1. Introduction

Mold flux is a vital material in continuous casting processes, where it is employed for various purposes; for example, to act as a lubricant between the melting iron and copper mold during continuous casting processes, to absorb nonmetallic interface inclusions, and to protect the interface of iron. High functional flux of a suitable viscosity that satisfies the purpose mentioned above is needed for the process efficiency and purification of iron. The functionality of flux is determined by its physical characteristics, such as viscosity, surface tension, thermal conductivity, and wettability. Especially, the flux’s viscosity and thermal conductivity are drastically changed by its solid volume fraction and crystallinity. Therefore, an understanding of the flux crystallization behavior is important in order to improve the efficiency of casting processes and materials. During continuous casting processes, flux is used during shear stress in order to keep the mold and molten iron interface lubricated, which is important as it prevents the steel surface from burning. Therefore, an investigation of flux crystallization as a function of shear rate is needed. Numerous studies on the crystallization behavior of flux have been conducted by various methods, including differential thermal analysis (DTA), scanning electron microscopy (SEM), and X-ray diffraction (XRD). However, these studies investigated the crystallization of heat-treated samples that were prepared using predetermined temperature profiles during a stationary state, in spite of demanding the effect of agitation. Few studies, however, have been conducted where crystallization was investigated during the agitation of the sample. The method of electrical capacitance measurements reported by Ohta et al., with which it is possible to observe the crystallization of oxide melts in-situ, was utilized in the present work in order to under-
stand the effects that agitation had on the crystallization of CaO–SiO$_2$–R$_2$O (R=Li, Na, or K)\textsuperscript{14} and CaO–SiO$_2$–CaF$_2$\textsuperscript{15}) systems.

Because of reports where a decreasing heat removal provided some control over the surface defects during iron casting\textsuperscript{23} using a flux that provides the iron used during the casting process and has suitable cooling characteristics is essential. In order to satisfy this, the effects of the basicity, fluorine, alkali metal oxides, and alkaline earth metal oxides on the crystallization of the flux have been studied. However, few studies have systematically reported the \textit{in-situ} effects of additive materials and agitation on the flux crystallization behavior. Recent studies have suggested that there is a change in the crystallization temperature and crystalline phase as a function of shear rate\textsuperscript{15}. With the purpose of improving the iron and steel making processes, a systematic investigation of crystallization and super-cooling of CaO–SiO$_2$–CaF$_2$–MgO slag under simulated actual operating compositions and conditions was performed. As part of this investigation, MgO was replaced with SrO since it is a similar alkaline earth metal oxide and may have a significant impact on the development of iron and steel fabrication processes. In the present work, the crystallization behavior of different CaO–SiO$_2$–CaF$_2$–RO (R=Mg, or Sr) slag systems, under the influence of shear rate, was investigated by the electrical capacitance method. The different slag systems were created by varying the amount of the MgO and SrO additive materials.

2. Experimental

Table 1 lists the chemical compositions of slag prepared using CaCO$_3$, SiO$_2$, MgO, SrCO$_3$ (99.9%, Sigma-Aldrich Japan Inc., Tokyo, Japan), and CaF$_2$ (99.9%, Kanto-Chemical Co. Inc., Tokyo, Japan) reagent powders. The initial powders were thoroughly mixed to produce the required basicity, C/S=1.2, premelted in a Pt crucible at 1 600°C under argon, and then quenched on a Cu plate. The premelted batch glasses were mixed with CaF$_2$ and MgO, or SrO to produce the sample batches. It is important to note that molten oxide samples containing CaF$_2$ are generally known to lose fluorine through reaction (a)\textsuperscript{22}:

\[
\text{CaF}_2 + \text{H}_2\text{O} = \text{CaO} + 2\text{HF} \quad \quad \quad \quad \quad \quad \quad \quad (a)
\]

Therefore, in order to prevent this loss of fluorine, the water from the sample batches was removed by placing the samples in a humidification drying machine at 105°C for 24 h. The capacitance measurements were conducted under dry Ar to prevent the loss of fluorine by reaction (a), and carried out using sulfuric acid, silica gel, and phosphorus pentoxide.

| C/S | CaO | SiO$_2$ | CaF$_2$ | MgO | SrO |
|-----|-----|--------|---------|-----|-----|
| 1.2 | 46.4| 38.6   | 10      | 5   | –   |
|     | 43.6| 36.4   | 10      | 10  | –   |

Three types of shear rate were applied on the slag samples, 0, 10.8 and 21.6 s$^{-1}$. The capacitance of the slag was measured using an impedance analyzer (IM3570, HIOKI E. E. Co., Nagano, Japan) at a constant frequency of 10 kHz. Both the crucible and rod were made with a Pt-20 mass% Rh alloy, and utilized as contact materials during the capacitance measurements. The detailed description of our experimental configuration can be found elsewhere\textsuperscript{14,15}. The capacitance was measured during the rotation of the rod by utilizing a slip ring. The capacitances were measured during a continuous cooling rate of 150°C/h.

