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Non-Newtonian behavior of solid-bearing silicate melts: An experimental study

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ABSTRACT

The non-Newtonian behavior and its mechanism have not been clarified for the solid-bearing silicate melts, leading to difficulties and even errors in estimating silicate melt viscosity. In this study, a typical metallurgical slag was employed as a model system of solid-bearing silicate melt. The flow behavior of the slag was measured via a rotational type rheometer at various shear rates. The results demonstrate that the slags exhibit non-Newtonian behavior for solid fractions exceeding a critical value (Φ_c, i.e. 0.33–0.40 for the investigated samples), at which an abrupt viscosity increase occurs. Shear thinning (the viscosity decreases with increasing shear rate), thixotropy (a time-dependent shear thinning) and an apparent yield stress of 0.2–74.4 Pa for the investigated samples are the non-Newtonian characteristics observed in this study. The higher the solid fraction, the more pronounced the shear thinning. The shear thinning is mainly attributed to the disruption of crystal clusters. Thixotropic behavior is found to be caused by the irreversible microstructural evolution within the experimental time scale. The apparent yield stress is mainly due to the formation of a solid network and is increased with increasing the solid fraction.

1. Introduction

Viscosity of silicate melt is a key parameter controlling many industrial processes, e.g. steelmaking [1], combustion and gasification [2,3], and ceramic welding [4]. An accurate viscosity model or measurement is vital for industrial process simulation and optimization. Numerous studies are available on the viscosity modeling and measurement of fully liquid silicate melts [5–7]. Despite of the fact that the solid-bearing system is also commonly met in actual production, the work on the viscosity of the solid-liquid coexisting silicate system is scarce [8,9], leading to difficulties and even errors in estimating and controlling silicate melt viscosity. A crucial reason is that the silicate melt exhibits various non-Newtonian (a viscosity that varies with applied shear rate) flow characteristics, e.g. shear thinning (viscosity decreases with increasing shear rate), with increasing solid fraction. Wright et al. [10] measured the viscosity of CaO-MgO-Al_2O_3-SiO_2 slag system saturated with $MgAl_2O_4$ particles. It was found that the slag viscosity decreases with increasing shear rate when the solid fraction exceeds approximately 8 wt%. Moreover, a yield stress (a finite stress to be exceeded for a material to flow [11]) up to 3 Pa was also observed at a solid fraction larger than 8 wt%. In their later study on CaO-FeO_x melt containing Fe_3O_4 particles [12], shear thinning and a yield stress were also observed but the solid fraction of the non-Newtonian behavior and its mechanism were not discussed. Zhen et al. [13] found that the CaO–MgO–Al_2O_3–SiO_2 system containing TiN particles exhibits shear thinning behavior once the particle fraction is above 3 vol%. All these studies merely observed non-Newtonian behavior in their experiment. Neither the underlying mechanism nor the threshold of the non-Newtonian flow was discussed in detail. It is thus significant to first clarify the various non-Newtonian flow characteristics in order to propose a correct viscosity model in future work.

In this work, an industrial basic oxygen furnace (BOF) slag with different additions of Al_2O_3 was studied as a model system for solid-liquid silicate system. In order to recycle BOF slags, a hot stage slag engineering has been proposed to inject Al_2O_3 powders into the BOF slag to achieve the desired chemistry for cement production [14,15]. However, injecting solid materials such as Al_2O_3 is prone to be stuck in case of high BOF slag viscosity during the hot-stage treatment [14,15]. Therefore, it is of practical value to investigate the flow behavior of BOF slag with Al_2O_3 addition. In this work, the slag viscosity was measured with a rotational type rheometer. The slag microstructure, i.e. crystal content and crystal morphology, at different temperatures was identified through quenching experiments in a vertical tube furnace. The slag microstructure was then combined with the measured viscosity in order (1) to investigate the transition from Newtonian to non-Newtonian behavior and (2) to identify the various non-Newtonian characteristics,

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Table 1
Chemical composition of the master BOF slag (wt%).

CaO	Fe[a]	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

[a] Fe is the total concentration of iron (element) in the slag.

e.g. shear thinning and yield stress, and to clarify the underlying mechanism.

2. Experimental methods

2.1. Sample preparation

The industrial BOF slag with its composition range measured by X-ray fluorescence spectroscopy (Panalytical PW2400) is shown in Table 1. The concentration of Fe^{2+} and Fe^{3+} in the slag was determined using chemical titration by potassium dichromate. Different quantities (5, 10, 15 and 20 wt%) of dried reagent grade Al_2O_3 powders were added to the master BOF slag to obtain a wide range of slag composition. For the sake of simplicity, sample BOF + x wt% Al_2O_3 is termed as xA (x is 5, 10, 15 and 20) hereinafter.

2.2. Viscosity measurement

The viscosity measurement was performed at a high temperature (up to 1600 °C) viscosity measuring apparatus. The standard rheometer Physica MCR 301 from Anton Paar has been integrated with a high frequency induction furnace. A technical description of the set-up and the dimension of the spindle and crucible have been reported in previous study [16]. The molybdenum crucible and spindle were enclosed in a graphite shell which served also as the heating element of the induction furnace. 30–40 g (depending on the density of slags) of slag powders were loaded in the Mo crucible. High purity argon (99.999 vol % Ar) was blowing into the furnace at a flow rate of 40 L/h during the viscosity measurement.

