Viscosity-structure-crystallization of the Ce$_2$O$_3$-bearing Calcium-aluminate-based Melts with Different Contents of B$_2$O$_3$

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In order to restrain the slag-metal interface reaction in the process of heat resistant steel continuous casting, the aluminate-based mold flux was devised. The effect of B$_2$O$_3$ on the viscosity, structure and crystallization property of the aluminate-based melts was studied. Appropriately adding B$_2$O$_3$ could decrease the viscosity of the melts. However, the viscosity could remain relatively constant when the addition of B$_2$O$_3$ exceeded 5 mass%. The structures of the melts, which were correlated to the viscosity, were confirmed through Fourier transformed infrared spectroscopy. The main network former of the melts was AlO$_4$-tetrahedral unit. With adding B$_2$O$_3$, B$_2$O$_3$ formed 2D BO$_3$-triangular unit, the bridging oxygen of the network combined by AlO$_2$-units was broken, the polymerization of the melts decreased, and the viscosity, the apparent activation energy decreased consequently. With no B$_2$O$_3$ addition, the main crystalline phase was CaO. Because of Ca–O have the strongest interaction force and the weakest irregular thermal motion. The crystallization of CaO could be restrained by adding B$_2$O$_3$, the crystalline phase transferred from CaO to LiAlO$_2$ and CaCeAlO$_4$. CaCeAlO$_4$ precipitated later than LiAlO$_2$ because of the different interactions and the irregular motion ability of different structure units.

KEY WORDS: aluminate-based melts; viscosity; structure; mold flux; crystalline phase; B$_2$O$_3$; rare earth.

1. Introduction

Heat-resistant steel has been widely used in the fields such as aerospace, shipping industry and petrochemical engineering for its excellent strength, high oxidation resistance and corrosion resistance under high temperature conditions. Rare earth has shown considerable effects on micro-alloying and improving performance of the steel, and it was introduced to heat-resistant steel production. For example, the target content of cerium is about 0.1 mass% in S30815 steel. High contents of reactive cerium in the steel could induce serious slag-metal interface reactions in the mold when using conventional mold fluxes. For example, SiO$_2$ was heavily reduced by cerium through the slag-metal interface reaction. As a result, the content of rare earth oxides in the mold fluxes increased, and the compositions of the mold fluxes changed, which could lead to deteriorated properties such as varying viscosity and surface tension during casting. What is worse, the surface defects and sticking breakout may be initiated in severe cases. In order to restrain the slag-metal interface reaction in the continuous casting process of heat-resistant steel, a new CaO–Al$_2$O$_3$–Li$_2$O–B$_2$O$_3$–Ce$_2$O$_3$ mold flux based on calcium aluminate system for heat resistant steel continuous casting has been devised by the authors. B$_2$O$_3$ is one of main typical component. And there are many published researches focusing on the effects of B$_2$O$_3$ in the silicate system. Wang et al. investigated the effect of B$_2$O$_3$ on melting temperature, viscosity and desulfurization capacity of refining flux, B$_2$O$_3$ was added as fluxing agent to substitute for CaF$_2$ and show better fluxing action. At the same time, the temperature range, in which the flux viscosity is low, is expanded as well as the stability of flux viscosity varying with temperature is improved obviously. The influence of B$_2$O$_3$ on viscosity of high Ti-bearing BF slag was studied by Ren et al. The results show that the addition of B$_2$O$_3$ can decrease the viscosity of high Ti-bearing BF slag, consequently improve its fluidity. At a lower temperature, B$_2$O$_3$ was easy to form a eutectic and decreased the viscosity of molten slag. At a higher temperature, some tetrahedron [BO$_4$]$^{5–}$ changed into triangle [BO$_3$]$^{3–}$ which would disintegrate the chains/molecules of molten matrix and decreased its viscosity. Li et al. reported that B$_2$O$_3$ are found to behave as network formers in Cr$_2$O$_3$-bearing CaO–SiO$_2$–Al$_2$O$_3$ slags, which was characterized by the decrease in NBO/Si (the number of non-bridging oxygen per Si atom) value. B$_2$O$_3$ addition also led to the formation of low melting point eutectics and weaker polymerization strength. In present new-designed slag system, B$_2$O$_3$ was added not only to decrease the melting temperature, but also to improve the inclusion absorption ability of the slag. According to Wan, the ability of
rare earth oxides dissolving can be improved by adding 
$\text{B}_2\text{O}_3$ composite as solvent. Wang et al.\textsuperscript{10} also found that not only the viscosity of mold fluxes can be reduced, but also the capacity to dissolve and absorb rare earth oxide can be increased by $\text{B}_2\text{O}_3$.

