Viscosity Measurements on Some Fayalite Slags

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In the present study, viscosity measurements on Fe–O–Si slags have been carried out using rotating cylinder method. The slag samples for viscosity measurement were prepared by pre-melting appropriate stoichiometric amounts of Fe, Fe₂O₃ and SiO₂ in an iron crucible under argon atmosphere, which ensured that Fe ions in the slag were predominantly in the valence state of +2. The viscosities of the pre-melted slag samples were measured in iron as well as nickel crucibles under argon atmosphere at different temperatures. The measured viscosity values obtained in the two kinds of crucibles were found to be in good agreement, indicating thereby that nickel crucibles can be successfully used for viscosity measurements. In order to investigate the effect of oxidation of Fe²⁺ to Fe³⁺, the binary Fe₂O–SiO₂ slag was kept in a nickel crucible under oxidising conditions using a CO/CO₂ atmosphere and viscosity measurements were carried out dynamically as a function of time at 1 623 and 1 673 K. With time, Fe³⁺ concentration in the slag increased and hence the viscosity changed progressively. The rate controlling step for the oxidation reaction was considered to be the mass transfer of CO₂ in the gas stream to the slag–gas interface. A simple kinetic analysis was used to predict the concentration of Fe³⁺ in the slag with time. The measured viscosity with time indicated that the viscosity remains almost the same during initial period of oxidation. The viscosity raises sharply when the Fe³⁺ concentration in the slag, calculated as Fe₂O₃ reached around 7 mass%.

KEY WORDS: slag; fayalite; viscosity; dynamic measurement.

1. Introduction

Viscosity is one of the important properties, which has a direct influence on the kinetics of slag–metal reactions in various smelting and refining processes. Hence, it is one of the key parameters used in various modelling techniques wherein various metallurgical processes are simulated to aid in better understanding, optimisation and control of processes.

Access to accurate viscosities of molten slags and description of the same as function of temperature and composition is an urgent need to meet the high demands of advanced technology. In view of this, the Department of Metallurgy, Royal Institute of Technology, Stockholm has been involved in viscosity measurements of various slag systems of technological importance. Efforts have been made to predict viscosities of various multicomponent systems as a function of composition and temperature. Along these lines, in the present work, viscosities of fayalite slags have been investigated. An understanding of the viscosity of Fe–O–Si system has great relevance even in copper metallurgy.

Very few measurements have been carried out in Fe–O–Si slag system and most of these measurements have been confined to FeO–SiO₂ region in which the Fe ions are predominantly in the valence state of +2. Formation of Fe³⁺ ions in the slag can cause large increase in viscosity during operation. The viscosities in the ternary system FeO–SiO₂–Fe₂O₃ were studied by Bodnar et al. as well as Toguri et al.

In the present study, viscosities were measured for Fe–O–Si system at different temperatures using rotating cylinder method. Initially, viscosity measurements were carried out in iron and nickel crucibles in the binary FeₙO–SiO₂ region of Fe–O–Si system as a function of temperature. Further, investigations were carried out to study viscosity of Fe–O–Si slags during oxidising conditions. For this, starting with binary FeₙO–SiO₂ slag in a nickel crucible, the viscosities were measured dynamically as a function of time under an oxidising atmosphere with CO/CO₂ gas mixture.

2. Experimental

2.1. Slag Preparations

In order to prepare the binary slag of SiO₂–FeₙO, Fe, Fe₂O₃ and SiO₂ in appropriate stoichiometry were first mixed. The materials used are listed in Table 1. SiO₂ was calcined at 1 273 K for more than 12 hr in a muffle furnace to decompose any residual carbonate and hydroxide. Fe₂O₃ was dried at 398 K for 12 hr before use. Iron and Fe₂O₃ were first mixed so that the total oxygen content in the mixture was 51 mole percent. This composition was so chosen that in liquid state at the temperature of approximately
1673 K, the mixture would be in equilibrium with $\delta$-Fe. The mixture was then thoroughly mixed with SiO$_2$ in an agate ball mill for more than one hour. Subsequently, the mixture was pre-melted in an iron crucible under argon atmosphere. For pre-melting, the mixture in a pure iron crucible was introduced into an alumina tube which is heated by U shaped Mo$_2$Si heating elements. An oxygen partial pressure between $2.5 \cdot 10^{-6}$ and $1 \cdot 10^{-9}$ atmosphere should be maintained in the gas phase to prevent any oxidation or reduction of the slag during pre-melting. This was ensured by passing the argon gas through a gas cleaning system before being introduced into the furnace. The oxygen partial pressure in the out going gas was monitored constantly by a ZrO$_2$–CaO oxygen probe and was found to be about $10^{-9}$ atm. The detail description for slag preparation using iron crucible has been discussed in earlier publications. The pre-melted samples were further used for viscosity measurements.

