THERMAL CONDUCTIVITY OF THE Na_2O-SiO_2 AND THE CaO-Al_2O_3-SiO_2 MELTS MEASURED BY HOT-WIRE METHOD

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ABSTRACT

The thermal conductivity of some silicate melts including the CaO-Al_2O_3-SiO_2 *system, which is a typical blast furnace slag system, was measured in their pure liquid region using non-stationary hot-wire method. Initially, the thermal conductivity of the* Na_2O-SiO_2 *melts was measured up to 1473 K and the measurement results showed a good agreement to previous studies. Further measurements were carried out at various compositions in pure liquid region of the* CaO-Al_2O_3-SiO_2 *system and iso-thermal conductivity line was drawn in iso-thermal sections at 1673 K, 1773 K, and 1873 K. Thermal conductivity drastically decreased as basicity increases when* CaO/SiO_2 *ratio is smaller than unity, whereas it showed rather constant value when* CaO/SiO_2 *ratio is larger. In the temperature range of interest, the thermal conductivity of each composition decreased as temperature rises. Temperature dependence in this study showed negative deviation from linearity with the reciprocal of absolute temperature, which has been conventionally understood to be valid to crystalline solid. The deviation was considered to be due to the thermally-induced deploymerization of the silicate structure at higher temperature. Infrared absorption analysis has confirmed the breakage of the silica tetrahedral structure as temperature rises. Furthermore, it could be well supported by a good linearity of the logarithm function of thermal conductivity against 1/T during deploymerization.*

INTRODUCTION

Most of processes in iron- and steel-making at high temperature involve heat transfer phenomena, and thermal properties such as thermal conductivities of slags and fluxes are very important for the proper control of each process and the product quality. The surface quality of final products is, for instance, greatly influenced by heat transfer though mould flux during continuous casting. Hence, thermal conductivity of mould powders has been intensively investigated [1, 2]. On the other hand, a huge amount of BF slag is generated in blast furnace process and the recycling of the blast furnace slag has been well established in the environmental sense. One of the most important recycling applications is the raw material of BF slag cement. In the BF cement production, the characteristics of wasted BF slags, such as degree of crystallization and granular size, strongly affect the final properties of products and it can be attained only under well-controlled heat transfer [3]. Also, utilization of latent heat of molten slag has been proposed [4], which will enable a significant reduction of CO_2 generation by applying the BF slag to the calcination of limestone.

Although thermal properties of molten slag and flux have great significance in iron- and steel-making process, the thermal conductivity data are not sufficient at present. Nagata *et al.* [5, 6, 7, 8] have measured the thermal conductivity of the Na_2O-SiO_2 binary system using non-stationary hot wire method, and they showed that the thermal conductivity of alkali silicate had the linear relationship with the reciprocal of absolute temperature [6]. However, thermal conductivity data of the CaO-Al_2O_3-SiO_2 system, a typical system of BF slags, have not been systematically measured over a wide range of composition. Moreover even few number of thermal conductivity data of BF slag, reported up to now were measured at temperature lower than 1773 K and showed disagreement each other. Difficulties on thermal conductivity measurement are often caused by convection and radiation at high temperature above melting point. Non-steady methods may be advantageous rather than steady ones due to the shorter measurement periods. Furthermore, it is well known that the thermal conductivity measured by laser flash method may involve larger contribution of radiation [9] compared with the hot wire method.

In the present study, measurements of the thermal conductivity with respect to various compositions of the CaO-Al_2O_3-SiO_2 system were carried out at temperature ranging from 1673 K to 1873 K using the hot wire method. Another objective is to clarify the relationship between thermal conductivity and structure of silicate melts based on the investigation of their composition and temperature dependencies of the thermal conductivity.

