

Thermal Diffusivity Measurements of Liquid Silicate Melts¹

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The effect of structure on the thermal diffusivities/conductivities for liquid silicates have been summarized based on recent experimental work carried out by the Royal Institute of Technology, Stockholm and the Tokyo Institute of Technology using the laser-flash and the hot-wire methods, respectively. In the former case, the effective thermal diffusivity was measured by a three-layer method. The relationship proposed by Mills that the thermal conductivity of silicates increases with a decrease in the ratio of NBO/T (number of non-bridging oxygens per tetrahedrally coordinated atom) has been well supported by the effective thermal diffusivity data for the liquid CaO-Al₂O₃-SiO₂ slags. However, it has been shown that for the slags having a higher CaO/Al₂O₃ ratio, the effective thermal diffusivity is roughly constant independent of the ratios of NBO/T. It has been concluded that when the silicate network is largely broken down, the phonon mean free path is not affected by the structure. It has been found by the hot-wire method that the magnitudes of thermal resistivity are in the hierarchy Li₂O-SiO₂ < Na₂O-SiO₂ < K₂O-SiO₂ despite their similar values of NBO/T. It has been concluded that the ionicity of non-bridging oxygen ions is also a factor controlling the thermal conductivity of silicates as well as the number of broken bridges in the silicate network. The effective thermal diffusivity was measured for the CaO-Al₂O₃-SiO₂-FeO system to elucidate the radiation contribution to the effective thermal diffusivity. It has been found that the effective thermal diffusivity increases with an increase in FeO content. It can be considered that the strong absorption and emission within the liquid slag films caused by the Fe²⁺ ions enhances the photon heat transfer.

KEY WORDS: effective thermal diffusivity; hot-wire method; laser flash method; phonon conduction; radiation conduction; thermal conductivity.

¹ Paper presented at the Sixteenth European Conference on Thermophysical Properties, September 1–4, 2002, London, United Kingdom.

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1. INTRODUCTION

Physical properties of metallurgical slags are essential for the design, modelling, and control of material processes, thus, creating an increased demand for more reliable measurements, over wider composition and temperature ranges. The thermal diffusivity is one of the most important properties and is, for example, required for the estimation of the rate of heat flow in slags and mold fluxes during refining and casting processes. The thermal diffusivity of metallurgical slags is also of scientific interest since it reflects the structure of the silicate network.

Generally, the thermal diffusivity is determined by lattice vibration (phonon conduction) in insulators. Debye [1] proposed that the thermal conductivity of insulators is expressed as $\lambda = C_v \nu l / 3$ by analogy with the kinetic theory of gases, where C_v is the heat capacity at constant volume in $\text{J} \cdot \text{K}^{-1} \cdot \text{m}^{-3}$, ν is the speed of sound, and l is the phonon mean free path. The value of l for silicates is considered to be affected by the number of broken bridges in a silicate network due to basic oxides. Ammar et al. [2] have reported that the thermal conductivities of silicates measured at 303 K decrease with increasing basic oxide content. They have suggested that higher content of basic oxides might cause further disordering of the silicate network structure which results in shortening of the phonon mean free path. Mills [3] has found a relationship for which the thermal conductivity of silicates at the melting point decreases proportionally with an increase in the ratio of NBO/T, i.e., the number of non-bridging oxygens per tetrahedrally coordinated atom. Consequently, systematic measurements of the thermal diffusivity of slag systems would enable an understanding of the structure of the silicate melts and how the polymerization of silicates is affected by basic and amphoteric oxides. However, in spite of the aforementioned practical and scientific importance, investigations of thermal diffusivity and conductivity for liquid silicate melts at high temperatures are still far from complete as shown in a review by Mills and Susa [4].

