Application of Laser-Pulse Technique to Determining Thermal Conductivity of Molten Oxides at High Temperature

Y. Waseda

Research Institute of Mineral Dressing and Metallurgy (SENKEN), Tohoku University, Sendai 980, Japan.

CONTENTS

	Page
ABSTRACT	56
1. INTRODUCTION	56
2. EXPERIMENTALS	56
3. PRINCIPLE OF DATA ANALYSIS	57
4. THERMAL CONDUCTIVITY OF HIGH TEMPERATURE OXIDE MELTS DETERMINED BY THE LASER-PULSE TECHNIQUE	58
5. THEORETICAL ASPECT ON RADIATIVE HEAT TRANSFER COEFFICIENT	59
6. LASER-PULSE CALORIMETRY	60
7. CONCLUDING REMARKS	61
ACKNOWLEDGEMENTS	62
REFERENCES	62

ABSTRACT

The supreme importance of thermal properties such as thermal conductivity or diffusivity of various inorganic materials at high temperature has recently been well-recognized and there have been several attempts on thermal conductivity measurements for relatively low conductive materials such as oxides and nitrides at high temperature. However, their accuracy is often not sufficient to allow quantitative discussion, mainly arising from experimental difficulties. For this purpose, the laser-pulse technique proposed in early 1960 has received much attention. Although some advantages of laser-pulse technique are strongly suggested, major progress has been obtained only in the last few years.

An attempt has been made in this paper to review current information on the principle and new data processing for the laser-pulse technique including some selected examples of its application to determining thermal conductivity of oxide melts at high temperature. The relevant significant theoretical aspect on the radiative heat transfer coefficient is discussed, in order to facilitate the understanding of the present status of fundamentals and powerful link between physical constant such as the reflective index of sample materials and the required formulae for determining thermal conductivity of high temperature melts by this technique. The laser-pulse calorimetry for high temperature materials has also been described for convenience of further investigation by this relatively new method of the laser-pulse technique.

1. INTRODUCTION

In recent years, the increasing importance of extensive and accurate knowledge of thermal properties such as thermal conductivity (or diffusivity) of relatively low conductive (less than 10 W/mK) materials at high temperature has been well-recognized, in parallel with application of various ceramics for making new refractory materials with severe temperature gradient and surface technology such as laser-flash annealing for several semiconductive devices. Such importance has also been emphasized in many metallurgical processes related to the production of high-quality steels by using the electroslag remelting (ESR) technique or the accurate control of continuous casting in steel-making [1-3]. Thus, there have been various attempts on thermal conductivity measurements for relatively low conductive materials such as oxides and nitrides at high temperature. However, their accuracy was

often not sufficient to allow the quantitative discussion mainly arising from the experimental difficulties, particularly at temperature above 1000 K.

A new laser-flash technique proposed in early 1960 [4], has many advantages and even is a better method for determining thermal conductivity of high temperature materials than the conventional techniques such as the hot-wire method and the coaxial cylinder method. However, the full potential of a laser-pulse technique has been assessed only recently. One of the major reasons is as follows: the radiative heat flow is known to play a significant role at high temperature and the heat transfer should be described as a function of not only thermal diffusivity but also emissivity and absorption coefficients for semi-transparent materials, but such points are not established yet until recently [5-7].

The main purpose of this paper is to present the recent developments of the laser-pulse technique for thermal conductivity measurement of relatively low conductive materials together with some selected examples of oxide melts at high temperature.

2. EXPERIMENTALS

The schematic diagram of the laser-pulse apparatus in the Research Institute of Mineral Dressing and Metallurgy (SENKEN), Tohoku University for measuring thermal conductivity and its cell-assembly are given in Figures 1 and 2, respectively. The cell-assembly is enclosed in a bell jar under vacuum of an order of 10^{-4} Pa ($\approx 10^{-6}$ Torr).

Fig. 1. Schematic diagram of the experimental layout for the laser-pulse technique.

Fig. 2. Schematic diagram of the cell-geometry for measuring thermal conductivity of oxide melts by the laser-pulse technique.