Focusing on the influence of $\text{B}_2\text{O}_3$ on the properties of slag systems with low content of $\text{SiO}_2$, some investigations have been reported. Huang et al.\textsuperscript{11} studied the effect of $\text{B}_2\text{O}_3$ addition on the viscosity of $\text{SiO}_2$-30 mass% $\text{Al}_2\text{O}_3$-$\text{B}_2\text{O}_3$-$\text{Li}_2\text{O}$-$\text{CaO}$ mold slag system containing low silica content ($\text{CaO}/\text{SiO}_2=2.68-7.35$, $\text{B}_2\text{O}_3=0-9$ mass%). The viscosities of the slags decreased slightly with an increase in the content of additive $\text{B}_2\text{O}_3$ above the break temperature. The break temperature also decreased with increasing $\text{B}_2\text{O}_3$ content. The effect of $\text{B}_2\text{O}_3$ on the viscosity and structure in the $\text{CaO}$-$\text{Al}_2\text{O}_3$-$\text{Na}_2\text{O}$-based system was studied by Kim and Sohn.\textsuperscript{12} An increase in the $\text{B}_2\text{O}_3$ content at fixed $\text{CaO}/\text{Al}_2\text{O}_3$ ratio lowered the viscosity. At fixed $\text{CaO}/\text{Al}_2\text{O}_3$ ratio, $\text{B}_2\text{O}_3$ additions decreased the $[\text{AlO}_4]$-tetrahedral structural units and transformed the 3D network structures such as pentaborate and tetraborate into 2D network structures of boroxol and boroxyl rings by breaking the bridging oxygen atoms to produce non-bridging oxygen atoms leading to a decrease in the molten flux viscosity. Some reports of the effect of $\text{B}_2\text{O}_3$ on the $\text{CaO}$-$\text{Al}_2\text{O}_3$ based slag system can be found, but most of them were limited to the slag compositions. No investigations on the properties of $\text{CaO}$-$\text{Al}_2\text{O}_3$-$\text{Li}_2\text{O}$-$\text{B}_2\text{O}_3$-$\text{Ce}_2\text{O}_3$ slag system are of great significance.

In present study, the effects of $\text{B}_2\text{O}_3$ on the viscosity and structure of the aluminate-based $\text{CaO}$-$\text{Al}_2\text{O}_3$-$\text{Li}_2\text{O}$-$\text{B}_2\text{O}_3$-$\text{Ce}_2\text{O}_3$ melts were investigated, and the results could provide theoretical basis for devising mold fluxes for heat resistant steel continuous casting.

2. Experimental

2.1. Raw Materials and Slag Preparation

All slag samples were pre-melted using AR grade agents in Mo crucible in an electric furnace at 1 823 K (1 600°C) under argon atmosphere (>99% purity). The pre-melted samples were quenched immediately and used to measure the viscosity and slag structure. The granularity of the reagents and pre-melted samples is less than 0.074 mm. The composition range of the mold fluxes used in present study is shown in Table 1.