Recently, thermal diffusivity and conductivity measurements for liquid silicate melts have been carried out by the Royal Institute of Technology and Tokyo Institute of Technology using the laser-flash and hot-wire methods, respectively. The present paper is intended to summarize the results of their experimental work so as to develop the relationship between the thermal diffusivities of liquid silicate melts and their structures. The measured thermal diffusivity and conductivity of liquid slags could contain contributions from various heat transfer mechanisms, i.e., lattice (phonon) thermal conductivity, radiation (photon) conductivity, and convection. It is generally considered that the thermal conductivity measured by the hot-wire method is not affected by radiation [4]. However, the radiation

contribution to the effective thermal diffusivity obtained by the laser-flash method is significant. The radiation contribution is dependent on the absorption coefficient of slag samples and the sample thickness. In the present work, the thermal diffusivities for CaO-Al₂O₃-SiO₂ slags containing two different concentrations of FeO have been measured by the laser-flash method and compared with the data for CaO-Al₂O₃-SiO₂ slag to elucidate the radiation contribution to the effective thermal diffusivity.

2. EXPERIMENTAL

2.1. Laser-Flash Method

2.1.1. Sample Preparation

The thermal diffusivity was measured for five compositions of the CaO-Al₂O₃-SiO₂ system and two compositions of the CaO-Al₂O₃-SiO₂-FeO system. Table I shows the chemical compositions of the samples. Slags containing iron oxide were prepared by mixing of reagent grade CaO, Al₂O₃, and SiO₂ powders and synthesized FeO powders in required proportions. FeO was prepared by mixing appropriate amounts of Fe₂O₃ and iron powders. The mixture of Fe₂O₃ and iron powders was pressed into pellets, placed in an iron crucible with an iron lid, and was sintered for 24 h at 1273 K in an argon atmosphere. The crucible was then quenched. X-ray diffraction showed the absence of metallic iron as well as other oxides of iron. CaO, Al₂O₃, and SiO₂ were calcined at 1223 K for at least 24 h in air in a muffle furnace before use in order to decompose any carbonate or hydroxide present. About 1.5 g of these mixtures were pressed into a pellet of 16 mm in diameter and introduced into the laser-flash apparatus (Sinku-Riko Model TC-7000H/MELT) in order to facilitate the subsequent melting of the sample in the furnace of the apparatus.

Table I. Chemical Compositions of Samples. (Mole fractions)

Slag	AlO _{1.5}	SiO ₂	CaO	FeO	X _{CaO} /X _{AlO_{1.5}}
1	0.15	0.52	0.33	0.00	2.2
2	0.23	0.47	0.30	0.00	1.3
3	0.18	0.42	0.40	0.00	2.2
4	0.27	0.38	0.35	0.00	1.3
5	0.33	0.35	0.32	0.00	1.0
6	0.27	0.37	0.35	0.01	1.3
7	0.26	0.36	0.33	0.05	1.3

2.1.2. Measurement

The three-layered cell arrangement was employed for the thermal diffusivity measurement. The three layers consist of the liquid slag specimen having the form of a thin film, sandwiched between two platinum crucibles. Figure 1a shows the schematic diagram of the cell assembly. The lower platinum crucible containing the slag sample has an inner diameter of 17 mm and a height of 11 mm. The upper platinum crucible has an outer diameter of 14 mm and a height of 20 mm. The combined thickness of the two platinum crucibles is around 0.30 mm. Before the start of the thermal diffusivity measurements, the contact point between the upper and lower platinum crucibles was accurately determined in order to obtain an equal sample thickness for all measurements. The cell arrangement was then positioned in the even-temperature zone of the furnace. The sample was heated at the rate of $6 \text{ K} \cdot \text{min}^{-1}$ in a flow of pure argon. After the attainment of thermal equilibrium, the top surface of the upper platinum crucible was exposed to an instantaneous laser energy pulse by Nd glass laser (2.40 kV). The temperature of the rear surface of the lower platinum crucible was measured using a photovoltaic InSb infrared detector. The lower crucible containing the liquid slag sample was then raised by 0.2 mm, and the measurement was repeated to produce a second temperature response curve (Fig. 1b). The difference in the thickness of the slag layer between the first and second measurements was obtained by means of a micrometer screw gauge.

