

## 論文の内容の要旨

論文題目      Thermophysical Property of Molten Borate Systems and  
their Structural Factors  
(ホウ酸塩系融体の熱物性とその構造的因子)

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In order to elucidate the relationship between physical property and molten borate structure, thermal conductivity was measured in the various borate and borosilicate system along with structural investigation using MAS-NMR and Raman spectroscopy.

In introduction, the practical application and academic importance of the physical property and structure of  $B_2O_3$  system were reviewed. Along with the development of high  $Al_2O_3$  bearing steel and strict environmental regulation,  $B_2O_3$  bearing mold flux system has been paid attention. In addition, due to the various applications, borate glass is considered as one of the promising glass system. However, in spite of the importance of borate system, physical property of  $B_2O_3$  bearing system has not been fully understood owing to complicate structure; not only short-range order, but also intermediate range order structure. The borate structure observed in the various oxide systems was reviewed. The effect of molten oxide structure on the various physical properties was also surveyed. It was found that thermal conductivity of the molten borate system has not been fully understood in spite of the importance in the glassmaking and pyrometallurgy process. Following the survey for thermal conductivity measurement principle, thermal conductivity measurement technique was determined.

In Chapter 2, thermal conductivity in the pure  $B_2O_3$  and borosilicate system was investigated. Following the measurement, structural investigation was carried out using  $^{11}B$  and  $^{29}Si$  MAS-NMR along with Raman spectroscopy. The conflict temperature dependence of thermal conductivity was observed. Owing to increase in boroxol ring size, thermal conductivity gradually increases with higher temperature. However, above 1400 K, when *double bond-switching mechanism* terminates, thermal conductivity decreases with higher temperature due to shortening of phonon mean free path resulting from thermally broken bond. Although both  $B_2O_3$  and  $SiO_2$  are typical network forming oxide, measured thermal conductivity of

molten  $B_2O_3$ - $SiO_2$  system shows much lower value than weighted average. The short-range order and intermediate range order structure of borosilicate system was evaluated by an aid of  $^{11}B$  MAS-NMR, 3Q MAS,  $^{29}Si$  MAS-NMR and Raman spectroscopy. Findings show that although some borate structures are associated with fully polymerized silicate network, other borate structures exist as boroxol ring cluster. The formation of boroxol ring cluster results in decreasing of thermal conductivity by increase in thermal resistance. It was found that not only short range order structure but also intermediate range order structure are key factors determining thermal conductivity.

In chapter 3, thermal conductivity of various binary alkali borate systems and sodium silicate system was investigated. In addition, according to Debye model, phonon mean free was calculated with varying temperature. The simple linear relationship between thermal conductivity and the relative fraction of  $Q^4$  unit; which is the relative fraction of fully polymerized silicate structure, indicating that thermal conductivity is mainly determined by fully polymerized network structure. On the other hands, the linear relationship between thermal conductivity and the relative fraction of 4-coordinated boron was observed in the region where tetraborate and diborate dominant region. Below 10 mol% of alkali oxide concentration, due to the mixing between boroxol ring structure and tetraborate unit, disorder increases along with shortening phonon mean free path showing opposite relationship. In order to evaluate the thermal conductivity based on the borate structure, understanding of intermediate range of borate structure has to be preceded. The effect of cation on thermal conductivity was considered. Although observed relative fraction of 4-coordinated boron is almost same, different thermal conductivity was found depending on the cation type. The effect of cation was evaluated using ionization concept. At 1273 K, the positive linear relationship between thermal conductivity and ionization potential was obtained. Higher ionization potential results in stronger bond strength between not only alkali ion and non-bridging oxygen, but also alkali ion and  $BO_4^-$  tetrahedral units. As an increasing of structure rigidity, thermal conductivity increases.

In chapter 4, thermal conductivity was measured in the  $Na_2O$ - $B_2O_3$ - $SiO_2$  system in order to evaluate the effect of borate and silicate network on thermal conductivity, simultaneously. In addition to thermal conductivity measurement, structural investigation was carried out using MAS NMR and Raman spectroscopy. Although both silicate and borate structure change with addition of sodium oxide, thermal conductivity is mainly determined by the change of borate structure at the initial stage. Increasing of thermal conductivity was observed with higher relative fraction of 4-coordinated boron. Raman spectroscopy result shows the increasing of relative fraction of 4-coordinated boron leads to formation of tetraborate structure. On the other hands, above certain R ratio ( $Na_2O/B_2O_3$ ), thermal conductivity decreases as a result of depolymerization of both borate and silicate network structure. Increasing of thermal

conductivity was observed with higher K ratio, in spite of almost same short range order of silicate and borate structure. Higher  $\text{SiO}_2$  concentration leads to increase in thermal conductivity by better mixing between silicate and borate network. In addition, higher heat conduction through silicate network than borate network can be inferred.

In order to evaluate the effect of  $\text{B}_2\text{O}_3$  on thermal conductivity in the mold flux system, thermal conductivity was investigated in the  $\text{CaO-SiO}_2$  based system; major mold flux components. Conflicting effect of  $\text{B}_2\text{O}_3$  on thermal conductivity was observed depending on the  $\text{CaO/SiO}_2$  ratio. According to activity coefficient of  $\text{B}_2\text{O}_3$ , the state of  $\text{B}_2\text{O}_3$  in the silicate network was evaluated. It was found that boron is incorporated into silicate network structure at low basicity region, while  $\text{B}_2\text{O}_3$  behaves as acidic oxide in the high basicity region. Therefore, at low basicity, increase in  $\text{B}_2\text{O}_3$  concentration causes change the nature of silicate network along with disrupting phonon transfer. On the other hands, at high basicity, addition of  $\text{B}_2\text{O}_3$  increases in thermal conductivity due to the formation of network structure.

In chapter 6, thermal conductivity was measured in the alkali-borate glass. The conflicting temperature dependence of thermal conductivity was observed. The thermal conductivity initially increases with higher temperature. After it reaches maximum, thermal conductivity gradually decreases as increasing of temperature. The temperature where maximum thermal conductivity was observed is excellent in accordance with the calculated one-dimensional Debye temperature supporting the validity of Debye model. It can be inferred that thermal conductivity is mainly determined by specific heat capacity below one dimensional Debye temperature. However, above the temperature, thermal conductivity decreases resulting from the change of other variables; phonon mean free path, sound velocity along with network structure. The similar relationship between thermal conductivity and ionization potential was also observed at room temperature.

Finally, in chapter 7, practical importance of thermal conductivity prediction model for the mold flux design was reviewed. Following the literature survey for previous thermal conductivity prediction model, Debye model was chosen for present thermal conductivity prediction model. Considering the thermal effect on the phonon mean free path, Debye model was modified. The calculated thermal conductivity based on present model is well accordance with measured thermal conductivity at high temperature region.