2.2. Viscosity Measurement and Data Processing

The rotating cylinder method was adopted to measure the viscosity. An electric resistance furnace with MoSi\textsubscript{2} heating elements was employed for the heating system and an alumina tube of high-purity was used. The schematic diagram is shown in Fig. 1. The temperature was automatically controlled and measured by the controlling system through two B-type thermal couples. The measuring temperature error was within ±5 K. A 140 g of pre-melted slag was put into a graphite crucible (inside diameter: 40 mm; height: 80 mm) lined with Mo sheet and heated to make the samples completely melted. Then, after 30 minutes of heat preservation, the measurements of viscosity were carried out with a Mo spindle (diameter: 10 mm; height: 25 mm). The measurement was under argon atmosphere (>99% purity) and the data were automatically collected by computer. For viscosity measurement, the Mo spindle rotated with a speed of 200 rpm, meanwhile, the slag was cooled with a rate of −3 K/min, and the measurement was ended with a viscosity of 10 Pa s.

After obtaining the viscosity-temperature curves, the breaking temperature of the mold flux, which was the critical temperature when the viscosity changes abruptly during the continuous cooling process, can be determined by the tangent method. Detailed descriptions can be found in our previous studies.\textsuperscript{13,14} Moreover, when the temperature is above the breaking temperature, the molten mold flux is a Newtonian fluid. The temperature dependence of the viscosity can be described by Arrhenius-type equation which is shown as Eq. (1), and the apparent activation energy of

\begin{equation}
\ln \eta = -\frac{E_a}{R} \frac{1}{T} + \ln A
\end{equation}

Table 1. Chemical compositions of samples (mass%).

<table>
<thead>
<tr>
<th>Slag</th>
<th>CaO</th>
<th>Al\textsubscript{2}O\textsubscript{3}</th>
<th>Li\textsubscript{2}O</th>
<th>Ce\textsubscript{2}O\textsubscript{3}</th>
<th>B\textsubscript{2}O\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>51</td>
<td>34</td>
<td>10</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>02</td>
<td>48.45</td>
<td>32.3</td>
<td>9.5</td>
<td>4.75</td>
<td>5</td>
</tr>
<tr>
<td>03</td>
<td>45.9</td>
<td>30.6</td>
<td>9</td>
<td>4.5</td>
<td>10</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic diagram of the experimental apparatus.
the mold flux also can be calculated form the Arrhenius equation.  

\[ \eta = AT \exp\left( \frac{E_a}{RT} \right) \] .................................. (1)

where \( \eta \) is the viscosity, \( A \) is a constant, \( E_a \) is the apparent activation energy for viscous flow, \( R \) is the universal gas constant, and \( T \) is the temperature in K. The Arrhenius-type equation can be re-arranged after taking logarithm:

\[ \ln \left( \frac{\eta}{T} \right) = \frac{E_a}{RT} + \ln A \] .................................. (2)

The above equation shows that \( \ln \left( \frac{\eta}{T} \right) \) have a linear relationship with \( \frac{1}{RT} \) and the slope of the line is the apparent activation energy \( E_a \).

2.3. Fourier Transformed Infrared Spectroscopy Measurement

For structure measurement, a Fourier transform infrared spectrometer (Nicolet 380) was used. FT-IR spectra were recorded in the 4000–400 cm\(^{-1}\) range using a spectrometer. The spectrometer is equipped with a KBr and the chosen resolution is 0.5 cm\(^{-1}\). For each sample, 2.0 mg of pre-melt slag was mixed with 200 mg of KBr in an agate mortar, and then pressed into pellets of 13 mm diameter for measurement.

2.4. Crystalline Phase Analysis

To investigate the effects of crystalline phases in the solidification process, the slags with a temperature lower than the breaking temperature were sampled and quenched with ice water after viscosity measurement. Sample morphology was analyzed using scanning electron microscope (SEM), and detections of the elemental composition of different phases of samples were conducted by adopting the energy dispersive spectroscopy (EDS) linked to SEM. The phase composition of the samples was determined by method of X-Ray Powder Diffraction (XRD).