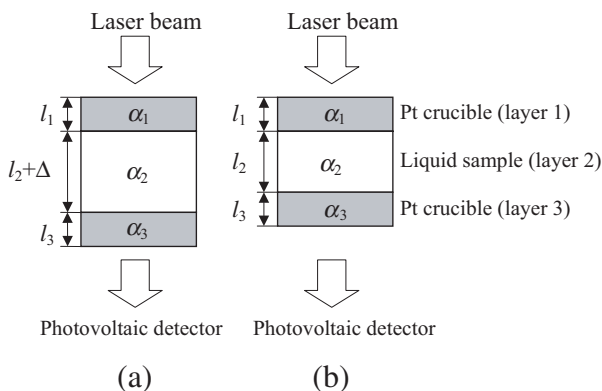


Fig. 1. Schematic diagram showing the three-layered cell arrangement (a) with the thickness of the liquid slag sample set to $l_2 + \Delta$ and (b) with the thickness of the liquid slag sample set to l_2 .

From the temperature response curves at the initial time region, obtained from the two laser irradiations of the three-layered cell, the thermal diffusivity of the slag sample was evaluated using the software based on differential three-layer analysis developed by Waseda et al. [5]. According to this,

$$\frac{\partial \ln(\theta \sqrt{t})}{\partial(1/t)} = \frac{(\eta_1 + \eta_2 + \eta_3)^2}{4} \quad (1)$$

where θ is the temperature response of the rear surface of the lower platinum crucible, t is the time, η_i is $l_i/\sqrt{\alpha_i}$, where l_i is the thickness, and α_i is the thermal diffusivity of the i th layer. A plot of $\ln(\theta \sqrt{t})$ versus $1/t$ would result in a straight line with $(\eta_1 + \eta_2 + \eta_3)^2/4$ as the slope. From Eq. (1), the following two equations can be derived:

$$\frac{l_2}{\sqrt{\alpha_2}} = 2 \sqrt{\frac{\partial \ln(\theta_{l_2} \sqrt{t})}{\partial(1/t)} - \eta_1 - \eta_3} \quad (2)$$

$$\frac{l_2 + \Delta}{\sqrt{\alpha_2}} = 2 \sqrt{\frac{\partial \ln(\theta_{l_2+\Delta} \sqrt{t})}{\partial(1/t)} - \eta_1 - \eta_3} \quad (3)$$

where $l_2 + \Delta$ and l_2 are the thicknesses of the liquid slag layer at the first and second laser radiations, respectively, Δ is the relative difference in the thickness of the liquid slag layer (Figs. 1a and 1b), and $\theta_{l_2+\Delta}$ and θ_{l_2} are the temperature response curves at the first and second laser radiations, respectively. With a knowledge of the thickness and the thermal diffusivities of layers 1 and 3, the thickness and thermal diffusivity of liquid slag samples can be determined. More details of the principle and the apparatus adopted here have been reported elsewhere [6]. The advantage of this measurement method is that the accuracy in the thickness of the liquid slag sample is not required to obtain the thermal diffusivity. The difference in the thicknesses of the two slag layers can be more accurately measured than can the absolute value of the sample thickness. The uncertainty in the difference in the thicknesses measured by the micrometer screw leads to an error of approximately $\pm 1\%$ in the thermal diffusivity.

Measurements were carried out over a temperature range between 1625 and 1825 K in a flow of pure argon. In order to reduce uncertainty in the measured values, the thermal diffusivity measurement was repeated at least ten times at each temperature.

