

A High-Temperature System Based on the Laser Flash Method to Measure the Thermal Diffusivity of Melts¹

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A high-temperature measuring system has been developed to undertake measurements of thermal diffusivity and specific heat up to 1900 K. The overall design allows measurements on solids to be undertaken using the accepted standard techniques and analytical procedures. The specific design for molten materials and especially slags is based on the differential threelayer technique utilizing a special cell which can be accommodated in the system. In this method, the liquid specimen is sandwiched between an upper inner platinum crucible and a lower outer platinum crucible, to provide a three-layered sandwich. A laser pulse irradiates the surface of the upper platinum crucible and the temperature response of the surface of the lower platinum crucible is observed. For the purpose of accurate measurement of specimen thickness at the measuring temperature, two runs are performed in which the thicknesses are l and $l + \Delta l$, where l is unknown but Δl can be set accurately with a built-in micrometer. The thermal diffusivity is obtained through a curve-fitting method by a personal computer using a three-layer analysis with a correction for the radiative component based on the transparent body assumption. Following verification of the basic performance, using solids of known properties and water and ethanol, a continuous casting mixture has been evaluated. The initial results on the fluids are in good agreement with those in the literature.

KEY WORDS: flash method; melts; radiation correction; slags; three-layer analysis; thermal conductivity; thermal diffusivity.

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1. INTRODUCTION

The thermophysical properties of molten materials, in particular thermal conductivity and thermal diffusivity, are especially important parameters required both for the design of plants that utilize heat-transfer fluids and for manufacturing processes in many industries. Furthermore, precise values of these heat transfer properties can play an important role in obtaining a better understanding of the basic physical and chemical behavior of fluids.

The properties of molten slags are especially important for practical application to the design of continuous casting processes to produce improved materials in the steel and other metal industries. More recently, they are necessary for the design of large scale incinerators used particularly for waste disposal.

The measurement of thermal properties of molten materials, especially at the high temperatures involved in many of these practical applications, is not a simple exercise, principally because of materials compatibility problems, radiation heat losses, and possible convective effects, which may all be exacerbated by time and particular temperatures.

Over the past 30+ years, the flash method [1] has become the most widely used measurement technique for measuring thermal diffusivity of all types of solid materials to very high temperatures [2]. The method is particularly attractive for such purposes because of its relatively simplicity in principle and specimen configuration combined with the very short times involved. The continuing development of improved laser and other instrumentation and computer hardware and software have provided the means to obtain more precise values from more complex analysis. These factors thus make the flash method attractive for measurements on fluids.

The basic flash method utilizing a laser source with a two-layer analysis to obtain results was first proposed some 20 years ago for undertaking measurements on low-melting point metals in a simple container [3]. Since that time, the technique has been extended to many different materials over a broad temperature range using various means of containment and a fixed specimen thickness [4–6]. Analysis of the experimental curves has been based on either the improved two-layer analysis [7] or its extension to the three-layer system developed for solid composites [8]. The latter was developed for high-temperature applications owing to the loss of accuracy of the two-layer procedure due to increased effects of radiation heat losses from specimen to the container. However, even with the three-layer case for a fixed specimen thickness, the absolute value of the latter can be uncertain because of the effects of thermal expansion and distortion

and any creep of the containment cell material and supports that may occur.

The present paper describes the essential features of the design and use of a high-temperature laser flash measurement system developed by Sinku Riko, Inc., in cooperation with the Institute of Advanced Materials Processing, Tohoku University. The system can include a special cell for fluids and molten materials. In this, the thickness of a fluid specimen can be changed simply and this relative change in thickness can be measured more accurately than the absolute value. With the use of a modification of the three-layer analysis [9], the method provides a means to determine the thermal diffusivity without knowing the absolute thickness of specimen. In addition, with the application of a new data processing technique, it is possible to determine thermal diffusivity values over a broader time regime of the temperature response curve.

2. MEASUREMENT PRINCIPLE

The principle is illustrated schematically in Fig. 1. The test specimen consists of a thin layer contained between the bottom plate of a slightly larger containment crucible and in contact with the lower plate of a similar smaller diameter crucible which is inserted into the fluid. The thickness of the specimen can be changed simply by moving the lower crucible up or down by small increments as required with the molten material remaining between the walls of the crucibles. A laser pulse irradiates the upper crucible surface and the temperature response of surface of the bottom crucible is monitored with an infrared detector. Measurements are made at two thicknesses, l_2 and $l_2 + \Delta l$, respectively, by lowering the lower crucible and measuring the small length change with a micrometer attached to the support system.

