International Journal of Thermophysics, Vol. 26, No. 1, January 2005 (© 2005)
DOI: 10.1007/s10765-005-2361-3

Thermal Diffusivity Measurements of Candidate Reference Materials by the Laser Flash Method[1]

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The National Metrology Institute of Japan (NMIJ) in AIST has investigated the laser flash method in order to establish a thermal diffusivity standard for solid materials above room temperature. A uniform pulse-heating technique, fast infrared thermometry, and a new data analysis method were developed in order to reduce the uncertainty in thermal diffusivity measurements. The homogeneity and stability of candidate reference materials such as isotropic graphite were tested to confirm their qualification as thermal diffusivity reference materials. Since graphite is not transparent to both the heating laser beam and infrared light for thermometry, the laser flash method can be applied to graphite without black coatings. Thermal diffusivity values of these specimens with different thicknesses, were measured with changing heating laser pulse energies. A unique thermal diffusivity value can be determined for homogeneous materials independent of the specimen thickness, by extrapolating to zero heating laser pulse energy on the plot of apparent thermal diffusivity values measured with the laser flash method as a function of heating laser pulse energy.

KEY WORDS: laser flash method; reference material; solid material; thermal diffusivity.

1. INTRODUCTION

The laser flash method is generally acknowledged as the standard and most popular method to measure the thermal diffusivity of solid materials above room temperature [1,2]. Because of the popularity of the laser

[1]Paper presented at the Fifteenth Symposium on Thermophysical Properties, June 22–27, 2003, Boulder, Colorado, U.S.A.

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flash method, there is an urgent need for reference materials for thermal diffusivity to verify proper equipment operation. Although several studies have been carried out to establish reference materials for thermal diffusivity, as of now, no reference material is available that is certified by official national and international organizations. The National Metrology Institute of Japan (NMIJ) in AIST has a plan to establish reference materials as an SI traceable thermal diffusivity standard.

When the thermal diffusivity is measured with the laser flash method, it is preferable that the material is optically nontransparent and dark colored (ideally black) in order to absorb the light of the pulse heating in a thin surface and to obtain high emissivity for radiative detection of the transient temperature change after the pulse heating. From this point of view, carbon materials have been proposed as candidates for reference materials of thermal diffusivity.

One candidate reference material for thermal diffusivity above room temperature up to 2000 K is POCO AXM-5Q1 graphite. Round-robin measurement of the thermal conductivity and thermal diffusivity of POCO AXM-5Q1 graphite were conducted under the auspices of AFML-AGARD from 1965 to 1972, and the recommended values were reported [3]. Later on, several leading laboratories participated in a cooperative project under the auspices of CODATA to measure the thermal diffusivity of POCO AXM-5Q1 graphite. However, POCO AXM-5Q1 graphite is not uniform enough since it was reported that the thermal diffusivity of POCO AXM-5Q1 graphite showed differences of more than 20% for different specimens [4–7].

In the National Research Laboratory of Metrology (the predecessor of NMIJ), the grade GC-20 of glass-like carbon was selected as a candidate for a reference material for a thermal diffusivity standard [8]. Glass-like carbon, which was produced by Tokai carbon Co. Ltd., Japan, is noncrystalline. However, since glass-like carbon is a very hard material, the method to cut and polish glass-like carbon to specimens suitable for laser flash measurements free from damage to the specimen surface has not been established.

Therefore, we have started to determine a reference material for laser flash measurements other than GC-20 glass-like carbon and POCO AXM-5Q1. We have investigated the homogeneity and stability of a number of graphite materials produced by different manufacturers to select a candidate for a thermal diffusivity reference material, and a grade IG-110 produced by Toyo Tanso Co. Ltd. was selected. In this paper, a study on thermal diffusivity measurements of IG-110 is reported.

