**Relationship Between Thermal Conductivity and Structure for the CaO-BO$_{1.5}$-AlO$_{1.5}$ Melts**

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The physical properties of a mold flux, such as its viscosity and thermal conductivity, affect continuous casting processes. Therefore, it is important to systematically evaluate these properties to understand the structure of the melt. The present study used hot wire method to measure thermal conductivity. Raman spectrometry and magic angle spinning nuclear magnetic resonance (MAS-NMR) were used to clarify the relationship between the thermal conductivities and structures of CaO-BO$_{1.5}$-AlO$_{1.5}$ melts with a wide composition range. Furthermore, effects of the covalency of each chemical bond in the melts, which was estimated using first-principle calculations, on the thermal conductivity were investigated.

Keywords: Thermal conductivity, Structure, Mold flux, Molten oxide

**INTRODUCTION**

In the continuous casting process, a mold flux is added to the surface of the molten steel. The mold flux acts as a lubricant and controls the cooling rate of the surface of the molten steel to prevent cracking due to the temperature difference between the interior and exterior of the molten steel. In other words, the thermal conductivity of the molten flux determines the quality of the final product and is one of the most important properties. The conventional mold flux contains CaO, SiO$_2$, and BO$_{1.5}$. In the case of a SiO$_2$-based flux, the Al in the molten steel behaves as a reductant, and the Si concentration in the molten steel increases as follows:

$$3(\text{SiO}_2) + 4\text{Al} = 3\text{Si} + 2(\text{Al}_2\text{O}_3).$$  (1)

This effect is a significant issue for high-Al steels, such as transformation induced plasticity (TRIP) steel. To prevent this reaction, mold fluxes with high concentrations of AlO$_{1.5}$ have been developed$^1$. However, it is difficult to accurately measure the thermal conductivity of a molten mold flux due to the large effect of convection and radiation at high temperature$^2$. The transient hot wire method is an effective measurement method to reduce these effects and has been adopted for measuring thermal conductivity of molten oxides$^3$-$^7$. In addition, the effects of the flux composition on the thermal conductivities of fluxes that contain BO$_{1.5}$ and AlO$_{1.5}$ are unknown because of their structural complexity. The coordination numbers of B and Al in the flux change with the composition. Therefore, the thermal conductivity of the mold flux cannot be predicted simply from its composition.

The authors studied BO$_{1.5}$ or AlO$_{1.5}$ containing systems. (Na$_2$O-BO$_{1.5}$, CaO-BO$_{1.5}$, BO$_{1.5}$SiO$_2$, CaO-AlO$_{1.5}$SiO$_2$, CaO-BO$_{1.5}$SiO$_2$, and CaO-BO$_{1.5}$AlO$_{1.5}$ (CBA)$^8$) In this study, thermal conductivity measurements were conducted using hot wire method and structural analyses were conducted using Raman spectrometry and MAS-NMR for various CBA system compositions. Thereafter, the relationship between the thermal conductivity and molten structure was evaluated quantitatively. In addition, the covalency of each bond in the molten mold flux was evaluated using first-principle calculations to consider the effects of the covalency of these bonds on the thermal conductivity.
EXPERIMENTAL PROCEDURES

The thermal conductivity of the flux was measured for compositions with a uniform homogeneous liquid phase at 1773 K using the transient hot wire method. Figure 1 shows a schematic of the experimental setup for the thermal conductivity measurement. A Pt-10%Rh crucible was used to hold the sample and was set in an electric resistance furnace (heating element: SiC). The furnace was then heated to 1773 K. After the sample melted, a thin Pt-13%Rh wire was inserted into it. A constant current of 1.0 A was applied to the wire by a galvanostat, and the change in voltage with respect to time was measured using a digital multimeter. This voltage change, which reflected an increase in the specific resistance of the Pt wire, was then used to calculate the temperature increase of the Pt wire, and the thermal conductivity was estimated. The measurement temperature was changed from 1773 to 1473 K in 50 K steps.

![Fig 1. Schematic of the experimental setup for thermal conductivity measurements](image)

Structural analysis was conducted for the quenched glass sample that was melted at 1773 K in a Pt crucible. Raman spectrometry (NRS-5100, JASCO) was used with an excitation provided by a laser with a wavelength of 532 nm operated at 5 mW. The resulting Raman signal was collected in the wavenumber range of 400 to 1600 cm\(^{-1}\). The \(^{11}\)B and \(^{27}\)Al spectra of each sample were collected using MAS-NMR spectroscopy (ECA-500, JEOL, Tokyo, Japan) under a magnetic field strength of 11.7 T. The detailed measurement conditions for each nucleus are listed in Table I.