3. Results and Discussion

3.1. Viscosity of the Mold Fluxes

Figure 2 shows the viscosity-temperature curves of mold fluxes with different content of \( \text{B}_2\text{O}_3 \). The mold flux has a high viscosity and breaking temperature with no \( \text{B}_2\text{O}_3 \) addition. With adding \( \text{B}_2\text{O}_3 \) to the mold flux, the breaking temperature decrease obviously. And the addition of \( \text{B}_2\text{O}_3 \) increases, the breaking temperature show continuous decreasing trend. The above change of the breaking temperature can be explained by the fluxing action of \( \text{B}_2\text{O}_3 \) and the superheat degree of the slag. When the contents of \( \text{B}_2\text{O}_3 \) are 0 mass%, 5 mass% and 10 mass%, the melting temperatures of the slags are experimentally measured as 1 463 K, 1 413 K and 1 390 K, respectively. That is, at a certain temperature, increasing the content of \( \text{B}_2\text{O}_3 \) decreased the melting temperature of the slag, and the superheat degree (the difference between the actual temperature \( T \) and the melting temperature \( T_m \) of the slag, it can be expressed as \( T - T_m \)) of the slag increased. As a result, the slag with higher \( \text{B}_2\text{O}_3 \) addition could keep the molten state more easily, the ‘sharp increase’ of the viscosity was restrained and the breaking temperature decreased with increasing the \( \text{B}_2\text{O}_3 \) addition. Additionally, the basicity of the slag decreased with increasing the \( \text{B}_2\text{O}_3 \) content. And the decrease of basicity also can restrain the crystallization tendency, resulting in the decrease of breaking temperature.  

The mold flux has a high viscosity and breaking temperature with no \( \text{B}_2\text{O}_3 \) addition. With adding 5 mass\% \( \text{B}_2\text{O}_3 \) to the mold flux, the viscosity show obvious decreasing trend, however, further increasing the content of \( \text{B}_2\text{O}_3 \) to 10 mass\%, the viscosity of the mold flux show no significant changing trend.

Based on the experimental data, the temperature dependence of the viscosity of the mold fluxes were calculated according to Arrhenius equation. The results are shown in Fig. 3. It can be noted that all the three slags with a temperature higher than the breaking temperature in the present study follow the Arrhenius behavior. The apparent activation energy show obvious decreasing trend with adding 5 mass\% \( \text{B}_2\text{O}_3 \), however, further increasing the content of \( \text{B}_2\text{O}_3 \) to 10 mass\%, the viscosity of the mold flux has no obvious change.

Appropriately adding \( \text{B}_2\text{O}_3 \) could decrease the viscosity of the melts in the silicate system. However, the viscosity can stay relatively stable when adding \( \text{B}_2\text{O}_3 \) from 5 mass\% to 10 mass\%. The apparent activation energy also shows the same changes.

Generally, the viscous properties of the slags are influenced by the components and the structure of the molten slags. The above results indicate that network of the molten melts was loosened with increasing the \( \text{B}_2\text{O}_3 \) content from 0 to 5 mass\%, and the frictional resistance of the molten slags was reduced. With increasing the \( \text{B}_2\text{O}_3 \) content from 5 to 10 mass\%, the network and the frictional resistance of the molten slags reach a relatively stable condition. That is, the degree of polymerization of the slags decreased firstly and then kept stable with increasing the \( \text{B}_2\text{O}_3 \) content. To do further explanation, the slag structure of the mold fluxes was also investigated, and it will be discussed in the following section.

3.2. Slag Structure of the Mold Fluxes

Figure 4 shows the FTIR spectra of the mold fluxes
The spectra can be separated into three regions: 1250–1150 cm\(^{-1}\), 850–700 cm\(^{-1}\) and 600–500 cm\(^{-1}\). Referring to previous published results, different band groups were determined. The absorption peaks at 1250–1150 cm\(^{-1}\), at 850–700 cm\(^{-1}\) and at 600–500 cm\(^{-1}\) correspond to the asymmetric stretching vibrations of [BO\(_3\)]-triangular unit, [AlO\(_4\)]-tetrahedron and [AlO\(_6\)]-octahedron, respectively.