2. EXPERIMENTAL

2.1. Measurements

We have been studying the laser flash technique to establish a thermal diffusivity standard for solid materials above room temperature [8]. An advanced laser flash technique has been developed after technical improvements in order to make thermal diffusivity measurements under well-defined initial and boundary conditions as follows:

(i) uniform pulse heating of a specimen by an improved laser beam using an optical fiber (reduction of the nonuniform heating error) [8,9];

(ii) development of a fast infrared radiation thermometer with an absolute temperature scale (reduction of the nonlinear temperature detection error) [8,10]; and

(iii) introduction of a new data analysis algorithm, "a curve-fitting method", where the entire regions of the temperature history curve is fitted by a theoretical solution under the real boundary condition (reduction of the heat loss error) [8,11].

Thermal diffusivity measurements were made using a laser flash instrument (LAF-502N, Kyoto Electronics Manufacturing Co., Ltd.) as shown in Fig. 1. This instrument was developed based on the above technical improvements [12]. A specimen is set on a specimen holder placed at the center of a carbon/carbon composite heater inside a vacuum chamber. The chamber has a vertical cylindrical shape, a pulsed laser beam impinges on the front surface of the specimen through the top window, and an infrared radiation thermometer detects the rear surface of the specimen through the bottom window. The specimen is supported by one ring in order to suppress heat loss to the specimen holder. There is a diaphragm above the specimen with the same aperture size as the specimen diameter. A Nd-YAG laser, with a wavelength of 1064 nm, is used for pulse heating the specimen. The laser beam is homogenized through a step-index optical fiber and mode mixer in order to heat the specimen surface uniformly. The temperature history curve of the rear surface of the specimen is detected using an infrared radiation thermometer. The laser-pulse intensity is monitored using a photodetector simultaneously with the temperature history curve of the specimen.

Measurements were carried out from room temperature to 1200 K. The output voltage of an infrared radiation thermometer is proportional to the spectral radiance. Nonlinearity of the Plankian equation, the relation between the spectral radiance and temperature, is larger for lower

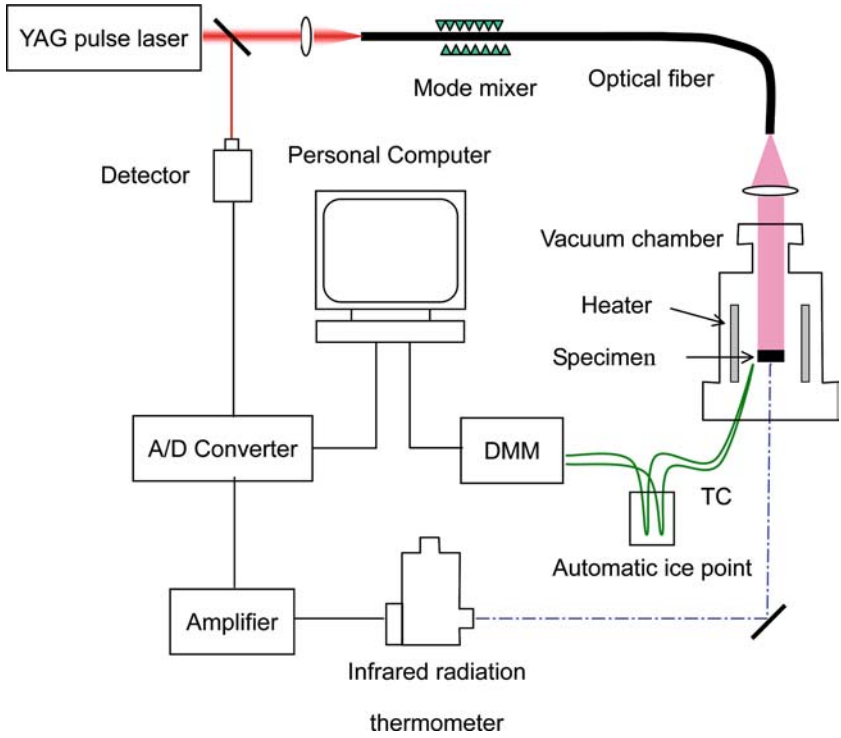

Fig. 1. Schematic diagram of measurement system.

temperatures. Therefore, for the measurements at lower temperatures, the output voltage was converted to the absolute temperature based on the temperature scale of the radiation thermometer. On the other hand, the spectral radiance was approximated by a linear function of temperature for higher temperatures. Then the thermal diffusivity was directly determined using the output voltage data for the measurements at higher temperatures since the change of the temperature is proportional to the change of output voltage.

