International Journal of Thermophysics, Vol. 20, No. 3, 1999

Thermal Diffusivity by Modified ac Calorimetry Using a Modulated Laser Beam Energy Source[1]

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Modified ac calorimetry, a variation of the Angstrom method, has been shown to be a precise tool for measuring the in-plane thermal diffusivity of thin films (thickness less than 300 μm) of a wide variety of materials and layered composites. The property is determined from an analysis of the decay curve of the ac temperature waves generated by irradiation of a specimen using uniform chopped light (at frequencies from 1 to 20 Hz) from a halogen lamp source. To address certain limiting factors, especially to improve the signal-to-noise ratio and to eliminate heat losses, an improved form of measurement instrument has been developed. It is based on the use of a modulated laser beam heating to provide a higher intensity energy source plus a special optical system to ensure that one-dimensional ac temperature wave propagation is obtained. Measurements can now be made using frequencies in the range of 0.01 to 10 Hz, i.e., 10 times lower than in the traditional method. The performance of the improved measurement instrument will be illustrated by results on various materials of known thermal properties such as nickel and stainless steel, proposed reference materials such as a glassy carbon and alumina, plus a comparison of results obtained on CVD diamond films used in an international round-robin series with those obtained by the traditional technique.

KEY WORDS: ac calorimetry; CVD diamond; modified Angstrom method; reference materials; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

Modified ac calorimetry has been used for over 10 years to measure the in-plane thermal diffusivity and derived thermal conductivity of thin films.

[1] Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22–27, 1997, Boulder, Colorado, U.S.A.

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0195-928X/99/0500-0977$16.00/0

The basic method and its verification have been described in detail [1–3]. Essentially the partially masked surface of a small rectangular piece is irradiated by uniform chopped light generated by a halogen lamp, and the ac temperature on the opposite surface is monitored as the specimen is moved in small increments. The thermal diffusivity is obtained from the linear decay curve of the ac temperature waves.

The method has been used to measure the thermal diffusivity of films of a variety of materials including CVD diamond, metals, alloys, ceramics, and polymers covering a wide range of thermal diffusivity. For very thin films or for materials having very low values of thermal diffusivity, a high precision of measurement requires vacuum conditions in order to minimize the effect of the gaseous layer at the surface.

A limiting factor in the traditional method is the selection of the optimum heating frequency. It needs to be low enough to ensure that the specimen thickness is smaller than the effective diffusion length while it also has to be high enough to avoid heat loss effects. Chopped halogen light from a lamp is used to obtain uniform ac light irradiation to yield ac temperature amplitudes greater than 0.01°C. In some cases, the amplitude is found to be insufficient for reliable measurement and the light source intensity needs to be increased. In order to accomplish this, use of a modulated laser beam scanning the surface in a direction perpendicular to the surface was considered as a replacement for the halogen lamp [4]. For this case of nonuniform light irradiation of finite width instead of uniform ac irradiation, a solution of the thermal conduction equation was obtained and validated experimentally [5]. This calculation verified that the intensity profile did not need to be uniform in the direction of the ac temperature wave propagation (x) but did need to be uniform in the perpendicular direction (y) to ensure that the ac temperature wave propagation was unidirectional. The neceessary uniformity can be attained by sweeping a narrow laser beam across the specimen surface at a high frequency with an appropriate optical system.

The issues of surface air layer effects necessitating the use of a vacuum for some specimens of low thermal diffusivity and of edge reflection affecting the thermal wave propagation in high-thermal diffusivity materials have been addressed by Gu and colleagues [7, 8]. Their analysis confirmed original work [9, 10] which showed that the surface heat loss term can be eliminated by simultaneous measurements of the "effective" thermal diffusivities obtained from both the amplitude decay, D_a^*, and the phase shift, D_p^*. The true thermal diffusivity, D, is determined from the geometric mean of the two "effective" thermal diffusivities. Initial experimental verification using a thermoelectric heat source indicated that this was possible. However, some later experiments using direct laser heating showed that nonuniform heating

was quite significant in the perpendicular direction (y) due to the use of nonscanning laser heating. More recently, it has been shown that the geometric mean relationship will still apply even with nonuniform heating provided measurements are made sufficiently far from the source [11].