The main network units are [AlO\(_4\)]-tetrahedron, [AlO\(_6\)]-octahedron and [BO\(_3\)]-triangular unit. [BO\(_3\)]-triangular unit has a 2D structure and plays as a network modifier. With no B\(_2\)O\(_3\) addition, the main structure unit is [AlO\(_4\)]-tetrahedron. [AlO\(_6\)]-octahedrons also exist in the molten slag. With increasing the content of B\(_2\)O\(_3\), the [BO\(_3\)]-triangular unit is formed and its absorbance intensity had a relatively increasing trend, the width of the peak of [BO\(_3\)] also increases and moves to lower wavelength. Moreover, the peak of [AlO\(_4\)]-tetrahedron firstly moves to the lower wavelength in which the molten slag has a lower polymerization, then, the peak show no obvious changes. It can be inferred that the polymerization of the mold flux maybe decreases firstly and then keeps relatively constant with increasing the content of B\(_2\)O\(_3\). This inference corresponds to the results in section 3.1 well, and it should be further confirmed by the change of the relative fraction of different structure units.

Using the software Origin 8.5, the spectra were analyzed by data smoothing and baseline correction. The relative area fractions of [AlO\(_4\)]-tetrahedron, [AlO\(_6\)]-octahedron and [BO\(_3\)]-triangular units can be calculated from the line by the integral method. McMillan \textit{et al.} and Kim \textit{et al.} have reported that Q\(_n\) unit (different [AlO\(_4\)]-tetrahedrons can be connected by bridging oxygen, and superscript \(n\) denotes the number of bridging oxygen in different units) in the AlO\(_4\) groups could be clarified as Q\(_4\), Q\(_3\) and Q\(_2\) units. Hence, the different units of [AlO\(_4\)]-tetrahedrons can be further analyzed. Using the software Origin 8.5, the baseline of the curve in the interval of [AlO\(_4\)]-tetrahedron was firstly subtracted, and then the curves were treated using the Gaussian-Deconvolution function in the software. During curve-fitting, the line parameter of wavenumber was assigned to 740 cm\(^{-1}\), 780 cm\(^{-1}\) and 800 cm\(^{-1}\) for Q\(_2\), Q\(_3\) and Q\(_4\), respectively. The spectrum was treated statistically by minimization of the residuals. And the relative area fraction of different units also could be obtained from the Gaussian-Deconvolution results.

Figure 5 shows the Gaussian-deconvolution result of the infrared spectroscopy, the relative area fraction of different units for the quenched slag with different contents of B\(_2\)O\(_3\) is shown in Fig. 6. With increasing the B\(_2\)O\(_3\) content from 0 to 5 mass\%, the [AlO\(_6\)]-octahedron units disappear, however, the relative fraction of the 2D BO\(_3\)-triangular unit increases. This indicates that the O\(^{2-}\) in the slag could easily combine with B\(_2\)O\(_3\). The 2D BO\(_3\)-triangular unit is formed through Eq. (3).

\[
\text{BO}_3^2^- + \text{B}_2\text{O}_3 = 2\text{BO}_3^4^- \quad \text{................. (3)}
\]

The 2D BO\(_3\)-triangular unit has a loose structure. It could further break the network of the molten slag.

With increasing the B\(_2\)O\(_3\) content from 0 to 5 mass\%, the highly polymerized [AlO\(_4\)]-tetrahedron (Q\(_4\)) decreases significantly, and the little polymerized units such as Q\(_3\) increase obviously. Judging from the deconvolution results, the highest intensity peak of the [AlO\(_4\)]-tetrahedron moves from Q\(_4\) to Q\(_3\), the polymerization degree of the mold flux decreases with increasing the B\(_2\)O\(_3\) content. And the frictional resistance of the molten slag decreases too. The above changes in the microstructure unit induce the decrease of the viscosity and the decrease of the apparent activation energy (section 3.1).

Further increasing the content of B\(_2\)O\(_3\) from 5 mass\% to 10 mass\%, the relative fraction of [AlO\(_4\)]-tetrahedron and
highly-polymerized units $Q^4$ increase slightly with a percent of 0.5% to balance the change caused by the increase of $Q^2$. As a result, different changes of $Q^2$, $Q^3$, and $Q^4$ could reach a relative equilibrium. The network structures and the frictional resistance have no obvious variations. Consequently, the viscosity and the apparent activation energy of the mold flux keep relatively constant with the content of $B_2O_3$ increasing to 10 mass% as shown in Fig. 2.

