Measuring and Modeling of Viscosity and Surface Properties in High Temperature Systems

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In order to be able to understand and model the kinetics of heterogeneous reactions and transport phenomena it is necessary to have experimental data of physical properties like viscosity, surface energy and interfacial energy. In this study viscosity of high-melting slags containing chromium oxides were measured. Central results and observed relationships and modelling are described. The results showed that addition of chromium oxide into the slag decreases the viscosity but the influence becomes weaker at high CrO\textsubscript{x} contents. The viscosity–composition relation was evaluated by a modified Iida’s model and a good agreement between the experimental and calculated results was observed.

Interfacial phenomena between liquid metal and slag with gas bubbles entering through the metal–slag interface were investigated by X-ray transmission technique. Bubble behaviour at metal–slag interface and dispersion of metal droplets into the slag were measured as a function of interfacial tension, gas bubble size and slag viscosity. The effect of different parameters on metal entrainment is discussed.

KEY WORDS: viscosity; slag; metal melts; chromium oxide; interfacial tension; bubbles; bursting.

1. Introduction

Physical properties like viscosity, thermal and electrical conductivity, density and surface energy have a decisive role to kinetics of reactions and transport phenomena in liquid metal–slag systems at high temperatures. In order to be able to understand and model these phenomena it is necessary to obtain experimental data of the properties. Viscosities for the normal steelmaking or refining slags have been extensively studied, and many models have been established, however, data of the slags containing chromium oxide, are quite scanty. The other important factor which influences the rate of chemical reaction at slag/metal interface is the interfacial energy. A situation when gas bubbles ascend up through the interface, makes the process very interesting but also complicated. Most of the available information on the bubble bursting is based on investigations at low temperatures. To quantitatively study the bubble bursting phenomenon in a high temperature system is of great interest to metallurgists. In the Laboratory of metallurgy at Helsinki University of Technology extensive studies on measurement of viscosity of high-melting slags and interfacial phenomena between liquid metal and slag as well as gas bubble passing through the metal–slag interface have been investigated.\textsuperscript{1–7} The paper discusses both experimental technique and results as well as observed relations and their modeling.

2. Viscosity of Slags Containing Chromium Oxide

Viscosity is a physical property which is related to the structural and physical properties of the melt. In slags, viscosity is dominated by the silicate structure; an acid slag with large polymerized silicate ions is highly viscous whereas a basic slag with small de-polymerized silicates is much more fluid. Except the presence of net-forming and non-net-forming oxides in the slag, complicated interactions between the cations and anions make the predicting and modeling of slag viscosity often quite problematic. Due to its strong structural dependence viscosity can often be expressed with a mathematical formulae similar to thermodynamic functions of a liquid slag. That is possible although viscosity has not any direct relation to e.g. Gibbs energy. In general, modeling of slag viscosity meets serious problems due to shortage of reliable experimental data. In production of ferrochromium and stainless steel the slags have exceptionally high melting temperature, typically over 1650°C but can be even over 1700°C. That makes measuring of the viscosity and its temperature dependence a very demanding task. In the case of multi-component slags it can be difficult to separate between homogeneous melt and a heterogeneous liquid-solid two phase region owing to deficient data of liquidus temperatures in chromium oxide containing slags. Another characteristic is that chromium in slags appears both as three-valent Cr\textsuperscript{3+} and two-valent Cr\textsuperscript{2+} ions. The ratio of different valences depends on the ambient oxygen partial pressure which thus has an influence on slag properties e.g. viscosity and should be, therefore, strictly
controlled. In the present study a special emphasis was directed to control the furnace atmosphere for its oxygen partial pressure.

2.1. Experimental

For viscosity measurements a vertical furnace with MoSi₂ heating elements and corundum furnace tube were used. The slag specimens were melted in a molybdenum or chromium crucible. A rotational viscosimeter type Brookfield LVDV-II+ was equipped with a molybdenum rod and a spindle which was immersed into the liquid slag after its melt down. Measurements were performed under purified argon atmosphere. The slags were equilibrated either by Cr metal located onto the crucible bottom or by using a chromium metal crucible. Viscosity measurements were first started at the highest temperature 1750°C in order to melt and equilibrate the slag, properly by keeping the sample at least for one hour at 1750°C before the first measurement. Then the furnace was let to cool down 3°C per minute to a selected temperature, where it was let to settle for 30 min before each measurement. At each temperature the viscosity was measured using several rotational speeds (60, 50, 30, 20 rpm). The measurements were continued until the slag started to solidify. After the experiment the slag was cooled down, crushed and analyzed for oxide components by XRF and for two- and three-valent Cr by a wet-chemical method.