METHODOLOGY

Measurement Principle

In the present study, non-stationary hot wire method is employed for the measurement of thermal conductivity of silicate melts. From the one solution of heat transfer equation, thermal conductivity, λ (W/mK), can be obtained as Equation 1 [10].

$$\lambda = \frac{Q}{4\pi} \Bigg/ \frac{d\Delta T}{d\ln t} \tag{1}$$

Here, Q (W/m) denotes the heat generation rate of hot wire per unit length. The thermal conductivity of sample can be obtained from Q and the slope of ΔT (K) versus ln t. In measurement, 0.15mm ψPt-13%Rh wire plays a role of thermocouple as well as heating element. The circuit for thermal conductivity measurement consists of hot wire, Galvanostat, 10 mΩ standard resistor and 0.5 mmψPt wire. Supplying a constant electric power with about 1.5A to hot wire immerged into the center of sample, the voltage change of hot wire between 2 terminals was monitored for no longer than 30 s. From stored data, a curve of ΔV versus ln t was plotted. Since the voltage change deviates from linearity presumably due to the convection, the linear range was to be determined by differentiating the curve and the slope of the straight line was evaluated. Recorded voltage change with time (*lnt*) can be converted to the slope of ΔT versus ln t using temperature coefficient of resistance.

Experimental Procedures

The apparatus used in the measurement are illustrated in Figure 1. Slag sample filled in a crucible was set in an electric resistance furnace with the heating element of MoSi2. The upper level of sample was adjusted to the highest temperature position in order to eliminate free convection during the measurement.

The thermal conductivity measurements of the Na_2O-SiO_2 system were carried out at every 20 K in the temperature range from liquidus temperature up to 1473 K. While mullite tanmann tubes were used as a crucible in the measurement of the Na_2O-SiO_2 system, the CaO-Al_2O_3-SiO_2 slag sample was held in alumina tanmann tube or manufactured Pt-10%Rh crucible (ϕ_{in}=32 mm) to avoid significant composition change by Al_2O_3 dissolution. The measurement was carried out at every 50 K in the temperature range from 1573 K (or around each liquidus temperature) to 1873 K.

After each measurement, slag sample cooled in the furnace was subject to chemical analysis. The chemical compositions of the sample were determined by gravimetric analysis for Si and ICP-Atomic Emission Spectroscopy for other elements. In order to investigate the structure of silicate melt, some selected samples were analyzed by IR Absorption Spectroscopy. Each sample was quenched in Ar flow, and 0.2 mg of the samples was well-ground and mixed with 200 mg of KBr, and then pressed into a pellet with the diameter of 8 mm. A spectral resolution was set as 4 cm^{-1}, and data of 64 scans were averaged.

Sample Preparation

Slag samples for measurement were prepared by mixing each reagent grade Na_2CO_3, SiO_2, Na_2SiO_3 (anhydrous), Al_2O_3 and CaO calcined from $CaCO_3$, aiming desired compositions. Two compositions of the Na_2O-SiO_2 system were prepared to be 51wt%Na_2O-49wt% SiO_2 (0.5Na_2O-0.5SiO_2 in mole fraction and m.p.: 1361K) and 34wt%Na_2O-66wt%SiO_2 (0.33Na_2O-0.67SiO_2 in mole fraction and m.p.: 1147 K). For the CaO-Al_2O_3-SiO_2 system the measurement compositions were chosen so that CaO/SiO_2 ratio could be fixed to several values as shown Figure 2. Well-mixed powder mixture was held in platinum crucible and premelted for 20 min. in the kanthal furnace at 1573 K and 1873 K for the Na_2O-SiO_2 and the CaO-Al_2O_3-SiO_2 system, respectively. After quenching, pre-melted samples were prepared by crushing finely.