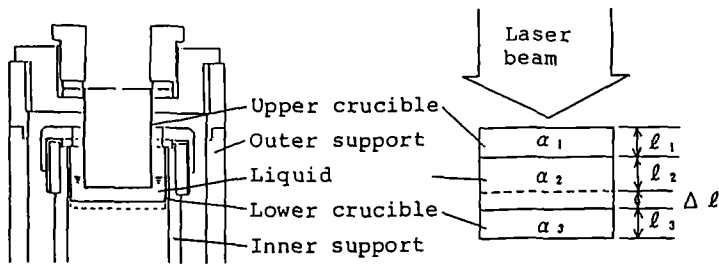


Fig. 1. Schematic diagram of the principle and measurement section for thermal diffusivity measurement on a fluid.

The temperature response at the initial time region of the temperature response of a three-layer system can be given in the form

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

where $\eta_i = l_i/\alpha_i$.

Plotting $\ln(\theta t^{1/2})$ against $1/t$ gives a straight line having the slope $-\frac{1}{4}(\eta_1 + \eta_2 + \eta_3)^2$. Thus, α_2 can be determined if the thermal diffusivity and thickness of the crucible material are known and the thickness l_2 is known.

For an infinite slab consisting of the three layers in Fig. 1, the temperature response of the back surface of the third layer can be described by Eq. (1) and the following can be obtained for the two measurement cases

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

$$(l_2 + \Delta l)/\alpha_2^{1/2} = \frac{2\sqrt{-\partial I_n(\theta l_2) t^{1/2}}}{\partial(1/t)} - \eta_1 - \eta_3 \quad (3)$$

The relationship between l_2 and α_2 are shown in Fig. 2 and the intersection of the two lines provides values of α_2 and l_2 .

However, Eq. (1) is valid only over a very limited region of the initial temperature response curve. In practice, a curve-fitting calculation procedure using the time region in the range 0.3 to 0.5 t_{\max} is utilized. Thus, the temperature response is obtained at one thickness l_2 as shown schematically in Fig. 3a and values of θ obtained at t_a and t_b (i.e., in the

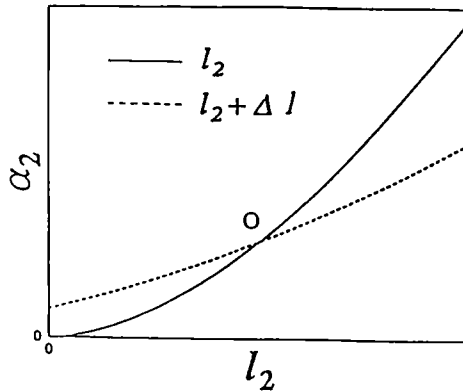


Fig. 2. Relationship of α_2 as a function of thickness estimated from Eqs. (2) and (3).

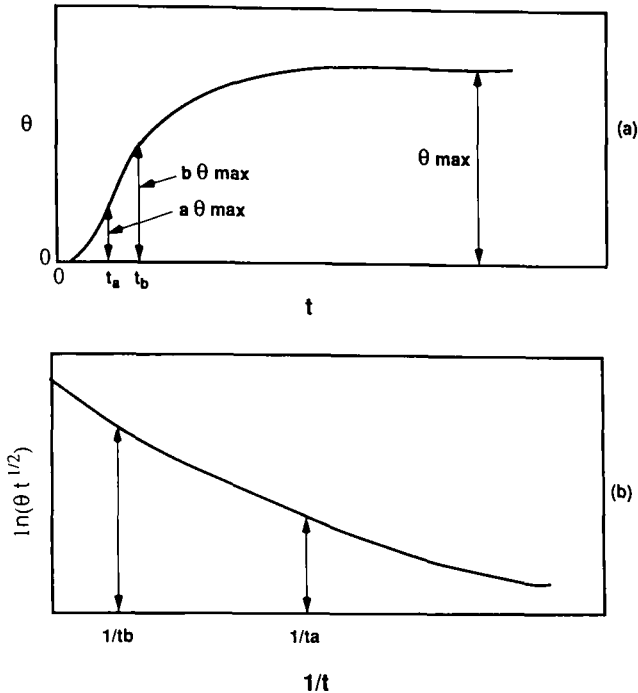


Fig. 3. Principle of data analysis from experimental output of θ vs t . (a) Determination of t_a and t_b in the range 0.2 to $0.4 \theta_{max}$. (b) Plot of l/t vs $\ln(\theta t^{1/2})$ to determine slopes β_1 and β_2 .

above range). The same procedure is applied using the time response for a thickness $l_2 + \Delta l$.

