Viscosity of SiO₂-CaO-CrOₓ slags in contact with metallic chromium and application of the Iida model

L. FORSBACKA and L. HOLAPPA

Laboratory of Metallurgy, Helsinki University of Technology, Finland

Viscosities of quasi-ternary CaO-SiO₂-CrOₓ melts in contact with metallic chromium were measured by the rotating cylinder method up to 1750°C. Twelve slag compositions were selected in the composition range 20–55 wt% SiO₂, 10–45 wt% CaO and 10–60 wt% CrOₓ. Estimation of the amounts of CrO and Cr₂O₃ was made by regression analysis based on the earlier data. Professor Iida’s (Osaka University) viscosity model was applied and model parameters (µCrO, αCrO and αCr₂O₃) were evaluated. The Iida model gave good consistency with the measured viscosity values.

Introduction

Knowing the properties of chromium containing slags is very valuable for the metallurgical industry, especially for stainless steel and ferro-chromium production. Still, not enough has been done in order to find out the viscosity values of chromium containing slags. One reason is that chromium slags have very high melting points. The other is that chromium appears in two oxidation stages in metallurgical slags: Cr²⁺ and Cr³⁺, with corresponding oxides CrO and Cr₂O₃ (CrO 1.5 ), which makes the measurement more complicated. The distribution of the total chromium content (CrOₓ) into CrO and Cr₂O₃ depends on the oxygen partial pressure, the temperature, and the total amount of chromium and the other oxide species in the slag.

In this study the chromium slag was put in contact with metallic chromium in order to equilibriate the system. This equilibrium would have the lowest oxygen partial pressure possible at the particular composition. A similar condition is found in metallurgical processes when chromium oxide is reduced from slag to metal.

Because viscosity measurements are time consuming and expensive, or even impossible because of the too high melting points, there is an ongoing attempt to develop viscosity models that can predict viscosities of various oxide combinations, also extrapolated into the temperature ranges that cannot be measured. Applicable work has been accomplished, for example, in the Royal Institute of Technology, Sweden (KTH-model)¹, Brisbane University of Queensland, Australia (modified Urbain model)² and Osaka University (Iida model), Japan, which has been adapted for this study.

Experimental techniques

The furnace is an Entech ETF 50–175V, with MoSi₂ heating elements having a maximum continuous temperature of 1750°C. A controller unit contains a Eurotherm 903P-unit, where the temperature control programs are made.

The programmable Brookfield LVDV-II+ viscometer is designed for measurement of viscosity at given shear rates. The principle of operation is to drive a spindle, which is immersed in the test fluid, through a calibrated spring. The viscous drag of the fluid against the spindle is measured by the spring deflection, which is detected with a rotary transducer.

The measurement range is defined by the rotational speed of the spindle, the size and shape of the spindle, the container in which the spindle is rotating, and the full scale of rotating spring.

The viscometer is installed in the lift, which enables immersion in and removal of the spindle from the liquid slag.

The spindle and the crucible were made of molybdenum, which has a melting point of 2623°C. Unfortunately, molybdenum oxidizes readily and the oxide evaporates rapidly at high temperatures. The furnace has to be hermetically sealed and an inert or a reducing atmosphere has to be applied in order to prevent detrimental oxidation. During experiments argon was used. A piece of graphite was placed in the furnace tube at the proper temperature zone to eliminate the small amount of oxygen eventually leaked into the furnace.

Dimensions of the crucible and spindle are presented in Figure 2. The 20 mm deep hole in the bottom of crucible is made for an alumina stand. The container is 90 mm deep, which may seem to be too deep. However, when the crucible is filled and treaded with a slag powder, it is almost completely full. After melting, the volume of the slag is less than 50% of the powder’s volume.