The so-called two layered cell system consists of two parts: a detector plate for measuring the temperature response curve and a column of sample liquid adhered to the metal plate. In the experiment for molten oxides, a platinum circular plate (0.2 mm in thickness and 6 mm in diameter) is usually employed as a detector plate which is suspended by three fine platinum wires just attached to the surface of sample melt. A platinum sample vessel is placed on the tantalum pedestal which has an elevator mechanism to precisely adjust its position. The temperature of a detector plate is measured by a Pt/Pt-13% Rh thermocouple, 0.1 mm in diameter, spot-welded to the center of the plate. In order to protect the signal from external noises, all circuits connecting to the thermocouple are electrically insulated from ground. The sample vessel is also insulated by a sapphire disc from the pedestal. The cell system is placed in a tungsten mesh heating element and to reduce an inductive effect caused by the heater, direct current was used with a bias by -50 V, at which the noise was minimized.

At a desired temperature, the pulse laser beam is flashed on the top surface of a detector plate and the temperature response curve is recorded in a digital transient memory from which the data is read by a micro-computer for determining thermal conductivity. After the run, the sample vessel is lowered and detached from a detector plate for direct observation of the melt. More detailed information including operational procedure and sample preparation have been given elsewhere /6, 7/ and is not duplicated here.

3. PRINCIPLE OF DATA ANALYSIS

As has already been suggested, one of the major disadvantages of the laser-pulse technique is the experimental difficulty arising from the fact that the radiative heat flow from a detector metal plate becomes serious, when this technique is applied to high temperature melt at temperature above 1000 K, but the separation of such radiative component from measured temperature response curve which involves both radiative and conductive heat flows is not established until recently. A new data processing for this purpose has been proposed with some successful results /6, 7/ and thus the essential points of this new data processing are given below.

Before triggering of a pulse laser beam, a metal detector plate is in thermal equilibrium with a liquid sample layer and then a laser pulse is flashed on the detector plate. Thus the absorbed heat of the plate discharges into liquid sample and surroundings by both conduction and radiation, as schematically illustrated by Figure 3. It is noted that only conduction

Fig. 3. Model for two layered cell-geometry in the laser-pulse technique.

heat flow was considered in the previous work /5/ for measuring thermal conductivity of molten salts by the laser-pulse technique. As is given by Ohta *et al.* /7/, the heat transport equations for the case involving both radiative and conductive heat flows can be obtained as equations (1) and (2) with initial and boundary conditions expressed by equations (3) and (4), respectively.

For metal plate:

$$-\rho_d C_{pd} l_d \frac{\partial T_d}{\partial t} = -\lambda_s \frac{\partial T_s}{\partial t} \Big|_{x=0} + RT_d(t) \quad (1)$$

For liquid layer:

$$\frac{\partial T_s(x, t)}{\partial t} = K \frac{\partial^2 T_s(x, t)}{\partial x^2} \quad (2)$$

Initial conditions:

$$T_d = T_0 \quad (3)$$

$$T_s = 0 \quad (x = 0)$$

Boundary conditions:

$$T_s(\infty, t) = 0 \quad (4)$$

$$T_s(0, t) = T_d$$

where, the suffixes s and d indicate the sample and the detector plate, t is time, x distance from the detector plate, l is the thickness of the plate, T is a temperature rise from the equilibrium temperature at time t, and C_p , ρ , λ , and K denote specific heat capacity, density, thermal diffusivity, respectively. In the present experimental conditions, the radiative heat flow can be assumed as linear process with respect to the temperature difference, because an increase of temperature is of the order of 10 K. Consequently, the coefficient (R) of radiative heat flow, depending upon the temperature of the metal plate and the refractive index of the sample, are considered to be constant for T_d .

The transport equations of (1) and (2) are normalized by time (t_n) and distance (x_n) and then the solutions for the cases of various radiative effects have been numerically obtained by the finite difference method with the following normalized form.

$$-\frac{\partial T(0, t_n)}{\partial t_n} = -\frac{\partial T(0, t_n)}{\partial x_n} + R_n T(0, t_n) \quad (x_n = 0) \quad (5)$$

$$\frac{\partial T(x_n, t_n)}{\partial t_n} = \frac{\partial^2 T(x_n, t_n)}{\partial x_n^2} \quad (x_n > 0) \quad (6)$$

where,

$$\begin{aligned} x_n &= (C_{ps} \rho_s) x / \rho_d C_{pd} l_d, \\ t_n &= (\lambda_s \rho_s C_{ps}) t / \rho_d^2 C_{pd}^2 l_d^2, \\ R_n &= (\rho_d C_{pd} l_d) R / \lambda_s \rho_s C_{ps}, \\ T(x_n, t_n) &= T_s(x_n, t_n) / T_0 \end{aligned} \quad (7)$$

Examples of numerical solution are shown in Figure 4

Fig. 4. Theoretical temperature response curves with various radiative effect.

together with the result of Tada *et al.* [5] for the case where the effect of radiative heat transfer is negligible. The basic idea of a new data processing proposed by Ohta *et al.* [7] is to evaluate thermal conductivity of sample liquid as well as the radiative component parameter, denoted by R in this paper, by comparing measured temperature response curve with those of theoretical solutions using the common least-square fitting technique.