2.2. Hot-Wire Method

Recently the thermal conductivities of M_2O-SiO_2 ($M = Li, Na, \text{ and } K$) and $M_2O-MF-SiO_2$ ($M = Li \text{ and } Na$) systems were measured at the Tokyo Institute of Technology by means of the transient hot-wire method. In this method the electrical power is supplied to a thin metal wire (hot wire) placed in the sample and the temperature rise (ΔT) of the wire is measured continuously. The thermal conductivity (λ) is obtained from the equation, $\lambda = Q/4\pi/(d \Delta T/d \ln t)$, where Q is the heat generation rate per unit length of the wire and t is the time. The thermal conductivity is derived using the slope of the linear portion of the relation between ΔT and $\ln t$. The details of the apparatus have been reported elsewhere [7, 8]. In this method, the generation of heat convection caused by the heating wire can be detected by the onset of the deviation from the linear portion in the ΔT versus $\ln t$ curve. The advantage of the hot-wire method is that the influence of heat convection can be excluded from the thermal conductivity data. Hayashi et al. [7] have measured the thermal conductivities for 33(mol%) $M_2O-67SiO_2$ ($M = Li, Na, \text{ and } K$) over a temperature range between room temperature and 1573 K, and Susa et al. [8] have measured the thermal conductivities over a temperature range 1050 to 1550 K, for the following six compositions: $Li_2O-2SiO_2$, $Na_2O-2SiO_2$, $0.7Li_2O-0.6LiF-2SiO_2$, $0.9Na_2O-0.2NaF-2SiO_2$, $0.7Na_2O-0.6NaF-2SiO_2$, and $0.5Na_2O-0.6NaF-2SiO_2$.

3. RESULTS AND DISCUSSION

3.1. Relation between Thermal Diffusivities of Liquid Silicate Melts and Their Structures

Figures 2 and 3 show the temperature dependences of the effective thermal diffusivity for two different slag samples with constant $CaO/AlO_{1.5}$ ratios of 1.3 and 2.2, respectively. The error bars represent the standard deviation of the experimental values. The effective thermal diffusivity obtained by the laser-flash method contains the contribution of the radiative heat transfer mechanism. However, in the present work, all the measurements were carried out for the same sample thickness, and it has been reported that the $CaO-Al_2O_3-SiO_2$ liquid slags can be successfully regarded as transparent bodies independent of composition [5]. Therefore, it can be assumed that the radiation effects on the effective thermal diffusivity are the same for all $CaO-Al_2O_3-SiO_2$ slag samples at the same measurement temperature and that the difference in the effective thermal diffusivity corresponds to the difference in the phonon thermal diffusivity reflecting the

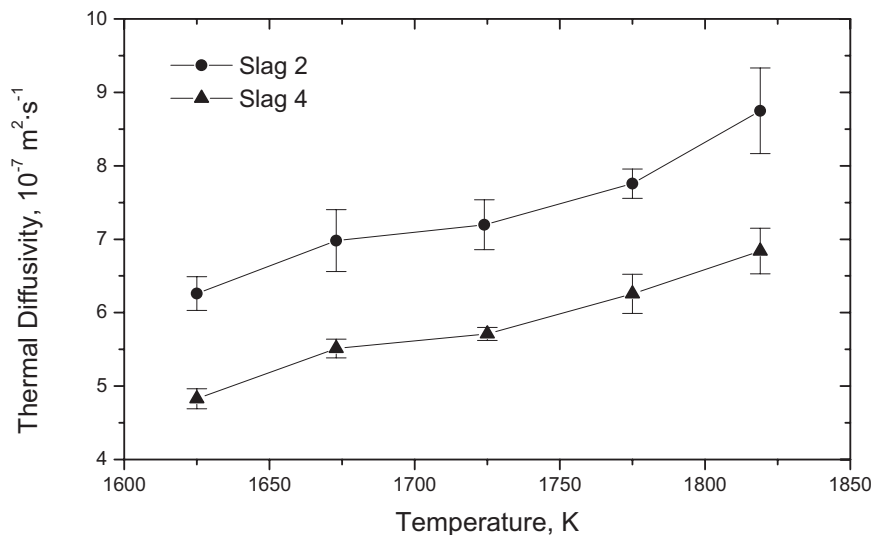


Fig. 2. Temperature dependences of the effective thermal diffusivity for slags 2 and 4.