The two response curves are converted as illustrated in Fig. 3b and the respective gradients β_1 and β_2 are obtained by the least-squares method. A value is chosen for l_2 and an approximate value of α_2 calculated for each case. This value is then put into the thermal diffusion equation, and using Laplace transformation and then the inverse Laplace transformation values of βLAP_1 , and βLAP_2 are calculated. By successive approximations, values of α_2 for the two cases are obtained that satisfy

$$\beta_1 = \beta LAP_1 \quad \text{and} \quad \beta_2 = \beta LAP_2$$

By a process of iteration using different values of l_2 , values of α_2 are calculated to provide curves of $l_2 + \alpha_2$, from which a final value of α_2 can be obtained from the intersection of the two curves.

3. APPARATUS

The apparatus is illustrated schematically in Fig. 4. In general, the basic components, operation, and analysis of results including corrections for finite pulse width, radiation, etc., for the measurement system are similar to those for typical high-temperature flash diffusivity apparatus used for solids. A 10-mm-diameter specimen is held in a horseshoe ring tantalum holder supported on three molybdeum pins in an alumina tube. However, to allow measurements to be made on fluids using the fluid cell, the lower end of the support tube is not fixed but is connected to an elevating mechanism and micrometer to enable the thickness of specimen to be changed by small increments and measured precisely (± 0.005 mm). The assembly is contained in an outer pure alumina tube with an upper calcium fluoride window through which energy from a 15-J/pulse neodymium glass laser (wavelength, 1054 nm; pulse width, 0.5 ms) irradiates the upper surface of the specimen stack.

The temperature response on a 3-mm-diameter area of the lower specimen surface is measured by an external indium antimonide sensor. For measurements of specific heat, the temperature is measured using a platinum rhodium/platinum thermocouple.

A d.c.-powered silicon carbide tubular furnace consisting of eight rods arranged in a circle surrounds the whole assembly to enable the system to attain temperatures up to the order of 1770 K. The use of d.c. power is chosen to allow more precise specific heat measurements to be made at high temperatures due to the fact that it significantly reduces noise fluctuations in the temperature response. However, for temperatures up to 1900 K, an a.c.-powered lanthanum chromide heater is used. Noise in the

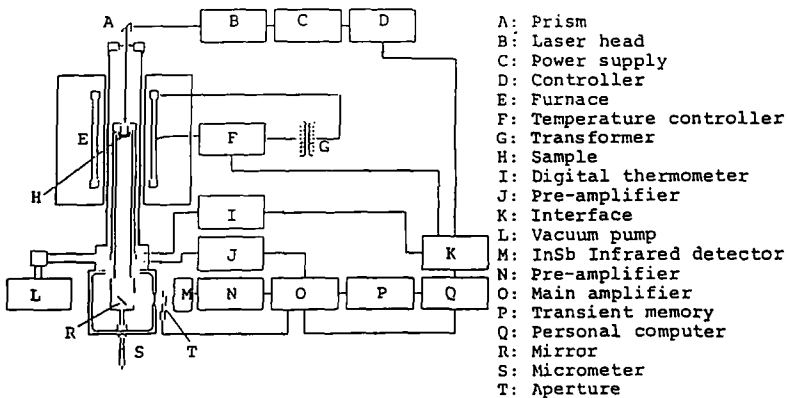


Fig. 4. Simplified schematic of the laser flash apparatus.

measuring circuit for specific heat is minimized by the inclusion of appropriate filters when a.c. power is used.

For measurement on fluids, a special cell is used to replace the solid specimen holder. This consists of two thin-walled (0.2-mm) platinum or platinum rhodium alloy crucibles. The outer one is 18.5 mm in diameter and 20 mm high, supported on the alumina tube. The inner one is 13.5 mm in diameter and of a similar height. This is fixed to a second high-purity alumina tube such that a layer of fluid can be formed between the lower platinum surfaces of each crucible by submerging the inner crucible into the outer one. At each temperature of a measurement cycle, the thickness of the fluid layer is adjusted manually by the micrometer to the two levels required for the determination. Finally, the results are obtained using the three-layer analysis described earlier.

4. MEASUREMENTS

In order to evaluate the functionality and efficacy of the apparatus, some preliminary measurements have been undertaken on solid stainless-steel and tantalum reference materials and on water, ethanol, and one continuous casting powder.

4.1. Solids

Thermal diffusivity and specific heat measurements were made in vacuum up to approximately 1200 K on a 304 stainless-steel reference material. For thermal diffusivity, the maximum deviation from the recommended values was 3.5% at the highest temperature of measurement. For specific heat, the deviation ranged from -4.5% at room temperature to $+1.5\%$ at 1280 K. Measurements of thermal diffusivity of pure tantalum (99.97%) from 300 to 1870 K gave an invariant thermal diffusivity value of $2.39 \pm 0.05 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$. This behaviour is in excellent agreement with recommended values for this metal [10].

