Effect of Crystallization on the Abrupt Viscosity Increase during the Slag Cooling Process

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The abrupt viscosity increase during the slag cooling process may jeopardize the stability of industrial operation. However, the underlying mechanism has not been completely understood yet. In the present work, the viscosity of basic oxygen furnace (BOF) slags with different additions, i.e., Al₂O₃ and SiO₂, was measured via a rotational rheometer. The slag crystallization behavior was observed in-situ via confocal laser scanning microscope (CLSM). Microstructural features, i.e., crystal fraction, shape and size in the slag, were identified through characterizing the water-quenched slag sample. The present results show that the abrupt viscosity increase occurs only when the crystal fraction exceeds a threshold (defined as critical volume fraction of solid, \( \Phi_c \)), at which crystals start to interfere with each other and form solid aggregates/clusters. The critical solid fraction varies between 0.33 and 0.51 for the investigated samples and is found to decrease with increasing crystal aspect ratio, which varies between 1.43 and 2.17 in our samples.

KEY WORDS: viscosity; slag.

1. Introduction

An abrupt viscosity increase during the cooling process is commonly met in slags. This sudden viscosity change may jeopardize the stability of industrial operation. For example, the dramatic viscosity increase in the basic oxygen furnace (BOF) slag gives rise to a problematic operation (e.g., difficulties in oxygen blowing) in converter smelting. The abrupt viscosity increase of mould flux in continuous casting process can cause a lubrication failure between the steel shell and mould and therefore deteriorates the steel surface quality. Despite of its vital role in practical production, the underlying mechanism, i.e., slag microstructural transition, of the abrupt viscosity increase has not been completely understood yet. Wright et al. and Lee et al. stated that the sharp viscosity increase is due to the onset of crystallization. In contrast, Vorres and Reid found the viscosity leap was only observed when the system contains predominantly crystalline phases. However, the critical solid phase content for the abrupt viscosity increase was not quantified.

Therefore, in this work, an industrial basic oxygen furnace (BOF) slag with different additions, i.e., SiO₂ and Al₂O₃, was studied as an example to investigate the effect of crystallization on the sharp viscosity increase in detail. The slag viscosity was measured via a rotational rheometer. The crystallization behavior was observed in-situ using a confocal laser scanning microscope (CLSM) under continuous cooling conditions. The structure of the sample was then quantified through the quenching experiments conducted in a tube furnace. The purpose of the present work was to identify and quantify the structural change that leads to the abrupt viscosity increase.

2. Experimental Methods

2.1. Sample Preparation

The master BOF slag composition measured via X-ray fluorescence spectroscopy (Panalytical PW2400) is shown in Table 1. The concentration of Fe²⁺ and Fe³⁺ in the slag was determined using chemical titration by potassium dichromate. Different quantities (5, 10, 15 and 20 wt.% ) of the dried reagent grade SiO₂ and Al₂O₃ powders were mixed with as-delivered BOF slag powders for the viscosity measurement. This is because a hot stage treatment is recently applied to valorize BOF slag by adding SiO₂ or Al₂O₃ at high temperature in order to make cements. The viscosity of BOF slag with the addition of SiO₂ or Al₂O₃ is thus significant as the slag viscosity controls the stability of the hot stage operation. For the sake of simplicity, sample BOF+x wt.% SiO₂ and BOF+x wt.% Al₂O₃ (x is 5, 10, 15 and 20) are termed as xS and xA hereinafter, respectively.

2.2. Viscosity Measurement

As shown in Fig. 1, a standard rheometer Physica MCR
301 from Anton Paar was upgraded for measuring the slag viscosity at high temperatures (up to 1,650°C). The molybdenum (99.9% Mo) crucible and spindle were enclosed in a graphite shell which served also as the heating element of the high frequency induction furnace. Specific dimensions of the crucible and spindle used in this work are shown in Fig. 2. In order to minimize the influence of liquid surface (i.e., the motion of the liquid surface) and crucible base (there is an additional torque if the spindle is too close to the crucible bottom) on the measurement, the positioning of the spindle was optimized to be approximately 7 mm below the liquid surface and 13 mm above the bottom of the crucible according to the measurement by Heller et al.\(^8\) It is feasible if the liquid slag surface is approximately 40 mm high after the immersion of the spindle, as shown in Fig. 2. 30–40 grams (depending on the density of slags) of slag powders were loaded in the Mo crucible. The furnace was heated to 1,600°C at a constant rate of 50°C/min and held for 30 min to melt and homogenize the slag. The spindle was then lowered down to the liquid melt while rotating at 5 rpm. The viscosity was measured at 30 rpm under a continuous cooling condition with a cooling rate of 5°C/min until the torque reached the preset maximum value, which corresponds to a maximum viscosity of 200 Pa·s. The furnace was purged with high purity argon (99.999 vol.% Ar, < 2 ppm O\(_2\), 60 L/min from the top and 200 L/min from the bottom of the furnace) during the measurement. The viscosity, torque, shear stress, shear rate/rotational speed and temperature were all recorded continuously via the software RheoPlus.

