Effect of Agitation on Crystallization Behavior of CaO–SiO₂–R₂O (R = Li, Na, or K) System Characterized by Electrical Capacitance Measurement

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The effect of agitation on the crystallization behavior of molten 50CaO–50SiO₂ and 45CaO–45SiO₂–10R₂O (R = Li, Na, or K, mol%) fluxes were systematically investigated by the measurement of their electrical capacitance over a wide temperature range from liquid region to well below the liquidus temperature. It is well known that the electrical capacitance of liquids is generally much higher than that of solids owing to the differences in their respective polarization mechanisms. These differences were exploited as a sensitive indicator of the crystallization of molten calcium silicates in an experimental furnace equipped with an electrical capacitance measuring system. The system comprised a Pt-based alloy crucible and a rotating rod that allowed evaluation of the effect of agitation generated by the rod, connected to a capacitance meter (LCR meter).

As expected, at a particular temperature, the electrical capacitance of the molten calcium silicates underwent a precipitous decrease by roughly three orders of magnitude, which was dependent on the chemical composition. This indicated the presence of crystallization and this was confirmed by corresponding microstructural characterization. It was also found that, for the measurements acquired with rotating rod agitation, the temperatures at which the capacitance underwent the sharp decrease were higher than that identified without the agitation. This suggests that the agitation effect induced by the rotating rod accelerates the crystallization of molten calcium silicates.

KEY WORDS: electrical capacitance; crystallization; agitation; calcium silicates; viscosity; non-Newtonian fluid.

1. Introduction

Modern steelmaking involves the handling of slags and fluxes, mostly in the temperature region between liquidus and solidus, i.e., the region of liquid and solid coexistence or multi-phase flux, to fully exploit their functional capabilities for the refining and casting processes. Therefore, numerous researchers have adopted various methods, including hot-thermocouple,¹–⁴) differential thermal analysis,⁵–¹⁰) heat-treatment using a crucible and furnace,¹¹,¹²) among others,¹³–¹⁹) to study the crystallization behavior of super-cooled slags and fluxes. However, most of these studies concerned the crystallization behavior of oxides at rest in crucibles or other containers, despite the fact that slags and fluxes are generally handled not only in the liquid–solid coexistence region, but also under a significant shear stress field created by agitation, stirring, or sliding in converters and continuous casting molds.

In the continuous casting process of steel making, the mold flux, which is mainly composed of calcium silicate, has the role of both lubricant and insulator between the solidifying steel shell and the water-cooled copper mold. Research involving this process has provided varying results that depend on both the grade of steel and the experimental design. Reported thicknesses of the mold flux film are in the range of a few hundreds of microns to a few millimeters.¹⁶–²⁸) Hanao et al. developed mold fluxes for high-speed continuous casting of a hypo-peritectic steel slab, and investigated the thickness of the mold flux based on CaF₂- and Na₂O-containing calcium silicates below the meniscus. They reported that the film thickness of the mold fluxes was found to be 0.8–1.6 mm.²²) Kajitani et al. investigated the effect of casting speed and viscosity of the flux on film thickness using a cold model, and found that the film thickness increased with increasing casting speed and flux viscosity, and varied in the range of 0.4–0.6 mm depending on the conditions.²⁷) These earlier studies suggest that the effect of agitation on the crystallization behavior of mold flux could be considerable, because the shear stress generated on the thin flux film by the oscillation of the copper mold could be huge.

Ionic liquids, like molten oxides (mold flux), have a much
higher electrical capacitance than their corresponding solids. This is attributed to the difference in their polarization mechanisms. Ionic liquids demonstrate ionic, orientational, and interfacial polarization. However, solids do not show orientational and interfacial polarization mechanisms, and have very limited ionic polarizability. Consequently, solids such as crystallized slags and fluxes have a much smaller electrical capacitance than their liquid counterparts. Ohta et al. recently proposed the feasibility of using electrical capacitance measurements to detect crystallization in a glass matrix during the fabrication of “nanoglass,” i.e., nanosized crystal grains dispersed in a glass matrix. They reported the successful detection of the precipitation of nanosized crystal grains in a Na2O–SiO2 glass matrix heated above its glass transition temperature (Tg), on the basis of a drastic decrease in capacitance of several orders of magnitude due to the above-mentioned difference in the polarization mechanism. In the present study, the same method was employed, but was extended to the detection of crystallization in supercooled oxide melts under agitation generated by rotational motion. The effect of agitation on the crystallization behavior of molten calcium silicate-based fluxes was systematically investigated.