4. THERMAL CONDUCTIVITY OF HIGH TEMPERATURE OXIDE MELTS DETERMINED BY THE LASER-PULSE TECHNIQUE

A new data processing including radiative component has been applied to determine thermal conductivity of oxide melts at high temperature between 800 and

1700 K. Some selected examples are given below, for demonstrating the usefulness of this data processing.

Figure 5 provides an example of the curve-fitting scheme in the case of molten sodium silicate at 1373 K.

Fig. 5. Comparison of the experimental temperature response curve with theoretical ones with or without radiative effect.

It is obvious from this example that the present data processing including the radiative component ($R_n \neq 0$) gives good reproducibility for the experimental temperature response curve over a wide time range measured. On the other hand, the experimental temperature response curve can be reproduced only in the very limited range of time by the case where no radiative component ($R_n = 0$) is considered as exemplified by dashed and chain lines in Figure 5. These results clearly indicate the importance of the radiative effect in the measurement of thermal conductivity by the laser-pulse technique.

The systematic results of thermal conductivity of sodium silicate melts determined by this data processing for the laser-pulse technique are illustrated in Figure 6 together with the values reported by other techniques [8, 9]. All data fall within the same order of magnitude and this implies that the agreement is rather good except for the difference in temperature dependence, although the definite reason could not be drawn from the presently available information. Thermal conductivity values of some silicate melts at high temperature have been obtained along the line of this idea and the results are summarized in Table 1.

The experimental uncertainty of these results is difficult to estimate. However, the following points may be mentioned:

Fig. 6. Thermal conductivity of sodium silicates. X: mol % Na_2O ; mp: melting point; sc: super cooled liquid [7].

(1) Random errors are mainly caused by the electrical noise in the measurement of the temperature response curve.

(2) The uncertainty due to dimensional measurement of the detector metal plate is 0.1% at most.

(3) Theoretical temperature response curves evaluated by numerical calculation of the heat transport equations is found to include an uncertainty of less than 1%.

A total uncertainty of $\pm 7\%$ in thermal conductivity values summarized in Table 1 may be suggested from these errors including the uncertainty of the heat capacity data.

5. THEORETICAL ASPECT ON RADIATIVE HEAT TRANSFER COEFFICIENT

Thermal conductivity and the radiative component parameter of R_n are determined simultaneously by a curve fitting procedure in the present data processing of measured temperature response curve. Hence, the

TABLE 1. Thermal Conductivity of Silicates Determined by the Laser-pulse Technique, $\lambda = a + b \times 10^{-4} T$ ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) [6, 7]

Composition (mol %)	Temperature range (K)	a ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	b ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$)
50Na ₂ O – 50SiO ₂	1310 (l) – 1410 (l)	1.03	—
40Na ₂ O – 60SiO ₂	900 (sc) – 1400 (l)	–0.068	5.2
30Na ₂ O – 70SiO ₂	800 (sc) – 1400 (l)	0.184	2.4
50K ₂ O – 50SiO ₂	1210 (l) – 1310 (l)	0.32	—
40K ₂ O – 60SiO ₂	950 (sc) – 1300 (l)	0.19	0.85
30K ₂ O – 70SiO ₂	900 (sc) – 1350 (l)	0.04	2.0
39CaO – 14Al ₂ O ₃ – 47SiO ₂	1210 (sc) – 1310 (l)	0.32	0.33
54CaO – 11Al ₂ O ₃ – 35SiO ₂	1720 (l) – 1800 (l)	0.74	–1.1
46CaO – 54SiO ₂	1200 (sc) – 1800 (l)	0.52	–0.52