2.2. Results and Discussion

The slag compositions are shown in Table 1 and Fig. 1, where also the liquid slag region at 1700°C is given. Measured viscosities as a function of temperature are shown in Fig. 2. The effect of CrOₓ on the viscosity of different slags at different temperatures is seen in Fig. 3. It is evident that chromium oxides behave like basic oxides as the viscosity decreases although the slag basicity decreases when moving from slag 1 to slag 7.

At high temperatures, the chromium in a slag is distributed both as divalent and trivalent oxides the ratio of which depends on the experimental conditions. For the present study the oxygen partial pressure under the experiments was defined by the equilibrium with metallic chromium. The reaction can be written:

\[
2(CrO_{1.5}) + Cr = 3(CrO) \quad \text{(1)}
\]

Here the 3-valent oxide was written as CrO₁.₅ instead of Cr₂O₃. The slag compositions were calculated based on the results of previous studies and are presented in Table 1.

Numerous models have been presented to estimate and present the dependence of slag viscosity on its chemical composition. Problems arise especially when slags having amphoteric oxides are described. In the previous study the authors applied the model presented by Iida. Iida’s viscosity model is based on the Arrhenius type equation, where network structure of the slag is taken into account by using a basicity index Bi

\[
\mu = A\mu_0 \exp \left( \frac{E}{B_i} \right) \quad \text{(2)}
\]

For a CaO–SiO₂–CrO–Cr₂O₃ slag the basicity index, Bi can be written:

\[
Bi^{(j)} = \frac{\alpha_{CaO}W_{CaO} + \alpha_{CrO}W_{CrO} + \alpha_{SiO₂}W_{SiO₂}}{\alpha_{CaO}W_{CaO}} \quad \text{(3)}
\]

In the equations, \(\mu\) = hypothetical viscosity, \(\mu_0\) = hypothetical viscosity of pure oxide, \(\alpha_i\) = specific coefficient, and \(W_i\) = weight percentage. The terms \(A\) and \(E\) are temperature dependent parame-
The modified basicity index corresponds to the conventional basicity index, but was specifically defined for the amphoteric oxides, thus $\alpha_i$ changes according to the overall basicity of the slag.

The modified model takes into account the amphoteric behaviour of oxides like $\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3$ as shown by Eq. (2). Figure 3 shows that addition of chromium oxide into the slag decreases the viscosity but the influence becomes weaker at high $\text{CrO}_x$ contents. Due to the choice of slag compositions the basicity ($\text{CaO}/\text{SiO}_2$ ratio), however, is decreased when $\text{CrO}_x$ increases and therefore, the total dependence is more complex and can be explained only by a model which takes into account both the effect of basicity and the effects of chromium oxides and their relative fractions. In Fig. 4 the viscosity–temperature relationships were calculated for six chromium oxide containing slags and compared with experimental results. Good agreement is observed in general, thus verifying the validity of the model. An error analysis was given by Forsbacka, previously. Also it is noteworthy that the viscosity values at the lowest measuring temperatures in some cases deviate upward from the trend line as is seen in Fig. 2. That is due to partialsolidification of the slag in which case the measurement was done in two-phase region and the viscosity does not any more obey the general relation for a corresponding, fully liquid slag. These results were removed from the data used for model assessment.

Figure 1 showed the liquid area at 1700°C in $\text{CaO}–\text{SiO}_2–\text{CrO}_x$ slags in equilibrium with $\text{Cr}$ metal. At higher oxygen partial pressure more Cr$^{3+}$ ($\text{Cr}_2\text{O}_3$ or $\text{CrO}_{1.5}$) is present in the slag, melting point rises up and the liquid area is suppressed from the $\text{CrO}_x$ corner towards the $\text{CaO}–\text{SiO}_2$ side. Realizing the complexity between the shape of the liquidus surface, the overall slag composition and the $\text{Cr}_2\text{O}_3$ and $\text{CrO}$ fractions in the slag it is evident how difficult it is to representatively describe the viscosity of Cr containing slags.

