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Thermal Diffusivity Measurement of Molten Calcium Ferrite Slags

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CONTENTS

ABSTRACT

Thermal diffusivities of calcium ferrite slags have been measured by the laser flash technique over the temperature range between 1003 and 1673°K. The logarithmic method for analysing the initial short time region of temperature rise of the back surface was employed for reducing the deviation of thermal diffusivity by both radiation and radial heat flows.

The thermal diffusivities of molten calcium ferrite slags are represented by the following equations:

33 mol% CaO:

$$\alpha = 3.99 \times 10^{-3} - 5.54 \times 10^{-7}\ T \quad (1573 - 1645°\mathrm{K})$$

40 mol% CaO:

$$\alpha = 1.49 \times 10^{-2} - 7.63 \times 10^{-6}\ T \quad (1563 - 1630°\mathrm{K})$$

45 mol% CaO:

$$\alpha = 1.16 \times 10^{-2} - 5.37 \times 10^{-6}\ T \quad (1578 - 1655°\mathrm{K})$$

50 mol% CaO:

$$\alpha = 8.66 \times 10^{-3} - 3.23 \times 10^{-6}\ T \quad (1575 - 1673°\mathrm{K})$$

55 mol% CaO:

$$\alpha = 2.46 \times 10^{-2} - 1.27 \times 10^{-5}\ T \quad (1613 - 1659°\mathrm{K})$$

where α is the thermal diffusivity (cm^2/s) and T is the absolute temperature (K). Thermal diffusivities of molten ferrite slags increase as the CaO content increases. This behaviour is consistent with the formation of a certain local ordering suggested from the structural data obtained by the X-ray diffraction.

1. INTRODUCTION

Recently, ferrite slags have attracted much concern in non-ferrous metallurgy as a promising slag to prevent the precipitation of magnetite in the reverberatory furnace and to remove inherent inconvenient elements.

Ferrite slags have many advantages compared with silicate based slags: 1) high holding capacity for iron oxides, even under the high oxygen partial pressures such as air atmosphere; 2) low viscosity, which reduces the favourable metal loss to the slag phase due to mechanical entrainment; 3) efficient removability of arsenic and phosphorus.

Thermodynamic properties with respect to the phase equilibrium between matte and ferrite slag has been investigated by Park *et al.* /1/. Sumita *et al.* have measured physical properties of ferrite slags such as density, surface tension /2/, viscosity /3/ and electrical conductivity /4/.

Slag systems are known to participate to a great extent in the heat transfer processes. It should also be emphasized that an understanding of the heat transfer properties of slags is paramount for the determination of optimum furnace operation. However, the thermal diffusivity of ferrite slags has not yet been investigated.

It has been recognized that the measurement of thermal diffusivity of molten sample above 1000°K is difficult so that a quantitative discussion is restricted because of these experimental limitations. For example, the radiative heat flow is known to play a significant role in heat transfer problem at higher temperatures /5/. However, the effect of radiation is difficult to evaluate accurately.

In laser flash experiments, several attempts have already been made to measure the thermal diffusivity or thermal conductivity of liquid samples by Schriempf /6/, Bates /7/, and Taylor *et al.* /8/. However, there are strong reservations regarding the quantitative accuracy of these results because of the leakages of heat due to conduction to the crucible wall and radiation at high temperature /9/.

The main purpose of this work is to present thermal diffusivity data of calcium ferrite slags obtained by the laser flash technique coupled with associated data processing using the logarithmic method. The results are also discussed in terms of the mean free path of phonons and the structure of ferrite slags.

2. LASER FLASH TECHNIQUE AND LOGARITHMIC METHOD FOR THE DETERMINATION OF THERMAL DIFFUSIVITY OF OPAQUE LIQUID SAMPLES

The two-layered sample cell system as shown in Fig. 1 was employed for the present purpose. The front surface of a small disc-shaped cell is subjected to a single pulse from a laser beam source. The re-