Based upon the above considerations, a measurement system was developed to take advantage of scanning laser heating to provide a highly uniform and high intensity energy source combined with the application of an advanced method of analysis using both the amplitude decay and the phase shift to eliminate the effects of heat loss. The major advantages of the improved technique are the ability to use much lower measuring frequencies, provided the thermal diffusion length is sufficiently long, and much improved temperature uniformity of the test specimen, thereby ensuring one-dimensional temperature wave propagation. The following sections describe the experimental system and the verification of its performance using a range of materials having known thermal diffusivities covering a wide range of values.

2. EXPERIMENTAL APPARATUS AND PROCEDURES

The system is illustrated schematically in Fig. 1. The ac thermal energy source is a laser diode having a total output power of 30 mW with an output

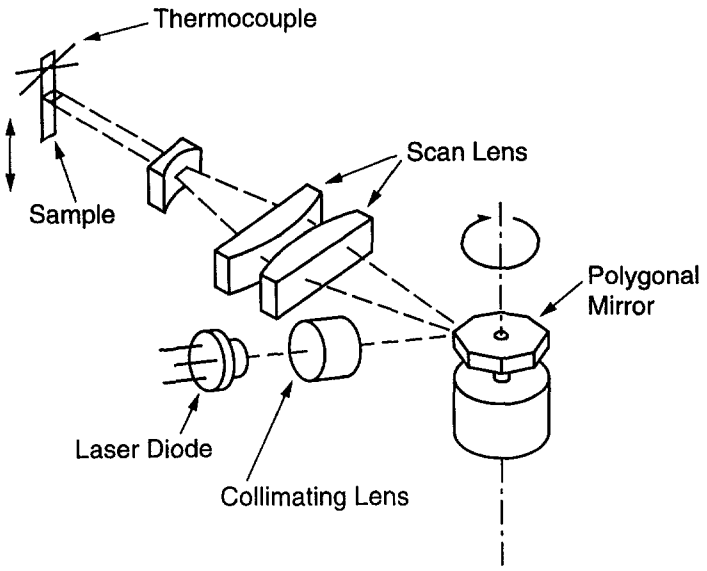

Fig. 1. Schematic arrangement of laser diode source and rotating polygonal mirror system to irradiate test samples.

instability less than 0.24%/°C and operating at 680 nm. The modulated beam is focused to a spot diameter of less than 100 μm. A polygonal mirror having 24 flat polished faces is used to sweep the laser beam over an angular range of 30°. This spreads the beam into a narrow strip approximately 0.5 mm wide and 5 to 6 mm long as shown in Fig. 2. The mirror is rotated at 6000 rpm such that the sweeping frequency is 2400 Hz, which is sufficiently fast compared to the laser modulation frequencies normally used (0.01 to 10 Hz).

The "ideal" test piece is rectangular, some 20 to 30 mm long and 4 to 5 mm wide, with a thickness that can vary from approximately 1 to 1000 μm. One specimen surface is coated uniformly with a thin film of graphite, which is sprayed on to provide a high emittance surface that is needed to