The size of the spindle has to be designed so that it is applicable in the required viscosity range. The coned ends of the spindle help the molten slag to drain off when the spindle is lifted from the slag.
Experimental methods

Calibration of viscometer
The viscometer was calibrated using three silicon oils with nominal viscosities of 10, 50 and 500 cP at 25°C, and at high temperature with a standard reference material developed in the BCR program of the EU (19.46% Li2O, 14.06% Al2O3 and 63.8% SiO2). For the room temperature calibration, the crucible was placed in a water bath (Haake DC-30), so that exactly 25°C was reached. It was found that the very low viscosities of CaO-SiO2-CrOx slags required such a combination of the size of the spindle and rotational speed that the spindle started to sway slightly during the measurement. The effect increased with higher rotational speeds and lower viscosities (remarkably below 5 cP). Therefore, the system constant was determined at four rotational speeds (60, 50, 30, 20 rpm), and the average was used as a system constant. During the measurement the same procedure was applied, so that the viscosity was a calculated average of four different speeds. The 100 rpm was not used because it caused extra resistance because of the increased sway. Also, the lowest speed used was limited by the requirement of 10 per cent of the torque of the calibrated spring of the viscometer.

Preparation of samples
The powders of CaO, SiO2 and Cr2O3 were heated at 800°C in an oven for 4 hours in order to remove moisture and carbon. SiO2 and CaO were carefully weighed in a micro-scale and blended to produce binary ‘base slags’. Cr2O3 and Cr powders were similarly weighed and blended to produce ‘addition slag’ with a nominal composition of CrO. The idea was to fill the crucible with base slag for the first measurement, and then after each measurement, take a sample for compositional analysis and add a predetermined amount of CrO to change the composition for the next measurement. As a result, there are two sets of measurements: Slags 1–6 and Slags 7–12, with target compositions represented in Table I and Figure 3.

The intention of the present study was to put the slag in contact with metallic chromium and drive the system in equilibrium. Therefore, 10 grams of metallic chromium flakes was placed in the bottom of the crucible before the first measurement. The crucible was then filled with 100 g of hydraulically pressed cylindrical pellets made of the base slag.

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**Table I**

Target compositions and estimated amounts of CrO and Cr2O3 (weight-%)

**Figure 1. Experimental arrangement**

**Figure 2. Crucible, spindle and coupling to viscometer**
Measurement procedure

The crucible filled with the slag was placed in the furnace, and the furnace was programmed to heat up 4º per minute up to 1750ºC. Circulation of cooling water and argon flow was verified. The furnace was kept at the maximum temperature at least for one hour before the first measurement. Then the furnace was programmed to cool down 3º per minute to a selected lower temperature and the temperature was allowed to settle for 30 minutes before each measurement. At each temperature the viscosity was measured using several rotational speeds (60, 50, 30, 20 rpm). The measurements were continued until viscosity started to rise rapidly and the position of the spindle proved the existence of solid phase in the slag. The viscosity was measured only during the cooling cycle, because earlier experiences show that once the solid phase has segregated on the bottom and walls of the crucible, it might take a very long time at high temperatures to achieve a homogenous liquid slag again. After the last measurement the spindle was lifted out of the slag and the furnace was allowed to cool down to room temperature. The crucible was weighed after the measurement and a few grams of slag were drilled from the top of the crucible for compositional analysis. After the sample was taken, the crucible was weighed again, and a suitable amount of addition slag (CrO) was added to change the composition for the next measurement.

Results

Chromium appears in two oxidation stages in metallurgical slags: Cr^{2+} and Cr^{3+}, with corresponding oxides CrO and Cr_2O_3 (CrO_{1.5}). The relative amount of these oxides depends on the other oxide species in the slag, the oxygen partial pressure, the total amount of chromium, and the temperature of the slag. Both of these oxides affect viscosity in different ways and are usually considered as different oxide species, like SiO_2 and CaO. It is therefore necessary to know how much CrO and Cr_2O_3 there are in the slag.

Compositional analysis

The analysis of CaO, SiO_2 and total CrO_x was made by X-ray fluorescence at AvestaPolarit Chrome. The amount of CrO was analysed by wet-chemical analysis in Delft, The Netherlands. The idea of wet chemical analysis is to dissolve the slag in HCl in an inert gas in the presence of Fe^{3+} chloride (FeCl_3).

Cr^{2+} is oxidized to Cr^{3+} and the same amount of Fe^{3+} is reduced to Fe^{2+}. The amount of Fe^{2+} ions can be determined by titration with standard permanganate solution.

