RHEOLOGICAL TRANSITIONS OF THE SOLID-BEARING METALLURGICAL SLAG DURING COOLING

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Introduction

Slag viscosity plays a vital role in metallurgical processes as it directly affects the kinetics of chemical reactions, metal-slag separation, slag foaming, *etc.* A reasonable viscosity estimation of fully liquid slags is achievable nowadays thanks to numerous viscosity models[1]. However, the flow behaviour of partially liquid slags is not understood well (*e.g.,* shear thinning and yield stress)[2] and a validated viscosity model for solid-bearing slags is still absent. In this work, the viscosity of modified basic oxygen furnace (BOF) slag was measured as a case study to understand the rheology of solid-bearing slags. The slag viscosity was measured under both continuous cooling condition (*i.e.* constant shear rate) and isothermal condition (*i.e.,* various shear rates). The non-Newtonian behaviour during cooling is thus measured and the underlying mechanism is discussed.

Experimental

The industrial BOF slag sample with the composition range shown in Table 1 was used for master slag. Different quantities of Na_2CO_3 (corresponding to 1 wt%, 3 wt%, and 5 wt% Na_2O) were added into the modified BOF slags with the addition of 10 wt% Al_2O_3 or 20 wt% SiO_2 to examine the effect of Na_2O on the slag viscosity[3]. For the sake of simplicity, BOF (100 g) + SiO_2 (20 g) + Na_2O (x g, x = 1, 3, and 5) is termed as 20SxN and BOF (100 g) + Al_2O_3 (10 g) + Na_2O (x g, x = 1, 3, and 5) is termed as 10AxN hereinafter.

Table 1: Chemical composition of the master BOF slag (measured *via* XRF, wt%)

CaO	*Fe	Fe^{2+}	Fe^{3+}	SiO_2	MnO	MgO	Al_2O_3	P_2O_5	CaO/SiO_2
42-55	18-22	8-12	8-12	12-18	0-8	0-5	0-3	0-2	3.5-4.6

*Fe is the total concentration of iron (element) in the slag; Fe^{2+} and Fe^{3+} in the slag was determined using chemical titration by potassium dichromate

The viscosity measurement was performed *via* a high temperature (up to 1650°C) rheometer. A technical description of the present apparatus has been reported in previous studies[4]. Two types of experiments were performed. (1) Viscosity measurements under continuous cooling condition at constant shear rate. The furnace was heated up to 1600°C at a constant rate of 50°C/min and was held for 30 min. The sample was then cooled down at 5°C/min. The viscosity measurement was performed during cooling at a constant rotational speed of 30 rpm. (2) Viscosity measurements under isothermal condition at various shear rates. In this experiment, after holding the temperature for 30 min at 1600°C, the viscosity was measured at an increasing shear rate from 2 rpm to 120 rpm (up-ramp). The spindle was rotating at 120 rpm for another 30 seconds before starting a gradual decrease in rotational speed to 2 rpm (down-ramp). After the completion of the measurement at 1600°C, the sample was cooled to the next desired temperature (varying with samples) and held for 30 min before rotating the spindle again.

Results and discussion

Viscosity measured under continuous cooling condition at constant shear rate

The measured viscosity under continuous cooling and at a shear rate of 30 rpm is shown in Figure 1. The effect of the addition of Na_2O on the slag viscosity was discussed elsewhere[3]. With the decrease in temperature, the viscosity gradually augments and then undergoes a sharp increase. The solid fraction and temperature at the moment of the sharp increase in viscosity are indicated as the critical solid fraction Φ_c and the temperature of critical viscosity T_{cv}, respectively[5]. To further examine the characteristics of the three flow regimes, the samples are reorganised into three regimes, as shown in Figure 1 (see the shaded areas) and Table 2.

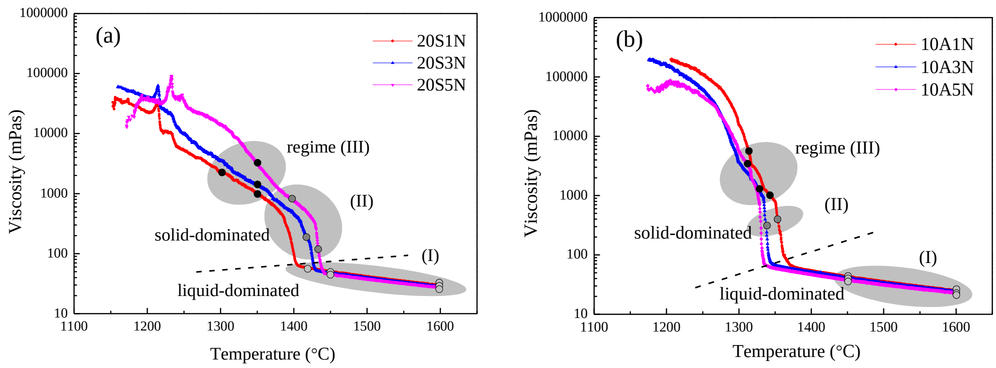

Figure 1: Three regimes distinguished by different flow properties; The round dots indicate the temperature at which the viscosity was measured isothermally (see Table 2 and Figure 2); The dashed line represents the boundary separating the solid-dominated (sharp viscosity increase) and liquid-dominated regime (gradual viscosity increase)

