ionically. The greater the current efficiency, the greater proportion of the current carried by ions in the slag (as opposed to electronic conduction).

From the conductivity and current efficiency results on iron silicate slags measured in iron crucibles, it can be shown that, as the iron oxide content of the slag increases, so too does the electronic contribution. If one considers the ternary FeO-Fe_2O_3-SiO_2 phase diagram at iron saturation, it is seen that a decrease in silica content of an iron silicate increases the amount of ferric content. Therefore the increase in the electronic contribution is likely to be due to the increase in the ferric content.

The conductivity and current efficiency measurements on calcium ferrite slags in iron crucibles, has shown that the majority of the conduction is electronic. If one again studies the ternary CaO-FeO-Fe_2O_3 phase diagram at iron saturation, it is seen that there is considerably more ferric iron than for iron silicate slags. This explains why there is significantly more electronic conduction in calcium ferrite slags and why the percentage of electronic conduction does not decrease much with addition of lime.

Conductivity at oxidized conditions

The measured conductivity data on the calcium ferrite slags in air showed the conductivity to be lower than at reduced conditions. The benefit of studying calcium ferrite slags was that they have been very well characterized. Both Sumita *et al.*[11] and Yazawa *et al.*[18] have provided structural information on calcium ferrite slags in air. Sumita *et al.* suggested that in pure FeO_x, the ferric ions were octahedrally co-ordinated (Fe^{3+}\{6\}) and with addition of CaO the ferric ions became progressively more tetrahedrally co-ordinated (Fe^{3+}\{4\}). A correlation was provided by Sumita *et al.* which suggested that the conduction mechanism was primarily ionic and due to the Ca^{2+}, Fe^{2+} and Fe^{3+}\{6\} ions. The Fe^{3+} \{4\} cations present polymerize the slag and inhibit conduction. Therefore, as more CaO was added to the slag, the conductivity decreased as a result of greater concentrations of Fe^{3+}\{4\} cations.

Unfortunately no data were found concerning the conductivity of iron silicate slag at oxidized conditions (most likely due to the formation of magnetite).

Conductivity with varying oxidation state

Sumita *et al.*[11] provided ion distributions for calcium ferrite slags as a function of the CaO content. For a slag with ~50 mol% CaO, the ferric ions were equally distributed between octahedral and tetrahedral co-ordinations. The calcium ferrite studied in this investigation had ~48 mol% CaO (~25 wt% CaO), therefore it can be expected that in air approximately half the ferric ions were in tetrahedral co-ordinations and half in octahedral co-ordinations. Therefore, considering the low conductivity at oxidized conditions (see Figures 2 and 3), it is likely that the majority of the current is carried by Fe^{3+} \{6\} and Ca^{2+} cations and a small amount is carried by the few Fe^{2+} cations that are present. As the slag becomes more reduced, the number of Fe^{2+} cations increase and, hence, electronic conduction is enhanced. It is not currently known how the distribution of octahedral and tetrahedral ferric cations is affected by the oxidation state.

Considering iron silicate slags and the data presented in Figure 1, it was shown that the increase in the conductivity with increasing p_{O2} was due to an increase in the ferric ion content in the slags. The increase in the ferric iron content leads to an increase in the amount of electronic conduction that takes place. The distribution of the ferric cations between octahedral and tetrahedral co-ordinations is