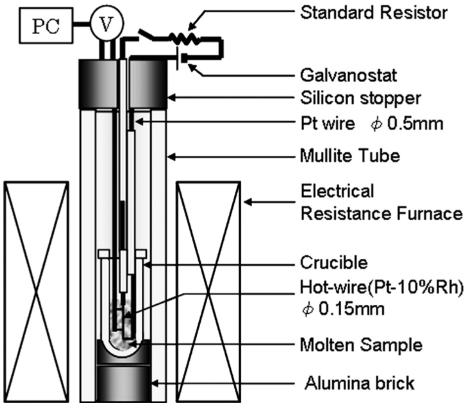


Figure 1: Schematic representation of the experimental apparatus

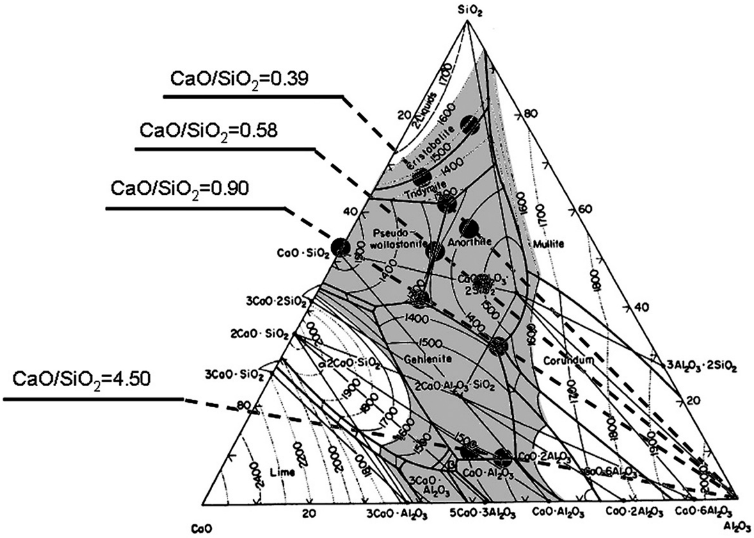


Figure 2: Liquid region and measurement compositions in the iso-thermal cross section of the CaO-Al_2O_3-SiO_2 ternary system

RESULTS AND DISCUSSION

Thermal Conductivity of the Na_2O-SiO_2 System

After the thermal conductivity measurement, the composition of each sample was analysed by ICP and silica gravimetric analysis. The result of composition analysis for both of the Na_2O-SiO_2 system showed that the whole composition was hardly different from the charge composition. And the dissolution of alumina from a crucible was found to be no more than 1 mol% (1.6 wt%), which can be negligible.

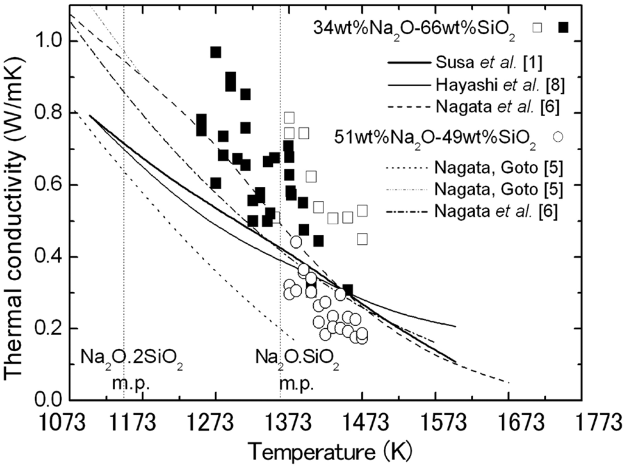


Figure 3: Temperature dependence of thermal conductivity of the Na_2O-SiO_2 system

The measurement results of thermal conductivity for the Na_2O-SiO_2 system are represented as a function of temperature in Figure 3. In the figure, open and solid symbols stand for the thermal conductivity obtained in heating and cooling cycle, respectively. In respect to both compositions, literature data investigated by several researchers were also shown in Figure 1, 5, 6 & 8. The results of this study generally exhibit good agreement in spite of a slight positive deviation from the reported data. In the range of experimental temperature, it is apparent that the thermal conductivities of the Na_2O-SiO_2 system with both compositions decrease as temperature rises. And any considerable difference in thermal conductivities from heating and cooling cycle did not appear. If the thermal conductivities of both compositions are compared each other at the same temperature, 1373~1473 K, the thermal conductivity of 34wt%Na_2O-66wt%SiO_2 is larger than that of 51wt%Na_2O-49wt%SiO_2.