Unfortunately, the compositional total analysis failed because the sample for the compositional analysis was taken only from the top of the solidified slag. It seemed afterwards that segregation during relatively slow solidification had altered the composition quite considerably. The only sample whose analysis showed a composition close to the target composition was Slag 6 (Table II), in which case the crucible was split vertically in two parts after the viscosity measurement. One half was used in SEM-EDS analysis and the other half for compositional analysis. It showed clearly that only a large sample is representative at a solidified slag. In the reference study sampling was done from the liquid slag.

Estimation of compositions

As discussed above, the intermediate samples were not representative of the ambient slag compositions (1–5, 7–11). Therefore the target (weighed) compositions were adapted as real compositions. For the same reason, the relative amounts of CrO and Cr_2O_3 were also estimated. This was done by using the data in the study by Yanping Xiao on CrO_x containing slags. The data consists, among other things, of analysed CrO compositions of 70 slags in a CaO-SiO_2-CrO_x system in equilibrium with chromium metal. This data may be used to construct a regression equation.

The fraction of Cr^{2+} of total chromium content depends on (1) the other oxide species in the slag, (2) the oxygen partial pressure, (3) the total chromium content, and (4) temperature. The other oxide species may be related to the basicity of the slag (NCaO/NSiO_2), and the oxygen partial pressure and the total chromium content are interrelated (Cr+1/2O_2 CrO_x). In consequence, the basicity, the total chromium content, and temperature, as parameters, are enough for constructing an adequate regression equation for the calculation of the Cr^{2+} fraction. The calculated equation is:

\[
\frac{N_{Cr^{2+}}}{N_{totalCr}} = -0.22557 \left( \frac{N_{CaO}}{N_{SiO_2}} \right) - 0.01184 \cdot N_{totalCr} \quad [1]
\]

The statistical significance of the regression coefficients (T-test) and the entire equation (R^2=0.84, significance F=1.27·10^{-26}) are acceptable.
Viscosities

Measured viscosities of the Slags 1–12 are represented in Table III and in Figures 4 and 5. It is commonly known that SiO₂ is a strong acid oxide, which increases viscosity, and CaO and CrO are basic oxides, which decrease viscosity. The behaviour of Cr₂O₃ is not so clear; in general it is assumed to be a weak basic oxide with amphoteric characteristics like Fe₂O₃. It is also assumed that the relative amount of CrO decreases and Cr₂O₃ increases as the total amount of CrOₓ increases. This is also verified by Equation [1.]

Keeping these in mind, the measured viscosities seem to behave logically: as the amount of acid SiO₂ decreases and the total amount of basic oxides CaO, CrO and Cr₂O₃ increases, the viscosity decreases.

In addition, as stronger basic oxides CaO and CrO are replaced with weaker Cr₂O₃, the viscosity decreases relatively less. The other reason for this behaviour might be that the silica network depolymerizes as the total amount of basic oxides increases, and when it has depolymerized totally, the viscosity does not decrease by addition of more basic oxides. This is represented in Figure 6, where viscosities seem to level when 60 per cent of CrOₓ is approached.
The viscosities are also represented on a logarithmic scale against reciprocal absolute temperature in Figure 5. According to the Arrhenius equation, the viscosities of homogeneous liquid should be represented as lines on these graphs. The viscosity values, which were obtained obviously below liquidus temperature, were not used in the regression analysis. The regression equations were used to calculate the viscosities of different slags at the same temperatures, which makes the table form illustration much simpler and the viscosity modelling easier in a spreadsheet program.

The Iida model

Prof. Iida’s viscosity model is based on the Arrhenius type of equation, where network structure of the slag is taken into account by using the basicity index \( B_i(j) \). The original Iida model (Equations [2–8]), which divided all the oxides into basic and acid oxides, has been modified to take account the amphoteric behaviour of certain oxides (Equations 10–13). This improved model is commonly known as the modified Iida model.

