IN-SITU STUDY ON CaO-Al_2O_3-SiO_2-MgO (CASM) SLAG SOLIDIFICATION BY USING ELECTRICAL CONDUCTIVITY MEASUREMENTS

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Introduction

To enable the valorisation of slag in high added value applications, its mineralogy can be modified during solidification by controlling the cooling process. It is, however, difficult to direct the cooling as the solidification behaviour cannot be measured online. Since the electrical conductivity (EC) ($\sigma = 1/\rho$) is sensitive to a minor change in the microstructure of the slag it can be used to monitor the change in the composition of the liquid phase and the precipitation during slag solidification. In the past decades, EC measurement is a well-developed method used for indicating the melt distribution and melt fraction in the upper mantle and for monitoring the microstructure evolution in cement-based materials[1-3]. Several reports focused on the EC of molten slags[4,5]. However, to date there has been no study on the change in EC of slags during solidification, which is affected by temperature, melt fraction, melt composition, melt distribution and melt connectivity. Therefore, it is essential to understand how these factors affect the EC of slags during solidification. In this study, Confocal Scanning Laser Microscope (CSLM) has been employed for the in-situ observation of the slag solidification and simultaneous measurement of the EC of slags. Firstly, the accuracy of the EC measurement set-up in the CSLM was evaluated by measuring the EC of CaO-Al_2O_3-SiO_2 (CAS) melts. Next, the in-situ EC measurement and CSLM observation were performed on CAMS slag under isothermal condition to investigate the influence of melt fraction and melt composition on the EC of the slag.

Experimental Procedure

Slag Preparation

Two slag compositions, indicated with A and B, were prepared by mixing reagent grade CaO, SiO_2, Al_2O_3 and MgO powders (Table 1). 20 g of each mixed oxide powder was melted in a platinum crucible at 1600°C for 2 hours in air using a bottom loading furnace. Then, the molten slags were quenched on a steel plate, followed by drying in a muffle furnace at 80°C for 10 h.

Table 1: Chemical composition of the slag samples and liquidus and solidus temperatures

Slag	CaO (wt%)	SiO_2 (wt%)	Al_2O_3 (wt%)	MgO (wt%)	Liquidus (°C)	Solidus (°C)
A	35	55	10	0	1398	1184
B	34	39	19	8	1361	1246

In-situ EC Measurement and CSLM Observation

In the present study, a special set-up was developed in a CSLM (technical description elsewhere[6]), which enables to measure the EC of the slag during the in-situ CSLM observation of the sample, as shown in Figure 1a. The EC cell assembly is illustrated in Figure 1b. Two platinum foils which served as electrodes were inserted into a cubic boron nitride (BN) crucible. Figure 1c presents the heating history of the measurement. Temperature calibration has been performed using pure copper. A temperature difference of 130 ± 5°C was measured between the thermocouple temperature and the sample temperature in the BN crucible.

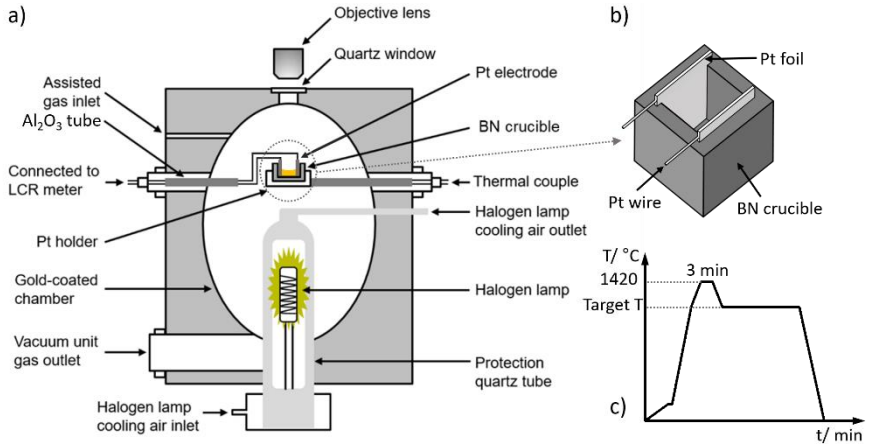

Figure 1: a) Schematic diagram of apparatus; b) EC cell; c) Heating history

The slag was first pre-melted at 1420°C for 3 min to homogenise the chemical composition and then fast cooled to the target temperature for in-situ EC measurement and observation of the isothermal crystallisation. The EC of slag A was measured after holding at every 10 degrees from 1370°C to 1330°C for 3 min in order to evaluate the accuracy of the set-up. Additionally, the EC of slag B was measured at 1160°C for 30 min in order to investigate the effect of crystallisation. EC measurements were conducted using the impedance spectroscopy technique with the two-electrode method. The EC cell was connected to a precision LCR meter (E4980A) for electrical impedance measurements over the frequency range 20 Hz to 300 kHz with a voltage of 1 V. The measured complex impedance Z is the sum of a real part Z' and an imaginary part Z", where the real part corresponds to the electrical resistance R of the sample[1]. The corresponding EC value was obtained by using the following relation:

$$\sigma = l / (R \cdot A) \quad (1)$$

where σ is the bulk EC of the sample (S/m), R is the sample electrical resistance (Ω), l is the sample thickness (m), and A is the cross-section area of the sample (m^2).