Thermal Conductivity of the CaO-Al_2O_3-SiO_2 System

First of all, the analysis result for the composition of the CaO-Al_2O_3-SiO_2 system is tabulated in Table 3. The difference in compositions turned out to be within 1wt% in most cases. And measured thermal conductivities of the CaO-Al_2O_3-SiO_2 system with various compositions are plotted as a function of temperature in Figure 4. All results were obtained from the measurements above respective liquidus temperatures. They show a good agreement with reported thermal conductivity data of similar compositions [5]. Even though these temperature dependences show slightly different behavior, a drastic decrease appears just above the liquidus temperature of every oxide composition. Thermal conductivity of the oxide shows higher values with increasing silica content at a certain temperature.

Table 2: Result of chemical analysis and measurement conditions for the CaO-Al_2O_3-SiO_2 system

Charge Measurementcomposition (wt%)			**Analysed composition (wt%)**			**CaO SiO_2**	**Liquidus temperature (K)**	**temperature** (K)
CaO	Al2O3	SiO2	CaO	Al2O3	SiO2			
11.0	11.0	78.0	11.0±0	11.0±1	78.0±0	0.14	1773	1773~1873
26.0	8.0	66.0	22.0±1	9.0±1	65.5±1	0.39	1673	1723~1873
24.0	15.0	61.0	24.0±0	15.5±0	60.0±1	0.39	1443	1573~1873
22.0	22.0	56.0	25.0±1	22.0±1	55.0±1	0.39	1673	1673~1873
30.0	18.0	52.0	28.0±1	22.0±2	50.0±2	0.58	1573	1573~1873
26.0	30.0	44.0	24.5±1	30.0±1	45.0±1	0.58	1773	1773~1873
47.5	0.0	52.5	47.0±0	1.0±1	53.0±1	0.90	1810	1823~1873
42.0	11.5	46.5	28.0±1	19.0±1	43.0±1	0.90	1673	1673~1873
38.0	20.0	42.0	36.5±1	21.0±1	42.5±1	0.90	1538	1623~1873
29.0	39.0	32.0	28.0±1	40.0±2	32.0±2	0.90	1673	1673~1873
45.0	45.0	10.0	40.5±1	45.5±1	10.0±0	4.50	1723	1723~1773
40.5	50.5	9.0	45.0±1	50.5±1	9.0±0	4.50	1773	1773~1873

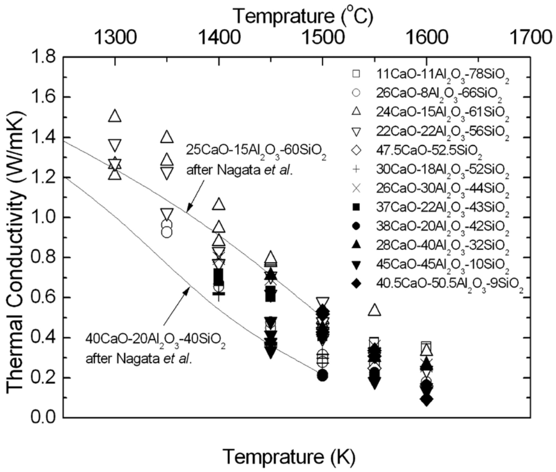


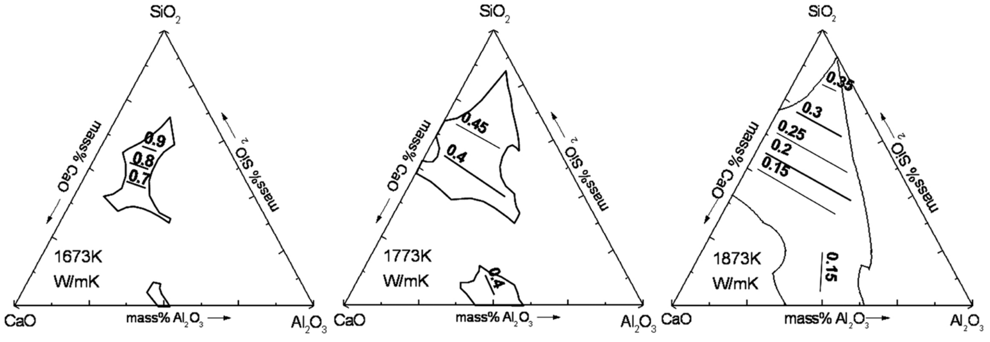
Figure 4: Temperature dependence of thermal conductivity of the CaO-Al_2O_3-SiO_2 system

Composition Dependence of the Thermal Conductivity of Silicate Melts

Thermal conductivities of the CaO-Al_2O_3-SiO_2 system are represented in its iso-thermal sections at 1673 K, 1773 K and 1873 K as shown in Figures 5(a), (b) and (c). As was previously mentioned, they show smaller values at the higher temperature and increase with basicity decrease.