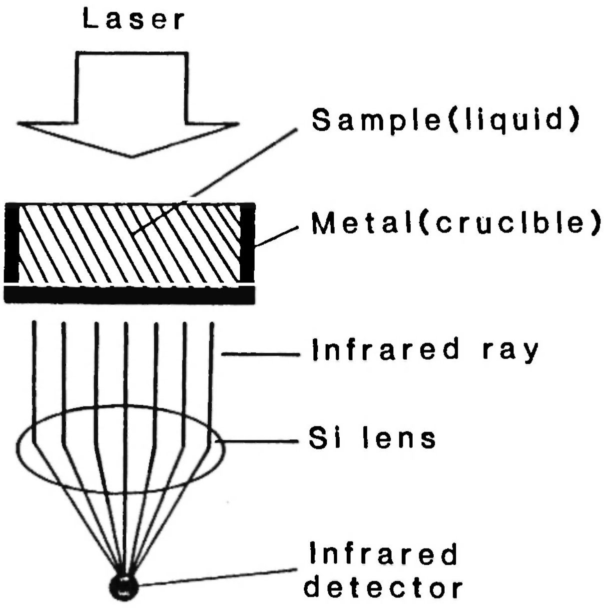

Fig. 1. Schematic diagram of the cell assembly.

sulting temperature rise of the back surface of the sample cell is detected and thermal diffusivity is computed from these temperature rises versus time data.

The $t_{1/2}$ method, first proposed by Parker *et al.* /10/, has been widely employed as a simple method for determining thermal diffusivity of solid material from the temperature response curve of the back surface. In calculating thermal diffusivity from the temperature responses, the $t_{1/2}$ method requires the time (for the back surface temperature) to reach 50% of its maximum value. Thus, the $t_{1/2}$ method requires relatively long time temperature responses. As the time period necessary for the determination of thermal diffusivity becomes long, the heat loss by radiation increases at high temperature. Therefore, it is desirable to analyse the initial short time region of the temperature response curve where the heat leakage due to the radiation is small.

When only uni-dimensional heat conduction is assumed, as is the case with a single-layer slab, the temperature response of the back surface can be represented as follows /11/:

$$T/T_{max} = 2\ell^2/\pi\alpha t)^{1/2}$$

$$\times \Sigma \exp[-(2n+1)\ell^2/4\alpha] \qquad (1)$$

where T is the temperature rise of the back surface of the slab, α is the thermal diffusivity, ℓ is the thickness of the slab and t is the elapsed time after flashing a laser beam. The series on the right hand side of Eq. (1) can be approximated by ranging the first term from t = 0 to the maximum temperature rise. Taking the natural logarithm of both sides of Eq. (1), the following useful equation is readily obtained:

$$\ln(t^{1/2}\cdot T) = \ln[2(\ell^2/\pi\alpha)^{1/2}\cdot T_{max}] -$$

$$- \ell^2/4\alpha t \qquad (2)$$

A plot of $\ln(t^{1/2}\cdot T)$ as a function of $1/t$ gives a straight line, with slope $-\ell^2/4\alpha$, and thermal diffusivity is estimated from the slope. Thermal diffusivity can be determined from any parts of the temperature rise if the time region is not too near T_{max}. This logarithmic method was first proposed by James /11/.

In the case of the two-layered sample cell system, the slope of the straight line is $-(n_1 + n_2)^2/4$, where n_i is the square root of the diffusion time or $n_i = \ell_i/\alpha_i^{1/2}$. The subscript i indicates the i-th layer, where the interfacial thermal contact resistance between sample and crucible is negligibly small.

Fig. 2 illustrates the temperature responses obtained by the numerical calculation of Eq. (2); t_n is the non-dimensional time defined by $\alpha t/\ell^2$. In the present work, the logarithmic analysis was carried out in the time zone between 10% and 30% of the maximum temperature rise, to prevent the effect of radiation heat loss at high temperature and radial heat flow due to conduction to the crucible wall. The slope of the straight line plot of $\ln(t^{1/2}\cdot T)$ versus $1/t$ was determined by the least squares method.