The liquidus temperatures of all compositions were difficult to investigate with a phase diagram because the slag was a quaternary system. Therefore, the liquidus temperatures were measured using the Hot-Thermocouple method\textsuperscript{23,24} as follows. A paste was first made by mixing a small amount of sample powder and 2-propanol, and afterwards it was applied to the top of Pt/Pt-13Rh filaments (JIS R-Type, 0.25 mm). The slag was uniformly melted by Joule heat generated with electric current through the filament. Thereafter, the melted slag was gradually cooled and crystallized. Then, the slag was observed during its gradual heating. The temperature at which the crystal was completely melted was defined as the liquidus temperature, $T_L$. It was assumed that the slag was uniformly melted at temperatures higher than the measured liquidus temperature. Liner approximations were estimated between the starting measurement temperature (1 500°C) and the liquidus temperature. Furthermore, the standard deviations of the measured values were calculated from five before and after plots where each plot is in the range from 1 500°C to the liquidus temperature. The crystallization temperature ($T_c$) was defined as the temperature at which the difference between the liner approximations and measured capacitance values was larger than the calculated standard deviation. Figure 1 shows an example of our definition of crystallization temperature. The difference between the liquidus and crystallization temperatures was defined as the super-cooling degree, $T_s$.

To clarify the morphology of the crystalline phases, SEM observations were performed on the polished sections of selected samples. These samples were prepared by first

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Table 1. Initial compositions (mol%) of the slag samples utilized in this study.

Fig. 1. An example of the definition of the crystallization temperature ($T_c$): the point where temperature differences exceed the standard deviations in the range of 1 500°C to $T_L$ in 46.4CaO-38.6SiO$_2$-10CaF$_2$-5MgO slag at 0 s$^{-1}$.

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melting the powder batches in a crucible, and then continuously cooling them in the same manner as for the capacitance measurements. The melt samples in the crucible were taken from the furnace, and then quenched on a Cu plate. Thereafter, the 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 deposited with a magnetron sputtering apparatus. The SEM images were obtained using an acceleration voltage of 20.0 kV. XRD analyses were also conducted on the quenched samples in order to identify the crystalline phase.

3. Results and Discussion

3.1. Electrical Capacitance Measurements of CaO–SiO2–CaF2–RO Melts

The rotating cylinder shear rate was calculated from the rotational speed and the dimensions of the crucible and rod, in accordance with the following Eq. (b):25)

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

where \(\gamma\), \(\omega\), \(r_o\), and \(r_i\) are the shear rate, angular rate, inner radius of the outer cylinder (crucible), and radius of the inner cylinder (rod), respectively.

Figures 2–5 show the capacitance measurement results of the additive materials, MgO and SrO, as a function of shear rate. As shown in these figures, although the measured capacitances exhibited insignificant changes above the liquidus temperatures, they drastically decreased below the liquidus temperatures in all the samples, showing a two-stage variation with decreasing temperature. These capacitance decreases indicate that the super cooled melts were drastically crystallized at these temperatures. Additionally, some shear rate effects generated by the rotating rod were found in some samples, which will be discussed in Section 3.2.

3.2. Effect of Shear Rate on the Crystallized Temperature and Super-Cooling Degree

Figure 6 shows the calculated crystallized temperatures of slag with different added amounts of MgO, SrO, or CaO–SiO2–CaF2 from the capacitance measurements results. As shown in Fig. 6, the crystallization temperatures increased with increasing amounts of MgO when the shear rate was 0 s\(^{-1}\). As with slag samples containing MgO, slag containing SrO exhibited an increase in crystallization temperatures with increasing SrO amounts when the shear rate was 0 s\(^{-1}\). These results indicate that the additions of alkaline earth metal oxides like MgO and SrO accelerate
crystallization at higher temperatures.