The composition dependence of the thermal conductivity measured in the present could be explained in the structural consideration. As is well known, heat conduction is transferred mainly by lattice conduction, which is carried out through lattice vibration with a specific mode, so-called phonon. The thermal conduction in silicate melt is considered to depend strongly on the structure. Since acidic oxide, such as SiO_2, forms network with strong covalent bond in the silicate melt, while basic oxide breaks Si-O covalent bond to form ionic bond with cations, the present result indicates that the thermal conduction in silicate melt is effective through covalent bond rather than ionic bond. This result is consistent with those reported by previous researchers [8]. The thermal conductivity of Na_2O-SiO_2 system was found to increase at higher SiO_2 content as well. This dependence would be also caused by the modification of network structure, as well understood.

Effect of basicity, CaO/SiO_2 ratio, on the thermal conductivity of silicate melt is represented in Figure 6. As the basicity increases, thermal conductivity shows a drastic decrease, which is caused by the reduction in the number of covalent bonds in the melt. At CaO/SiO_2=4.5, however, thermal conductivity turned out to be much higher than what could be extrapolated from the acidic region. This may be due to the saturation of non-bridging oxygen when silicate melts is basic enough. Also it may suggest the network forming behavior of Al_2O_3 in highly basic melts.



(a) (b) (c)

Figure 5: Iso-thermal conductivity lines for the CaO-Al_2O_3-SiO_2 system at (a) 1673 K, (b) 1773 K, (c) 1873 K

Relationship between Thermal Conductivity and the Change of Structure in High Temperature

Thermal conduction in silicate melts is carried out mainly by phonon vibration, and the phonon conduction in crystalline materials can be figured out by Debye's expression for thermal conductivity based on the kinetic theory of gases, as following Equation 2 [11].

$$\lambda = \frac{Cvl}{3} \tag{2}$$

Here, C, v, and l denote the heat capacity, the sound velocity, and the phonon mean free path of the sample, respectively. Since the mean free path becomes shorter in proportion to the number of phonon increases, thermal conductivity is considered to be inversely proportional to absolute temperature assuming heat capacity and sound velocity of silicate melt are almost constant [12]. As a matter of fact, Nagata and Hayashi [7] have proposed the linear relationship between thermal conductivity and the reciprocal of absolute temperature in the study on the thermal conduction of simple binary silicate melts. In the present study, the thermal conductivities of the 30wt%CaO-18wt%Al_2O_3-52wt%SiO_2 and 38wt%CaO-20wt%Al_2O_3-42wt%SiO_2 oxide melts were representatively plotted versus reciprocal of the absolute temperature in Figure 7. According to phonon conduction theory, the straight line which is approaching the origin at infinite high temperature was expected. The measurement results, however, show negative deviation from the linearity. Comparing two compositions, the negative deviation at higher temperatures becomes more remarkable with higher SiO_2 content. This disagreement may be caused by the change of network structure.

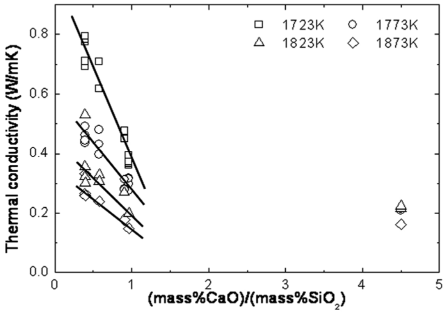


Figure 6: Relationship between thermal conductivity and CaO/SiO_2 ratio at various temperatures