\[
\mu = A \mu_0 \exp \left( \frac{E}{B_i(j)} \right). \]

\[ A = 1.029 - 2.078 \times 10^{-3} T + 1.050 \times 10^{-6} T^2. \]

\[ E = 28.46 - 2.0884 \times 10^{-2} T + 4.000 \times 10^{-4} T^2. \]

\[ \mu_0 = \sum \mu_0 X_i. \]

\[ \mu_0 = 1.8 \times 10^{-5} \left[ M(T_m) \right]^{1/2} \exp \left( H_j / RT \right) \left( V_m \right) \exp \left( H_j / R T_m \right). \]

\[ H_j = 5.1 \left( T_m \right)^{1/2}. \]

\[ B_i(j) = \frac{\sum (\alpha W_j) \left( \alpha_{Cr_2O_3} \right) W_{Cr_2O_3}}{\sum (\alpha W_j) \left( \alpha_{Cr_2O_3} \right) W_{Cr_2O_3}}. \]

where \( \mu \) = viscosity, \( T \) = absolute temperature, \( \mu_0 \) = hypothetical viscosity of pure oxide, \( X_i \) = mole fraction, \( T_m \) = melting temperature, \( R \) = universal gas constant, \( V_m \) = molar volume at melting point, \( B_i(j) \) = modified basicity index, \( \alpha_i \) = specific coefficient, and \( W_i \) = weight percentage.

The modified basicity index is similar to the basicity index \( B_i \), but the amphoteric oxides \( \alpha_i \) are replaced with \( \alpha_i^* \). The basic-acid behaviour of amphoteric oxides changes according to the overall basicity of the slag. So, one \( \alpha \) is not sufficient to represent slags with different basicities. For quaternary \( \text{CaO-SiO}_2-\text{CrO}-\text{Cr}_2\text{O}_3 \) slag, \( B_i(j) \) is written as:

\[ B_i(j) = \frac{\alpha_{CaO} W_{CaO} + \alpha_{CaO} W_{CaO} + \alpha_{Cr_2O_3} W_{Cr_2O_3}}{\alpha_{SiO_2} W_{SiO_2}}. \]

Because the behaviour of \( \text{Cr}_2\text{O}_3 \) is not certain, it has been marked as amphoteric oxide with \( \alpha^* \) parameter. A positive value of \( \alpha^* \) would indicate that \( \text{Cr}_2\text{O}_3 \) acts as a basic, whereas in the case of a negative \( \alpha^* \) value it behaves as an acid oxide, and the bigger the value, the stronger the behaviour.

The parameter of a slag can be calculated by the following procedure:

\[ \mu_{sec} = A \mu_0 \exp \left( \frac{E}{B_i} \right). \]

When the slag contains only an amphoteric oxide of \( \text{Cr}_2\text{O}_3 \),

\[ B_i = \sum (\alpha W_j) + \alpha_{\text{Cr}_2\text{O}_3} W_{\text{Cr}_2\text{O}_3}. \]

By combining the above equations we have:

\[ \alpha_{\text{Cr}_2\text{O}_3} = \frac{1}{E W_{\text{Cr}_2\text{O}_3}} \left[ \ln \left( \frac{H_j}{A \mu_0} \right) \sum (\alpha W_j) - E \sum (\alpha W_j) \right]. \]
So, it is assumed that \( \alpha^*_{\text{Cr}_2\text{O}_3} \) correlates linearly to the weight percentage of \( \text{Cr}_2\text{O}_3 \) (\( W_{\text{Cr}_2\text{O}_3} \)) and the basicity index (\( B_i \)), and a correlation equation is formed at each temperature.

\[
\alpha^*_{\text{Cr}_2\text{O}_3} = aB_i + bW_{\text{Cr}_2\text{O}_3} + c \tag{13}
\]

Using this correlation equation it is possible to calculate \( \alpha^*_{\text{Cr}_2\text{O}_3} \) for a slag that has no experimentally measured viscosity value. In addition, equations correlating the coefficients \( a, b \) and \( c \), and the temperature may be formed.

**Application of the Iida model**

**Determination of the Iida model parameters**

As a first approximation \( \text{Cr}_2\text{O}_3 \) is kept as a constant basic oxide. In order to perform a calculation, the \( \mu_{\text{Cr}_2\text{O}_3} \) and \( \alpha_i \) parameters have to be known. The parameters for \( \text{SiO}_2 \), \( \text{CrO}_2 \), \( \text{CaO} \) (\( \mu_{\text{Cr}_2\text{O}_3} \), \( \mu_{\text{Cr}_2\text{O}_3} \), \( \alpha_{\text{SiO}_2} \), and \( \alpha_{\text{CaO}} \)) have been used in many earlier viscosity studies, and their validity has been verified. Also, \( \mu_{\text{CrO}_2} \) and \( \alpha_{\text{CrO}} \) parameters have been given in earlier articles, but \( \mu_{\text{Cr}_2\text{O}_3} \) and \( \alpha_{\text{Cr}_2\text{O}_3} \) are missing. Because, \( \text{Cr}_2\text{O}_3 \) rarely exists without co-existence of \( \text{CrO} \), it is probable that at least a \( \text{Cr}_2\text{O}_3 \) parameter is a compromise that includes the effect of \( \text{CrO} \).

