Delayed Melt Crystallization of Cuspidine by Addition of Li$_2$O

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INTRODUCTION

Mold fluxes are usually designed based on CaO-SiO$_2$-CaF$_2$ multicomponent oxides to control heat transfer and lubrication during continuous casting of steel. Mold fluxes offer solidification between mold and solidified shell to allow control of overall heat transfer, so success of the continuous casting process requires appropriate melt crystallization behavior of mold fluxes. Several studies have investigated the melt crystallization behavior of commercial mold fluxes under various conditions, but few studies have reported the effects of Li$_2$O addition on the crystallization kinetics in mold fluxes. The crystallization rate of mold fluxes is increased by addition of alkali oxides, which provide free oxygen to the silicate network, and thus facilitate diffusion of silicate. However, in our study, crystallization of Cuspidine has been suppressed obviously by addition of Li$_2$O despite its expected function as an alkali oxide to increase the number of free oxygen.$^{1,2}$ In order to clarify the details of delayed crystallization, we investigated both the isothermal and non-isothermal melt crystallization kinetics of mold fluxes with various Li$_2$O content by applying the Johnson-Mehl-Avrami-Kolmogorov (JMAK) and Friedman equations to Differential Scanning Calorimetry (DSC) data. Raman spectroscopy and solid-state nuclear magnetic resonance (NMR) spectroscopy analyses were conducted to verify the structural effects of Li$_2$O. Also, molecular dynamics simulation has been carried out to assess the effects of Li$_2$O on cations-fluorine interaction.$^3$

DISCUSSION

1. Experimental

Five glasses were prepared; they had Li$_2$O contents (wt %) of 0 (denoted “L0”), 0.56 (“L0.5”), 1.09 (“L1”), 1.67 (“L1.5”) or 2.32 (“L2”) in CaO-SiO$_2$-CaF$_2$ mold flux (Table 1). Appropriate masses of raw materials were mixed for 2 h, then melted in carbon crucibles in a box furnace at 1623 K for 30 min to homogenize chemical composition. Immediately after homogenization, the samples were quenched on a cool copper plate to yield a partial glassy structure. The samples were ground by disk milling. The resulting powders were analyzed using XRF and ICP-AES to compare designed sample composition with the pre-melted sample composition (Table 1); ICP-AES was used to measure the content of Li and B, which are too light to measure using XRF.
Table 1. Basicity and Material Composition (wt %) of the Pre-Melted Mold Flux (Glass codes are explained in the text)

<table>
<thead>
<tr>
<th>Glass code</th>
<th>Measure</th>
<th>L0</th>
<th>L0.5</th>
<th>L1</th>
<th>L1.5</th>
<th>L2</th>
</tr>
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<tbody>
<tr>
<td>Basicity</td>
<td>1.74</td>
<td>1.75</td>
<td>1.74</td>
<td>1.70</td>
<td>1.74</td>
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<tr>
<td>Li₂O</td>
<td>0.00</td>
<td>0.56</td>
<td>1.09</td>
<td>1.67</td>
<td>2.32</td>
<td></td>
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<tr>
<td>SiO₂</td>
<td>27.28</td>
<td>26.68</td>
<td>26.39</td>
<td>26.89</td>
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<tr>
<td>CaO</td>
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<td>47.52</td>
<td>46.64</td>
<td>45.62</td>
<td>46.20</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>7.21</td>
<td>7.14</td>
<td>7.19</td>
<td>7.19</td>
<td>7.12</td>
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<tr>
<td>F</td>
<td>12.73</td>
<td>12.62</td>
<td>13.46</td>
<td>13.25</td>
<td>13.23</td>
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<tr>
<td>B₂O₃</td>
<td>5.35</td>
<td>5.48</td>
<td>5.23</td>
<td>5.38</td>
<td>5.21</td>
<td></td>
</tr>
<tr>
<td>Sum</td>
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<td>100.00</td>
<td>100.00</td>
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</tr>
</tbody>
</table>

2. Isothermal melt crystallization

Figure 1 shows the degree of relative crystallinity with time on various Li₂O composition. Obtained graph of sample L0 showed C-shaped curve which indicates instantaneous crystallization, while sample L0.5-L2 showed S-shaped curve which indicates sporadic crystallization[25, 26]. It is clearly shown that even the minor amount of Li₂O converted the mode of crystallization.

![Figure 1](image.png)

Figure 1. Relative crystallinity of samples with time (a) L0 (b) L0.5 (c) L1 (d) L1.5 (e) L2.