All measuring instruments in the laser flash system should be calibrated traceable to the national standard. For example, the time scale of the data acquisition system for recording the temperature history curve was calibrated by a reference sine wave from a calibrated function generator. Major sources of uncertainty in thermal diffusivity measurements are as follows: (i) uncertainty of specimen thickness, (ii) uncertainty of time scale, (iii) uncertainty of pulse width [13,14], (iv) nonuniform heating effect [8,15], (v) heat loss effect [11], (vi) uncertainty of infrared radiation

thermometry [10], (vii) drift of the specimen temperature, (viii) uncertainty of data analysis, and (ix) uncertainty of the specimen temperature measurement. Considering these sources and following the ISO Guide for the expression of uncertainty in measurement (GUM) [16], we have made a trial for evaluating the uncertainty of the measurement. The expanded uncertainty of a thermal diffusivity measurement at room temperature is estimated to be less than 3% with a coverage factor of $k=2$ in the typical case.

2.2. Specimens

IG-110 is a grade of isotropic high-density graphite manufactured by Toyo Tanso Co., Ltd., and was selected as a candidate for a thermal diffusivity reference material. We stock 200 rods of IG-110, which are 100 mm in length and 10 mm in diameter. These rods are separated into 20 lots. One lot consists of 10 rods from adjacent positions in one block. We sampled one lot from the stocks and tested the homogeneity and stability of the thermal diffusivity in order to judge qualification of IG-110 as a reference material. The bulk density of a rod sampled from this lot is 1.76 $\mathrm{Mg\cdot m^{-3}}$ and the electrical resistance is 1050 $\mu\Omega$ according to the manufacturer.

We have prepared six specimen sets and three specimens from a rod as shown in Fig. 2. Each set includes four specimens that were 10 mm in diameter and 1.4, 2.0, 2.8, and 4.0 mm in thickness. Specimens were cut from rods, and then polished to make both surfaces parallel. The thickness of the specimens is measured using a linear gauge. The thickness variation of a specimen is several micrometers. These processes are necessary to define the specimen thickness with a small uncertainty.

2.3. Analysis

A curve-fitting method [8,11] is used to determine the thermal diffusivity from the temperature history curve obtained by the laser flash measurement. The entire set of experimental data is fitted by Cape and Lehman's theoretical curve [17] corrected by Josell et al. [18], which gives an analytical solution under the heat loss boundary condition. Both the thermal diffusivity and the Biot number are simultaneously determined by this curve-fitting method.

One advantage of the curve-fitting method is that the quality of experimental data can be checked by observing deviations between the experimental data and the theoretical curve. Poor quality data resulting from nonuniform heating, drift of the specimen temperature, or slow