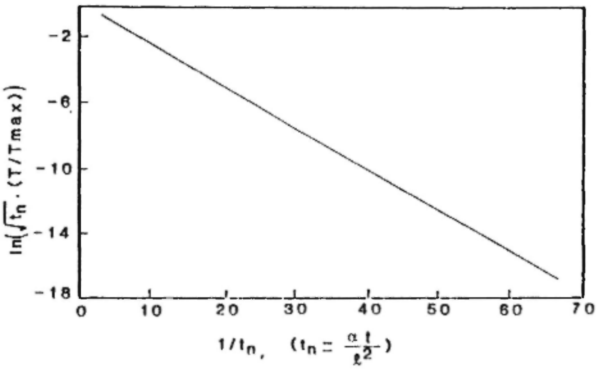

Fig. 2. Temperature-time response curve by the logarithmic method.

The effect of the pulse width on thermal diffusivity was estimated in a similar manner to the method proposed by Yamamoto *et al.* /12/. Since the thermal diffusivity of calcium ferrite slags is relatively low (10^{-2} to 10^{-3} cm^2/s), the pulse width effect is found negligibly small in the present experimental conditions.

3. EXPERIMENTAL PROCEDURES

3.1. Apparatus

Experimental apparatus and procedures of data analysis have already been described in detail /13/. Thus, only the essential features are presented here for the convenience of discussion. Fig. 3 shows a schematic diagram of the experimental apparatus employed for measuring the thermal diffusivity of ferrite slags. A sample cell assembly is placed on four alumina pins to minimise conductive heat leakage.

The cell system is heated (by alternating current) using a platinum wire heating element wound around an alumina pipe. The temperature of the sample before flashing a laser pulse is measured by a Pt–Pt 13%-Rh thermocouple located slightly above the front surface of the sample. Temperature response of the back surface of the cell is measured by a remote optical sensing device. Infrared rays from the back surface of the sample cell, including the radiative flux from the heater, are focused by a gold mirror and a silicon lens on a InSb infrared detector cooled by liquid nitrogen through a pedestal of alumina pipe. The temperature response is stored in a digital transient memory connected to a microcomputer.

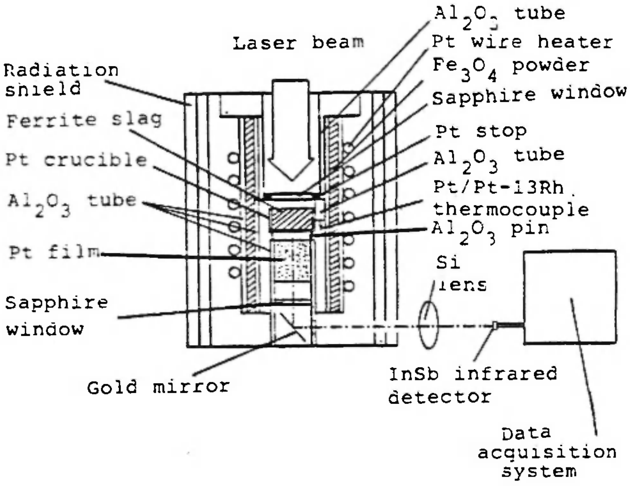

Fig. 3. Schematic diagram of the experimental apparatus.

Since the alumina pipe is radiation penetrative at high temperatures, the radiative heat flux through the alumina pipe appears to fluctuate mainly because of the alternating current for the following reason. Infrared rays emitted from the back surface of the cell are incident to the infrared detector. The multiple reflection of the penetrative radiative heat flux from the platinum heating element takes place between the wall of the alumina pipe and the back surface of the sample cell. This fluctuating radiative heat flux is also incident to the infrared detector. Thus, a significant noise with the same cycle as the power source is induced. This fluctuation of the measured temperature response curve could be greatly reduced by employing magnetite powder as a radiation absorber in the space between the alumina pipe wound by the platinum heating element and the inner alumina pipe. The measurements were made in a normal air atmosphere. To decrease heat loss by air convection, the top and bottom faces of a sample chamber were covered with sapphire windows.

3.2. Preparation of Samples

Calcium ferrite slags were prepared from calcium carbonate and ferric oxide powders of 99% purity. The composition was in the range of 33 to 55 mol% CaO. The weighed reagents were intermixed in an acetone medium. They were then pelletized and calcined in a platinum crucible for more than 20 hours at about 1273°K. Next, they were kept in the molten state for about 6 hours at 1800°K in air, cooled down to room temperature, and then crushed and ground into the powder form. The quantity of the premelted powder sample was estimated from the density value [2] in advance and charged into the Pt cell in order to make the calcium ferrite sample layer flat by melting. The dimensions of the Pt cell were 0.2 mm thickness; 1.3 mm depth and 10 mm diameter.