structure. It can be seen from Fig. 2 that the effective thermal diffusivity increases with an increase in the SiO_2 content. This result is in agreement with Mills' proposal [3] that the thermal conductivity of silicates increases with an increase in the ratio of NBO/T. On the other hand, as shown in Fig. 3, slags 1 and 3 exhibit roughly the same effective thermal diffusivities in spite of the different SiO_2 content, i.e., the different ratios of NBO/T. It is considered that for the slag samples having a $\text{CaO}/\text{AlO}_{1.5}$ ratio of 2.2, because the silicate network is largely broken down, there is not a significant change of structure between two samples, which results in little change in the phonon mean free path. Therefore, the thermal diffusivity is not significantly dependent on the SiO_2 content, i.e., the ratio of NBO/T.

Figure 4 shows the temperature dependence of the effective thermal diffusivities of slags 1 and 5, which have similar CaO content and different ratios of $\text{AlO}_{1.5}/\text{SiO}_2$. It is found that slag 5 having the higher ratio of $\text{AlO}_{1.5}/\text{SiO}_2$ exhibits a higher thermal diffusivity than slag 1. For slag compositions of the present work, it can be considered that there are enough non-bridging oxygen ions such that $\text{AlO}_{1.5}$ is allowed to behave as a network-forming oxide. However, when $\text{AlO}_{1.5}$ behaves as a network-forming oxide, Ca^{2+} ions are consumed to compensate for the charge of Al^{3+} ions which result in polymerization. Therefore, it can be considered that polymerization of the silicate network caused by the substitution of $\text{AlO}_{1.5}$ for SiO_2 yields an increase of the thermal diffusivity.

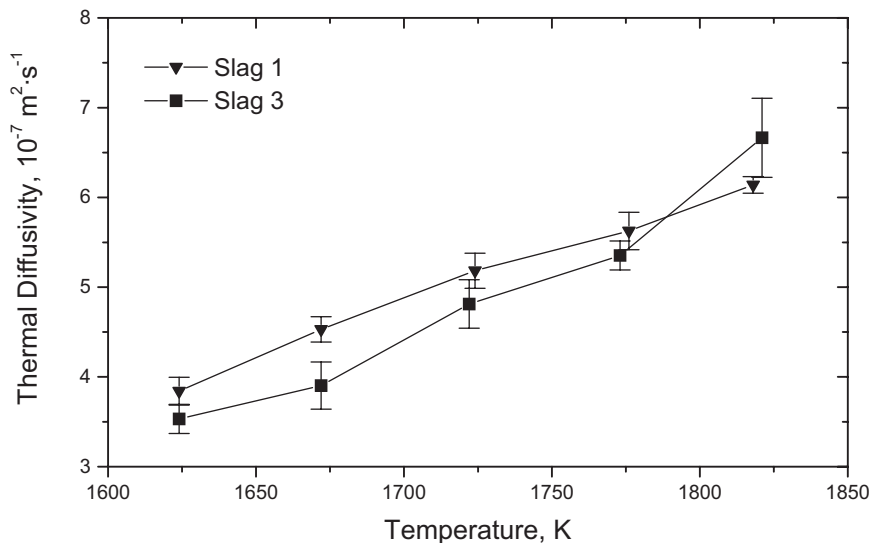


Fig. 3. Temperature dependences of the effective thermal diffusivity for slags 1 and 3.