<table>
<thead>
<tr>
<th>Nuclear Property</th>
<th>(^{11})B</th>
<th>(^{27})Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuclear spin</td>
<td>3/2</td>
<td>5/2</td>
</tr>
<tr>
<td>Larmor frequency [MHz]</td>
<td>160.4</td>
<td>130.3</td>
</tr>
<tr>
<td>Repetition times</td>
<td>256</td>
<td>4096</td>
</tr>
<tr>
<td>Flip angle [rad]</td>
<td>30°</td>
<td>30°</td>
</tr>
<tr>
<td>Delay time [s]</td>
<td>1.25</td>
<td>0.17</td>
</tr>
<tr>
<td>Spinning rate [kHz]</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Reference standard</td>
<td>Saturated H(_3)BO(_3) solution (+19.49 ppm)</td>
<td>Al(NO(_3))(_3) solution (0 ppm)</td>
</tr>
</tbody>
</table>

Table I: Detailed measurement conditions for MAS-NMR spectroscopy
RESULTS AND DISCUSSION

1. Relationship between thermal conductivity and structure

The results showed a negative effect of the temperature on thermal conductivity. Figure 2 shows the results of thermal conductivity measurements at 1673 K for the CBA system. For the compositions where CaO/AlO\textsubscript{1.5} = 1.38, the thermal conductivity showed a local maximum with an increase in the BO\textsubscript{1.5} content (Figure 3(a))\textsuperscript{11}. In addition, the relative fraction of the B[3]–O–Al[4] bond, which consists of three coordination B atoms (B[3]) and four coordination Al atoms (4[Al]), was observed via Raman spectrometry and showed a similar change based on the BO\textsubscript{1.5} concentration (Figure 3(b))\textsuperscript{11}. The vibrational assignments for each peak position are listed in Table II\textsuperscript{12,13}. The results suggest that the AlB\textsubscript{3}O\textsubscript{7} structure (Figure 4) contributed to the heat conduction in the molten CBA system. Therefore, MAS-NMR measurements were conducted to evaluate the relative fraction of the coordination numbers of B and Al. It was confirmed that in the CBA system, the main coordination numbers of B and Al were 3 and 4, respectively. Figure 5 shows an example of the peak separation of \textsuperscript{11}B and \textsuperscript{27}Al for 14.8 mol\% CaO-73.7 mol\% BO\textsubscript{1.5}-11.5 mol\% AlO\textsubscript{1.5}. The relative fractions of B[4] and Al[4] in all the cations were calculated using the MAS-NMR measurement results. Figure 6 shows the relationship between the thermal conductivity and relative fractions of B[4] and Al[4]. This figure shows that in the low BO\textsubscript{1.5} concentration range, the main network former was Al[4], while in the high BO\textsubscript{1.5} concentration range, B[4] was the main network. The AlB\textsubscript{3}O\textsubscript{7} structure has one B[4], one Al[4], and more than two B[3] per unit structure (Figure 5). Therefore, the probability of forming the AlB\textsubscript{3}O\textsubscript{7} structure is determined by the lower concentration of B[4], and Al[4] had a local maximum with respect to BO\textsubscript{1.5} because a sufficient number of B[3] existed in the compositions of this study. As shown in Figure 7, the thermal conductivity had a local maximum similar to the probability of forming the AlB\textsubscript{3}O\textsubscript{7} structure. A structural analysis using NMR could provide a semi-quantitative evaluation of the relationship between the fraction of the AlB\textsubscript{3}O\textsubscript{7} structure and the thermal conductivity, which was originally suggested by Raman spectrometry.

Table II: Reference peak positions of Raman spectrum and assignments for the CaO-BO\textsubscript{1.5}-AlO\textsubscript{1.5} system\textsuperscript{12,13}

<table>
<thead>
<tr>
<th>Reference position (cm\textsuperscript{-1})</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>480–550</td>
<td>Al–O\textsuperscript{0} stretching vibration in [AlO\textsubscript{4}]\textsuperscript{4−}; Al–O–B stretching vibration in the aluminate network</td>
</tr>
<tr>
<td>600–650</td>
<td>B–O–B stretching vibration in ring-metaborates</td>
</tr>
<tr>
<td>700–720</td>
<td>Al–O or Al–O–B stretching vibration in the aluminate network; \textsuperscript{11}Al–O–\textsuperscript{0}B bending vibration</td>
</tr>
<tr>
<td>770</td>
<td>B–O\textsuperscript{0} stretching vibration in six-membered borate rings with 1 or 2 [BO\textsubscript{2}]\textsuperscript{2−} (di-triborates, triborates, tetraborates, and pentaborates)</td>
</tr>
<tr>
<td>860</td>
<td>Symmetric B–O\textsuperscript{0} stretching vibration in [BO\textsubscript{3}] pyroborate</td>
</tr>
<tr>
<td>890–940</td>
<td>B–O\textsuperscript{0} stretching vibration in orthoborates</td>
</tr>
<tr>
<td>960–980</td>
<td>\textsuperscript{11}Al–O–\textsuperscript{0}B stretching vibration in the aluminoborate network</td>
</tr>
<tr>
<td>1200–1300</td>
<td>B–O\textsuperscript{0} stretching vibration in pyroborates; B–O\textsuperscript{0} stretching vibration in [BO\textsubscript{4}] (various borate groups)</td>
</tr>
</tbody>
</table>
Fig 2. Thermal conductivity of the CBA system at 1673 K
(a)