The \( \mu_{\text{Cr}_2\text{O}_3} \) can be calculated using Equation [6], where approximation of \( \mu_{\text{Cr}_2\text{O}_3} \) was found in the literature and \( V_{m\text{Cr}_2\text{O}_3} \) was approximated by calculating the density \( \text{Cr}_2\text{O}_3 \) using linear regression of densities of \( \text{Cr}_3\text{O}_4 \), \( \text{Cr}_2\text{O}_3 \), \( \text{CrO}_2 \) and \( \text{CrO}_3 \) related to oxidation stages of chromium ions (\( R^2=0.97 \)). Some error may be due to the fact that the density should have been calculated at the melting point. The \( \alpha_{\text{Cr}_2\text{O}_3} \) and \( \alpha_{\text{CrO}} \) parameters were found by iteration so that the average error of the model (global \( \Delta \)) was minimised (Equations [14] and [15]). The parameters are represented in Table IV.

\[
\delta_n = \frac{(\mu_{\text{meas}})_n - (\mu_{\text{cal}})_n}{(\mu_{\text{meas}})_n} \times 100 \tag{14}
\]

\[
\Delta = \frac{1}{N} \sum_{n=1}^{N} |\delta_n| \tag{15}
\]

The average error of the model between temperatures 1750°C and 1550°C is 13.1 per cent. The average error of the model decreases a little if temperature rises and increases if the model is used under 1550°C. The reason might be the relatively weak temperature dependence of the \( \mu_{\text{CrO}} \) parameter. The error is calculated only between the measured values and calculated values above the liquidus temperatures. The comparison of the measured viscosities and calculated viscosities are represented in Figure 7.

**Application of the modified Iida model**

It was tried to improve the model by assuming amphoteric behaviour for \( \text{Cr}_2\text{O}_3 \), by using Equations [10–13], and the above determined values \( \alpha_{\text{Cr}_2\text{O}_3} \) and \( \mu_{\text{Cr}_2\text{O}_3} \). This method raised the average error. Therefore, it is better to assume that the \( \text{Cr}_2\text{O}_3 \) is a basic oxide. If the total chromium content (\( \text{Cr}_2\text{O}_3 \)) had been used in modelling instead of separate oxide species \( \text{CrO} \) and \( \text{Cr}_2\text{O}_3 \), the \( \text{CrO} \) behaves like amphoteric oxide. The reason, of course, is the two oxidation stages of chromium in the slag. If the Iida model is constructed this way, it is only useful in this particular system in contact with metallic chromium.

**Discussion**

**Error sources of viscosity values**

The error of the viscosity measurement apparatus.

According to the instruction manual, the error is within \( \pm 1\% \) of the full-scale range. Full-scale means that the calibrated spring of the viscometer is strained up to its limit (100 torque-\%). Consequently, a particular spindle, in the
same fluid, has different error limits in each rotational speed used. The higher the speed used and the closer the 100%-torque is, the more accurate is the measurement. The viscometer cannot be used under 10 torque-% because the calibrated spring does not get enough resistance and the viscosity reading fluctuates back and forth. Even at 10 torque-% the error limit would be ±10%.

The error due to the spindle construction.
The measurement arrangement causes restrictions to the spindle construction. The spindle cannot be changed during the measurement at high temperature and it has to cover a wide viscosity range. The spindle must fit in the crucible, and it is better that there is an adequate gap between the walls of the crucible and the spindle to minimize the boundary effects. The long shaft of the spindle is one of the major error sources. A heavy spindle in the tip of the long shaft sways easily, especially at high rotational speeds. Measurement of low viscosity requires a bigger spindle and higher rotational speed in order to get enough resistance for a calibrated spring. Both of these requirements also cause more sway of the spindle, which increases the error. The best spindle size is an optimum, which minimizes error. During the measurements the highest rotational speed used was 60 rpm. The error was minimized by taking many viscosity measurements using different rotational speeds and calculating an average value. The same method was used when the system constant was determined.