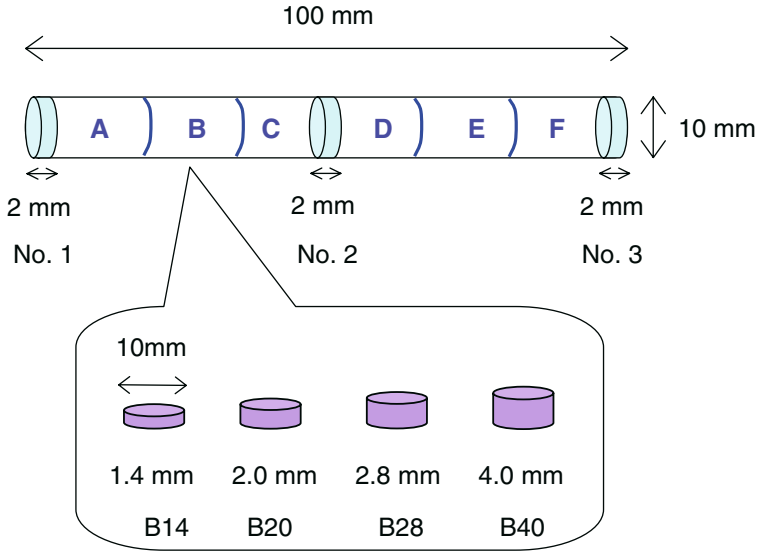

Fig. 2. Sampling locations of specimens cut out of a rod of IG-110 graphite.

response of the temperature-detection system can be checked immediately. Thus, only good quality experimental data are selected, and therefore, thermal diffusivity values with smaller uncertainty are obtained.

The origin of the time was set at the center of gravity of the observed laser-pulse intensity distribution when the observed temperature history curve is fitted to a theoretical curve [13].

3. RESULTS AND DISCUSSION

Figure 3 shows an example of a temperature history curve of IG-110 graphite at room temperature. The initial temperature of the specimen is kept at 25.6 °C before pulse heating. The specimen temperature rises from 25.6 °C to about 28 °C, after heating by a laser pulse. The thermal diffusivity is determined as $9.76 \times 10^{-5}\,m^2 \cdot s^{-1}$ from this curve based on the curve-fitting method. The value of $9.76 \times 10^{-5}\,m^2 \cdot s^{-1}$, however, cannot be directly assigned to 25.6 °C because the thermal diffusivity is a temperature-dependent property, and the temperature of the specimen rises during a measurement. It is difficult to determine the effective specimen temperature that corresponds to the thermal diffusivity. There have been a few investigations to assign the effective temperature that corresponds to the

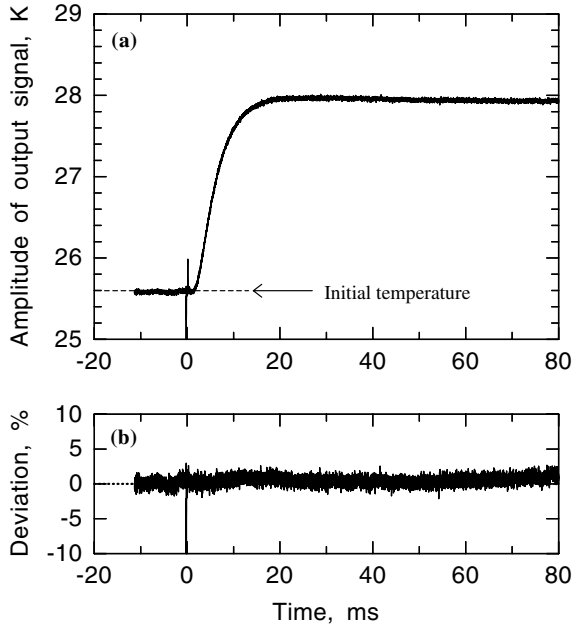

Fig. 3. Temperature history curve of rear surface at room temperature for the IG-110 specimen R2-E20: (a) experimental data, (b) deviation of the experimental data from the theoretical curve. Output signal is calculated in temperature from output signal of infrared radiation thermometer.

thermal diffusivity value determined from the temperature history curve observed by the laser flash method [19].

The thermal diffusivity determined from a temperature history curve is conventionally regarded as the value corresponding to the initial temperature. This approximation is reasonable when the temperature rises after pulse heating is small since the thermal diffusivity with the infinitesimal temperature rise is equal to the value corresponding to the initial temperature. Experimentally, a series of measurements under different heating laser pulse energies is carried out and apparent thermal diffusivity values are plotted as a function of amplitude of the output signal, which is equivalent to the temperature rise. The fitted curve to the data was determined using the least-squares method. Then the intrinsic thermal diffusivity corresponding to the initial temperature can be determined by extrapolation to zero amplitude of the output signal along the least-squares curve as shown in Figs. 4 and 5. The measurements were made at

five different heating laser pulse energies and repeated three times at each level of the heating energy. All data were plotted in these figures.

