THERMOPHYSICAL PROPERTIES OF SILICATE MELTS AND GLASSES

Hiroyuki SHIBATA[1], Sohei SUKENAGA[1], Tsuyoshi NISHI[2], Hiromichi OHTA[2]

[1] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 980-8577, Sendai, Japan
[2] Department of Mater. Sci. and Eng., Ibaraki University, 316-8511, Hitachi, Japan

hiroyuki.shibata.e8@tohoku.ac.jp, sohei.sukenaga.d3@tohoku.ac.jp, tsuyoshi.nishi.75@vc.ibaraki.ac.jp, hiromichi.ohta.ys@vc.ibaraki.ac.jp

Introduction

Heat transfer properties of metallurgical slags are very important to control and design solidification and refining processes of metals. These properties, especially thermal conductivity or thermal diffusivity of slags in molten and glassy states play important role to control the solidification process of molten slags for recycling of solidified slags. Ta *et al.* reported that a continuous blast furnace slag solidification process has been developed[1]. The thermal history of the slag was simulated using the thermal conductivity value of the slags to estimate the thickness of the glassy and crystalline phases for finding the suitable conditions to obtain an air-cooled slag coarse aggregate for concrete. In the continuous casting process of the steels, mould flux is a key to obtain a high quality surface of the solidified slabs *etc.* In this process, thermal conductivity plays also a very important role to control heat transfer from solidifying steel shell to a copper mould. It has been reported that the value of thermal conductivity of the silicate in molten and glassy states depends on the chemical composition[2,3,4]. This means that the thermal conductivity of the silicate in both states depends on the structure. In order to discuss the differences in the thermal conductivity, we should have a precise measurement technique of thermal conductivity of the silicate in both states.

In this paper, we would like to show the laser flash technique to obtain the thermal conductivity of molten silicate at high temperature and the obtained results. The relationship between the structure and the thermal conductivity of the silicate is discussed.

A front heating-front detection laser flash (FH-FDLF) method

The laser flash method is recognised as a versatile technique to measure the thermal diffusivity of various materials such as metals and oxides in a wide temperature range. It was rather difficult to measure thermal diffusivity or thermal conductivity of

silicate in molten state due to handling of the molten materials and correlation of radiative heat transfer effect on the obtained values. To overcome these difficulties, we have developed a front heating-front detection laser flash method. A brief outline of this technique is given below. The schematic diagram of the sample cell employed in this technique is shown in Figure 1.

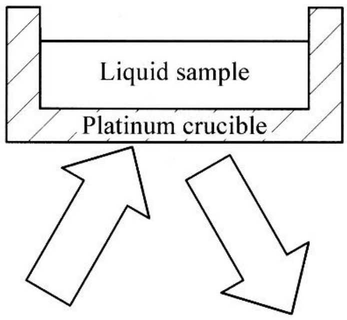

Figure 1: Schematic diagram of the cell of front-heating front-detection laser flash method

The molten silicate was contained in the platinum cell with 0.1 mm thickness, 5 mm depth and 20 mm in diameter. After melting the sample, the pulsed laser beam irradiated the bottom of the platinum crucible. Then, the absorbed energy at the bottom of the crucible propagated upward from the bottom to the molten sample. The temperature of the bottom of the crucible decayed with time depending on the thermal conductivity of the molten sample. The temperature response of the bottom surface of the platinum crucible was measured by an InSb infrared detector.
The temperature decay T_d (t) can be given by:

$$T_d(t) = T_0 \exp(h^2 t) \mathrm{erfc}\left(h\sqrt{t}\right) \tag{1}$$

$$h = \frac{b_s}{\rho_d C_d l_d} \tag{2}$$

where T_0, C, ρ, b, l are the maximum temperature rise of the temperature response, specific heat, density, thermal effusivity and the thickness of the platinum crucible respectively. Subscriptions of s and d are sample and platinum cell, respectively. Time t is defined as the elapsed time after irradiating a laser pulse. The value of T_0 and h in Equation (1) should be estimated by least square fitting of the theoretical temperature response to the measured temperature response. Thermal diffusivity value of the sample liquid, α_s, is obtained from the following equation with respect to thermal effusivity, b_s:

$$b_s = \sqrt{\alpha_s} \rho_s C_s \tag{3}$$

The thermal conductivity is obtained by Equation (4) with the value of density and heat capacity.

$$\lambda_s = \alpha_s \rho_s C_s \tag{4}$$

Thermal conductivity of Al_2O_3-CaO-SiO_2 and CaO-Na_2O-SiO_2 oxide melts[2,3]

The measured thermal conductivities of Al_2O_3-CaO-SiO_2 and CaO-Na_2O-SiO_2 oxide in molten state are shown in Figure 2, which have already been reported. The chemical composition of the oxides is listed in Table 1. The obtained values of the thermal conductivity were dependent on the chemical compositions of the oxides. No significant temperature dependence was detected for all oxides in the temperature range investigated.