Fig 3. Effect of BO$_{1.5}$ addition on the thermal conductivity and the percentage of each structure (CaO/AlO$_{1.5}$ = 1.38)
2. Relationship between thermal conductivity and covalency of bonds

Homonuclear diatomic molecules, such as H₂ and O₂, have pure covalent bonds. However, the bonds of heteronuclear diatomic molecules are both covalent and ionic. If the deviation of the electron distribution of a bond is large, the bond is ionic rather
than covalent and weak. To evaluate the strengths of bonds that contain B[4], Al[4], and Al[6] and form a 3D network in the CBA system, the covalency of the bonds was estimated using first-principle calculations. In the calculations, it was assumed that B[4] and Al[4] combine with O atoms to form a regular tetrahedral structure, and Al[6] combines with O atoms to form a regular octahedral structure. The lengths of B–O and Al–O were calculated from the covalent radius of a single bond and fixed at 1.48 and 1.89 Å, respectively. The structures for the calculations were then prepared by combining any two of these structures. The isosurfaces of the electron density in the calculation results are shown in Figure 7. These show that the electron density around the B atoms was higher than those of Al[4] and Al[6], and B–O bonds were more covalent than the Al–O bonds. These results agreed with the fact that in a chemical bond with a large difference in electronegativity, an atom with higher electronegativity attracts more electronic charge, and the electron density around it increases, while the electron density around an atom with lower electronegativity decreases. The electronegativities of O, Al, and B are 3.44, 1.61, and 2.04, respectively. Therefore, an Al–O bond has a larger difference in electronegativity values and is more polarized and less covalent than a B–O bond.

Fig 7. Electron density distribution of each unit structure in the CBA system
To evaluate the covalency of the bonds involving B[4], Al[4], and Al[6] more quantitatively, calculations with Wannier functions were conducted. The Wannier functions describe the electron states. The square of the Wannier functions represents the electron distribution, and its mean position represents the center of the electron distribution. The Wannier functions are non-unique. Therefore, maximally localized Wannier functions (MLWF), which are transformed to minimize the spread of the Wannier functions, are used to describe the electron state. The change in polarization can be interpreted as polarization occurring in the case of electron localization at the center of the MLWF (WFC: Wannier function center). Therefore, the distance, D (Å), between the WFC and the chemical bond center of a bond is considered to be an indicator of the strength of covalency. Table III lists the results for D, and Figure 8 shows the WFC and D in the B[4]–O–Al[4] structure, which has the least D and is the most covalent structure. The D values in Table III suggest the following. First, the B[4]–O bonds were the most covalent, and the Al[6]–O bonds were the least covalent. Second, comparing the D values of the B[4]–O bonds, the B[4]–O(−Al[4]) bond was more covalent than the B[4]–O(−Al[6]) bond. Notably, when the chemical bond lengths of the compared bonds are significantly different, the degree of polarization differs, and an evaluation of the covalency using D is expected to be difficult even if they have the same D. However, in the case of the B–O and Al–O bonds, their chemical bond lengths are not significantly different. Therefore, this evaluation method was considered to be possible.

Table III: D (Å) values of X–O bond in X–O–Y bond

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<tr>
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<tbody>
<tr>
<td>B[4]</td>
<td>0.317</td>
<td>0.299</td>
<td>0.417</td>
<td></td>
</tr>
<tr>
<td>Al[4]</td>
<td>0.548</td>
<td>0.532</td>
<td>0.705</td>
<td></td>
</tr>
<tr>
<td>Al[6]</td>
<td>0.604</td>
<td>0.600</td>
<td>0.571</td>
<td></td>
</tr>
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</table>

The above results suggested that the B[4] atoms had a strong effect on the increase in thermal conductivity, and replacing Al[4] with Al[6] weakened the covalency of the B[4]–O bond. This confirmed the relationship between the thermal conductivity and BO<sub>1.5</sub> of the CBA system (Figure 6). For compositions with Ca/Al = 1.38, the relative fraction of the B[4]–O bond increased with the BO<sub>1.5</sub> concentration at low BO<sub>1.5</sub> concentrations. In contrast, when the BO<sub>1.5</sub> concentration was more than 55 mol%, the Al[4] content decreased and the Al[6] content increased, and therefore, the thermal conductivity decreased.

CONCLUSIONS

Thermal conductivity measurements were conducted on the CaO-BO<sub>1.5</sub>-AlO<sub>1.5</sub> system. Thereafter, the relationship between the thermal conductivity and structure was investigated using Raman spectrometry and MAS-NMR and first-principle calculations. The results can be summarized as follows.

- The structural analysis using Raman spectrometry and MAS-NMR semi-quantitatively suggested that the AlB<sub>3</sub>O<sub>7</sub> structure (B[4]–O–Al[4] bond) contributed to increase thermal conductivity.
REFERENCES