With the measured torque, rotational speed and the known geometry of measuring crucible and spindle, the shear stress \(\tau\) and shear rate \(\dot{\gamma}\) can be calculated as

\[
\tau = \frac{M}{2\pi R_0^2 L} \quad \cdots \quad (1)
\]

\[
\dot{\gamma} = \frac{2\Omega_0 R_0^2}{R_i^2 - R_o^2} \quad \cdots \quad (2)
\]

The viscosity is thus obtained as

\[
\eta = \frac{\tau}{\dot{\gamma}} = \frac{M}{4\pi L \Omega_0} \frac{R_o^2 - R_i^2}{R_i^2 R_o^2} \quad \cdots \quad (3)
\]

with \(M\) the measured absolute torque, N·m; \(\Omega_0\) the rotational speed of the spindle, rad/s; \(R_o\) and \(R_i\) the inner radius of the crucible and the radius of the spindle, respectively; \(m\) the depth of the immersed spindle in liquid slag, m.

As in the present rheometer, the torque and spindle rotational speed are measured in absolute values, the viscosity is directly obtained according to Eq. (3).\(^8\) However, the following errors can lead to a deviation between the measured and actual viscosity values.

1. The additional torque caused by the immersion of rod. The liquid slag surface was 7 mm above the spindle to minimize the effect of surface motion (see Fig. 2) in this work. The immersed rod gives rise to an additional torque of 1.43% and an immersion error of 1 mm would cause a torque change of 0.2%.\(^8\)

2. The tumbling, eccentricity, misalignment of spindle during viscosity measurement. In the present apparatus (see Fig. 1), the rod position above the furnace was recorded via a software NATIONAL INSTRUMENTS Vision Builder 2012 for Automated Inspection.\(^9\) The spindle was centered and adjusted until the obliquity and eccentricity was less than 1.5° and 1.5 mm, respectively, from the axis of rotation before each experiment.\(^9\)

3. The geometrical error of spindle and crucible. This was minimized by critically measuring the dimension of crucible and spindle before each measurement.

4. High temperature expansion of Mo spindle and crucible. The error is negligible as the linear thermal expansion of Mo at 1,600°C is 1.1% according to Suh et al.\(^10\)

The comparison between the measured and the provided viscosity of a reference silicone oil at room temperature indicates a deviation of 3%, which is fairly acceptable.\(^8,11\)

2.3. CLSM in-situ Observation of the Slag Solidification Behavior

In order to correlate crystallization behavior of the slag with its viscosity, a high temperature confocal laser scanning microscopy (CLSM, Lasertec, 1LM21H-SVF17SP) was applied to provide an in-situ observation of the slag solidification during cooling. A platinum crucible was used herein, as shown in Fig. 3.

The samples after viscosity measurement were dried and...
ground into powders with size < 80 μm. Approximately 5 mg powders were loaded into the platinum crucible, which was placed on a platinum holder. Before heating, the furnace chamber was first evacuated to ca. 10 Pa and then filled with pure argon gas for three times to eliminate the residual oxygen in the furnace. This results in an atmosphere that is similar with the viscosity measurement, in which a graphite heating element ensures the absence of oxygen. The sample was heated up to 1600 °C and held for 5 minutes to melt and homogenize the slag. Then, the sample was cooled down at a cooling rate of 5°C/min in order to be consistent with the cooling rate in viscosity measurement. The crystallization temperature \( T_{\text{cry}} \) is defined as the temperature at which the nucleation of the crystal is first observed during the cooling trajectory. The crystal precipitation, growth and clustering were monitored during cooling and the images were captured at a frequency of 60 frames/second via the HiTOS software. The in-situ observed crystallization process was then combined with the measured viscosity to investigate the mechanism of distinct flow characteristics.