When comparing composition as a function of shear rate, the crystallization temperatures of slags containing 5 mol% MgO and 10 mol% SrO increased with increasing shear rates, meaning that the crystallization process was accelerated by the agitation generated from the rod’s rotation. The differences in the crystallization temperatures between the 0 and 10.8 s\(^{-1}\) shear rates were more remarkable than that between the 10.8 and 21.6 s\(^{-1}\) shear rates. By contrast, the changes in the crystallization temperatures of slags containing 10 mol% MgO and 5 mol% SrO exhibited insignificant changes over all the shear rates used. Detailed discussions of these results are mentioned in section 3.3.

Comparing crystallization temperature as a function of composition, the crystallization temperatures of slag that contained MgO were lower than those of slag that contained SrO. Therefore, the crystallization temperature increased with respect to the cationic radius (\(\text{Mg}^{2+} < \text{Sr}^{2+}\)), which corresponds well with the results of a previous study of the CaO–SiO\(_2\)–R\(_2\)O (R\(_2\)O = Li, Na, or K) system.\(^{14}\) In comparison with the base slag of the CaO–SiO\(_2\)–CaF\(_2\) system (C/S = 1.2, CaF\(_2\) = 10 mol%),\(^{15}\) the crystallization temperatures of the slag containing MgO were lower than those of the CaO–SiO\(_2\)–CaF\(_2\) system. In contrast, the crystallization temperatures of the slag containing SrO were higher than those of the CaO–SiO\(_2\)–CaF\(_2\) system. These results were caused by differences in the liquidus temperature of the compounds; the tendency of the crystallization will be discussed in the next paragraph.

Figure 7 shows the calculated super-cooling degrees of slags containing MgO, SrO, or the CaO–SiO\(_2\)–CaF\(_2\) system, obtained from the results of the crystallized temperature and liquidus temperature, which were measured using either the Hot-Thermocouple method or the phase diagram of the CaO–SiO\(_2\)–CaF\(_2\) system. As shown in Fig. 7, the super-cooling degree of slag containing 5 mol% MgO decreased with increasing shear rate. On the other hand, the super-cooling degrees of slag containing 10 mol% MgO exhibited little change with changes in the shear rate. In case of the slag with SrO, the super-cooling degrees of slag with 5 mol% SrO did not change with shear rate changes. By contrast, the super-cooling degrees of slag with 10 mol% SrO decreased with increasing shear rate. In comparison, the super-cooling degrees of MgO containing samples were lower than those of SrO containing samples, except for the sample containing 5 mol% MgO tested with a 0 s\(^{-1}\) shear rate. The super-cooling degrees of slags that contained MgO were more affected by increases in the shear rate than those of slags that contained SrO. It is considered that the heat or mass diffusion of slags containing MgO, whose crystallization was affected, were drastically encouraged by the agitation generated by the rod’s rotation. In comparison with the base slag made up of the CaO–SiO\(_2\)–CaF\(_2\) system, the super-cooling degrees of slags with MgO or SrO were higher, meaning that these slags were more difficult to crystallize.

### 3.3. XRD and SEM Analyses

Figures 8, 9 reveal the X-ray diffraction patterns of
Fig. 9. XRD patterns of quenched samples of CaO–SiO$_2$–CaF$_2$–SrO system slag quenched at the temperatures shown in the figure for a shear rate of 0 s$^{-1}$.