2.2. Experimental Set Up

The rotating cylinder method was adopted in the present study. The experimental set up consisting of a high temperature furnace, a gas cleaning system and a viscometer as well as the experimental procedure adopted have been explained in detail in earlier publications.

The gas cleaning system and experimental setup are shown in Fig. 1. CO/CO$_2$ mixture was used to maintain oxidising condition during dynamic viscosity measurements on Fe–O–Si slag. CO gas used for the present experiments was passed through columns of silica gel and Mg(ClO$_4$)$_2$ to remove any traces of moisture. Further, it was passed through a column of copper turnings at 773 K to remove the traces of oxygen. The CO$_2$ impurity in CO gas was removed by ascarite kept in the gas stream. For CO$_2$ gas, the traces of moisture were removed by passing through columns of silicate gel and Mg(ClO$_4$)$_2$. The gas flow rates were controlled and monitored using flow controllers, model F-201C-FA, supplied by Bronkhorst High-Tech B.V., the Netherlands.

The viscometer was calibrated at room temperature using mineral oil standard with viscosities 0.0985, 0.960, 4.850 and 12.500 Pa·s. Calibrations were also carried out at experimental temperature using a reference slag consist of Al$_2$O$_3$–Li$_2$O–SiO$_2$ developed for BCR program of European Union.

Crucible-spindle assembly made of pure iron was used for viscosity measurements under argon atmosphere, wherein the slag melt was in equilibrium with metallic iron. For viscosity measurements at higher oxygen partial pressures in the gas phase, it was necessary to choose an alternative material for the crucible and the rotating spindle. Some attempts were made with platinum crucibles and corresponding spindle. But the crucibles developed cracks during the measurements resulting in extensive damage to the experimental assembly due to slag leakage. In the absence of other suitable materials, pure nickel was chosen as the crucible and spindle material for viscosity measurements under oxidising conditions. It is admitted that even though the $P_{O_2}$ in the gas phase can be kept below the Ni–NiO equilibrium oxygen pressure at the experimental temperatures during the oxidation experiments, the lowering of the activity of NiO by dissolution in the slag phase would still lead to an oxidation of the crucible. In the absence of other

Table 1. Materials used in the present study.

| Materials                  | Purity        | Supplied by                   |
|---------------------------|---------------|-------------------------------|
| Iron (Fe)                 | pro analyse grade | E. Merck, Darmstadt, Germany |
| Iron Oxide (Fe$_2$O$_3$)  | Anhydrous, AR grade | Fisher Scientific, New Jersey, USA |
| Silicon Oxide, (SiO$_2$)  | pro analyse grade | E. Merck, Darmstadt, Germany |
| Argon, (Ar)               | Argon Plus    | AGA Gas, Stockholm            |
| Carbon monoxide (CO)      | CO 99.99 %    | AGA Gas, Stockholm            |
| Carbon dioxide (CO$_2$)   | CO$_2$ 99.9 % | AGA Gas, Stockholm            |

1-Valve, 2-Silica gel, 3-Cu, 4-Ascrate, 5-Mg(ClO$_4$)$_2$ 6-Mg, 7-Flow meter, 8-Gas-mixer, 9-Oxygen probe 10-Viscometer and high temperature furnace

Fig. 1. Setup of high temperature viscometer system.
suitable materials, nickel was opted by the authors as the best choice. The dimensions of the two kinds of crucibles and spindles are the same and are listed in Table 2.

Initially, measurements were carried out on the binary Fe₉O–SiO₂ slag in iron crucible under argon atmosphere. Subsequently, the viscosity measurements were repeated by replacing the iron crucible with a nickel crucible. Once, the viscosity measurements in nickel crucible under argon atmosphere were carried out for the binary, the atmosphere was switched to CO₂/CO in order to measure the viscosity of slag under oxidising conditions. With time, CO₂ oxidises the Fe²⁺ to Fe³⁺ and the slag composition changes with time and hence the viscosity. In the present work, the experimental temperatures were chosen to be 1 673 and 1 623 K. The ratio of $P_{CO_2}$ to $P_{CO}$ was 9.81, which would lead to oxygen partial pressure of $2.5 \cdot 10^{-7}$ atmosphere at 1 673 K and $7.2 \cdot 10^{-8}$ atmosphere at 1 623 K. The minimum partial pressures of oxygen to oxidize nickel was calculated to be $2.5 \cdot 10^{-8}$ atmosphere at 1 673 K and $8 \cdot 10^{-7}$ atmosphere at 1 623 K. However, as mentioned earlier, there is a likelihood of the oxidation of nickel due to the lowering of the activity of NiO formed due to the dissolution in the slag. The volume flow rates of CO and CO₂ were chosen to be approximately 0.021 and 0.206 Nl/min. After viscosity measurements, the slag was cooled in argon atmosphere. Before and after viscosity measurements, slag samples were taken for chemical analysis.