The error in temperature measurement.
The temperature was measured with a B-type thermocouple, which has an error limit of ±1°C below 1700°C. During the measurements it was found that the error increased by time, maybe because it was used above 1700°C for long periods. The thermocouple was checked against a new thermocouple and a correction was made to measured values.

The error in composition.
In spite of the fact that the compositional analysis failed, it is probable that the error is no more remarkable than the error in viscosity measurement itself. The pure oxides have less than 0.5% impurities, and the weighing was done very carefully. Some error was caused, because between measurements about 5 grams of sample were drilled from the top of the slag, whose composition was not the same as the rest of the slags due to the segregation during solidification. Even though the total chromium content is probably very close to that intended, the amounts of CrO and Cr₂O₃ were estimated by using data from different measurements. In addition, chromium metal at the bottom of the molybdenum crucible slowly dissolved into molybdenum, which may change the Cr/CrOₓ equilibrium. The magnitudes of these errors are difficult to verify. The correlation equation used in estimation had R²=0.84. The biggest errors obviously occur at the lowest viscosity values. The spindle construction at high rotational speed is not any more optimal for viscosities below 5 cPaaS.
Inaccuracy of the temperature measurement and composition are relatively smaller, except for the amounts of CrO and Cr2O3.

Validity of the Iida model
The Iida model was modified by adjusting the $\alpha_{\text{CrO}}$ and $\alpha_{\text{Cr2O3}}$ parameters and calculating the $\mu_{\text{CrO}}$ parameter. The $\alpha_{\text{Cr2O3}}$ parameter has been reported to be a basic oxide and have a value of 0.13\textsuperscript{6,7}. This is quite near the reported $\alpha_{\text{Fe2O3}}$ value, which is 0.08\textsuperscript{6,7}. In this study Cr2O3 was found to have much stronger basic characteristics with the $\alpha_{\text{Cr2O3}}$ parameter as large as 0.71.

As a first approximation, CrO was assumed to behave like FeO and have the same value of $\alpha$ ($\alpha_{\text{FeO}}$=0.96). However, the value of $\alpha_{\text{CrO}}$ was found to be much higher (1.48), which indicates that its basic behaviour is nearly as strong as that of MgO ($\alpha_{\text{MgO}}$=1.51). These parameters should be verified with more extensive study including more oxide species.

It was also noticed that the error became larger as the temperature decreased. One reason for this might be that the temperature dependence of the hypothetical viscosity of pure CrO ($\mu_{\text{CrO}}$) was very weak. The other oxides had much stronger temperature dependence of $\mu_{\text{CrO}}$. Therefore, the data used in the calculation of $\mu_{\text{CrO}}$ should be verified.

Anyway, the lida model gave moderate consistency with the measured values above liquidus temperatures (global $\Delta$ = 13.1%).

Conclusions
Experience gained in these measurements will help to make more accurate viscosity measurements in the future. The spindle construction has to be improved in order to decrease the error margin at low viscosities. Compositional analysis has to be made using all the slag in the crucible to avoid errors caused by the segregation. If measurements are made in equilibrium with metallic chromium, a crucible made of more oxide species.

Specific coefficients ($\alpha_{\text{CrO}}$, $\alpha_{\text{Cr2O3}}$) of the lida model were found by minimizing the average error (global $\Delta$), using viscosities of wide compositional range (10–60 weight-% of CrO). The determined values of $\alpha_{\text{CrO}} = 1.48$ and $\alpha_{\text{Cr2O3}} = 0.71$ indicate unexpectedly strong basic behaviour, and should be verified with larger data consisting of other oxide species. The hypothetical viscosity of pure CrO ($\mu_{\text{CrO}}$) was calculated using data found in the literature survey. The temperature dependence of the $\mu_{\text{CrO}}$ was very small, and may have contributed to the increased error at lower temperatures.

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References
11. NAKAJAMA, K. Tetsu to Hagane, 80, p. 593. 1994