To remove bubbles in a sample before measurements, the sample-cell system was held for an hour in the vacuum furnace at temperatures about 100°K above the liquidus.

Since the thermal expansion of calcium ferrite slags is of the order of 1% in the range from room temperature to melting point, no shrinkage was observed in solid samples so that thermal expansion corrections were not necessary in the present work.

4. RESULTS AND DISCUSSION

4.1. Effects of Radial and Radiative Heat Flows on Thermal Diffusivity

As previously reported, calcium ferrite samples are opaque and both the permeation depth of a laser beam and the radiation effect of the sample inside are negligibly small /13, 14/. The interfacial thermal resistance between ferrite slags and the Pt plate appears insignificant /13/.

To evaluate the effect of the radial heat flow on thermal diffusivity, two series of experiments were carried out. Fig. 4 shows the measurements carried out for three solid samples with different diameters of 17, 13 and 10 mm over the temperature range 490 – 660°K. As can be seen in Fig. 4, agreement is found to be satisfactory. This implies that difference in sample size does not affect the thermal diffusivity value within the present experimental conditions.

The variation of thermal diffusivities measured by the different laser beam diameters both in air and in vacuum is given in Fig. 5 using the results of ferrite slag containing 45 mol% CaO at 293°K. Almost constant values were obtained when the laser beam diameter was larger than 7 mm. Fig. 5 also suggests that the heat leakage by convection is negligibly small. From these results, the effect of radial heat flow due to conduction to the crucible walls appears insignificant and, therefore, the assumption of uni-dimensional heat flow is justified for the present experimental conditions.

The effect of radiative heat loss on thermal diffusivity in this work using the logarithmic method was estimated for a slag containing 50 mol% CaO at temperatures of 1500° and 1673°K. The back surface temperature responses are given by Heckman /15/ as follows. Assuming that the heat losses are from both front and back surfaces:

$$T(\ell,t) = T_{\circ} \Sigma_{n=1}^{\infty} Y_n(0) Y_n(\ell) \times \exp(-\beta_n^2 \alpha t/\ell^2) \tag{3}$$

where

$$Y_n(x) = \frac{2^{1/2}(\beta_n^2+L_2^2)^{1/2}[\beta_n \cos(\beta_n x(\ell) + L_1 \sin(\beta_n x/(\ell))]}{[(\beta_n^2+L_1^2)(\beta_n^2+L_2^2+L_2) + L_1(\beta_n^2+L_2^2)]^{1/2}} \tag{4}$$

and the β_n (n = 1, 2, 3, . . .) are the positive roots of:

$$(\beta^2 - L_1 L_2)\tan\beta = \beta(L_1 + L_2) \tag{5}$$

L_1 and L_2 in Eq. (4) are the radiative heat loss factors

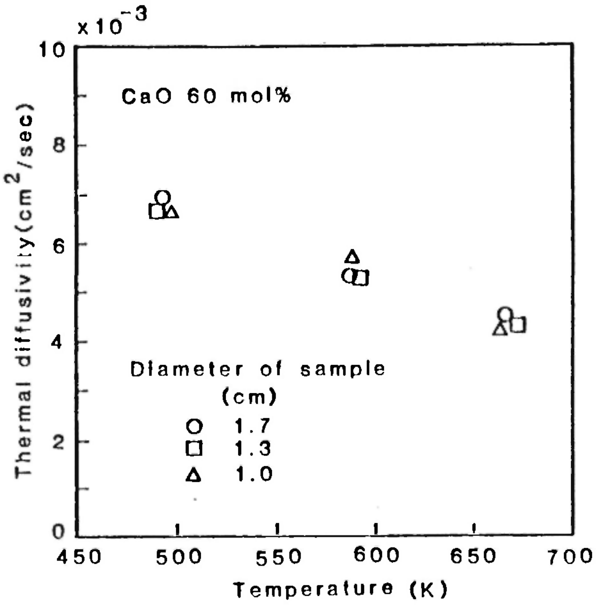

Fig. 4. The effect of sample diameter on thermal diffusivity.