2. Experimental Procedure

2.1. Electrical Capacitance Measuring System under Agitation

As schematically illustrated in Fig. 1, the measurement system consisted of a rotating rod powered by a variable speed motor, that was connected to a slip ring that transferred the electrical signal traveling from the rotating rod, and a PID-controlled electric furnace with six U-shaped MoSi2 elements (Kyoei Rikaki, Fukuoka, Japan). The capacitance of the molten oxides was measured using an LCR meter (LCR High–tester 3522–50, HIOKI E. E. Co., Nagano, Japan) at a constant current of 10 mA and an AC of frequency 10 kHz.

![Fig. 1. Schematic of the electrical capacitance measuring furnace with rotating rod system.](image)

Both crucible and rod were of high purity Pt-20 mass% Rh alloy (Tanaka Kikinzoku K. K., Tokyo, Japan), the dimensions of which are shown in Fig. 1(a). A B-type thermocouple, set just underneath the crucible, measured the temperature of the sample melt. Both the crucible and the thermocouple were within the homogeneous temperature zone of the furnace.

2.2. Sample Preparation

As listed in Table 1, an eutectic composition of the CaO–SiO2 binary system, 50CaO–50SiO2 (mol%) slag was employed as the mother composition, then 10mol% R2O (R = Li, Na, or K, whose ionic radii are 0.076, 0.102, and 0.138 nm, respectively) was added. Powder batches of CaCO3 and SiO2 (99.9%, Sigma-Aldrich Japan Inc., Tokyo, Japan) were thoroughly mixed to achieve the required composition. The mixture was then placed into a Pt crucible. The sample batch was pre-melted in an air furnace at 1 600°C for 30 min and then quenched on a water-cooled copper plate. Just prior to the capacitance measurements, R2CO3 (R = Li, Na, or K, 99.9%, Sigma-Aldrich Japan Inc., Tokyo, Japan) was added and mixed to form the required compositions.

2.3. Procedure for Capacitance Measurement

The sample batch was placed in the Pt-20Rh crucible, which was set in the furnace (Fig. 1) and heated to 1 600°C for 30 min. Then, precisely 10 mm of the Pt-20Rh rod was immersed into the homogeneous and bubble-free sample melt after the holding, and the electrical capacitance was measured and logged under continuous cooling at 50°C/h at various revolution speeds (0, 30, 60, or 90 rpm) by the LCR meter.

2.4. Microstructural Characterization

To clarify the morphology of the precipitates, SEM observations were performed on polished sections of quenched samples. Powder batches of 50CaO–50SiO2 and 45CaO–45SiO2–10R2O were melted in a Pt-20Rh crucible with a 60 rpm rotating rod and continuously cooled in the same manner as for the capacitance measurements. At several temperatures, samples of the melt in the crucible were taken from the top of the furnace, and then quenched on a water-cooled copper plate. Quenched samples were fixed in epoxy and then progressively polished with SiC paper, followed by finishing with a 1 μm diamond slurry. Prior to visualization, the polished surfaces were coated with a thin gold conducting layer using magnetron sputtering apparatus (MSP–1S, Shinku Device, Japan). Images were obtained using a SEM (VE–8800, Keyence, Japan), which was operated at an acceleration voltage of 5 kV. XRD analyses were also conducted on the quenched samples in order to identify the crystalline phase (MultiFlex, Rigaku, Japan).

| Table 1. Chemical compositions (mol%) of oxide samples for capacitance measurements, where R = Li, Na, or K. |
|-----------------|-----------------|-----------------|
| CaO            | SiO2            | R2O             |
| 50             | 50              | 0               |
| 45             | 45              | 10              |
3. Results and Discussion

3.1. Electrical Capacitance of Molten Calcium Silicates in a Resting State

Electrical capacitance measurements for a 50CaO–50SiO$_2$ flux are shown in Fig. 2 as a function of measurement temperature on continuous cooling. During the early stages of the cooling period, the electrical capacitance remained fairly constant at approximately 100 nF, with only a slight decrease between 1600 and 1360°C. A further decrease in temperature caused a precipitous drop of roughly three orders of magnitude. The melting temperature (eutectic temperature) is 1544°C, which suggests that the 50CaO–50SiO$_2$ flux demonstrates 180°C of supercooling under the experimental conditions of the present study.

