Thermal Conductivity of R-Na_2O-SiO_2(R=Al_2O_3, CaO) Melts

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Abstract: Reliable values of thermal conductivity of molten silicates are strongly requested to establish a model which can describe the relationship between thermal conductivity and structure of the molten silicates. Thermal conductivity of Na_2O-SiO_2-CaO-Al_2O_3 molten slags has been measured by using the novel laser flash method. A thin platinum crucible was filled with silicate melt and the bottom surface of the platinum crucible at high temperature was irradiated by a pulsed laser. After irradiation, a temperature decay of the bottom surface of the platinum crucible was measured with an InSb infrared detector. The value of the thermal conductivity was determined by fitting the measured temperature response curve to theoretical one with a least square method. Measured thermal conductivity slightly depends on temperature in molten state with the chemical compositions of the slags presently investigated. On the other hand, the thermal conductivity was found to decrease with increasing NBO/T (Non-Bridging Oxygen ions / Tetrahedrally coordinated cation) values.

Key words: thermal conductivity, molten silicate, laser flash method

1. Introduction

Physical properties of metallurgical slags are essential for the design, modeling, and control of manufacturing processes of various materials. Despite the importance of thermal conductivity values of slags, a few works has been available in the literature [1]. Several researchers measured thermal conductivity of molten oxides by using mainly two techniques. One technique is a hot wire method which is widely used to measure thermal conductivity of liquid. Obtained values of thermal conductivity of molten silicate sometimes show a negative temperature dependency at high temperature by using the hot wire method [2,3,4,5]. The other technique is a laser flash method which is recognized as a versatile technique for measuring thermal diffusivity of the materials. The measured thermal conductivity of molten silicates at high temperature by the laser flash method often show a positive temperature dependency without considering radiative heat transfer component[6,7]. It is known that the thermal conductivity values measured by conventional laser flash method at high temperature involve significant contribution of radiative heat transfer. Ohta *et al.* [8,9,10] measured the thermal conductivities of molten silicates using a three layer laser flash method with data processing to remove radiative heat transfer component and the results were found to show a small temperature dependency. Millls [11] has pointed out that the thermal conductivity of a silicate melts is a function of the non-bridging oxygen in the melt. The available data of thermal conductivity of silicate melts prevent us to discuss the effect of the structure of the melts on heat transfer properties in detail. Therefore, accurate value of thermal conductivity of the silicates melts is strongly required.

Recently a novel flash technique has been developed to break through the experimental difficulties for the measurement of molten oxide at high temperature [12,13]. A single laser pulse is flashed on the bottom of the platinum crucible and the infrared ray irradiated from the same bottom surface is measured to obtain the temperature decay, from which the thermal conductivity of the liquid sample can be determined. In the initial time region of temperature decay, conductive heat transfer is dominant, since the temperature gradient in the melt is steep. It may also be noted that the effect of radiative heat flow from the bottom surface of the crucible on the temperature response is relatively insignificant [14]. Measurement in a short initial time region is also preferable to avoid the onset of convection in the liquid layer. This novel laser flash technique is named a front heating-front detection laser flash method.

In the present work, high temperature thermal conductivity measurements were carried out on synthetic slags containing Al_2O_3, CaO, SiO_2 and Na_2O, often used in metal production process, by the front heating-front detection laser flash method. The slag compositions have been chosen systematically in order to consider thermal conductivity in relation to liquid structure.

2. Experimental

2.1 Principle of the front heating-front detection laser flash method

A schematic diagram of the platinum crucible employed in this work is shown in Figure 1. A liquid sample was contained in a platinum crucible. A bottom surface of the platinum crucible was irradiated by a single pulse laser. Then, the absorbed energy at the surface propagated into the liquid sample through the crucible. Then, a resultant temperature response of the same bottom surface was measured by an InSb infrared detector. Theoretical temperature decay is determined under the following conditions.

(1) The entire sample set consists of the liquid sample and the crucible is under thermal equilibrium before laser irradiation.

(2) The heat flow is one dimensional from the crucible to the liquid sample.

(3) The thickness of the liquid sample is semi-infinite.