3. Results

Figure 2 shows the viscosity measured both in iron and nickel crucibles for the binary 68% Fe₉O–32%SiO₂ as a function of temperature. As expected, the viscosity decreases with temperature. The measured viscosity values are in the range recommended by Slag Atlas. Reproducibility of the viscosity values was found to be good as can be seen in the figure. It was also found that the viscosities measured in iron and nickel crucibles are in good agreement. This would suggest that nickel components can be employed for the viscosity measurements of slags.

After measuring the viscosity values for the binary Fe₉O–SiO₂ slag, investigations were carried out to study the variation of viscosity under oxidising conditions in a CO₂/CO atmosphere. These measurements were performed by using nickel crucible and spindle. The measured viscosity values are listed in Table 3. As the oxidation progresses, the Fe³⁺ concentration in the slag increases and hence the viscosity varies with time. Figure 3 shows the measured viscosity varying with time at 1 673 and 1 623 K. It can be seen that reasonable reproducibility of measurements has been reached. The viscosity of the slag almost remains the same during initial part of oxidation with a slight decrease at 1 623 K. A somewhat more pronounced decrease has been found with increasing Fe₂O₃/FeO ratios by Toguri et al.
al.17) for the slag with 35% SiO₂ at 1 573 K. The viscosity values in the ternary system FeO–SiO₂–Fe₂O₃ are in the range reported by earlier workers.16,17) At much longer oxidation time, there is a sharp raise in viscosity. This raise in viscosity occurs at a much shorter time at 1 673 K compared to that at 1 623 K.

After viscosity measurements, the slag samples for analysis were taken along the height of the slag. Figure 4 shows the sampling places as well as the compositions (Fe³⁺ concentration expressed as wt% Fe₂O₃) at different points. The slag compositions are fairly uniform along the height of the slag. However, very close to the vicinity of top surface, the concentration of Fe³⁺, expressed as Fe₂O₃, was found to be very low. This can be attributed to the reduction of Fe³⁺ at the surface layer during cooling of slag using argon gas wherein the partial pressure of oxygen was low.

4. Discussion

The chemical reaction which occurs in the gas–slag interface can be assumed as

\[
\text{CO}_2(g) + 2\text{Fe}^{2+} \text{(slag)} + 2\text{O}^2- \text{(slag)} = \text{CO}(g) + 2\text{Fe}^{1+} \text{(slag)} + 3\text{O}^2- \text{(slag)} \quad \text{............(1)}
\]

It is reasonable to assume that reaction (1) occurring at the slag–gas interface could be quite fast as well as the compositions (Fe³⁺ concentration expressed as wt% Fe₂O₃) at different points. The slag compositions are fairly uniform along the height of the slag. However, very close to the vicinity of top surface, the concentration of Fe³⁺, expressed as Fe₂O₃, was found to be very low. This can be attributed to the reduction of Fe³⁺ at the surface layer during cooling of slag using argon gas wherein the partial pressure of oxygen was low.

If the partial pressure of oxygen in equilibrium with the slag phase is known, then for \(X_{\text{O}_2,i,}\), the mole fraction of CO₂ at the gas–slag interface can be determined from the above gas equilibrium as

\[
\rho \frac{dX_{\text{FeO}}}{dt} = -Ak\rho \varepsilon (X_{\text{CO}_2,i} - X_{\text{CO}_2,b}) \quad \text{............(2)}
\]

where \(\rho\) is the molar density of slag and \(V\) is volume of the slag in the crucible, \(X_{\text{FeO}}\) is the mole fraction of FeO in the slag, \(A\) is the area of slag–gas interface, \(k\) is the mass transfer coefficient, \(\rho \varepsilon\) is the gas density, \(X_{\text{CO}_2,b}\) is the mole fraction of CO₂ in the bulk and \(X_{\text{CO}_2,i}\) is the mole fraction of CO₂ at the slag–gas interface. It has been further assumed in the present analysis that the molar density of slag and total volume of slag do not change significantly during oxidation.