Results and Discussion

Figure 2 presents the logarithm of the EC as a function of the reciprocal temperature for slag A, which is compared with the EC data of the slag measured by H. Winerhager *et al.*[7]. It has been widely accepted that the temperature dependence of the EC can be expressed by the Arrhenius law[5]:

$$ln\ \sigma = lnA - E/(RT) \quad (2)$$

where σ is the electrical conductivity (S/cm); A is the pre-exponent factor; E is the activation energy ($J \cdot mol^{-1}$); R is the gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$); T is the absolute temperature (K). The temperature dependence of the EC follows the Arrhenius law and the measured EC of slag A is consistent with the EC data by H. Winterhager *et al.*[7] It can be concluded that the developed EC measurement in the CSLM is reliable.

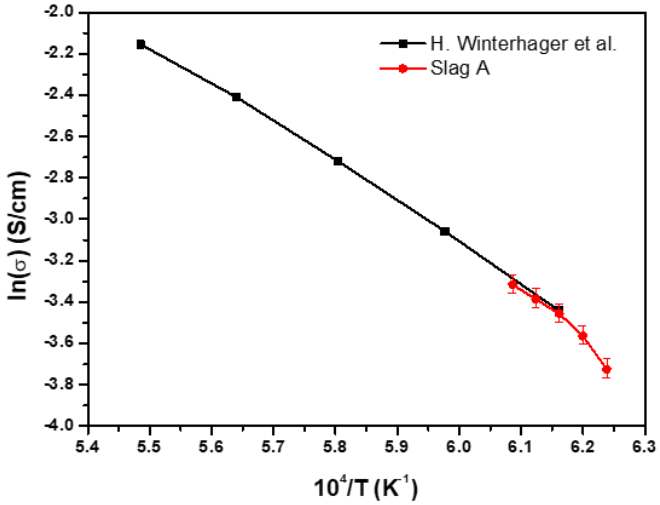

Figure 2: Comparison of EC data of this study with that obtained by H. Winterhager *et al.* [7]

Figure 3 shows the measured resistance curve of slag B during isothermal crystallisation. The measured resistance increases with time. The first solid crystal appeared at 156 s. The growth of the subsequently precipitated crystals and the resulting decrease in melt fraction result in an increase in electrical resistance. After 15 min, the slag surface solidified from left to right and completely solidified at about 25 min. As shown in the CSLM image at 20 min, left of the dashed line is the solidified slag. The increase in the solid fraction is considered to be a significant factor for the increase of the electrical resistance of the slag. In order to quantify the effect of the

melt fraction and melt composition variations on the EC of slag, the microstructure and compositions of the quenched slag need to be further analysed by SEM and EPMA.

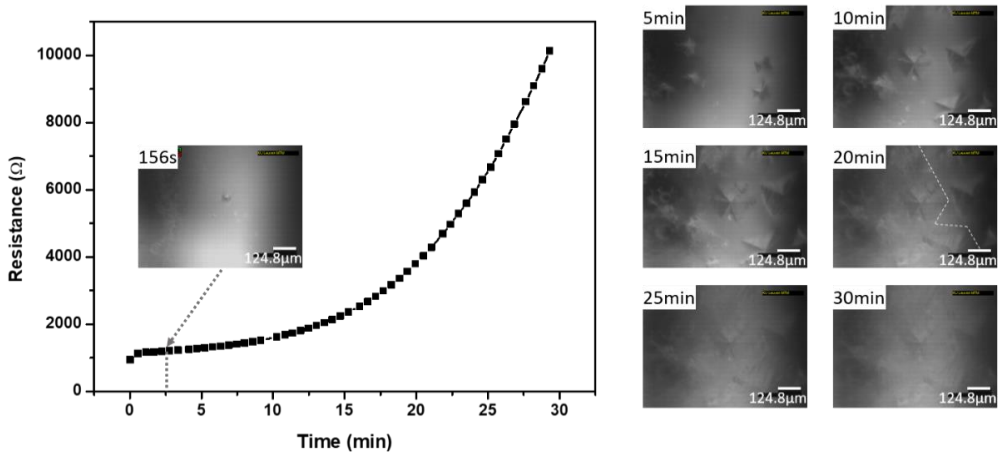

Figure 3: Measured resistance of slag B as a function of isothermal time at 1160°C and CSLM images of crystallisation at different isothermal times

Conclusion

Confocal Scanning Laser Microscope (CSLM) has been successfully applied for an in-situ observation of slag solidification and a simultaneous measurement of its electrical conductivity. An increase in solid fraction of the slag has a significant impact on the electrical resistance of the slag during isothermal crystallisation.

References

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