Table 2: Sample/measurement and the corresponding number in Figure 2

Regime	Sample	T (°C)	Number	Regime	Sample	T (°C)	Number
(Ⅰ)	10A1N	1600	1	(Ⅱ)	10A1N	1355	13
		1450	2		10A3N	1338	14
	10A3N	1600	3		20S3N	1420	15
		1450	4		20S5N	1435	16
	10A5N	1600	5			1400	17
		1450	6	(Ⅲ)	10A1N	1340	18
	20S1N	1600	7			1315	19
		1420	8		10A3N	1325	20
	20S3N	1600	9		10A5N	1315	21
		1450	10		20S1N	1350	22
	20S5N	1600	11			1300	23
		1450	12		20S3N	1350	24
-	-	-	-		20S5N	1350	25

Viscosity measured at isothermal condition with various shear rates

As shown in Figure 1, the slag successively undergoes regime (Ⅰ), (Ⅱ) and (Ⅲ) as temperature decreases. The regime (Ⅰ) is defined as the liquid-dominated regime whereas (Ⅱ) and (Ⅲ) are termed as the solid-dominated regime. To quantify the rheological behaviour in each regime, the power law model[6] (Equation (1)) was used to calculate the flow index.

$$\tau = m\dot{\gamma}^n \qquad (1)$$

with τ the shear stress, Pa; $\dot{\gamma}$ the shear rate, s^{-1}; m the flow consistency, $Pa{\cdot}s^n$; n the flow index, dimensionless. The flow index is obtained by fitting Equation (1) to the measured data for the shear rate in both the up- and down-ramp. The relative flow index difference (Δn) is proposed to characterise the shear thinning difference between the two ramps, as shown in Equation (2).

$$\Delta n = \left| n_{down} - n_{up} \right| \times 100\% / n_{up} \qquad (2)$$

As shown in Figure 2, the flow index n is around 1 in regime (Ⅰ) in the shear rate of both the up- and down-ramp, confirming the Newtonian flow for this regime. According to our previous analysis[3], although the crystallisation already takes place in this regime, the crystal-crystal interaction is negligible as the crystals are far apart from each other. In regime (Ⅱ), the temperature range is just below T_{cv} (Figure 1, regime (Ⅱ)) and the flow index n is below 1 (Figure 2 (a), regime (Ⅱ)), suggesting a shear thinning behaviour. The flow index difference Δn between the up and down ramp shear rate is negligible (see Figure 2 (b), regime (Ⅱ)). This indicates that the viscosity evolution with shear rate in these two ramps is symmetric, namely the structural deformation is reversible. According to our previous work,[3] as the quantity

of crystals exceeds the critical solid fraction Φ_c, solid aggregates and clusters are formed. The complicated crystal-crystal interaction in a shearing field gives rise to the non-Newtonian behaviour. In regime (Ⅲ), the flow index is also found to be smaller than 1 (Figure 2a, regime (Ⅲ)). However, the flow index in the shear rate up-ramp is generally smaller than that in the down-ramp (measurement 20 in Figure 2a can be an experimental error). The flow index difference Δ*n* is up to 350% (Figure 2b, regime (Ⅲ)), indicating an evident time-dependent shear thinning, *i.e.,* thixotropy. As discussed in previous study,[3] this thixotropy is attributed to the unrecoverable slag microstructure deformation.

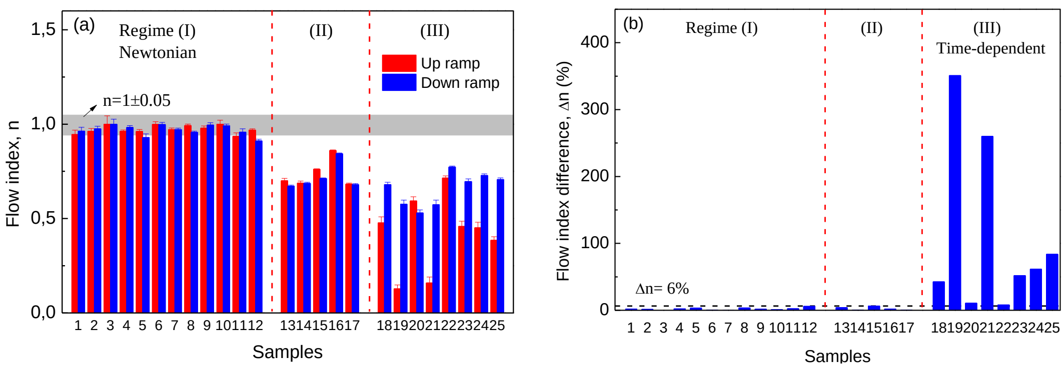

Figure 2: The calculated (a) flow index (both up ramp and down ramp) and (b) relative flow index difference in the three regimes; The relation between numbers 1-25 and the measurements is shown in Table 2

Conclusions

Based on the present experimental study of the rheological properties of the modified BOF slag, it was found that the slag undergoes the Newtonian, shear thinning, and thixotropy regimes as the temperature decreased from above slag liquidus. The shear thinning regime was observed as crystal content exceeds the critical solid fraction Φ_c, at which the viscosity increases abruptly.

References

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