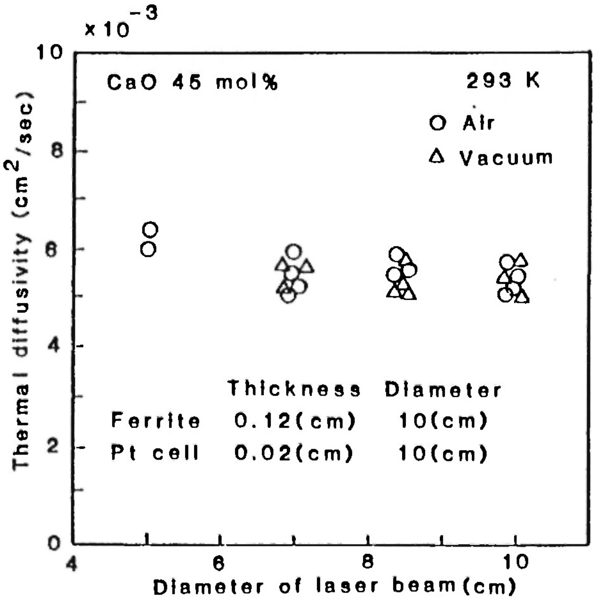

Fig. 5. The effect of laser beam diameter on thermal diffusivity.

from the faces at x = 0 (front surface) and ℓ (back surface), respectively, and can be represented by:

$$L = 4\ell\sigma\epsilon_i T_A^2/\lambda \qquad (i = 1,2) \qquad (6)$$

where σ is the Stephan-Boltzmann constant, ℓ is sample cell thickness (slag: 0.13, Pt: 0.02 cm), ϵ_i is emissivity, [ϵ_1: 0.8 (assumed), ϵ_2: 0.2] /16/, and T_A is temperature of the environment (1500 or 1673°K). Thermal conductivity (λ) can be obtained from the experimental data of heat capacity /17/, density /3/ and thermal diffusivity.

James /11/ reported that the back surface temperature responses of the two layered sample cell, of which thermal diffusivities are α_1 and α_2, and thicknesses are ℓ_1 and ℓ_2, can be obtained by substituting Eq. (7) for l^2/α in Eq. (3) so that:

$$\frac{l^2}{\alpha} = (\ell_1/\sqrt{\alpha_1} + \ell_2/\sqrt{\alpha_2})^2 \qquad (7)$$

In the present experimental conditions, the square roots of diffusion time are $\ell_1/\sqrt{\alpha_1} = 2.20$, and $\ell_2/\sqrt{\alpha_2} = 0.04$. Since the platinum plate is very thin and its thermal diffusivity is very high, compared with ferrite slag, the platinum layer only affects the shape of the temperature responses by less than 2%. Thus, a single layer slab of ferrite slag (when emissivity is different at the two surfaces) was assumed, to investigate the influence of the radiative heat loss on the temperature responses.

Fig. 6 shows the influence of radiative heat loss on thermal diffusivity measurement. The solid line is the experimental temperature responses at 1500°K. The dotted line is the calculated temperature responses taking into account radiative heat loss calculated from Eq. (3) for the physical constants of the cell at 1500 and 1673°K. The results show that the thermal diffusivity values determined by the logarithmic method involve an uncertainty due to the radiative heat loss of only less than 0.5% at 1500°K and 0.6% at 1673°K, respectively. Thus, the excluding radiative heat loss appears almost insignificant on the determination of thermal diffusivity using the logarithmic method employed in this work.