Figure 4 shows results for the IG-110 specimen R3-C14 at various levels of temperature. The thermal diffusivity corresponding to each initial temperature, along with the standard deviation, is determined by extrapolation. For this specimen, R3-C14, the intrinsic thermal diffusivity values are $(3.76 \pm 0.02) \times 10^{-4}\,m^2 \cdot s^{-1}$ at 506 K, $(2.66 \pm 0.03) \times 10^{-4}\,m^2 \cdot s^{-1}$ at 816 K, $(2.15 \pm 0.02) \times 10^{-4}\,m^2 \cdot s^{-1}$ at 995 K, and $(1.84 \pm 0.01) \times 10^{-4}\,m^2 \cdot s^{-1}$ at 1203 K.

Since the thermal diffusivity is a physical property intrinsic to a material, a unique thermal diffusivity value should be obtained independent of the specimen thickness of the same material. Figure 5 shows the signal amplitude dependence of the thermal diffusivity of four specimens from the specimen set R3-C at 299 K. In fact, four extrapolated values agree within 5% in spite of different thickness. This deviation is comparable to

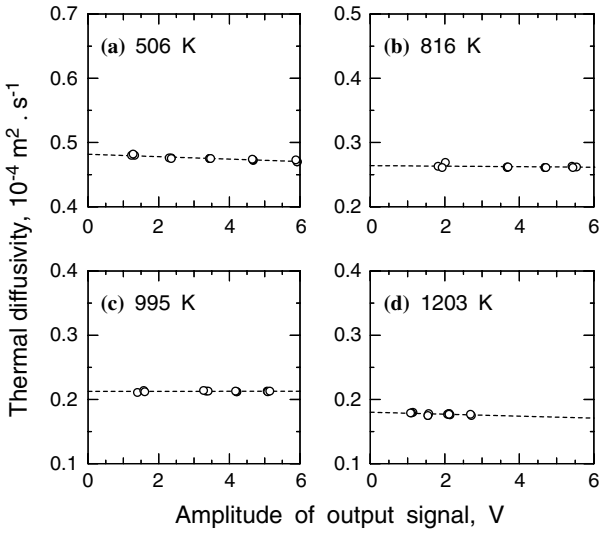

Fig. 4. Heating laser pulse energy dependence of thermal diffusivity at various temperatures for the IG-110 specimen R3-C14: (a) 506 K, (b) 816 K, (c) 995 K, and (d) 1203 K. Horizontal axis represents amplitude of output signal of infrared radiation thermometer. Dashed lines are the best fit to all data points. An intrinsic thermal diffusivity is determined by extrapolating to zero amplitude of the output signal along these lines. This figure indicates that the intrinsic thermal diffusivity can be estimated at each temperature.

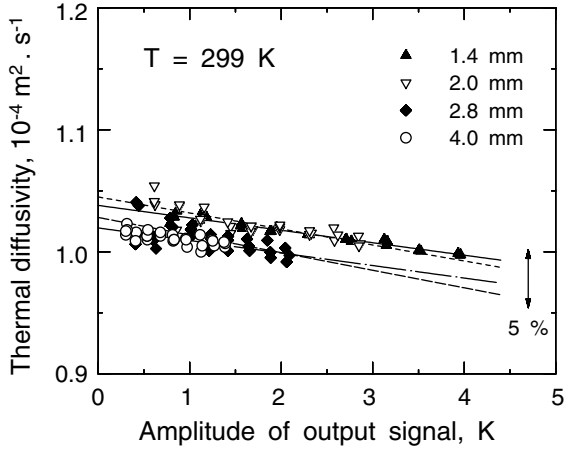

Fig. 5. Heating laser pulse energy dependence of thermal diffusivity at room temperature for the IG-110 specimen set R3-C. Horizontal axis represents amplitude of output signal of infrared radiation thermometer. Lines are the best fit to all data points. The intrinsic thermal diffusivity is the value extrapolated to zero amplitude of the output signal. This figure shows that the thermal diffusivity values of the different thickness specimens from the same rod agree within about 5%.

the intra-rod heterogeneity which is as large as 5%, as discussed in detail later. So, a significant dependence of the thermal diffusivity value on specimen thickness could not be found.