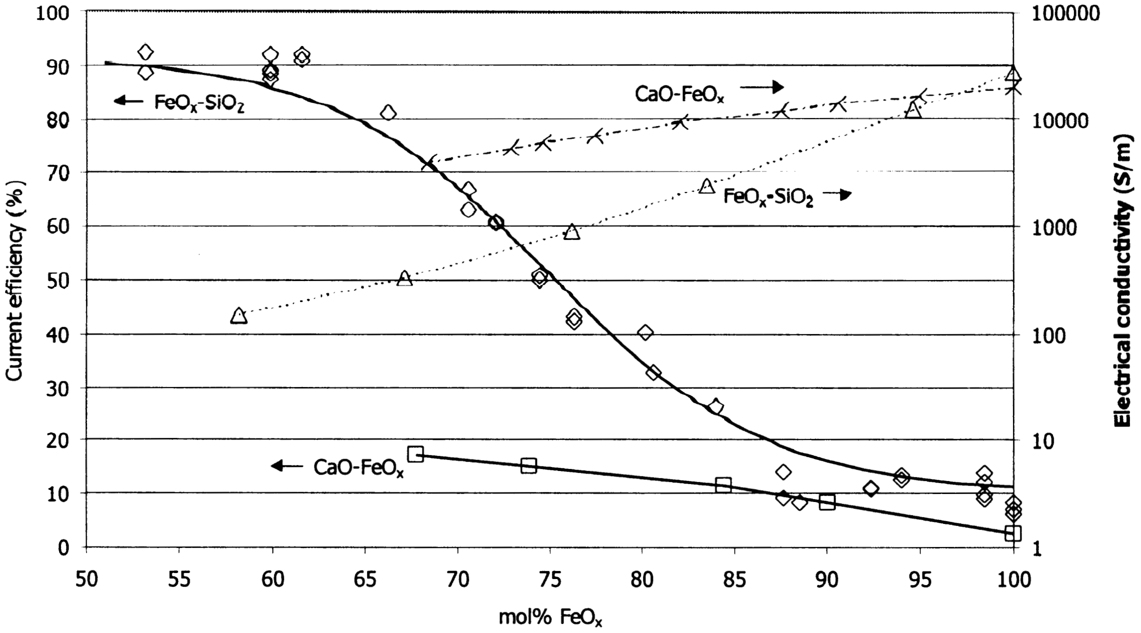

Figure 4: Current efficiency measurements on iron silicate and calcium ferrite slags by Simnad *et al*[17]. and Dancy and Derge[10], respectively. Measurements were carried out in iron crucibles at 1300 and 1200°C, respectively. Electrical conductivity measurements at 1400°C on iron silicate and calcium ferrite slags by Inouye *et al.*[3] and Dancy and Derge[10], respectively (in iron crucibles)

unknown, however Mysen *et al.*[19] showed that the ferric ions in silicate melts were predominantly tetrahedrally co-ordinated at oxidized conditions but as the Fe^{3+}/Fe_{total} fraction decreased from 0.5 to 0.3, the ferric ions changed co-ordination to octahedral. This work was carried out on slags with low iron contents (up to 10 wt% FeOx) so its applicability to high iron containing slags is uncertain.

Effect of slag basicity

The slag basicity affects the proportion of ferric and ferrous ions and also the co-ordination of the ferric ions at a given oxidation state. At iron saturation for slags containing the same amount of iron, the conductivity should increase with increasing basicity as the ferric fraction (and electronic conduction) increases. As the oxidation state of the slags is increased, the conductivity should increase as more ferric iron is formed. However, as was seen in the case of the calcium ferrite slag, the conductivity was already at a maximum at iron saturation and the conductivity started decreasing with increasing oxidation state. Therefore, one expects that for an intermediate basicity slag, the conductivity will increase as it is oxidized, reach a maximum and then start decreasing with further oxidation (as shown by Hundermark *et al.*[1] and Engell and Vygen[20]).

Conclusions

The electrical conductivity of a calcium ferrite slag was measured at a range of oxidation states at 1300°C. The electrical conductivity in air was approximately 300 S/m and increased to approximately 1900 S/m at a p_{O2} of 10^{-10} atm. The increase in the conductivity is likely to be due to increased electronic conduction between ferric and ferrous ions. The results for the calcium ferrite slag were compared to results for iron silicate slags, in order to understand the effect of basicity on the oxidation state dependence of the electrical conductivity in high iron containing slags.

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