Isothermal crystallization kinetics can be described by Johnson-Mehl-Avrami-Kolmogorov (JMAK) with obtainable parameters; Avrami and crystallization rate constant [27, 28]. Avrami constant implies how nucleation and growth proceed and crystallization rate constants literally indicates how fast the crystallization proceeded. JMAK equation can be expressed by equation (1).

$$X(t) = 1 - \exp(-kt^n)$$

where $X(t)$ indicates relative crystallinity at time $t$, $k$ represents the speed of crystallization, and $n$ is the Avrami constant, which indicates how nucleation and growth proceed. Parameters $k$ and $n$ can be acquired from the negative of the logarithm.

Figure 2 shows the plots of $\ln[-\ln\{1-X(t)\}]$ versus $\ln t$ with different Li₂O composition based on equation (1). It is evident that both the crystallization rate constant $k$ decreased and the crystallization half-time $t_{1/2}$ increased with an increase of isothermal temperature in all samples. The crystallization was delayed with the increment of isothermal temperature, which indicates that
the overall crystallization will be governed by nucleation. Effective activation energy also can be calculated through the Arrhenius equation with the crystallization rate constant $k$ and isothermal temperature $T_i$ as shown in equation (2), where $k_0$ is a temperature-independent pre-exponential constant, $E_a$ is the effective activation energy. It should be emphasized that all of the samples showed negative effective activation energies, which also implies that the overall crystallization should be limited by nucleation

$$\frac{1}{n} \ln(k) = \ln(k_0) - \frac{E_a}{RT_i}$$

(2)

The ratio of the crystallization half time ($t_{1/2}$) to the crystallization end time ($t_{max}$) was calculated from Figure 1. The ratio is about 0.2 in the sample not containing Li$_2$O, whereas the samples containing Li$_2$O were frequently more than 0.5. Considering the substantial slopes (degree of crystallinity vs. time) were similar for all samples in Figure 1, it is reasonable to say that Li$_2$O addition suppressed the crystallization seriously at the initial stage. The negative effective activation energy and inversely correlated behavior between the crystallization rate constant, half time and temperature imply that Li$_2$O was a stumbling block restraining nucleation. As Li$_2$O is one of network breaking agents, increased diffusivity and decreased viscosity will raise the mobility of atoms for crystallization; this change should induce an increase in crystallization temperature and accelerate nucleation. However, the results did not conform to these expectations, so some other critical factors must govern the crystallization process.

3. Molecular dynamics and NMR/Raman spectroscopy

One promising mechanism for the crystallization delay is selective interaction between F$^-$ and Li$^+$ ions. Added Li$^+$ ions lower the activity of F$^-$ ions with their high affinity to F$^-$, which can retard the crystallization by decreasing the available fluorine content. If added lithium considerably interacted with fluorine and degraded the activity of fluorine, cuspidine formation could be delayed regardless of the silicate kinetics. To test the validity of the explanation, an analysis should focus on fluorine. The peak positions of 19F NMR spectra located between -165 to -115 ppm indicate the tetrahedral structure of fluorine with mixed cations. As shown in Figure 3(a), 1st peak (black arrow, near 130 ppm) was observed, and 2nd peak (red arrow, near -161 ppm) became gradually prominent as the amount of added Li$_2$O increased. Therefore, the tetrahedral structures of fluorine are likely to be dominant in all samples (L0-4). Simulation results also showed that the sum of fluorine’s CNs with cations was around 4 in all Li$_2$O content (Figure 3(b)), in good agreement with the NMR result. Interestingly, CNs of F-Li pairs increased whereas F-Ca pairs decreased (Figure 3(b)) with Li$_2$O addition, implying that lithium replaced calcium and complexed with fluorine.
CONCLUSIONS

The crystallization of silicate-containing melt has been directly related to the polymerization degree and viscosity of the silicate network. Our analysis also demonstrated that Li$_2$O depolymerized the silicate structure and decreased the viscosity of the glass melts. However, Li$_2$O addition retarded crystallization even with the increased kinetics. Our structural investigation showed that lithium had significant interaction with fluorine, and these could cause crystallization delay by disrupting the Ca-F interaction and lowering the activity of fluorine. In both simulations and 19F NMR measurements, lithium displaced calcium then interacted with fluorine and distributed tetrahedral structure. Most of the displaced calcium interacted with NBO of silicate, resulting in the decreased motion of calcium. Therefore, we strongly suspect that lithium disrupted Ca-F interaction and caused significant structural changes, and the lithium-release or structural normalization process to form a pure cuspidine appeared in the form of a high level of undercooling and crystallization delay.

REFERENCES