Therefore, we have confirmed the intrinsic thermal diffusivity value independent of specimen thicknesses and heating pulse energies. We will determine the thermal diffusivity of the reference materials using this procedure. This procedure is also useful for the verification of the measurement system. If a set of reference specimens with different thicknesses of the same material is available, laser flash thermal diffusivity measurement instruments can be verified systematically over wide ranges of response and temperature with systematically changing specimen thickness and heating laser pulse energy. If only one reference specimen is available, verification is just effective for the specimen whose thermophysical properties and dimensions are similar to the reference specimen. Judging from the result of the verification, we may need to improve the instruments and/or revise the analysis.

Reference materials for thermal diffusivity should be stable with time, homogeneous, and resistive to heat treatment. In order to obtain

one-dimensional heat diffusion after pulse heating, a reference material should be dense. Although the laser flash technique can be applied to transparent materials if both surfaces are covered with black coating, the coating behaves as a thermal resistance and introduces additional uncertainty in the measurement. Thus, candidates for reference materials for laser flash thermal diffusivity measurements should have high absorptance to the heating laser beam and high emissivity to radiative temperature detection in order to be measured without black coatings. Isotropic graphite such as IG-110 graphite meets these requirements.

We have investigated the homogeneity and stability of IG-110 specimens to examine their qualifications as thermal diffusivity reference materials. Figure 3a shows a typical temperature history curve observed for the IG-110 specimen R2-E20 at room temperature. The output signal of the infrared radiation thermometer is converted to temperature based on the temperature scale calibrated by a blackbody furnace. The experimental data show good signal-to-noise ratio. This curve was analyzed by the curve-fitting method to determine the thermal diffusivity.

The deviations of the experimental data from the fitted theoretical equation are plotted in Fig. 3b. The deviations are very small, and the estimated thermal diffusivity value is not sensitive to the fitting area. Thus, the specimen is expected to be sufficiently homogeneous for the intrinsic thermal diffusivity to be defined. Figure 3 also demonstrates that the measurements have been carried out under the initial conditions of rather uniform heating by the pulsed laser beam and the boundary condition of a small drift of temperature, and good temporal responsivity of a fast infrared radiation thermometer, etc. by using this instrument.

Figure 6 shows the thermal diffusivity of IG-110 specimens at room temperature cut from three rods. All specimens have the same shape and size of 10 mm in diameter and 2.0 mm in thickness. The sampling locations of specimens are also shown in Fig. 6. Intra-rod homogeneity can be estimated from the thermal diffusivity values of three specimens from R3. Inter-rod homogeneity can be estimated from the thermal diffusivity values of R1-No. 1, R1-B, R2-B, and R3-No. 1. Figure 6 suggests that both intra-rod and inter-rod heterogeneity of IG-110 are about 5% and much smaller than the heterogeneity of POCO-AXM5Q1 graphite, which is more than 20% [4–7].