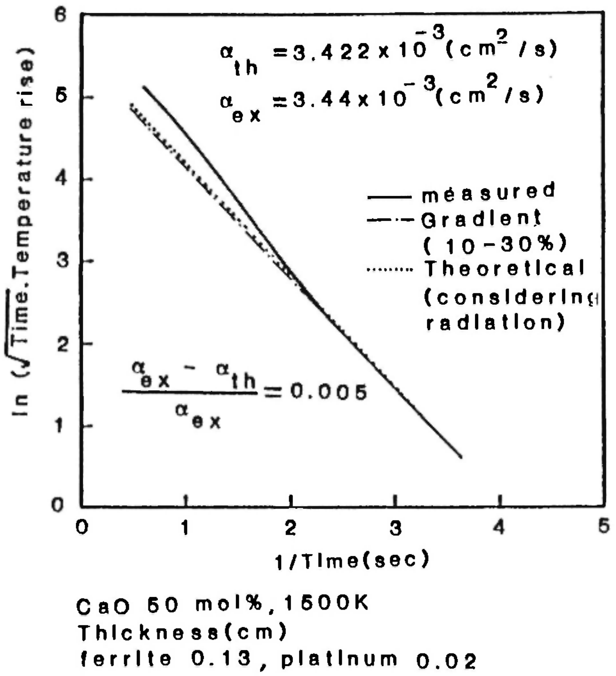

Fig. 6. The effect of radiative heat loss on thermal diffusivity.

4.2. Thermal Diffusivities of Calcium Ferrite Slags

By the logarithmic method discussed in Section 2, the thermal diffusivities of calcium ferrite slags in the composition range of 33 to 55 mol% CaO were measured over the temperature range 1003 to 1673°K.

Reproducibility was examined in both solid and liquid phases. The sample-cell system used for the second measurement was constructed in the same manner as the first one. The reproducibility has been well confirmed, as exemplified by Fig. 7 using the

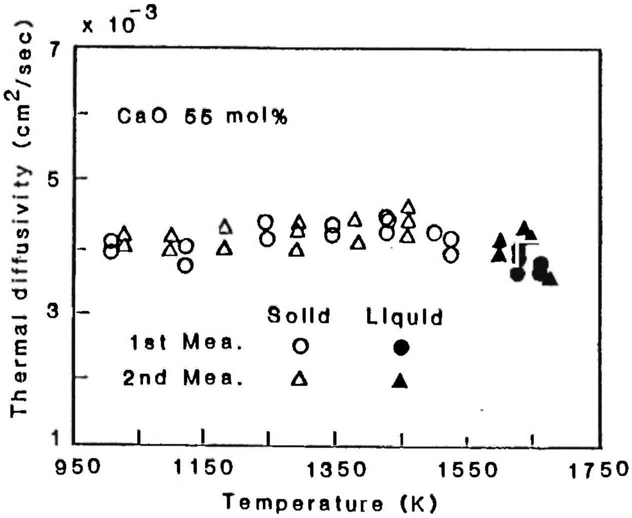

Fig. 7. Thermal diffusivity of ferrite slags containing 55 mol% CaO.

results of a ferrite slag containing 55 mol% CaO. The same degree of reproducibility was also obtained for the other ferrite slag samples.

Temperature dependence of the thermal diffusivity of calcium ferrite slags is illustrated in Fig. 8. Thermal diffusivity of ferrite slags is found to decrease as temperature increases in both the solid and the liquid phases. Thermal diffusivities of solid ferrite slags are known to be represented by the following form:

$$\alpha = A + BT + CT^2 \qquad (8)$$

where T is the absolute temperature (°K). The coefficients A, B and C of Eq. (8) are summarized in Table 1. Thermal diffusivities of molten ferrite slags are expressed by the following equation:

$$\alpha = A_1 + B_1T \qquad (9)$$

The coefficients A_1 and B_1 of Eq. (9) are listed in Table 2. It may be noted that these equations are applicable over the temperature range presently investigated.

TABLE 1
The values of coefficients A, B and C in Eq. (8)

CaO (mol%)	A	B	C	Temperature range (°K)
33	7.98×10^{-4}	6.66×10^{-6}	-3.47×10^{-9}	1009–1518
40	2.35×10^{-3}	4.06×10^{-6}	-2.46×10^{-9}	1003–1446
45	2.10×10^{-3}	3.09×10^{-6}	-1.66×10^{-9}	1031–1511
50	1.62×10^{-2}	-1.97×10^{-5}	7.42×10^{-9}	1013–1507
55	2.15×10^{-3}	2.64×10^{-6}	-7.97×10^{-10}	1009–1543

TABLE 2
The values of coefficients A_1 and B_1 in Eq. (9)