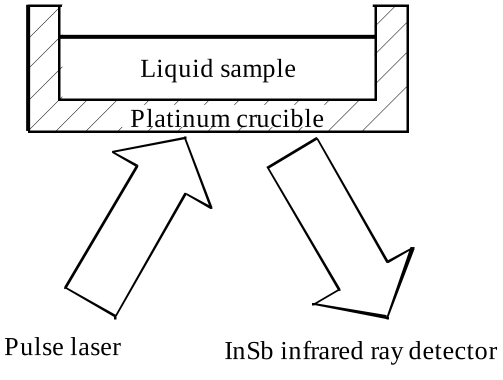

Fig.1 Schematic diagram of the sample cell of the front heating-front detection laser flash method.

The temperature decay T_d (t) is given by equation (1),

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

$$h = \frac{b_s}{\rho_d C_d l_d} \quad (2)$$

where T_0 , C_d , α_d , b_s , and l_d are the maximum temperature rise of the temperature response, the specific heat, density, the thermal effusivity, and the thickness of platinum crucible, respectively. The subscripts *d* and *s* indicate the platinum and the sample, respectively. Here, time *t* is defined as the elapsed time after irradiating a laser pulse. The values of T_0 and *h* in Eq. (1) are obtained by least square fitting of the measured temperature decay to theoretical temperature response. The thermal diffusivity value of the sample liquid, α_s , is then obtained from the following simple equation with respect to thermal effusivity, b_s :

$$b_s = \sqrt{\alpha_s}\rho_s C_s \quad (3)$$

The thermal conductivity is also obtained from the following relation (4).

$$\lambda_s = \alpha_s \rho_s C_s \quad (4)$$

2.2 Sample

Powders of Al_2O_3, SiO_2 ,$CaCO_3$ and Na_2O with high purity were mixed in desired quantities. The mixed samples were calcined in order to decompose carbonate or any hydroxide and melted at 150 K above its liquidus temperature for 60 minutes in a platinum crucible. The molten sample was quenched on a copper plate and crashed into small pieces which were put into a platinum crucible as shown in Fig.1 to facilitate the subsequent melting in the heating chamber of the laser flash apparatus.

Chemical compositions of the measured molten silicates are listed in Table 1. These compositions are marked in the phase diagram in Figures 2 and 3 for discussing the experimental results. In the case of series slag A, A and B lines represent fixed molar ratios between CaO and SiO_2 together with lines representing fixed molar ratios between CaO and Al_2O_3 (lines C through E). The compositions presently measured can also be divided into two other groups, according to the molar ratio between CaO and Al_2O_3 [15]. The chemical compositions denoted by B were also selected to investigate the effect of non-bridging oxygen on the thermal conductivity.

Table 1 Chemical composition of series A [15] and series B slags.

slag	Al_2O_3	CaO	Na_2O	SiO_2	CaO/SiO_2
A1	8.0	34.0	–	58.1	0.59
A2	13.1	31.5	–	55.4	0.57
A3	10.1	41.5	—	48.5	0.85
A4	16.0	39.0	–	45.1	0.86
A5	21.0	36.0	–	43.0	0.84
B1	–	9.1	13.6	77.3	0.12
B2	–	18.4	12.2	69.4	0.26
B3	–	23.1	34.6	42.3	0.55

The temperature decay curves were measured at one desired temperature of the sample at least ten times. Then, the ten temperature response curves were accumulated to obtain one temperature curve with a better signal to noise ratio. First, the value of h was estimated fitting Eq. (2) to the accumulated temperature response curve. Then, density and specific heat capacity of platinum [16] listed in Table 2 were used to obtain value of thermal effusivity, b_s, by equation (3). Finally, thermal conductivity was obtained from density and specific heat capacity of each slag listed in Table 3 which were taken from the literatures [17].