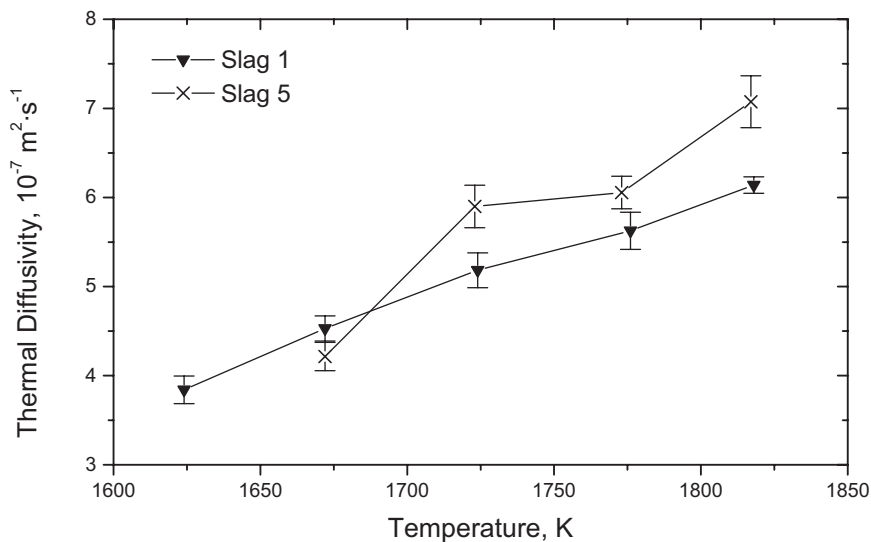


Fig. 4. Temperature dependences of the effective thermal diffusivity for slags 1 and 5.

Hayashi et al. [7] have found by hot-wire measurements that the magnitudes of thermal resistivity, i.e., the reciprocal of thermal conductivity at their respective melting points are in the hierarchy $\text{Li}_2\text{O-SiO}_2 < \text{Na}_2\text{O-SiO}_2 < \text{K}_2\text{O-SiO}_2$ despite their similar values of NBO/T . In silicates there are two types of chemical bonds, i.e., primary covalent bonds between silicon and oxygen in the network structure and ionic bonds between non-bridging oxygens via cations of basic oxides. Heat is transferred via these bonds. Thus, the thermal resistivity of silicates can be considered to be composed of the thermal resistivity due to covalent bonds and that due to ionic bonds. Hayashi et al. [7] have suggested that the magnitudes of thermal resistivity due to the ionic bonds are in the hierarchy $\text{Li}_2\text{O-SiO}_2 < \text{Na}_2\text{O-SiO}_2 < \text{K}_2\text{O-SiO}_2$ and that the difference of thermal resistivity due to the ionic bonds would be caused by the difference in bonding energies between cations of basic oxides and non-bridging oxygen ions which is dependent on the ionic character of chemical bonds, i.e., the ionicity of non-bridging oxygen ions. They have concluded that the ionicity of non-bridging oxygen ions is also a factor controlling the thermal conductivity of silicates as well as the number of broken bridges in the silicate network. In terms of the alkali silicates containing fluorides, Susa et al. [8] have found that addition of fluorides to the alkali silicate melts decreases the thermal conductivities of these melts, which leads to the conclusion that fluorides depolymerize the network structure.

The temperature dependence of slag structure could be elucidated from the temperature dependence of the thermal diffusivity and conductivity due to phonon conduction. Since the effect of the radiation heat transfer on the effective thermal diffusivity becomes more pronounced at higher temperatures, it is necessary to exclude the radiation effect completely in order to consider the temperature dependence of the slag structure. To eliminate the radiation contribution from the measured thermal diffusivity of the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ slag samples, the equations proposed by Waseda et al. [5] were applied. Waseda et al. [5] have estimated the effective thermal diffusivity for a sample of the thermal diffusivity of $4 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$ using the finite difference method in numerical computation assuming the transparent body approximation. They have obtained the following equation based on the dimensions of the liquid sample cell with $l_2 = 0.2 \text{ mm}$, and $\Delta = 0.2 \text{ mm}$, which is the same as those used in the present study.

$$\alpha_{\text{eff}} = (6.986 \times 10^{-7}T^2 - 1.466 \times 10^{-3}T + 1.883) \times \alpha_0, \quad (4)$$

where α_{eff} and α_0 are the effective thermal diffusivity and the thermal diffusivity due to phonon conduction. Figure 5 shows the corrected thermal diffusivity as well as the measured thermal diffusivity for slag 2. It is seen