CaO (mol%)	A_1	B_1	Temperature range (°K)
33	3.99×10^{-3}	-5.54×10^{-7}	1573–1645
40	1.49×10^{-2}	-7.63×10^{-6}	1563–1630
45	1.16×10^{-2}	-5.37×10^{-6}	1578–1655
50	8.66×10^{-3}	-3.23×10^{-6}	1575–1673
55	2.46×10^{-2}	-1.27×10^{-5}	1613–1659

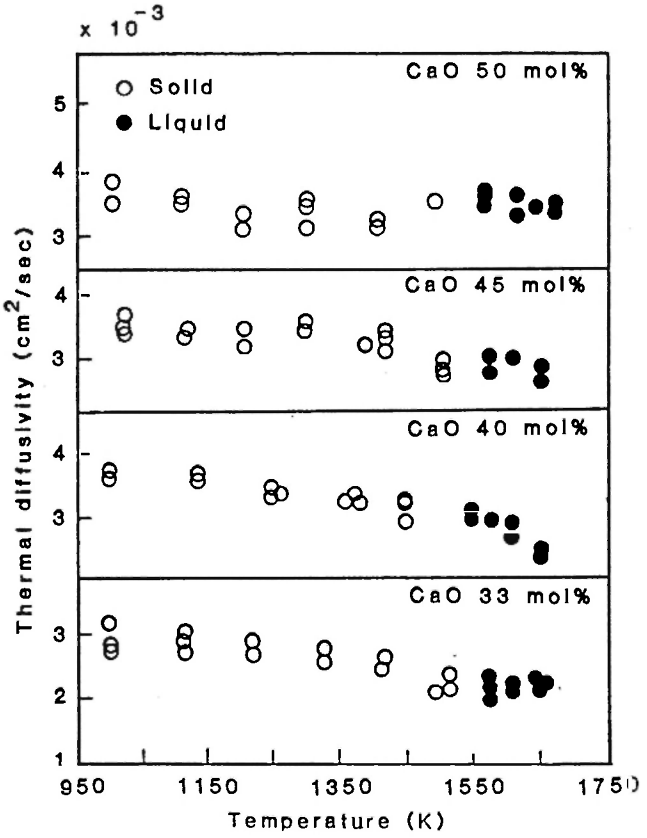

Fig. 8. Thermal diffusivity of ferrite slags containing 33, 40, 45 and 50 mol% CaO.

The thermal diffusivities of molten calcium ferrite slags at 1633°K are plotted as a function of the CaO content in Fig. 9. The minimum value is found in the composition of 40 mol% CaO, but composition dependence of thermal diffusivity is not distinctive in molten calcium ferrite slags.

4.3. Structural Features of Calcium Ferrite Slags and their Relation to Thermal Diffusivity

Kittel /18/ and Kingery *et al.* /19/ reported that the effects of composition and structure on thermal conductivity are well explained by consideration of mean free path and phonon theory. Thermal conductivity is defined by:

$$\lambda = \frac{1}{3} C_v v l_c \qquad (10)$$

where λ is the thermal conductivity, C_v the specific heat per unit volume, v the average sound velocity and l_c the mean free path of a phonon. The thermal diffusivity is proportional to the value of λ because of $\alpha = \lambda / C_p \rho$. In crystalline materials, the mean free path of a phonon tends to decrease as the temperature

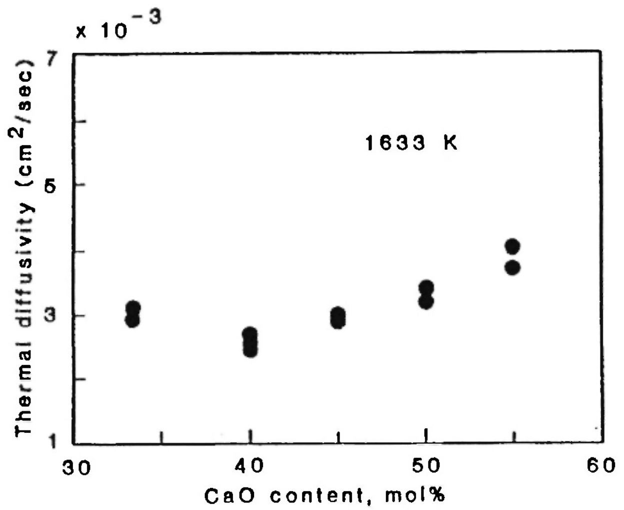

Fig. 9. Compositional dependence of thermal diffusivity of molten calcium ferrite slags at 1633°K.