(sc): super cooled liquid, (l): liquid

reliability of this data processing may be examined by comparing the theoretical value of R_n with the experimental one. The heat transfer coefficient of R_n can be expressed by the following equation [7] as a differential coefficient of the total radiative heat flux of the detector metal plate with respect to the radiative net flow per unit area for a minute rise in temperature from the steady-state temperature where the net heat flow is zero.

$$R_n = 4(1 + n^2) \epsilon \sigma T^3 \rho_d C_{pd} l_d / \lambda_s \rho_s C_{ps} \quad (8)$$

where ϵ and T are the hemispherical total emittance and the temperature of the detector plate, respectively and n is the refractive index of the sample liquid and σ is the Stefan-Boltzmann constant. The theoretical values of R_n from eq. (8) are given in Figure 7 with the experimental ones estimated from measured temperature response curve along the line of the data processing given in the previous session. Good agreement was found in temperature range between 1000 and 1400 K and thus the consistency of the present data processing including the radiative component could be quantitatively appreciated. More detailed discussion including theoretical calculation for other effects such as the effect of multiple reflection between the detector plate and the wall of vessel through semi-transparent sample of silicate melts and the absorption process of radiative heat flux in the sample liquid or the radiation process from liquid layer has been given [10, 11] and such effects are found to be less than 1% for the total radiative heat flux emitted from the detector plate. Taken all these points, the validity and usefulness of this new data processing for mea-

Fig. 7. Comparison of measured radiative heat transfer coefficient of R_n with theoretical value by eq. (8).

suring thermal conductivity of high temperature materials by the laser-pulse technique appears to be well-confirmed.

6. LASER-PULSE CALORIMETRY

The laser-pulse technique is known to also be useful for the heat capacity measurement of inorganic materials at high temperature. Several attempts [12-14] have been made to determine heat capacity (C_p) of some ceramics with an appropriate reference material. For future convenience of the measurements of high

temperature thermal properties, a brief description of the laser-pulse calorimetry for silicate melts is given below.

The heat capacity measurement is generally carried out by the following procedure. After the conductivity measurement, the liquid column of sample is cut by lowering the vessel, then the pulse laser beam is flashed on the detector metal plate with small amount of sample melt. The temperature response curve of the detector plate is analyzed to determine the initial temperature rise (T_s) in Figure 8A and compared to that of the blank run (T_d) in Figure 8B. From the

Fig. 8. Schematic diagram of the heat capacity treatment by the laser-pulse calorimetry.

difference of initial temperature rise between measurement and blank runs with the assumption of $Q_s = Q_d$ in Figure 8, the heat capacity of sample melt can be estimated by the use of the following equation:

$$C_{ps} = (\Delta T_d - \Delta T_s) C_{pd} M_d / \Delta T_s M_s \quad (9)$$

where M is the mass and the suffixes s and d denote the sample and the detector plate, respectively.

This simple method may be affected by the following factors:

- (1) Weight of sample melt adhered on the detector plate is relatively small compared with the plate itself.
- (2) The difference of heat content between the detector plate and the sample materials is distinct.
- (3) The disparity in both size and shape between measurement and blank runs is rather appreciable.

These factors enable us to introduce the experimental uncertainty and thus a high reliability of this method is not always obtained, in contrast to the conventional drop calorimetry [15]. In order to avoid these factors, the devised method [7] has been applied to increase the weight ratio of sample to cell and the fused silica was also employed as the reference material to keep

a good similarity between measurement and blank runs. Such similarity enables us to give higher reliability of the results.

The examples of the heat capacity measurement are given in Figure 9 using the results of sodium silicates.

Fig. 9. Heat capacity of sodium silicates [7].

The values obtained by the laser-pulse technique [7] agree well with the results determined by the drop calorimetry [15] within the error less than $\pm 3\%$. On the basis of these comparisons, the overall error of the laser-pulse calorimetry could be estimated less than $\pm 5\%$. The heat capacities of the silicate melts determined by this technique are summarized in Table 2, for further convenience.