### 3. Interfacial Phenomena at Liquid Metal–Gas and Metal–Slag Interface

Surface and interfacial properties have an essential role in metallurgical processes where reactions and transport phenomena take place between metal, slag and gas phase as well as ceramic lining materials. Deoxidation of steel, inclusion nucleation, growth and removal to the top slag are greatly influenced by interfacial energy between the inclusion and the steel, the inclusion and the slag as well as the metal/slag interface. In reoxidation and nitrogen pick-up phenomena or in reversed, degassing reactions (hydrogen or nitrogen removal) surface tension has been stated to be a dominating factor.

Gas is formed by reactions or injected into liquids in most pyrometallurgical processes, converter process and ladle metallurgical treatments being typical examples. When gas bubbles pass through the top surface of iron or iron/slag interface small iron droplets are burst into the surrounding atmosphere or into the covering slag, respectively. When entering to the atmosphere iron droplets are oxidized and form dust. Bubble bursting is one of the dust formation mechanisms. Bigger metal droplets cause build-up layers, skull formation and ejections at the mouth and outside the reactor vessel. Two different cases were studied and are discussed here: behaviour of gas bubble at metal–gas interface, and bubble transfer through the metal–slag interface.

In the present study the bubble behaviour inside liquid metal and at the metal surface or bubble transfer through the metal–slag interface was observed by X-ray transmission technique (Fig. 5). Droplets bursted by gas bubbles were collected and characterized as well.

#### 3.1. Bubble Behaviour at Metal–Gas Interface

When a gas bubble rises to the top of the liquid metal the surface tension decelerates and stops its movement, the bubble curves the surface for a certain shape with liquid metal film covering the protruding bubble until after a certain resting time the film is drained and the bubble bursts to
the atmosphere. Bubble bursting causes metal ejections to the gas phase by two main mechanisms. The first mechanism produces film droplets which are formed when the metal film covering the bubble passing through the surface collapses forming tiny droplets which are then spread to the surrounding atmosphere. Their diameter is scattered from submicron size to tens of micrometers. In the case of the flow of single bubbles through the free surface of iron melt, jet droplets are formed due to the collapsing of the crater. Jet droplets are relatively large, from hundreds of micrometers to several millimeters. An example of jet formation at the gas/iron interface is shown in Fig. 6. The two groups of metal droplets can be seen in Fig. 7. Large jet droplets are easily seen on the collector plate whereas tiny film droplets are observed as dust-like dark areas on the ceramic plate. The size distribution and the weight percentage of the two groups of droplets produced from 100 single argon bubbles with diameter of 11.8 mm are shown in Fig. 8. It can be seen from the figure that the number of film droplets was orders of magnitude higher than that of jet droplets, however, their weight percentage was much less.

According to the experimental observations, it was found that the mechanisms governing the droplet formation by gas bubbles bursting are quite similar in water and in molten iron systems. Under certain surface tension of a liquid phase, there exists a certain gas bubble size which can produce maximum mass of ejection by bubble bursting. This was called critical bubble size. For the pure air/water system, it was about 4 mm. For the argon/iron system, the critical bubble diameter can be found for iron melts with different surface tension values in Fig. 9. Hence, it is possible to build a link between these two systems providing that the critical bubble diameter in iron melt can be predicted at different surface tension levels. Papachristodoulou stated that the Eotvos number could be a suitable link to predict the critical bubble diameter in different low temperature systems. It was found, however, that the Eötvös number could not satisfactorily predict the critical bubble size in
iron melt based on the present experimental data. A probable reason is that the effect of viscosity was not considered. Another approach was made by Hinds and Kuo\(^{11}\) who presented a dimensionless number \(N_j = \sigma / (\mu g D_b)^{1/2}\) as a criterion for jet droplet formation also based on measurements at room temperature. There \(\sigma\) is surface tension of the liquid, \(\mu\) is viscosity, \(D_b\) is bubble diameter and \(g\) is gravity. The equation did not include density. By combining the Eötvös number and \(N_j\) a new dimensionless group was constructed to examine the relation between the critical bubble size and the physical properties, density, surface tension, acceleration due to gravity and viscosity. A new dimensionless number (\(B_j\)) containing all these variables was proposed as follows:

\[
B_j = \frac{\mu \rho D_b^{2.5} g^{1.5}}{\sigma^2} \quad \quad \quad (4)
\]