2.4. Quenching Experiment for Microstructure Identification

To measure phase fractions, a quenching experiment in a vertical tube furnace was performed to freeze the slag microstructure at the temperatures of interest. To avoid compositional variation, the slag sample after viscosity measurement was also used in the quenching measurement. A platinum tube made from 0.15 mm thick platinum foil (Pt-20 wt.% Rh) with size of 10 mm x 10 mm was used in this work. Approximately 20 mg slag powders were loaded into the tube and both ends were then folded like an envelope to prevent any liquid leak at high temperature (see Fig. 4). The Pt envelopes were then placed in a graphite crucible (height 50 mm, inner diameter 29 mm) which was also used to maintain a reducing atmosphere. Argon gas was used to purge the furnace during the experiment at a flow rate of 40 L/hour. The graphite crucible was then positioned in the hot zone of the vertical tube furnace with MoSi\(_2\) heating element (see Fig. 5). The furnace was heated to 1600°C at 5°C/min (instead of 50°C/min used in viscosity measurement and CLSM observation due to the limit of the furnace) and held for 30 min for the homogenization. Afterwards, the sample was cooled down to the desired temperature in the furnace at 5°C/min (same with the cooling rate in the viscosity measurement and CLSM measurement) and quenched in a bucket filled with cold water. The quenched sample was then dried and prepared for further analysis. In the CLSM and quenching experiment, the atmosphere was controlled under the same oxygen partial pressure, i.e. \( 10^{-14} \) to \( 10^{-15} \) ppm, to ensure the same atmosphere in the parallel experiments. In the viscosity measurement, the oxygen partial pressure was not measured as an oxygen sensor was not installed in the present apparatus. However, considering that graphite was both used in the viscosity measurement (graphite jacket covering the Mo crucible, see Fig. 1) and quenching experiment (graphite crucible), the oxygen content was assumed in the same range. Furthermore, according to FactSage calculation, the solid fraction decreases by 1.2% when oxygen partial pressure changes from \( 10^{-14} \) ppm to \( 10^{-8} \) ppm, which is 6 orders of magnitude difference, in the case of present BOF slag at 1500°C. Therefore, the effect of atmosphere deviation (within 6 orders of magnitude, which is believed to be the maximum deviation between viscosity measurement and quenching experiment) on the solid fraction is insignificant, thus its effect on viscosity is also limited.

The slag specimens were mounted in resin (Epofix), ground by silicon carbide papers and polished with diamond paste. The polished samples were then coated with carbon for compositional and microstructural analysis. The composition was analyzed with electron probe micro-analysis (FE-EPMA, JXA-8530F, JEOL Ltd, Japan), equipped with a wavelength dispersive spectroscope (WDS). The beam current and accelerating voltage were set as 15 nA and 15
kV, respectively. The microstructure was observed with a high resolution scanning electron microscope (FEI XL-40 LaB6). The obtained images were digitally analyzed with Image J software for analysis of crystal morphology (size and shape) and content.

### 3. Results and Discussion

#### 3.1. Viscosity Evolution under Continuous Cooling Condition

The measured slag viscosity under continuous cooling condition is shown in Fig. 6. An abrupt viscosity increase during the cooling of the liquid slag is clearly observed. The temperature at this sudden viscosity change, referred to as the temperature of critical viscosity ($T_{cv}$, as shown in Fig. 6(a)), has been employed to characterize the abrupt viscosity increase.\(^2,12–14\) The temperature-dependent viscosity curve can be characterized by two regimes, \(i.e.\) with decreasing temperature, viscosity increases gradually (first regime, \(T > T_{cv}\)), followed by a steep viscosity increase at \(T_{cv}\) (second regime). The viscosity of the second regime (\(T < T_{cv}\)) is several orders of magnitude higher than that of the first regime. At \(T < T_{cv}\), there are also a number of other steep viscosity increases. However, due to the difficulty to measure the corresponding large solid fractions and the complexity of crystallization, the abrupt viscosity increases at \(T < T_{cv}\) are not discussed in this work.

The crystallization temperature \(T_{cr}\) is determined with CLSM test and the comparison between \(T_{cr}\) and \(T_{cv}\) is shown in Fig. 7. Due to the temperature limit of the CLSM equipment, samples BOF, 5S, 10S, and 5A could not be completely melted during heating and were not measured in this study. The measured \(T_{cv}\) were found to be 24–213°C (varying with samples) lower than \(T_{cr}\) (1 444–1 563°C) for the present samples, indicating that the onset of crystallization does not immediately lead to the sharp viscosity change. The abrupt viscosity increase only occurs when the quantity of crystals exceeds a threshold and a particular microstructure is formed.

#### 3.2. Microstructural Transition under Continuous Cooling Condition

In order to understand the mechanism underlying the abrupt viscosity increase, slag microstructural evolution with decreasing temperature was observed in-situ via CLSM. The images captured at different temperatures of sample 15A at both heating and cooling processes are shown in Fig. 8.