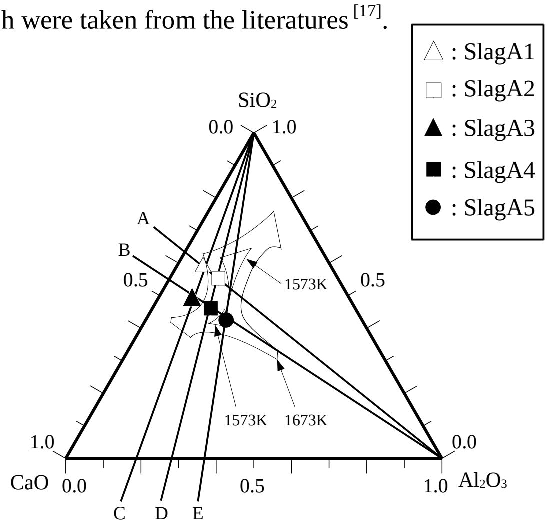

Fig.2 Chemical compositions of series A [15] and liquidus line of Al_2O_3-CaO-SiO_2 system.

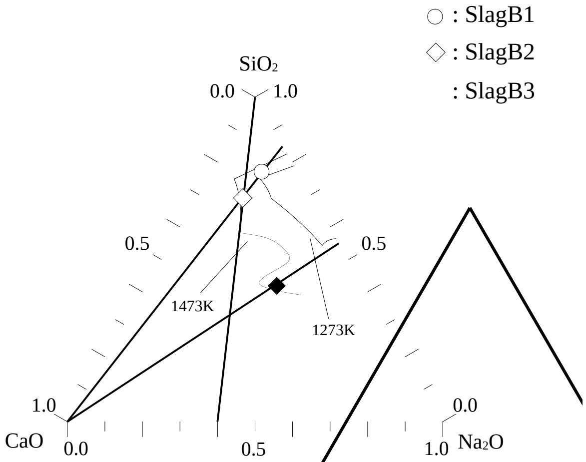

Fig.3 Chemical compositions of series B and liquidus line of Na_2O-CaO-SiO_2 system.

Table 2 Properties of platinum [16].

Temperature (K)	Density (kg m^{-3})	Specific heat capacity (J kg^{-1} K^{-1})
600	21200	141
800	21080	146
1000	20950	151
1200	20810	157

Table 3 Properties of slag sample estimated from reference [17].

Specimen	Density ρ_s (10^3 kg m^{-3})	Specific heat C_s (10^3 J $kg^{-1}K^{-1}$)
SlagA1	2.48	1.33
SlagA2	2.46	1.31
SlagA3	2.54	1.15
SlagA4	2.55	0.987
SlagA5	2.56	0.987
SlagB1	2.37	0.963
SlagB2	2.35	0.954
SlagB3	2.41	1.01

3. Results

The measured thermal conductivities are summarized in Table 4. The obtained thermal conductivity values of Slag A1 and Slag A3 show almost same values in the temperature range between 1623 K and 1823 K as demonstrated by Figure 4. Similar feature is also found in the values of Slag A2 and Slag A4. It is noted that the highest values are obtained in the case of Slag A5 among the measured slags. No significant temperature dependency is detected for all slag samples in the measured temperature range in the molten state.

The thermal conductivity values of Slag B2 and B3 are similar each other and slightly show negative temperature decency. The values of Slag B1 show the highest values among the series Slag B.

Table 4 Measured thermal conductivity of slags.

(a) slag A

Temperature	Thermal conductivity values, λs(Wm^{-1}K^{-1})					
T(K)	slag	A1	A2	A3	A4	A5
1623		1.78	2.31	1.80	2.39	2.79
1673		1.78	2.29	1.81	2.35	2.72
1723		1.74	2.27	1.82	2.30	2.64
1773		1.72	2.31	1.83	2.34	2.73
1823		1.65	2.28	1.74	2.29	2.77

(b) slag B

Temperature	Thermal conductivity values, λs(Wm^{-1}K^{-1})			
T(K)	slag	B1	B2	B3
1348		2.50	1.68	—
1373		2.46	1.63	—
1398		2.37	1.65	1.85
1423		2.52	1.61	1.61
1448		2.43	1.56	1.91
1473		2.28	1.57	1.50
1498		2.25	1.53	1.71
1523		2.24	1.56	1.56
1548		2.23	1.52	1.47
1573		2.19	1.55	1.44
1598		—	—	1.34
1623		—	—	1.00