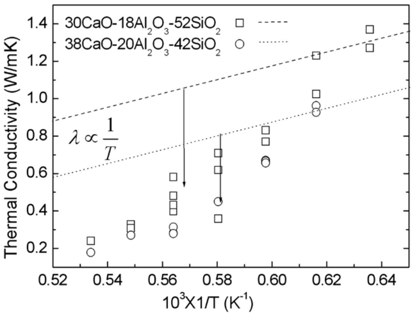


Figure 7: Dependence of the thermal conductivity of 30wt%CaO-18wt%Al_2O_3-52wt%SiO_2 and 38wt%CaO-20wt%Al_2O_3-42wt%SiO_2 melts on the reciprocal of absolute temperature

In order to consider a temperature effect on the network structure, the samples quenched from 1673 K, 1773 K, and 1873 K were subjected to infrared absorption analysis. The IR absorption patterns of 30wt%CaO-18wt%Al_2O_3-52wt%SiO_2 and 38wt%CaO-20wt%Al_2O_3-42wt%SiO_2 are shown in Figure 8. Wide band appeared at the range from 1200~800 cm^{-1}, showing the summation of IR absorptions of [SiO_4]-tetrahedra with various non-bridging oxygen per silicon (NBO/Si=1, 2, 3, 4).

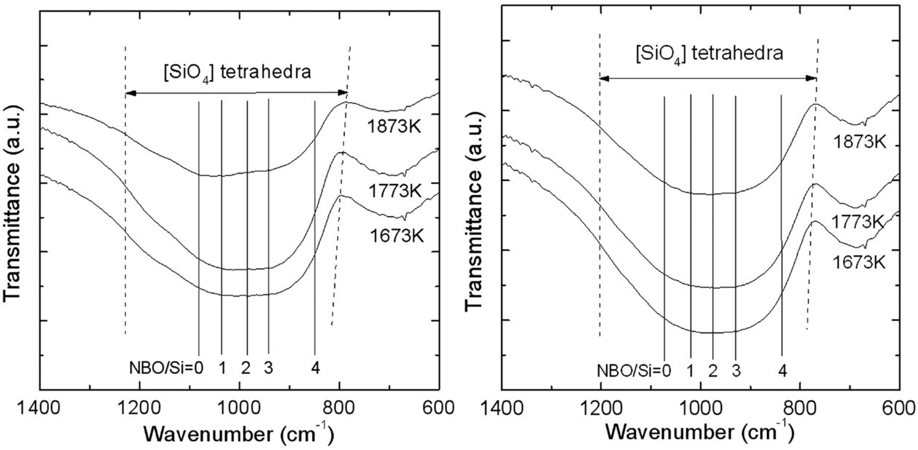


Figure 8: IR transmittance as a function of wave number
(a) 30wt% CaO-18wt%Al_2O_3-52wt%SiO_2 melts (b) 38wt%CaO-20wt% Al_2O_3-42wt%SiO_2 melts

While IR absorptions of the samples quenched from 1673 K and 1773 K showed similar spectra for both compositions, that of 1873 K demonstrated an increase in absorption at low wavenumber side of [SiO_4]-tetrahedra band, which can be interpreted as a depolymerisation of silicate network structure. Moreover, this was observed more significantly in case of the 30wt%CaO-18wt%Al_2O_3-52wt%SiO_2 melt compared with the 38wt%CaO-20wt%Al_2O_3-42wt% SiO_2 melt, indicating that the structure of silicate melt with higher SiO_2 content might be more sensitive to temperature.

Based on the fact that the thermal conductivity has the proportional relationship with phonon mean free path [11], it should be noted that mean free path may depends not only on thermal scattering but also on the network change. C. Kittel has proposed that the mean free path in solid glasses would be geometrically determined owing to the disorder of their structure. According to the author, a part of phonon energy is subject to be attenuated by the disordered structure, which limits mean free path [13]. Since the depolymerisation takes place in the network structure of the silicate melt above the liquidus temperature, mean free path certainly turns to dependent on the structure rather than the classical theory in crystalline solid. Obviously, the number of thermally-broken bonds, n_{broken}, which limit the decreasing of mean free path, is inversely proportional to the exponential of the reciprocal of the absolute temperature. If a bond is broken, the network structure reduces into pieces. Thus, it can be inferred that the volume of interaction, Ω inversely decreases as the number of broken bonds increase. Consequently, the relationship between mean free path and the absolute temperature can be obtained as Equation 3.

$$l \propto \Omega \propto \frac{1}{n_{broken}} \propto exp\left(\frac{B}{RT}\right) \tag{4}$$

Here, R and B denote the gas constant and the apparent activation energy for bond breaking to make the network pieces, which may directly reflect bonding energy.