The furnace was heated to 1600 °C at a constant rate of 50C/min (shown in Fig. 1) and held for 30 min to melt and homogenize the slag. The spindle was then lowered down to the pre-set position [16] in the crucible and started to measure the viscosity at various rotational speeds. The error of the viscosity measurement with the present set-up was calibrated as 3% using reference materials. The details of the calibration can be seen in reference [16]. After the completion of the measurement at 1600 °C, the sample was cooled down to the next desired temperature and held for 30 min again before the measurement.

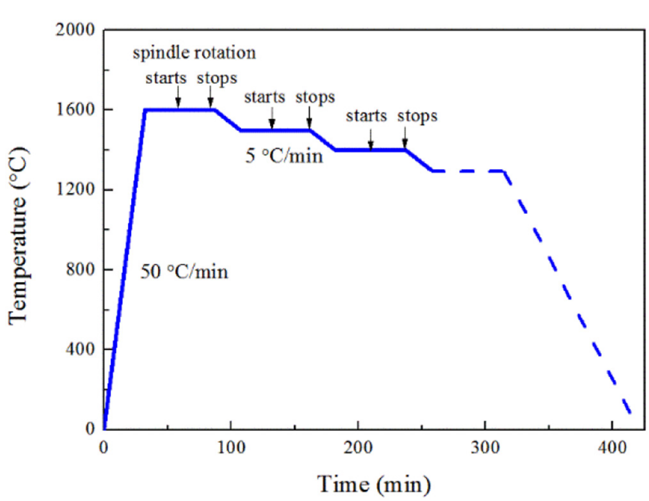
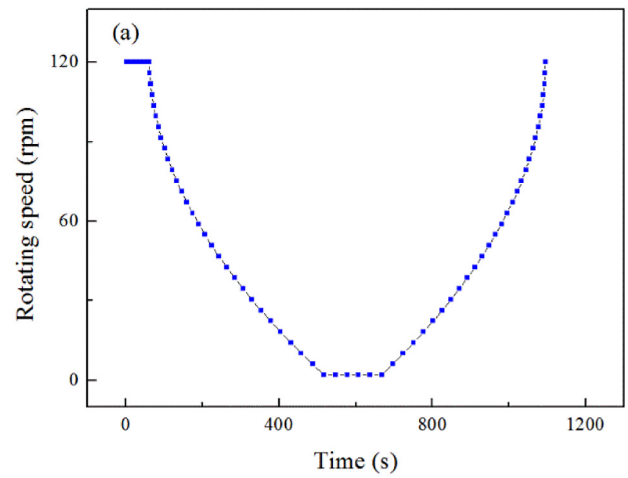


Fig. 1. Temperature profile of the viscosity measurement.



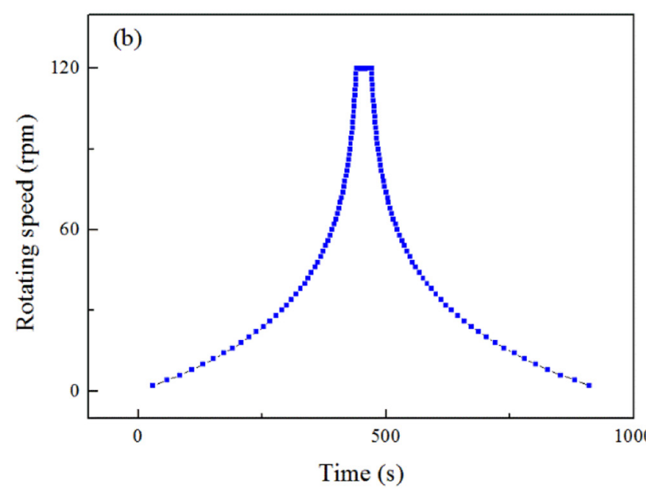


Fig. 2. Rotational speeds applied during viscosity measurement. The lines are drawn to guide the eyes.

The temperature profile is shown in Fig. 1.

In order to investigate the flow behavior under various shear rates at each desired temperature, the spindle first rotated at 120 rpm (39.3 s^{-1}) for 60 s (to stabilize the viscosity readings) and then slowed down gradually to 2 rpm (0.7 s^{-1}) within 458 s. The rotational speed was maintained at 2 rpm for 120 s (to stabilize the viscosity readings) before rising up again to 120 rpm, as shown in Fig. 2(a). In order to investigate the effect of shear history on the flow curve, an inverse shear rate changing profile was employed for sample 20A at 1235 °C. The rotation started at 2 rpm and gradually increased up to 120 rpm. After holding for 30 s, the rotational speed reduced to 2 rpm again, see Fig. 2(b). In the former case, the microstructure was sufficiently stirred prior to the shear rate decrease whereas in the latter case, the slag was kept static for 30 min before starting to rotate the spindle. In this way, the effect of shear history (or time) on viscosity can be examined [17].

The shear rate and shear stress were converted from the rotational speed and the measured torque via Eqs. (1) and (2), respectively.

$$\dot{\gamma} = \frac{2\Omega_o R_o^2}{R_o^2 - R_i^2} \tag{1}$$

$$\tau = \frac{M}{2\pi L R_i^2} \tag{2}$$

where M the measured absolute torque, Nm; Ω_o the rotational speed of the spindle, rad/s; R_o and R_i the inner radius of the crucible and the