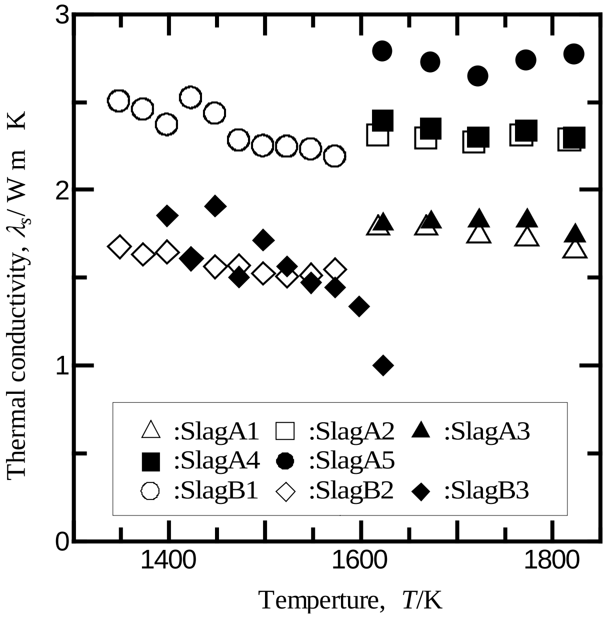

Fig.4 Measured thermal conductivity of series A [15] and series B slags.

4. Discussion

Ohta *et al.* [14] have already estimated by using a numerical method the effect of the radiative heat transfer is negligible during the measurement for the front heating-front detection laser flash method because the temperature gradient is steep during the measurement period which is from 4 ms to 12 ms after the laser irradiation. Therefore, the thermal conductivity obtained in this study is considered the true thermal conductivity due to conductive heat transfer alone in molten silicates. Therefore, it is concluded that the temperature dependence of molten silicates is insignificant.

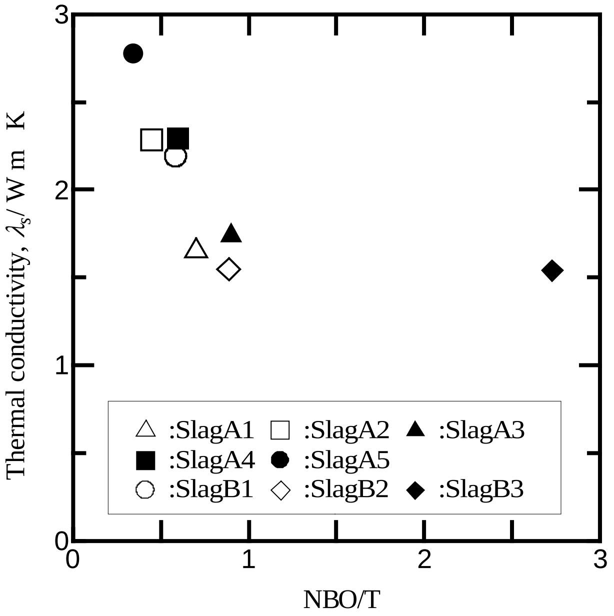

Fig.5 Relation between measured thermal conductivity of series A [15] and series B, and NBO/T.

The mean values of thermal conductivity for each slag sample were calculated in the measured temperature range and they are plotted in Figure 5 as a function of the NBO/T (Non-Bridging Oxygen ions / Tetrahedrally coordinated cation) value. The thermal conductivity decreases from 2.8 W/mK to 1.5 W/mK with increasing NBO/T value until it approaches to unity. A length of silicate chain is disconnected by addition of cation, such as Ca^{2+} or Na^{+}. Above unity of the NBO/T value, thermal conductivity of molten silicates would not decrease with increasing of NBO/T value. This result implies that the silicate chain is not modified by adding a certain amount of the cations and more.

5. Conclusions

The reliable thermal conductivity value of molten silicates have been measured by using the front heating-front detection laser flash method. The obtained thermal conductivity is intrinsic values governed by conductive heat transfer in molten silicates without radiative heat transfer component because of the remarkable feature of the presently applied measuring technique. The present results are summarized as follows;

(1) Thermal conductivity of molten silicates shows a weak temperature dependency for all investigated slags.