Based on the understanding that phonon mean free path would exponentially decrease as temperature rises, the logarithms of thermal conductivities of silicate melts with various compositions were plotted versus $1/T$. The plots show fairly good linearity in their pure liquid region as shown in Figures 9 and 10. The slope of the straight line was estimated to evaluate the apparent activation energy for bond breaking in network, which was found to be almost constant in the range of 150~170 kJ. Since it falls in approximately same order of viscous activation energy of silicate melts, it may indicate the average Si-O bond breaking bond energy. At constant basicity, to be stricter, it has been found that the activation energy for thermal conduction was smaller at lower SiO_2 content. The decrease of the activation energy can be caused by the increase of NBO/T with lower population of $[SiO_4]$-tetrahedron. More considerable tendency in CaO/SiO_2=0.9, may be a strong proof of the SiO_2 content dependence of the activation energy.

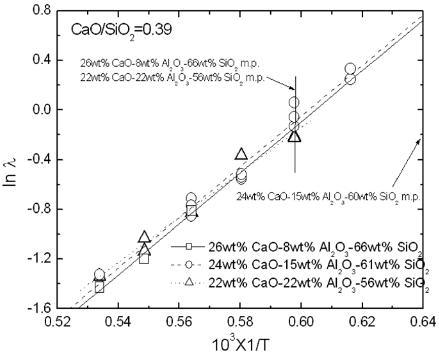


Figure 9: Dependence of logarithm of the thermal conductivity of some silicate melts whose CaO/SiO_2=0.39

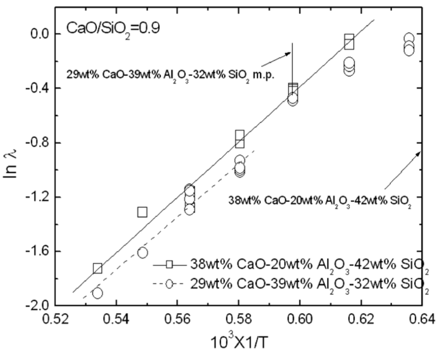


Figure 10: Dependence of logarithm of the thermal conductivity of some silicate melts whose CaO/SiO_2=0.9

CONCLUSIONS

Thermal conductivity of some silicate melts such as the Na_2O-SiO_2 and the CaO-Al_2O_3-SiO_2 system was measured using non-stationary hot wire method in the range from liquidus temperature up to high temperature. Based on the measurement result, effects of the composition and the temperature on thermal conductivity of silicate melts were investigated.

Thermal conductivity decreased with increase in the ratio of CaO/SiO_2, proving that the more acidic melts show the higher thermal conductivity due to more covalent bonds. However, when the silicate melts change to very basic melts up to a certain point, network modification is saturated and the dependence of thermal conductivity on basicity becomes insignificant. Furthermore, iso-thermal conductivity contours for the $CaO\text{-}Al_2O_3\text{-}SiO_2$ system were drawn in the iso-thermal sections at 1773 K, 1823 K, and 1873 K, respectively. As for all compositions, thermal conductivity sharply decreased as temperature rises from liquidus temperature to 1873 K. However, measured thermal conductivity showed a negative deviation from the conventional linearity with the reciprocal of absolute temperature due to the structure change of the silicate melts. The exponential relationship between logarithm of thermal conductivity and the reciprocal temperature enables the estimation of the average Si-O bond breaking energy for silicate melts. And it can be verified that the bond breaking activation energy is dependent on SiO_2 content of silicate melts.

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