The sharp decrease in capacitance should be consistent with the crystallization of the calcium silicate supercooled liquid according to the original literature on crystallization detection by capacitance measurement. Ohta et al. have previously reported a similar sharp decrease in the electrical capacitance of supercooled Na$_2$O–SiO$_2$ glass at a particular temperature above its $T_g$, and then confirmed the precipitation of nanometer-sized crystalline phases in the glasses quenched at this temperature using TEM observations. The results shown in Fig. 2, in combination with those described in the literature, indicate that the crystallization behavior of molten calcium silicate can be successfully detected by electrical capacitance measurement. In this study, the crystallization temperature ($T_x$) is defined as the temperature where the capacitance undergoes a sharp decrease.

The electrical capacitance data for 50CaO–50SiO$_2$ and 45CaO–45SiO$_2$–10R$_2$O fluxes are summarized in Fig. 3 as a function of temperature. With the addition of 10mol% R$_2$O, the electrical capacitance values similarly showed drastic decreases at certain temperatures: 1150°C for Li$_2$O, 1250°C for Na$_2$O, and 1310°C for K$_2$O, indicating that the $T_x$ of calcium silicate was significantly reduced by the R$_2$O addition. As can be seen in Fig. 4, it was found that the $T_x$ values of R$_2$O-containing fluxes decreased linearly with respect to the cationic radius of the alkaline additive. The order of the $T_x$ values correlates with viscosity variations that have been reported in relation to the alkaline cationic radius of a CaO–SiO$_2$–R$_2$O system, which would suggest that crystallization in a less viscous flux could be faster. These results indicate that the crystallization behavior of molten calcium silicates can be successfully detected by electrical capacitance measurement.

3.2. Electrical Capacitance of Molten Calcium Silicates under Agitation

Figure 5 reveals the temperature dependence of the electrical capacitance of the 50CaO–50SiO$_2$ flux with various revolution speeds (0, 30, 60, and 90 rpm) of the rotating rod. It can be seen that at the early stage of measurements taken whilst cooling, the electrical capacitance values varied very little at approximately 100 nF independent of on the revolution speed. At various temperatures below the liquidus temperature (1544°C), sharp decreases in the electrical capacitance occurred at all revolution speeds, and it was clear that the $T_x$ increased with the revolution speed of the rod. Figures 6–8 show the measured electrical capacitance values for calcium silicate fluxes containing 10mol% Li$_2$O,
Na$_2$O, and K$_2$O, respectively. As can be seen, even with the alkaline additives, it was found that the $T_x$ increased with the revolution speed of rod in a similar manner. These results suggest that the agitation generated by the rotating rod accelerates the crystallization of supercooled calcium silicate.

Figure 9 summarizes the $T_x$ values determined by the electrical capacitance measurement as a function of shear rate, calculated with the revolution speeds and the dimensions of crucible and rod in accordance with the following equation:

$$\gamma = \frac{2\omega}{1 - \left(\frac{r_o}{r_i}\right)^2}$$

where $\gamma$, $\omega$, $r_o$, and $r_i$ are the shear rate, angular rate, inner radius of outer cylinder, and radius of inner cylinder, respectively. As can be seen in Fig. 9, $T_x$ increased with the shear rate for each flux investigated in the present study. These
results corroborate the speculation that shear motion (agitation) generated by the rotating rod could accelerate the crystallization of supercooled calcium silicate melts. However, it should be noted that the range of shear stress that can be calculated with the shear rate and the viscosity will be in the order of ~10 Pa (= N/m²). Here, multiplying both the numerator and the denominator of N/m² by m gives J/m², then multiplying J/m² by m³/mol (= molar volume) provides “J/mol”. This back-of-the-envelope calculation can reveal the amount of energy generated by the rotating rod in the present study. The densities of calcium silicate-based melts are known to be in the order of ~10³ g/m³, thus the molar volume should be in the range of 10⁻³ m³/mol, depending on the system. Therefore, it would be assumed that the energy generated by the rotating rod would be in the order of 10⁻⁴ J/mol, which is extremely small and therefore not sufficient to overcome the activation energy of crystallization that is on the order of several tens to hundreds of kJ/mol.