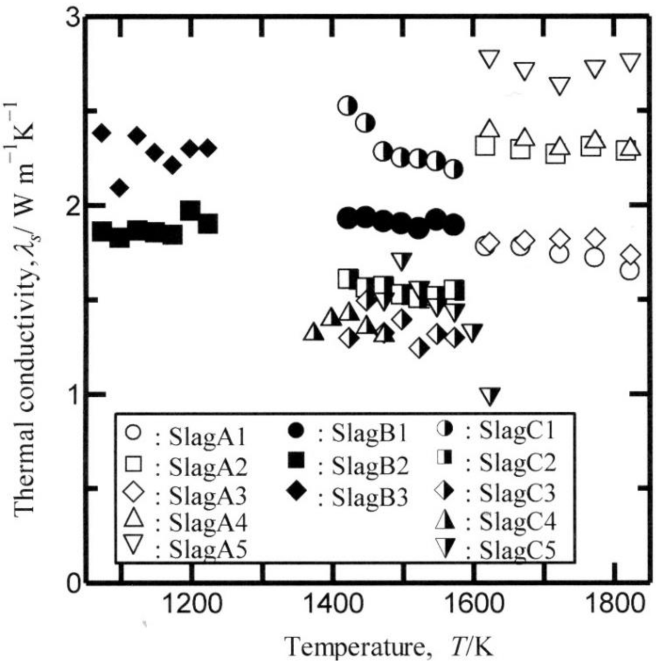

Figure 2: Measured thermal conductivity of oxides

From these results, the composition dependence of the thermal conductivity was given as a linear combination of fractions of components. An empirical equation of the thermal conductivity of the Al_2O_3-CaO-SiO_2 system was estimated as below:

$$\lambda = 57.1 - 0.48\ X_{Al2O3} - 0.57\ X_{CaO} - 0.55\ X_{SiO2}\ W/mK \tag{5}$$

where X is mol% of each oxide.

It has been suggested that if unconnected points of silicate network broken by alkaline or alkaline earth oxides become non-bridging oxygen as a barrier to thermal conduction, the thermal conductivity increases with decrease of number of non-bridging oxygen (NBO).[5] Nishi *et al.* have also reported the three-dimensional thermal resistor network model to evaluate the effect of non-bridging oxygen on the thermal conductivity.[6] Each silicon in silicate is tetrahedrally surrounded by four oxygen atoms and each bridging oxygen atom shared by two silicon atoms. CaO and Na_2O generate two non-bridging oxygen atoms. If Al_2O_3 were fewer than other oxides, Al_2O_3 binds the silicate network to form AlO_4 structure accepting O from other oxide. NBO/T, the ratio of non-bridging oxygen ions per tetrahedrally coordinated cations, is easily calculated from the chemical composition of silicate melts as follows.

$$\mathrm{NBO/T} = \frac{2\{(X_{CaO}+X_{Na2O})\text{-}X_{Al2O3}\}}{2X_{Al2O3}+X_{SiO2}} \qquad (6)$$

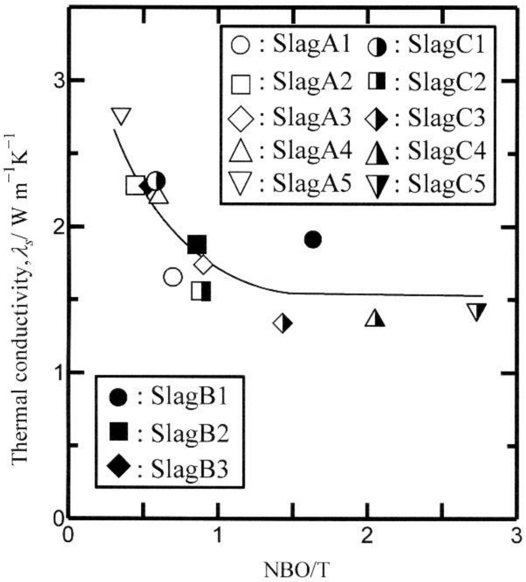

Figure 3: Relation between the measured thermal conductivity of oxides and NBO/T

The value of NBO/T is also listed in Table 1. The relation between average of the measured thermal conductivity of silicates melts and NBO/T is shown in Figure 3. The thermal conductivity values decreased from 2.8 W/mK to about 1.5 W/mK with increase of NBO/T until it reaches about unity. It was suggested that the heat transfer would be weakened by non-bridging oxygen region.