### 3.3. Crystallization Process of the Mold Fluxes

In the continuous cooling process, the crystallization process is another important property of the mold flux. It will greatly influence the heat-transfer in the mold and other related properties of the mold fluxes. In order to further investigate the properties of the mold flux with different contents of $B_2O_3$, the crystallization process of the mold fluxes was also studied experimentally. The results are shown in the following discussions.

**Figure 7(a)** shows the XRD pattern of the mold flux with no $B_2O_3$. There is only one crystalline phase, CaO, precipitated in the continuous cooling process. Based on the SEM-EDS analysis results shown in Fig. 7(b) and Table 2, CaO (phase P1) precipitated largely and distributed uniformly among the liquid matrix phase M. The above results can be explained as follows.

Considering the micro structure, ions and ions groups have irregular thermal motion all the time. There exists interaction force between different ions and ion groups. With adding no $B_2O_3$, the mold flux has a high basicity. The cations are $Li^+$, $Ca^{2+}$, and $Ce^{3+}$. The anions and anion groups are $O^{2-}$ and $AlO_4^{5-}$. Structure analysis show that $Al_2O_3$ plays a role of acidic oxide. The structure units $[AlO_4]$-tetrahedron is the main network former. In the molten slag, ions with positive charges should compensate the $[AlO_4]$-tetrahedrons. $Li^+$ ion, which has the minimum ionic radius, has just one positive charge, implying $Li^+$ could freely move in the space of $[AlO_4]$-tetrahedrons and $Li^+$ ions have the priority to compensate the highly-polymerized $[AlO_4]$-tetrahedrons. Moreover, ionic bonds between cations and anions also exist in the molten slag, such as Ca–O ionic bond and Ce–O ionic bond. **Table 3** shows the cell and symmetry information of related compounds. According to the cell and symmetry information, the crystal structures of the unit cell can be
drawn for related compounds using the software Materials Studio. The results are shown in Fig. 8. Judging from the given information and calculated results, CaO has the minimum crystal lattice size and the densest stacking. Consequently, CaO has relatively stronger tendency of forming a stable and dense structure. Besides, Ca$^{2+}$ has a large ionic potential. Hence, Ca$^{2+}$ and O$^{2-}$ have the strongest interaction force. Ca$^{2+}$ and O$^{2-}$ ions connected with ionic bonds will have the weakest irregular thermal motion. The above conditions facilitate the partial saturation of Ca$^{2+}$ ions and O$^{2-}$ ions. Consequently, CaO precipitated in the continuous cooling process.

**Table 2.** EDS analysis of quenched mold flux with no B$_2$O$_3$.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Compositions (at%)</th>
<th>Estimated phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>50.7 – – – 49.3</td>
<td>CaO</td>
</tr>
<tr>
<td>M</td>
<td>12.1 11.8 23.4 48.9</td>
<td>Liquid matrix phase</td>
</tr>
</tbody>
</table>

To be emphasized: the atomic number of Li is so small that Li cannot be detected by EDS.

**Table 3.** Cell and symmetry information of different compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>System</th>
<th>Space Group</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>cubic</td>
<td>Fm$ar{3}$m</td>
<td>4.797</td>
<td>4.797</td>
<td>4.797</td>
<td>21</td>
</tr>
<tr>
<td>Ce$_2$O$_3$</td>
<td>rhombohedral</td>
<td>P$ar{3}$_m1</td>
<td>3.891</td>
<td>3.891</td>
<td>6.063</td>
<td>22</td>
</tr>
<tr>
<td>LiAlO$_2$</td>
<td>tetragonal</td>
<td>P422</td>
<td>5.169</td>
<td>5.169</td>
<td>6.268</td>
<td>23</td>
</tr>
</tbody>
</table>