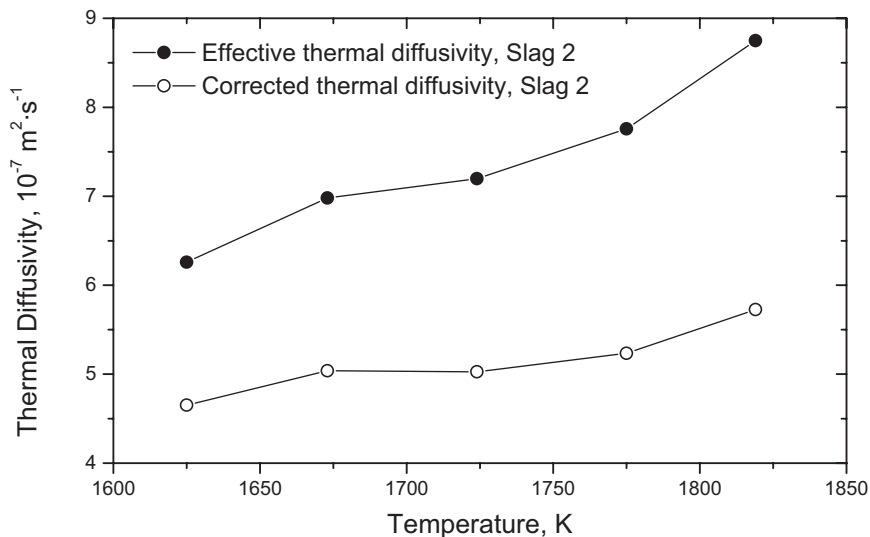


Fig. 5. Measured thermal diffusivity and thermal diffusivity corrected for the contribution due to radiation using the equation suggested by Waseda et al. [5] for slag 2.

that the corrected thermal diffusivity still shows the positive temperature dependence. Monaghan et al. [9] have shown a negative temperature dependence of the corrected thermal diffusivity obtained by the laser-flash method for the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ liquid slags. Waseda et al. [5] and Friedrichs et al. [10] have reported the negligible or weak positive temperature dependence for the molten mold fluxes and the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3$ slags, respectively. In contrast, the thermal conductivities measured by the hot-wire method show large negative temperature dependences for liquid slags [7, 8]. The discrepancy of the temperature dependence between the laser-flash and hot-wire methods may be due to two possibilities: (i) the radiation effect has not been successfully eliminated from the thermal diffusivity data obtained by the laser-flash method, and/or (ii) the linear portion between ΔT and $\ln t$ for the hot-wire method is only obtained during the small time region because of heat convection and Marangoni flow, which has provided the large error in data. An effort to understand the discrepancy of data between the two methods is in progress in the Division of Metallurgy, Royal Institute of Technology (KTH).

3.2. Effective Thermal Diffusivities of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-FeO}$ System

Figure 6 shows the temperature dependence of the effective thermal diffusivities for slags 4, 6, and 7, which have constant ratios of $\text{CaO}/\text{AlO}_{1.5}$

and CaO/SiO_2 and different FeO content. It can be seen that the effective thermal diffusivity increases with an increase in FeO content. The increase of the thermal diffusivity by FeO addition is considered to be attributed to the radiation effect. Since the FeO contents are small, the slag structure change caused by FeO addition could be negligible. When the effect of the slag structure change on the thermal diffusivity is considered, it could be expected that the thermal diffusivity due to the phonon conduction decreases with an increase in FeO content because the Fe^{2+} generally behaves as a network breaker. Ohta et al. [11] calculated the effective thermal diffusivity at 1573 K for the sample having a thickness of 0.3 mm and a phonon thermal diffusivity of $4 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$ as a function of the mean absorption coefficient using the gray-body approximation. According to their calculation, the effective thermal diffusivity obeys the transparent body approximation for an absorption coefficient less than 10^2 m^{-1} . However, they have reported that the effective thermal diffusivity increases with an increase in the absorption coefficient for the samples having an absorption coefficient higher than 10^2 m^{-1} . Therefore, it can be considered that the strong absorption and emission in the liquid slag films are caused by the Fe^{2+} ions, which would enhance the photon heat transfer in the present $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{FeO}$ slag compositions.