4.2. Fluids

Measurements were made at 300 K in air on distilled water and Class 1 reagent-purity ethanol. Average values of thermal diffusivity of $1.53 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$ and $1.16 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$ were obtained for water and ethanol respectively. The former value is some 4.5% higher than the recommended value and the latter some 31% higher. Subsequent analysis of the ethanol indicated that there was greater than 0.5% water present. This could account for some of the difference.

Finally measurements were undertaken on a proprietary casting powder D-12 containing silica, alumina, magnesia, calcia sodium oxide, and calcium fluoride. This material was chosen because it had been measured earlier by one of the present authors, who obtained values in the range of 4.98 to $5.39 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$ over the approximate temperature range 1400 to 1670 K . The present measurements were carried out in a protective argon atmosphere ($5 \times 10^4 \text{ Pa}$) and over temperature range from 1370 to 1670 K .

A correction for the radiative component in this nonopaque material was based on the transparent body assumption, which depends only on the thickness and temperature [11]. A correction based on the band approximation as a function of wavelength is more exact, but the calculation is lengthy and complex and also requires measured data on the sample absorptance versus wavelength. For slag systems having low levels of metallic impurity, the simpler correction is recommended since the differences between the two techniques were found to be less than 5% for the present material.

In general, the results indicated that the thermal diffusivity corrected for the radiation component increased with increased temperature from approximately 4.4×10^{-7} to $5.3 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$, and they agree reasonably well with the previous results. However, there was ± 5 to 6% deviation in value at each measurement level. Furthermore, on attaining the highest temperature, it was found that the value decreased with time, indicating possibly that some volatile component was diffusing out of the specimen.

5. DISCUSSION

The flash method utilizing a three-layer analysis of the results appears to be an appropriate technique to be used for measurements on fluids and on molten solids at high temperatures in particular. The present preliminary results indicate that reasonable thermal diffusivity values can be obtained by the technique. However, refinements of technique and further study are ongoing. In particular, a most urgent need is to have several fluids available as reference materials covering a broad temperature range in order to verify this and other techniques. As discussed by Nagashima [12], measurements at high temperatures are difficult and a number of uncertainties are present. Their impact can be resolved only by undertaking measurements on materials having known properties. His proposal for workers in this field to develop reference materials under a step-up confirmation program, e.g., H_2O and other liquids \rightarrow LiCl and other salts \rightarrow molten slags, is a most worthy objective.

REFERENCES

1. W. J. Parker, R. J. Jenkins, C. P. Butler, and G. L. Abbot, *J. Appl. Phys.* **32**:1979 (1961).
2. R. E. Taylor and K. D. Maglic, *Compendium of Thermophysical Property Measurement Methods Vol. I*, K. D. Maglič, A. Cezairliyan, and V. E. Peletsky; eds. (Plenum Press, New York, 1984), pp. 305–336 (see also Vol. II, 1992, pp. 281–314).
3. J. T. Schriempf, *Rev. Sci. Instrum.* **43**:781 (1972).
4. Y. Tada, M. Harada, M. Tanigaki, and W. Eguchi, *Indust. Eng. Chem. Fundam.* **20**:333 (1981).
5. M. M. Farooq, W. H. Giedt, and N. Araki, *Int. J. Thermophys.* **2**:39 (1981).
6. Z. Fang and R. Taylor, *High Temp. High Press.* **19**:29 (1987).
7. H. M. James, *J. Appl. Phys.* **51**:4666 (1980).
8. H. J. Lee and R. E. Taylor, *High Temp. High Press.* **15**:299 (1983). See also *Thermal Conductivity 14* (Plenum Press, New York, 1976).
9. Y. Waseda, M. Masuda, and H. Ohta, *Proceedings of Fourth International Symposium on Advanced Nuclear Energy Research*, JAERI-M 92-207 (Japan Atomic Energy Research Institute, Tokai, Ibaraki, 1992), pp. 298–301.
10. Y. S. Touloukian, C. Y. Ho, and P. E. Liley (eds.), *Thermophysical Properties of Matter* (Plenum Press, New York, 1971).
11. H. Ohta, G. Ogura, Y. Waseda, and M. Suzuki, *Rev. Sci. Instrum.* **61**:2645 (1990).
12. A. Nagashima; see R. P. Tye, *High Temp. High Press.* **24**:597 (1992).