is raised. This can be understood in terms of the number of phonons with which a given phonon can interact. The collision frequency of a given phonon should be proportional to the number of phonons and the total number of excited phonons is proportional to the temperature T at higher temperatures. Thus, the relation $\alpha \propto 1/T$ is well appreciated and this gives the decrease in thermal diffusivity as the temperature increases. At a sufficiently high temperature, the mean free path of a phonon decreases to a value almost equal to the lattice spacing and then the thermal diffusivity may become almost constant. Such behaviour is found, as shown in Figs. 7 and 8. However, it appears that the thermal diffusivities of solid ferrite slags only slightly decrease with temperature rise in the present experimental composition range.

Structural studies of molten calcium ferrite slags were made by X-ray diffraction /20, 21/. Fig. 10 shows the near neighbour correlations of Ca–O and Fe–O pairs. The correlation of Ca–O pairs is almost constant, but the Fe–O distance and its coordination number gradually decrease as the CaO content increases. The variation of the Fe–O pairs is attributed to a change in the position of Fe from an octahedral to a tetrahedral oxygen site, suggesting the formation of a certain local ordering such as FeO_4^{5-} or $Fe_2O_5^{4-}$ /20, 21/. The formation of such local ordering is consistent with the increase in viscosity and thermal diffusivity of molten ferrite slags. An increase in viscosity of molten calcium ferrite slags is detected as the CaO content increases /4/. As demonstrated in Fig. 9, a slight increase in thermal diffusivity is also found at higher CaO content, although the type of anionic species is not revealed from these data alone.

5. CONCLUSIONS

Thermal diffusivity of molten calcium ferrite slags has been measured by the laser flash technique. The effects of radial heat flow and radiative heat loss on the thermal diffusivity are found to be negligible in this method. The logarithmic method of analysing the initial short time region of temperature rise is also found effective for the determination of thermal diffusivity of an opaque liquid sample at high temperature.

Thermal diffusivities of calcium ferrite slags containing 33, 40, 45, 50 and 55 mol% CaO are in the range 0.0025–0.0043 (cm^2/s) for both the solid and the liquid phases. The thermal diffusivity values decrease as temperature is raised and slightly increase as a function of higher CaO content. The variation of thermal diffusivities of solid ferrite slags with respect to temperature may be interpreted by the change of mean free path using the phonon theory. Structural features of molten calcium ferrite slags and their relation to thermal diffusivity have been discussed on the basis of near neighbour correlations determined by X-ray diffraction.

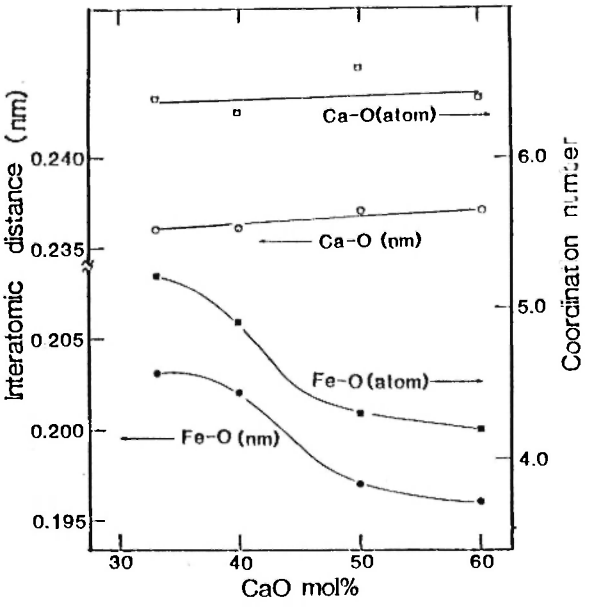

Fig. 10. Compositional dependence of the near neighbour correlations of Ca–O and Fe–O pairs in molten calcium ferrite slags /21/.

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