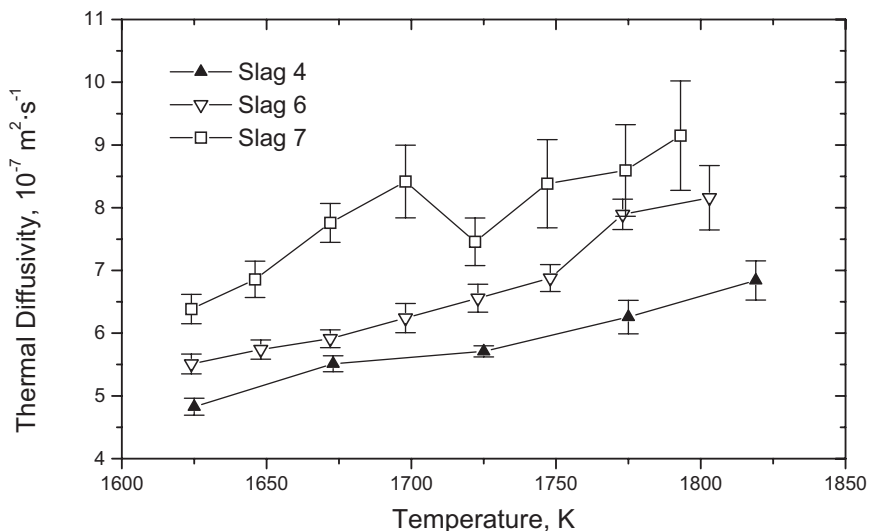


Fig. 6. Temperature dependence of the effective thermal diffusivities for slags 4, 6, and 7.

4. CONCLUSIONS

The results of the recent experimental work carried out by the Royal Institute of Technology and Tokyo Institute of Technology using the laser-flash and hot-wire methods, respectively, have been summarized so as to understand the relationship between the thermal diffusivities/conductivities of liquid silicates and their structures. The empirical relationship proposed by Mills [3] that the thermal conductivity of silicates increases with decreases in the ratio of NBO/T has been supported by the present effective thermal diffusivity data for the CaO-Al₂O₃-SiO₂ liquid slags. However, it has been shown that for these slags having the higher CaO/Al₂O₃ ratio the effective thermal diffusivity is roughly constant independent of the different ratios of NBO/T. It is considered that when the silicate network is largely broken down, the difference in SiO₂ content does not cause a significant change of structure, which results in little change in the phonon mean free path. Therefore, the thermal diffusivity is not significantly dependent on the ratio of NBO/T. Hayashi et al. [8] have reported that the magnitudes of thermal resistivity are in the hierarchy Li₂O-SiO₂ < Na₂O-SiO₂ < K₂O-SiO₂ despite their similar values of NBO/T. They have concluded that the ionicity of non-bridging oxygen ions is also a factor controlling the thermal conductivity of silicates as well as the number of broken bridges in the silicate network. Regarding the temperature dependence of the thermal diffusivities/conductivities, there is a discrepancy of data between the laser-flash and hot-wire methods. Further investigation is required in this area.

The radiation contribution to the effective thermal diffusivity has been elucidated for the CaO-Al₂O₃-SiO₂-FeO system. It has been found that the effective thermal diffusivity increases with an increase in FeO content. It can be considered that the strong absorption and emission in the liquid slag films caused by the Fe²⁺ ions enhances the photon heat transfer in the present CaO-Al₂O₃-SiO₂-FeO slag compositions.

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