As shown in Fig. 8(a), the slag is still solid at 999°C and is completely melted at 1 536°C (Fig. 8(b)). At 1 506°C (Fig. 8(c)), the first crystal is clearly observed and the temperature is defined as the crystallization temperature \(T_{cr}\).

When \(T_{cr} > T > T_{cv}\) (1 300°C), as shown in Figs. 8(c) and 8(d), the majority of crystals are randomly distributed and the distance between the neighboring crystals is a few times larger than the crystal size (approximately 20 μm). According to the rheology of a suspension, particles can translate and rotate independently without being influenced by their neighboring particles in the regime where particles are far apart\(^15,16\) from each other. The presence of solid particles in the liquid system gives rise to an extra energy dissipation through solid-liquid hydrodynamic interactions, \(e.g.\) altering the feature of the flow field around the solid particles. This influence is, however, inconspicuous compared to the viscosity of the liquid, namely it is the liquid that dominates the slag viscosity.\(^17,18\) This is consistent with the present observation, as shown in Figs. 8(c) and 8(d), and in Fig. 6 (see (b), the sample 15A, temperature range from 1 600°C to 1 300°C). On account of the microstructure and

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**Fig. 6.** Measured viscosity of SiO\(_2\) (a) and Al\(_2\)O\(_3\) (b) modified BOF slag under a continuous cooling (5°C/min) condition.

**Fig. 7.** The comparison between crystallization temperature \(T_{cr}\) and temperature of critical viscosity \(T_{cv}\).
the corresponding viscosity behavior, the temperature range between $T_{cv}$ and $T_{cry}$, e.g. between 1 300 $^\circ$C and 1 506 $^\circ$C for the sample 15A, is defined as the liquid-dominated regime in this study (see Fig. 9).

As $T_{sol}$ (the solidus of the slag, at which the slag is completely solid) $< T < T_{cv}$, a large quantity of crystals tend to be in contact with each other, coalesce and agglomerate into aggregates, as shown in Figs. 8(e)–8(f). In a shearing field, the anisotropic aggregates lead to a considerable obstruction exerted to the rotational spindle.\textsuperscript{19) This microstructure results in a large energy dissipation.\textsuperscript{16} As a consequence, an evident viscosity leap is observed. Therefore, the abrupt viscosity increase observed in the slag cooling process is essentially due to the formation of solid aggregates/clusters. As temperature decreases further, the liquid in the gap between crystals is either squeezed out or solidified to connect the neighboring crystals, forming a solid network structure (Figs. 8(g) and 8(h)). In this regime ($T_{sol} < T < T_{cv}$), the particle-particle interaction tends to dominate the flow behavior and therefore the regime is defined as the solid-dominated regime, as shown in Fig. 9.

With a further decrease in temperature, the residual liquid is crystallized and the solidification process is eventually completed at 1 196$^\circ$C (Fig. 8(i)).

The different microstructural features underlying the two flow regimes clearly demonstrate that it is the formation of solid aggregates that gives rise to the dramatic viscosity leap. This particular microstructural feature is formed until the solid fraction exceeds a threshold.

### 3.3. Critical Solid Fraction

To quantify the slag microstructure at the temperature where the abrupt viscosity increase occurs, the solid fraction at this temperature (sharp viscosity increase) was determined through analyzing the water-quenched samples. The SEM images of the quenched samples were digitally analyzed with Image J software. The area fraction is considered as the volume fraction of crystals ($\Phi$) assuming crystals are randomly distributed. The solid fraction at which the viscosity increases abruptly is defined as the critical solid fraction $\Phi_c$ herein. The largest length of the crystal is adopted to describe particle size. This is because it is the largest length than mainly influences the particle motion in a shear flow field.\textsuperscript{20) The aspect ratio of the ellipse with the equivalent area of the crystal in a two-dimension image is applied to characterize the particle shape as the aspect ratio governs the revolving motion of particles.\textsuperscript{21) Images of the microstructure of the quenched samples are shown in Fig. 10. The measured $\Phi_c$ and the corresponding average particle aspect ratio and the average largest length are shown.
in Table 2. The standard deviations in the averaging of the particle shape and size are also shown. As the SEM images in Fig. 10 demonstrate, the main crystals in sample BOF, 5S, 5A, 10A, 15A are CaSiO$_4$ (C$_2$S) and MgO, whereas in other samples, only C$_2$S is the principle crystal. Moreover, it is also noted that the C$_2$S in original BOF slag and the SiO$_2$ added slag is roughly round, as quantified by the measured aspect ratio, i.e. $1.43 \leq r_p \leq 1.88$. However, for Al$_2$O$_3$ added slag, the C$_2$S tends to be dendritic with aspect ratio varying between 1.93 and 2.17. The origin of the morphological difference of C$_2$S between the Al$_2$O$_3$ and SiO$_2$ added slags has not yet been clarified. In addition, the SEM images also clearly exhibit the microstructural features at the critical solid fraction. In BOF and the SiO$_2$ added slag, the round C$_2$S crystals are inter-connected and no clear boundary can be distinguished in a large number of crystals, indicating the formation of aggregates (Figs. 10(a)–10(e)). In the Al$_2$O$_3$ added slag, the dendritic C$_2$S crystals grow into large particle clusters. The clusters interfere with each other through their long dendrite arms. These features are consistent with the observation via CLSM. The measured $\Phi_c$ in present samples is between 0.33 and 0.51, varying with samples, as shown in Table 2.