(2) Thermal conductivity of molten silicates is suggested to correlate the NBO/T (Non-Bridging Oxygen ions /

Tetrahedrally coordinated cation) value in the wide range of chemical compositions.

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References

[1] K.C. Mills and M. Suza. Thermal conductivities of slags. Slag Atlas, 2nd ed., Verlag Sthahleisen GmbH, 1995, p 591-600.

[2] K. Nagata, M. Susa and K.S. Goto. Thermal Conductivities of Slags for Ironmaking and Steelmaking. *Tetsu to Hagane*, 1983, 69(11), p1417-1424, in Japanese.

[3] K. Nagata and K. S. Goto. Heat Conductivity and Mean Free Path of Phonons in Metallurgical Slags. Proc. 2nd Int. Symp. Metallugical Slags and Fluxes. 1st ed., Nov 11-14, 1984(USA), Metall. Soc. AIME, 1984, p875-889.

[4] Y. Kang and K. Morita. Thermal Conductivity of the CaO-Al_2O_3-SiO_2 System. *ISIJ Int.*, 2006, 46(3), p420-426.

[5] M. Susa, M. Watanabe, S. Ozawa and R. Endo. Thermal conductivity of CaO–SiO_2–Al_2O_3 glassy slags: Its dependence on molar ratios of Al_2O_3/CaO and SiO_2/Al_2O_3. *Ironmaking & Steelmaking*, 2007, 34(2), p124-130.

[6] R. Eriksson and S. Seetharaman. Thermal Diffusivity Measurements of Some Synthetic CaO-Al_2O_3-SiO_2 Slags. *Metall. Mater. Trans. B*, 2004, 35B(3), p461-469.

[7] T. Matsushita, M. Hayashi and S. Seetharaman. Thermochemical and thermophysical property measurements in slag systems. *Int. J. Mater. Prod. Technol.*, 2005, 22(4), p351-390.

[8] H. Ohta, Y. Waseda, and Y. Shiraishi. Effect of Radiative Heat Transfer in Thermal Conductivity Measurements for Molten Silicates by a Two-Layered Laser Flash Method. *J. High Temp. Soc.*, 1985, 11(2), p81-90.

[9] Y. Waseda, H. Ohta, H. Shibata, K. Wtanabe and K. Nkajima. Estimation of Heat Leak to the Side Wall of a Cell in the Differential Three Layered Laser Flash Method for Measuring Thermal Diffusivities of Liquids. *High Temp. Mater. Processes*, 1994, 20(3), p104-112.

[10] H. Ohta, M. Masuda, K. Wtanabe, K. Nkajima, H.Shibata and Y.Waseda. Determination of Thermal Diffusivities of Continuous Casting Powders for Steel by Precisely Excluding the Contribution of Radiative Component at High Temperature. *Tetsu to Hagane*, 1994, 80(6), p33-38.

[11] K.C. Mills. The Influence of Structure on the Physico-chemical Properties of Slags. *ISIJ Int.*, 1993, 33(1), p 148-155.

[12] H. Ohta, H. Shibata, A. Suzuki, and Y. Waseda. Novel laser flash technique to measure thermal effusivity of highly viscous liquids at high temperature. *Rev. Sci. Instrum.*, 2001, 72(3), p1899-1903.

[13] H. Shibata, A. Suzuki and H. Ohta. Measurement of Thermal Transport Properties for Molten Silicate Glasses at High Temperatures by Means of A Novel Laser Flash Technique. *Mater. Trans.*, 2005, 46(8), p1877-1881.

[14] H. Ohta, H. Shibata and T. Kasamoto. Estimation of Heat Transfer of A Front-heating Front detection Laser Flash Method Measuring Thermal Conductivity for Silicate Melts at High Temperatures. *ISIJ Int.*, 2006, 46(3), p434-440.

[15] *Metall. Mater. Trans. B*: to be submitted.

[16] Japan Society of Thermophysical Properties. Thermophysical properties of pure metals Thermophysical Properties Handbook, 1st ed. Yonendo, Tokyo, 1990, p24.

[17] B.J. Keene and K.C. Mills. Densities of molten slags. Slag Atlas, 2nd ed., Verlag Sthahleisen GmbH, 1995, p 329-331.