In the present work, the gas is assumed to be ideal. Hence, the mole fraction of CO₂ at the bulk can be determined from the input gas composition. In order to determine the mole fraction of CO₂ at the slag–gas interface, the following equilibrium in the gas phase has been considered

\[
\text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2 \quad \text{............(3)}
\]

If the partial pressure of oxygen in equilibrium with the slag phase is known, then for \(X_{\text{O}_2,i,}\), the mole fraction of CO₂ at the gas–slag interface can be determined from the above gas equilibrium as

\[
X_{\text{CO}_2} = \frac{k_{\text{eqm}} \sqrt{X_{\text{O}_2,i}}}{1 + k_{\text{eqm}} \sqrt{X_{\text{O}_2,i}}} \quad \text{............(4)}
\]

where, \(k_{\text{eqm}}\) is the equilibrium constant for reaction (3). However, the partial pressure of oxygen in equilibrium with FeO–SiO₂–Fe₂O₃ slag system (in the present analysis, Fe₂O₃ is considered as a component added to the FeO–SiO₂ binary) could not be computed directly due to the lack of
thermodynamic data. For the present calculation, the equilibrium partial pressure of liquid slag was obtained from the ternary diagram reported by Muan et al.\textsuperscript{27} at the liquidus temperature. It has been assumed that the partial pressures of oxygen in equilibrium with the slag at 1623 and 1673 K are not significantly different from that at the liquidus temperature. From the phase diagram, the logarithm of partial pressure of oxygen as a function of FeO composition of slag has been plotted in Fig. 5. The figure shows that it is possible to express logarithm of partial pressure of oxygen as a linear function of FeO mole fraction in the slag. Hence, the oxygen partial pressure in equilibrium with slag can be expressed as a function of mole fraction of FeO:

\[ P_{O_2,i} = X_{O_2,i} \exp(-119X_{FeO} + 46.1) \]  \hspace{1cm} \text{(5)}

Substituting Eq. (5) and Eq. (4) in Eq. (2),

\[
\rho V \frac{d(X_{FeO})}{dt} = -A k_{eqn} \left( X_{CO_{eqn}} \frac{\exp(-119X_{subFeO} + 46.1)}{1 + k_{eqn} \exp(-119X_{FeO} + 46.1)} \right)
\]

\hspace{1cm} \text{..........................(6)}

The above equation can be solved numerically from the start of the experiment to the end of the experiment. Since the compositions of FeO in the slag at the start of experiment and at the end of the experiment are known, the mass transfer coefficient can be estimated. Once the mass transfer coefficient is known the composition of FeO with time can be determined from Eq. (6).

Knowing the composition of the slag at the end of viscosity measurements, the kinetic model described in the previous section was used to estimate the composition of slag with time. Figure 6 shows the variation of Fe\textsubscript{2}O\textsubscript{3} content in the ternary system FeO–SiO\textsubscript{2}–Fe\textsubscript{2}O\textsubscript{3} with time computed using the model at 1623 and 1673 K. As expected, the oxidation rate is higher at 1673 K than at 1623 K.

Figure 7 shows the variation of viscosity of the slag as a function of the computed content of the component Fe\textsubscript{2}O\textsubscript{3} in the ternary system FeO–SiO\textsubscript{2}–Fe\textsubscript{2}O\textsubscript{3} at 1623 K, at which temperature more number of experimental points are available. The variation of viscosities with time can be classified into two parts. In the region where the Fe\textsubscript{2}O\textsubscript{3} content is low, the viscosities remain almost constant. When the Fe\textsubscript{2}O\textsubscript{3} content reaches around 7\%, there is a sharp rise in viscosity, marking the approach of the precipitation of magnetite. Further work need to be carried out in order to correlate the present dynamic studies with equilibrium data.

5. Conclusions

Nickel crucibles and spindles have been successfully used to measure the viscosity of Fe–O–Si slags prepared by pre-melting appropriate mixture of Fe, Fe\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} in pure iron crucible. The viscosities of binary 68\% Fe\textsubscript{2}O\textsubscript{3}–32\% SiO\textsubscript{2} have been reported as function of temperature in the present study. Dynamic viscosity measurements have been carried out on the above slag under a CO/CO\textsubscript{2} oxidising atmosphere to investigate the effect of Fe\textsuperscript{3+} content on viscosity. The results show that the viscosity remains constant during initial part of oxidation. However, when the
Fe₂O₃ content reaches approximately 7 mass%, there is sharp increase in viscosity suggesting the precipitation of magnetite.

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