It was found that the predictions made by this dimensionless number (marked as \(B_j\)) agreed with the experimental results better than if the pure Eötvös number was applied. For example, taking the critical bubble size in pure water as 4 mm, \(B_j = 0.0059\), the critical bubble size in molten iron gets the values 10.5 and 12.4 mm when the surface tensions are 1.4 and 1.8 N/m, respectively. The viscosity and density of iron melt were taken as 0.005 Pa s and 7.0 g/cm\(^3\). These \(B_j\) numbers in water and in molten steel were in a good agreement.

### 3.2. Bubble Behaviour at Metal–Slag Interface

The other interesting case is concerning bubble bursting at the iron–slag interface which is a very common case e.g., in converter process and ladle metallurgy treatments with gas bubbling. Also this phenomenon was studied by X-ray transmission technique and image grabbing by video or CCD camera. Controlled single bubble injection technique and collector plate for bigger metal droplets were applied.\(^5\)

Figure 10 shows bubble exiting from the metal/slag interface to the slag phase. Figure 11 also gives an evidence of jet formation. In the picture a bubble is released from the metal phase and the cavity is filled with metal forming a jet which collapses and produces metal droplets into the slag phase. Formation of film droplets is a similar process as at metal/gas surface resulting from the film drainage and collapse to form tiny droplets. The proposed mechanisms of metal droplets entrainment into slag were sketched in Fig. 12. As it is evident that the interfacial properties as well as viscosity have a decisive role in the bubble bursting phenomenon and droplet formation, the effect of these factors as well as bubble size were investigated. The experimental results are shown in Figs. 13–15. It is interesting to see in Fig. 13 that when the bubbles are smaller than 11 mm, it is practically no entrainment of metal into the slag whereas with larger bubble size the mass of entrained metal increased strongly with the bubble size. It is evident that with too small bubbles jet formation is prevented to take place. Figures 14 and 15 show that with increasing the interfacial tension of metal and/or slag viscosity, the metal entrainment into the slag is reduced. To sum up all the parameters which influence metal entrainment, a correlation was elaborated by using a similar formula developed by Reiter and Schwerdtfeger\(^{12}\) for room temperature systems and replacing the Eötvös number by \(B_j\). The schematic diagram representing the effect of all these factors on the mass of entrain-
ment based on Eq. (5) is shown in Fig. 16 where the dashed lines represent the start-of-entrainment curves at different slag viscosities.

\[
\frac{M}{\rho_m V_B} = 0.29 \left( \frac{D_{\text{b}}^{2.5} g^{0.5} \mu_m \rho_m}{\sigma_m^{2/3}} \right) \left( \frac{\mu_m}{\mu_s} \right)^{0.4}
\]  

The Equation (5) could roughly estimate the mass of metal entrainment due to a single gas bubble passing through the interface between the liquid slag and iron. \( V_B \) is volume of a bubble. Otherwise the symbols are the same as before. The subscript symbol \( m \) notes to metal, \( m-s \) to metal–slag interface and \( s \) to slag.

4. Conclusions

In order to understand, describe and model high temperature reactions and process phenomena the physical properties of materials and phases are of central importance. The paper describes some examples of measuring technique and experimental results. Viscosity measurements of high-melting slags containing chromium oxides were performed. The results showed that the addition of chromium oxide into the slag decreases the viscosity but the influence becomes weaker at high CrO₃ contents. The measured values were assessed to the modified Iida’s model for slag viscosity. Good agreement was found between the experimental values and the calculated ones based on the model.

Direct detection of gas bubble bursting at the surface of liquid iron was performed by X-ray transmission. The effects of bubble size, viscosity and surface tension were investigated. Interfacial phenomena when gas bubbles ascend through the metal–slag interface were observed as well. Bubble bursting phenomenon and the effects of bubble size, slag viscosity and interfacial tension on the metal entrainment into slag were measured too. It was stated that the mass of metal droplets entrained into slag by gas bubbles is decreased by increasing the interfacial tension of metal and slag viscosity, whereas it is increased with increasing the gas bubble size. A correlation between different parameters was constructed based on the experiments to estimate the mass of iron droplets entrained into slag by single gas bubbles.

REFERENCES