CaO–SiO$_2$–CaF$_2$–MgO and CaO–SiO$_2$–CaF$_2$–SrO systems, quenched at the temperatures shown in the figures, and at a 0 s$^{-1}$ shear rate. As shown in Fig. 8, the only diffraction peaks observed in the sample containing 5 mol% MgO, quenched at 1 220°C, belonged to dicalcium silicate (2CaO·SiO$_2$). At this temperature, the capacitance of this sample showed a steady decline. On the other hand, dicalcium silicate, merwinite (Ca$_3$Mg(SiO$_4$)$_2$) and cuspidine (3CaO·2SiO$_2$·CaF$_2$) diffraction peaks were found in the sample with 10 mol% MgO, which was quenched at 1 160°C. This was the temperature at which the capacitance showed a complete decrease. In order to clarify the primary crystalline phase, for a sample quenched at 1 190°C, which is when the capacitance began to decrease, the only peaks found were those of the dicalcium silicate phase. It is theorized that in the sample with 10 mol% MgO, dicalcium silicate crystallizes first, followed by the crystallization of the merwinite and cuspidine phases. Figure 9 reveals that dicalcium silicate and cuspidine diffraction peaks were found in the samples quenched at 1 240°C and 1 190°C, which is when the capacitances of slags with 5 and 10 mol% SrO started to decrease, were analyzed. From the XRD analysis results, cuspidine peaks were found in the sample quenched at 1 280°C, and dicalcium silicate peaks were found in the sample quenched at 1 220°C. Although the shear rate induced the accelerated crystallization of the dicalcium silicate crystalline phase, as shown in Figs. 8 and 9, its effect was insignificant for the crystallization of the cuspidine phase. In the previous study of the CaO–SiO$_2$–R$_2$O (R=Li, Na, or K) systems, and CaO–SiO$_2$–CaF$_2$ systems, the crystalline phase tended to change from CaO–SiO$_2$ to dicalcium silicate, or cuspidine, as the cationic radius of the added materials increased. Merwinite is a magnesium substitute of dicalcium silicate, so when merwinite was considered as one of the dicalcium silicates, the tendency of the crystalline phase was similar to that in the present and previous studies. Furthermore, the fact that crystallization of the dendritic phase is accelerated by agitation agrees with the conclusions of the present and previous studies of the CaO–SiO$_2$–CaF$_2$ system.

In order to observe the morphology of the crystalline phase, the surfaces of samples cooled to room temperature were observed by SEM. Figures 10, 11 exhibit SEM images of the polished section of the samples after a 0 s$^{-1}$ shear rate. As can be seen in Fig. 10, the morphology of the crystalline phase of samples containing 5 and 10 mol% MgO was similar to that of a non-uniform interface. This non-uniform interface crystalline phase was identified as dicalcium silicate (merwinite) through EDS. Figure 11 reveals that the crystalline phase of samples containing 5 and 10 mol% SrO was found to have a dendritic morphology and a sharp crystalline phase. These dendritic and sharp crystalline phases were identified with EDS as dicalcium silicate and cuspidine, respectively. A possible contribution to the morphology of the crystalline phases could be the influence of the agitation on the crystallization temperatures, since, as mentioned in Section 3.2, the crystallization temperature of slag compositions containing 5 mol% MgO and 10 mol% SrO increased with increasing shear rates from 0 s$^{-1}$ to 10.8 s$^{-1}$. Generally, the crystallization rate is limited by atomic or thermal diffusion when the crystal formed non-uniform interfaces, such as dendrites. As mentioned in Section 3.2, the primary crystallization of the dendritic dicalcium silicate in the slag containing 10 mol% SrO was accelerated as a consequence of the enhancement in mass and heat transfer by agitation generated by the rotating rod. In comparison with the previous study of the CaO–SiO$_2$–CaF$_2$ system, although the morphology results were similar in the case of dicalcium silicate in the slag containing SrO, i.e., the dicalcium silicate was shown to have a dendritic morphology, the dicalcium silicate in the slag containing MgO was observed to have a different morphology. We conclude that the dicalcium silicate and cuspidine in the slag had different crystallization mechanisms because the crystallization of the slags containing 5 mol% MgO and 10 mol% SrO were accelerated by agitation, whereas the slags containing 10 mol% MgO and 5 mol% SrO were not. However, the present study was not designed to investigate these possible mechanisms. For future work, the primary crystallization mechanisms of slags containing MgO or SrO should be examined.
4. Conclusions

The influence of agitation and the morphology of the crystalline phase on the crystallization behavior of supercooled slags (CaO–SiO$_2$–CaF$_2$–RO (R = Mg or Sr)) were systematically investigated using continuous electrical capacitance measurements over a wide temperature range. The major findings are as follows.

The crystallization behavior was changed by the morphology of the crystals and the presence of agitation. In addition, the formation of dendritic crystals in the slags was accelerated by agitation. This suggests that the crystallization behaviors were dependent on the morphology of their crystal phases. The supercooling degrees of the slag were barely changed by the agitation, so it is suggested that the crystallization proceeded without the rate controlling mass or heat transfer. The supercooling degrees of slag containing 10 mol% SrO exhibited insignificant changes with changing shear rates. On the other hand, the supercooling degrees of slag containing 10 mol% SrO decreased with increasing shear rate.

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