Since reference materials for laser flash measurements may be used repeatedly, the effect of heat treatment on IG-110 specimens should be checked. Figure 7 shows the thermal diffusivity at room temperature after annealing at 800 °C for 4 h in a vacuum. It is found that the thermal diffusivity of IG-110 increases after the first annealing and the change of thermal diffusivity from the first annealing was reproducible for a number

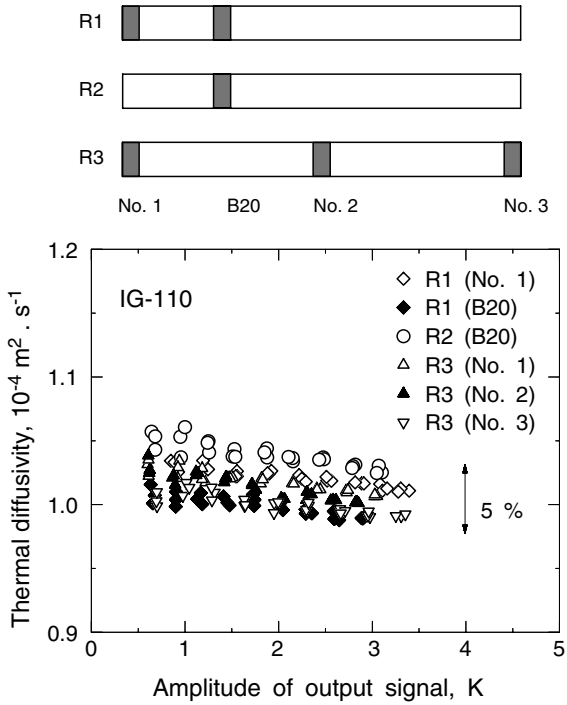

Fig. 6. Heating laser pulse energy dependence of thermal diffusivity at room temperature of IG-110 specimens cut from three rods. Sampling locations of specimens are also shown. Horizontal axis represents amplitude of output signal of infrared radiation thermometer. This figure shows the thermal diffusivity of the specimens with the same shape and thickness from three rods. It indicates that the intra-rod and inter-rod heterogeneity of IG-110 is about 5%.

of specimens. The piece-to-piece difference of the thermal diffusivity is reduced after annealing. The change from the second annealing is much smaller than the first change. Water absorbed by the process of cut and polish might explain the effect of annealing.

According to these experimental results, IG-110 is suitable for a thermal diffusivity reference material after annealing.

4. CONCLUSION

We have been studying the laser flash method in order to establish an SI traceable thermal diffusivity standard. We have investigated IG-110

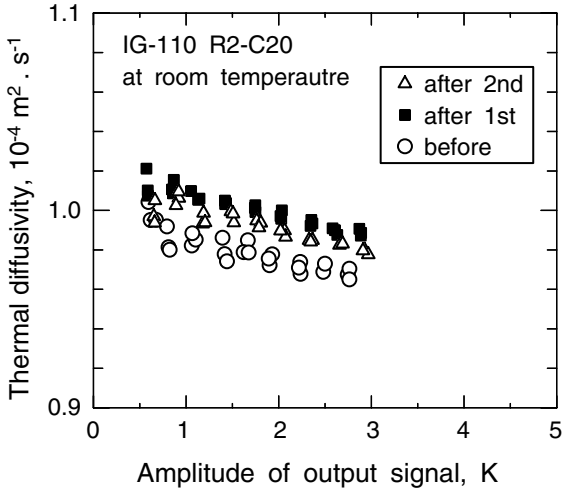

Fig. 7. Heating laser pulse energy dependence of thermal diffusivity at room temperature for the IG-110 specimen R2-C20 after annealing at 800 °C for 4 h in a vacuum. Horizontal axis represents amplitude of output signal of infrared radiation thermometer.

graphite as a candidate reference material. Thermal diffusivity values of IG-110 specimens of different thicknesses were measured as a function of the heating laser pulse energy. An intrinsic thermal diffusivity value can be determined for homogeneous materials independent of the specimen thickness by extrapolating to zero heating laser pulse energy on the plot of apparent thermal diffusivity values measured with the laser flash method as a function of the heating laser pulse energy. It is found that IG-110 is suitable as a reference material after annealing. Based on this research, we are preparing to supply IG-110 as a thermal diffusivity reference material.

ACKNOWLEDGMENT

We would like to thank M. Neda for her help with measurements.

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