Table 1: Chemical composition of silicate (mol%) and NBO/T

slag	Al_2O_3	CaO	Na_2O	SiO_2	NBO/T
A1	8.0	34.0	-	58.1	0.70
A2	13.1	31.5	-	55.4	0.45
A3	10.1	41.5	-	48.5	0.90
A4	16.0	39.0	-	45.1	0.60
A5	21.0	36.0	-	43.0	0.35
B1	-	-	45.0	55.0	1.64
B2	-	-	30.0	70.0	0.86
B3	7.0	-	27.9	65.1	0.53
C1	-	9.1	13.6	77.3	0.59
C2	-	18.4	12.2	69.4	0.89
C3	-	16.7	25.0	58.3	1.43
C4	-	10.1	40.5	49.4	2.05
C5	-	23.1	34.6	42.3	2.73

Thermal conductivity of B_2O_3-SiO_2 and CaO-B_2O_3-SiO_2 oxide and ^{11}B NMR MAS spectroscopy[4]

The thermal conductivity of B_2O_3-SiO_2 and CaO-B_2O_3-SiO_2 melts was also measured. In this system, it has been found that the thermal conductivity slightly linearly decreased with increasing temperature over the investigated temperature range of 1248-1723 K. When comparing two systems, thermal conductivity became higher by addition of CaO.

^{11}B NMR MAS spectroscopy of the glassy sample of B_2O_3-SiO_2 and CaO-B_2O_3-SiO_2 was carried out to find out the effect of CaO addition on the increase of the thermal conductivity. In the obtained results of ^{11}B NMR MAS spectra, by addition of CaO the structure of the glass without CaO was composed of the three coordinated boron. On the other hand, the structure with CaO was a mixture of the three and four coordinated boron structure indicating that $^{[3]}$B is transformed to $^{[4]}$B. Ca^{2+} may connect two negatively charged BO^{4-} based on the electro-neutrality rule.

Summary

The thermal conductivities of molten oxide have been measured by using a front heating-front detection laser flash method with wide range of chemical compositions. We now have the technique to evaluate the thermal conductivity of the slags. The mechanism of the heat transfer of molten silicate and silicate glass has not been completely understood yet. The structure of molten oxide and the thermophysical properties should be correlated in detail.

References

1. Y. Ta, T. Hoshino, H. Tobo, K. Watanabe, "Behaviour of Crystallization on Continuous Solidification Process of Blast Furnace Slag", *Tetsu to Hagané*, **104** (11) 708-716 (2018).
2. H. Hasegawa, Y. Hoshino, T. Kasamoto, Y. Akaida, T. Kowatari, Y. Shiroki, H. Shibata, H. Ohta, Y. Waseda, "Thermal Conductivity Measurement of Some Synthetic Al_2O_3-CaO-SiO_2 slags by Means of a Front-Heating and Front-Detection Laser Flash Method", *Metall Mater Trans B*, **43B** 1405-1412 (2012).
3. H. Hasegawa, T. Kowatari, Y. Shiroki, H. Shibata, H. Ohta, Y. Waseda, "Thermal Conductivity of Molten Silicate of Al_2O_3-CaO-Na_2O-SiO_2 slags by Means of a Front Heating-Front Detection Laser Flash Method", *Metall Mater Trans B*, **43B** 1413-1419 (2012).
4. T. Nishi, K. Tanaka, K. Ohnuma, T. Manako, H. Ohta, S. Sukenaga, H. Shibata, T. Kakihara, "Determination of thermal conductivities of B_2O_3-SiO_2 and CaO-B_2O_3-SiO_2 melts", *J Nucl Mater*, **510** 193-198 (2018).
5. K.C. Mills, "The Influence of Structure on the Physico-chemical Properties of Slags", *ISIJ Int*, **33** (1) 148-156 (1993).
6. T. Nishi, H. Ohta, S. Sukenaga, H. Shibata, "Estimation of Thermal Conductivity of Silicate Melts Using Three-dimensional Thermal Resistor Network Model", *J Non-cryst Solids*, **482** (15) 9-13 (2018).