**Figure 7.** Crystallization of mold flux with no B$_2$O$_3$ (a) XRD patterns and (b) SEM image.

**Figure 8.** Crystal structure of unit cells of (a) CaO, (b) Ce$_2$O$_3$ and (c) LiAlO$_2$.

**Figure 9(a).** shows the XRD pattern of the mold flux with 5 mass% B$_2$O$_3$. There are two crystalline phases precipitated in the continuous cooling process. The crystalline phases changed from CaO to LiAlO$_2$ and CaCeAlO$_4$. Based on the SEM-EDS analysis results shown in Fig. 9(b) and Table 4, LiAlO$_2$ (dark phases P1) precipitated among the liquid matrix phase M (the light grey phases), and it had a dendritic distribution. CaCeAlO$_4$ (bright white phase P2) precipitated with a needlelike distribution.

With adding B$_2$O$_3$, the cations are Li$^+$, Ca$^{2+}$ and Ce$^{3+}$. The anions and anion groups are O$^{2-}$, AlO$_4^{5-}$ and BO$_3^{3-}$. Structure analysis shows that Al$_2$O$_3$ plays a role of acidic oxide. Al$_2$O$_3$ still plays the role of acidic oxide, and [AlO$_4^{5-}$]-tetrahedron is the main network former. In the molten slag, the electronegativity of AlO$_4^{5-}$ ion group is stronger than that of BO$_3^{3-}$ ion group and interactions between cations and AlO$_4^{5-}$ ion groups is stronger than that between cations and BO$_3^{3-}$ ion groups. The interacted cations and AlO$_4^{5-}$ ion groups has the relatively weaker irregular motion, and they will combine with each other resulting in the crystallization of aluminate compounds. And B can exist in the liquid matrix phase. There is no compound with B precipitating in the continuous cooling process. Investigation indicated that B$_2$O$_3$ show better fluxing actions on CaO–based slags, and B$_2$O$_3$ addition also led to the formation of low melting point eutectics. Referring to the published phase diagrams, in
The present studied CaO-Al\textsubscript{2}O\textsubscript{3}-based slag system, B\textsubscript{2}O\textsubscript{3} may react with CaO and Al\textsubscript{2}O\textsubscript{3} to form CaO⋅Al\textsubscript{2}O\textsubscript{3}⋅B\textsubscript{2}O\textsubscript{3} (melting temperature: 1288 K) and 2CaO⋅Al\textsubscript{2}O\textsubscript{3}⋅B\textsubscript{2}O\textsubscript{3} (melting temperature: 1073 K). Moreover, B\textsubscript{2}O\textsubscript{3} also could react with Li\textsubscript{2}O to form LiBO\textsubscript{2} (melting temperature: 1119 K), Li\textsubscript{2}B\textsubscript{4}O\textsubscript{7} (melting temperature: 1187 K) and Li\textsubscript{4}B\textsubscript{10}O\textsubscript{17} (melting temperature: 1167 K). However, the melting temperatures of the above B\textsubscript{2}O\textsubscript{3}-bearing compounds are lower than the melting temperature of the slags used in this study (1463 K, 1413 K and 1390 K, respectively). Consequently, simple component such as CaO and Li\textsubscript{2}O did not precipitate in the continuous cooling process, and no B-bearing phases precipitated.

Judging from the structure analysis shown in section 3.2, the polymerization of the molten slag decreased after adding B\textsubscript{2}O\textsubscript{3}, and there are more little-polymerized [AlO\textsubscript{4}]\textsuperscript{-}tetrahedrons in the slag. As a result, more cations for charge compensation will be needed. Just as discussed above, Li\textsuperscript{+} ions will firstly compensate the most-polymerized [AlO\textsubscript{4}]-tetrahedrons (Q\textsubscript{4} units) to form LiAlO\textsubscript{2}, which can be expressed as Fig. 10. The process is essentially a formation of LiAlO\textsubscript{2}. As a consequent, LiAlO\textsubscript{2} precipitated in the continuous cooling process. The crystal structure of LiAlO\textsubscript{2} is also shown in Fig. 8.