Additionally, the dependences of the crystallization temperatures on shear rate were found to be dissimilar, as shown in Fig. 9. The crystallization temperature for 45CaO–45SiO₂–10Li₂O flux showed a linear dependence on the shear rate. However, for the other fluxes, it was found that the accelerative effect of agitation (shear rate) on the crystallization was diminished at the higher shear rates, which can be attributed to the difference in the morphology of precipitated crystal grains in the supercooled calcium silicates.

Figure 10 shows SEM images of polished sections of samples quenched at different temperatures. The XRD diffraction patterns of these same samples are shown in Figs. 11–14, respectively. As shown in Fig. 10, the samples...
quenched above the $T_x$ determined by the electrical capacitance measurements, contained no crystalline phase. The electrical capacitance values of the fluxes in these temperature regions were roughly 100 nF (Figs. 2 and 3), which slightly decreased with temperature but did not reveal any significant differences in the microscopic character. In contrast, the samples quenched at the $T_x$ clearly showed dendritic crystal grains for 50CaO–50SiO$_2$, 45CaO–45SiO$_2$–10Na$_2$O, and 45CaO–45SiO$_2$–10K$_2$O fluxes, and spherical crystal grains for the 45CaO–45SiO$_2$–10Li$_2$O flux. These morphological variations may account for the difference in shear rate dependency of $T_x$ displayed by the Li$_2$O-containing flux compared to the Na$_2$O- and K$_2$O-containing samples. These crystalline phases were identified as CaO·SiO$_2$ (wollastonite) for 50CaO–50SiO$_2$ and 45CaO–45SiO$_2$–10Li$_2$O fluxes, and 2CaO·SiO$_2$ (dicalcium silicate) for 45CaO–45SiO$_2$–10Na$_2$O, and 45CaO–45SiO$_2$–10K$_2$O fluxes, which corresponded to the primary crystalline phase in these systems.  

The non-faceted crystals shown in Fig. 10 can be formed by growth instabilities, e.g., transport of the solute in the matrix, diffusion of the latent heat of solidification, or elimination of impurities, which will occur when the growth rate is controlled by the diffusion rate. Therefore, it can be concluded that the accelerative effect of the rotating rod on the crystallization behavior of calcium silicates is explained by the shorter diffusion distance of solute required for the crystallization due to the agitation, and/or elimination of the latent heat by the agitation.

3.3. Crystallization and Viscosity

Figure 15 compares the temperature dependence of the capacitance and viscosities of the 50CaO–50SiO$_2$ flux. The viscosity data is taken from previous work on material with the same composition. The experimental conditions (temperature history of samples, cooling rate, dimensions and configuration of the contact materials, and rotation speed) employed were comparable with the measurement of electrical capacitance in the present study. The solid line in the figure is an extrapolation line assuming Arrhenius-type temperature dependence for the viscosity above the liquidsus temperature. The dashed line shows the transition temperature of Newtonian (in higher temperature) to non-Newtonian (in lower temperature) behavior induced by the presence of the crystal particles in the supercooled liquid matrix. The $T_x$ value determined by the capacitance measurement was much higher than the Newtonian to non-Newtonian transition temperature, but was closer to the temperature at which the viscosity started to deviate from Arrhenius-type temperature dependence. Although the size and distribution of the crystalline phases were not precisely characterized in the present study, the obtained results suggest that molten silicates that contain a tiny amount of crystalline phase that can be detected using capacitance measurements would behave as a Newtonian fluid, but not fit the Arrhenius-type temperature dependence, then after a certain amount of crystal precipitates, the molten calcium silicate displays non-Newtonian behavior.

4. Conclusion

The effect of agitation on the crystallization behavior of molten calcium silicate-based fluxes was investigated using continuous measurement of their electrical capacitance over a wide temperature range.

At a particular temperature, the electrical capacitance of the molten calcium silicate abruptly decreased by three orders of magnitude, which indicated clearly the crystallization. It was also found that, for measurements taken under agitation with a rotating rod, the crystallization temperatures were higher than those without the agitation. However, the shear stress calculated from the experimental conditions was quite small, meaning that it would not be sufficient to overcome the activation energy of crystallization. The results suggest that the agitation induced by the rotating rod would make the diffusion distance required for the crystallization shorter than that in the resting state.

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