Considering the morphology difference in the SiO$_2$ modified slag and Al$_2$O$_3$ modified slag, the dependence of $\Phi_c$ on crystal shape and size is presented in Figs. 11(a) and 11(b), respectively.

As displayed in Fig. 11(a), the critical solid fraction shows a decreasing trend with increasing particle aspect ratio. Due to their dendritic shapes, C$_2$S in Al$_2$O$_3$ added slag can easily interconnect, form aggregates and thus the slags exhibit an abrupt viscosity increase at a lower solid fractions than the system containing round particles, i.e. SiO$_2$ added slags. Therefore, $\Phi_c$ is larger in SiO$_2$ added slags than in Al$_2$O$_3$ added slags.

It is also noted in Fig. 11(b) that there is no clear correlation between $\Phi_c$ and the particle size, implying the negligible effect of particle size on the critical solid fraction.

### Table 2. Measured $\Phi_c$ at $T_c$, and the corresponding average particle aspect ratio and size (the standard deviation of particle size and shape measurement are also indicated).

| Sample | $T_c$ (°C) | $\Phi_c$ | Average aspect ratio ($r_p$) | Average largest length (µm) |
|--------|------------|----------|-------------------------------|-------------------------------|
| BOF    | 1567       | 0.40     | 1.88±0.65                     | 66.83±62.58                   |
| 5S     | 550        | 0.45     | 1.57±0.86                     | 51.28±23.93                   |
| 10S    | 548        | 0.51     | 1.43±0.30                     | 51.68±17.87                   |
| 15S    | 501        | 0.42     | 1.45±0.48                     | 48.76±17.01                   |
| 20S    | 420        | 0.50     | 1.57±0.43                     | 47.68±20.60                   |
| 5A     | 1440       | 0.34     | 1.97±0.86                     | 50.62±37.76                   |
| 10A    | 1375       | 0.39     | 2.17±1.02                     | 49.28±28.22                   |
| 15A    | 1300       | 0.37     | 1.95±0.80                     | 30.36±16.31                   |
| 20A    | 1260       | 0.33     | 1.93±0.79                     | 23.82±14.74                   |

### 4. Conclusions

The abrupt viscosity increase of slag can considerably jeopardize the stability of an industrial operation. This work aims to understand the underlying mechanism through the identification and quantification of the microstructural feature of the slag when viscosity increases abruptly. By
Fig. 11. Dependence of critical solid fraction on (a) particle aspect ratio and (b) particle size. The standard deviation of particle aspect ratio and size is calculated as an error bar. The relative error of critical solid fraction is estimated to be 10% and is also shown herein.

combining the viscosity-temperature curve and the microstructural evolution under the continuous cooling condition, the microstructural transition when viscosity increases abruptly is revealed and the critical solid fraction ($\Phi_c$) is proposed to characterize the sharp viscosity increase. The following conclusions are obtained:

1) The temperature of critical viscosity ($T_{cv}$), at which viscosity increases sharply, was measured to be 24–213°C (varying with samples) lower than the crystallization temperature (1,444–1,563°C) for the investigated samples.

2) The in-situ CLSM observation of the slag crystallization process indicates that the sharp viscosity increase is attributed to the formation of solid aggregates.

3) The critical crystal volume fraction at which the viscosity increases abruptly is defined as the critical solid fraction ($\Phi_c$). The critical solid fraction varies between 0.33 and 0.51 for the investigated samples and it increases with decreasing crystal’s average aspect ratio (from 2.17 to 1.43). No clear correlation was found between the critical solid fraction $\Phi_c$ and the crystal size.

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