Structure analysis show that the 2D BO\textsubscript{3}-triangular unit is formed through Eq. (3) after the B\textsubscript{2}O\textsubscript{3} is added to the slag. That is, more O\textsuperscript{2−} ions were consumed to form 2D BO\textsubscript{3}-triangular unit. Besides Li\textsuperscript{+} ions compensating the most-polymerized [AlO\textsubscript{4}]-tetrahedrons, cations such as Ca\textsuperscript{2+} and Ce\textsuperscript{3+} will compensate the little-polymerized [AlO\textsubscript{4}]-tetrahedrons and imply charge balance for BO\textsubscript{3−} units. Judging from the XRD analysis results, the precipitation of CaCeAlO\textsubscript{4} was a result of Ca\textsuperscript{2+} and Ce\textsuperscript{3+} together compensating the little-polymerized [AlO\textsubscript{4}]-tetrahedrons. Similar results were also obtained in the authors’ previous studies.\textsuperscript{24,26}

Based on the above discussions, the interaction between Li\textsuperscript{+} ions and the most-polymerized [AlO\textsubscript{4}]-tetrahedrons results in the crystallization of LiAlO\textsubscript{2}. And the interaction between Ca\textsuperscript{2+}, Ce\textsuperscript{3+} and the little-polymerized [AlO\textsubscript{4}]-tetrahedrons can lead to the crystallization of CaCeAlO\textsubscript{4}. In the molten slag, the most-polymerized [AlO\textsubscript{4}]-tetrahedrons combined with each other to form a chain structure or a net structure, and the most-polymerized [AlO\textsubscript{4}]-tetrahedrons have the weakest irregular motions. In the continuous cooling process, the connected Li\textsuperscript{+} ions and the most-polymerized [AlO\textsubscript{4}]-tetrahedrons have the lowest active energy, and LiAlO\textsubscript{2} firstly precipitated earlier than CaCeAlO\textsubscript{4}. This result corresponds well with the morphology shown in Fig. 9. LiAlO\textsubscript{2} precipitated early and had a bulky and sufficient growth. However, the later precipitated CaCeAlO\textsubscript{4} just has a tiny needlelike distribution, and the distribution was scattered.

4. Conclusions

Appropriately adding B\textsubscript{2}O\textsubscript{3} could decrease the viscosity
of the melts. However, the viscosity could remain relatively constant when the addition of \( \text{B}_2\text{O}_3 \) exceeded 5 mass%.

The main network former of the melts was \( \text{Al}_2\text{O}_3 \)-tetrahedral unit. With adding \( \text{B}_2\text{O}_3 \), \( \text{B}_2\text{O}_3 \) preferentially combined with \( \text{O}^{2-} \) to form 2D \( \text{BO}_3 \)-triangular unit, the bridging oxygen of the network combined by \( \text{Al}_2\text{O}_3 \)-units was broken to non-bridging oxygen, the polymerization of the melts decreased, and the viscosity, the apparent activation energy decreased consequently.

With no \( \text{B}_2\text{O}_3 \) addition, the main crystalline phase was \( \text{CaO} \). Because of \( \text{Ca}^{2+} \) has a large ionic potential, and \( \text{Ca}–\text{O} \) have the strongest interaction force and the weakest irregular motion. The interaction between \( \text{Li}^{+} \) ions and the most-polimerized \([\text{AlO}_4]^{-}\)-tetrahedrons has a large ionic potential, and the polymerized \([\text{AlO}_4]^{-}\)-tetrahedrons results in the crystallization of \( \text{LiAlO}_2 \). And \( \text{LiAlO}_2 \) firstly precipitated for \( \text{Li}^{+} \) ions and the most-polimerized \([\text{AlO}_4]^{-}\)-tetrahedrons have the lowest active energy and the weakest irregular motion. The interaction between \( \text{Ca}^{2+} \), \( \text{Ce}^{3+} \) and the little-polymerized \([\text{AlO}_4]^{-}\)-tetrahedrons can lead to the crystallization of \( \text{CaCeAlO}_4 \), and \( \text{CaCeAlO}_4 \) precipitats later than \( \text{LiAlO}_2 \).

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