7. CONCLUDING REMARKS

The new data processing for the laser-pulse technique has been reviewed for determining thermal conductivity of high temperature melts by making possible separation of the radiative component from measured temperature response curve. This method has been applied to the measurement of several silicate melts at temperatures between 800 and 1400 K and the reasonable agreement with the literature values was obtained. The laser-pulse technique employs small, easy to fabricate samples and the results can be obtained within a few seconds. The laser-pulse technique is also useful and a simple way to determine the heat capacity of inorganic materials at high temperature

TABLE 2. Heat Capacity of Silicates Determined by the Laser-pulse Technique, $C_p = a \times 10^3 + b \times 10^{-1} T$ ($J \cdot kg^{-1} \cdot K^{-1}$)

Composition (mol %)	Temperature range (K)	a ($J \cdot kg^{-1} \cdot K^{-1}$)	b ($J \cdot kg^{-1} \cdot K^{-2}$)
50Na ₂ O – 50SiO ₂	970 (s) – 1330 (s)	0.845	6.234
	1350 (sc) – 1450 (l)	1.778	—
40Na ₂ O – 60SiO ₂	970 (sc) – 1470 (l)	1.536	0.167
30Na ₂ O – 70SiO ₂	970 (sc) – 1470 (l)	1.435	0.314
50K ₂ O – 50SiO ₂	1200 (s) – 1220 (s)	0.983	—
	1300 (l) – 1400 (l)	1.004	—
40K ₂ O – 60SiO ₂	970 (sc) – 1470 (l)	1.247	0.343
30K ₂ O – 70SiO ₂	970 (sc) – 1470 (l)	1.264	0.209
39CaO – 14Al ₂ O ₃ – 47SiO ₂	1000 (sc) – 1700 (l)	0.741	0.962
54CaO – 11Al ₂ O ₃ – 35SiO ₂	1720 (l) – 1770 (l)	0.962	—
46CaO – 54SiO ₂	1000 (sc) – 1700 (l)	0.791	0.669

(s): polycrystalline solid; (sc): super cooled liquid; (l): liquid

as shown in this review. No other method has the versatility of the laser-pulse technique. It may be interesting to extend the present data processing for determining thermal conductivity of other inorganic materials at high temperature by the laser-pulse technique, so that the usefulness and validity of the results presented in this paper will be tested.

ACKNOWLEDGEMENTS

A significant part of this paper is based on the recent results of a collaboration by Dr. H. Ohta. His valuable contribution should be greatly appreciated.

REFERENCES

1. FINE, H.A., ENGH, T. and ELLIOTT, J.F., *Met. Trans.*, **7B**: 277 (1976).
2. MITCHELL, A., SZEKELY, J. and ELLIOTT, J.F., *Electroslag Refining 3*, Iron and Steel Institute, London (1973).
3. MILLS, K.C., POWELL, J.S., BRYANT, J.W. and KEENE, B.J., *Can. Met. Quart.*, **20**: 93 (1981).
4. PARKER, W.J., JENKINS, R.J., BUTLER, C.P. and ABBOTT, G.L., *J. Appl. Phys.*, **32**: 1979 (1961).
5. TADA, Y., HARADA, M., TANIGAKI, M. and EGUCHI, W., *Indust. Eng. Chem. Fundam.*, **20**: 333 (1981).
6. SAKURAYA, T., EMI, T., WASEDA, Y. and OHTA, H., *Japan Inst. Metals*, **46**: 1131 (1982).
7. OHTA, H., WASEDA, Y. and SHIRAIISHI, Y., *Proc. 2nd Inter. Conf. on Metallurgical Slags and Fluxes*, Lake Tahoe, Nevada (1984). *The Met. Soc. AIME*, 863 (1984).
8. OGINO, K., NISHIKAWA, K. and YAMOMOTO, T., *Tetsu-to-Hagane*, **65**: S683 (1979).
9. ISHIGURO, S., NAGATA, K. and GOTO, K.S., *Tetsu-to-Hagane*, **66**: S669 (1980).
10. OHTA, H., WASEDA, Y. and SHIRAIISHI, Y., *J. High Temp. Soc. Japan*, **11**: 81 (1985).
11. OHTA, H. and WASEDA, Y., *Bull. Japan Inst. Metals*, **24**: 805 (1985).
12. MOSER, J.B. and KRUGER, O.L., *J. Appl. Phys.*, **58**: 3215 (1967).
13. TAKAHASHI, Y., *J. Nucl. Mater.*, **51**: 17 (1974).
14. TAKAHASHI, Y., YOKOKAWA, H., KADOKURA, H., SEKINE, Y. and MUKAIBO, T., *J. Chem. Thermodynam.*, **11**: 379 (1979).
15. See for example: TAKAHASHI, Y. and YOSHINO, T., *Yogyo Kyokai Shi*, **81**: 524 (1973).