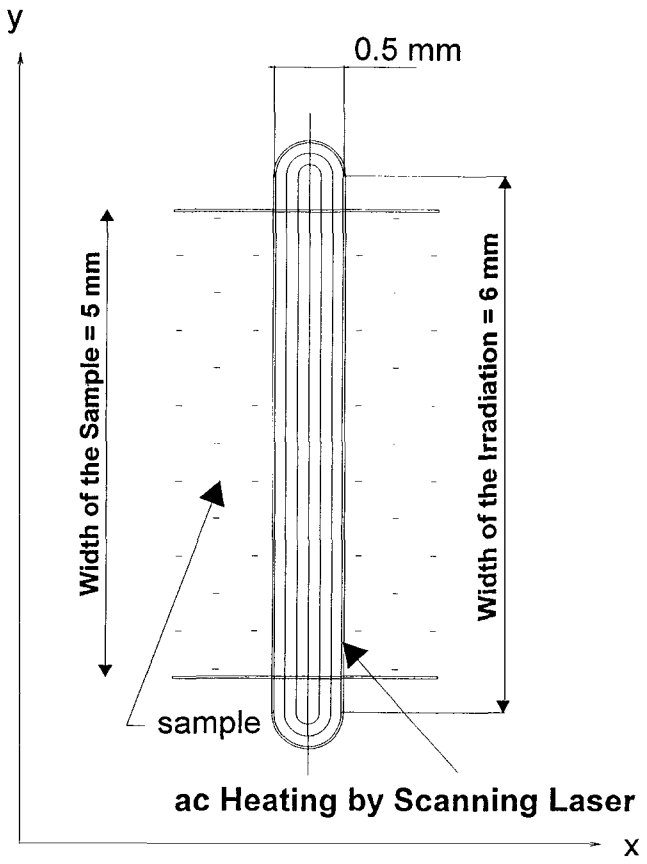

Fig. 2. Distribution of thermal energy across a test sample.

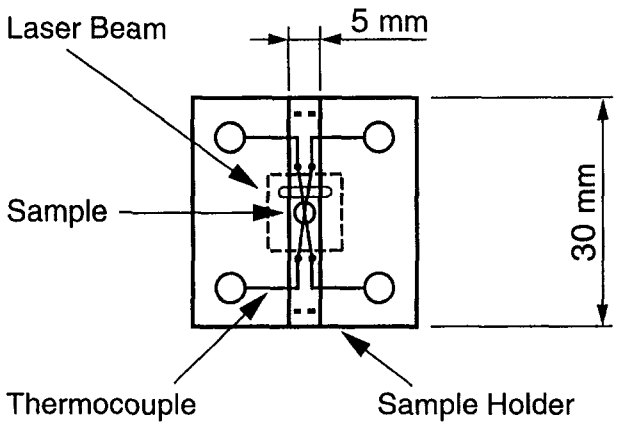

Fig. 3. Sample holder.

ensure efficient and uniform absorption of the incident energy. The test piece is then fixed into a special holder [shown in Fig. 3] with both ends supported and with the black surface facing the laser. A thermocouple approximately 0.1 mm in diameter is attached to the opposite surface by means of a spot of silver paste so that both the ac temperature excursion and the dc temperature can be monitored continuously.

The ac signal is amplified using an input transformer and a low-noise amplifier. In traditional ac calorimetry using a halogen lamp source, the input transformer produced high signal-to-noise ratio signals at normal frequencies of operation (2 to 20 Hz) but could not be used at such low frequencies as those used in the present system. However, the laser diode produces much higher power levels (factor of 10 to 50 or so), thus allowing use of the input transformer. The amplifier has a band width of 10 Hz but with a noise level of only 10 nV at 0.1 to 10 Hz. The system is operated automatically using a microcomputer and personal computer with an RS232C interface.

In a measurement the thermal diffusion length is selected to fall in the range 2 to 4 mm, by the choice of an appropriate frequency, f, which is determined by trial measurements. Measurements are then made at three or more frequencies, but at least at f, $f/2$, and $2f$. Data are collected and averaged either over a large number (60) of data points over the measured distance at a slow ramp rate, or for very high diffusivity materials, such as diamond, measurements are made for a long time (600 s) at two discrete measurement positions. A program to perform discrete Fourier transformation of the averaged signals in the frequency range 0.01 to 10 Hz then provides the appropriate amplitude decay and phase shift data to the

personal computer at a rate of 1 data point per 10 s. Analysis of the resultant data is undertaken using MS-Windows 3.1 or MS-Windows 95/NT to provide separate values of D_a^* and D_p^*, from which D is then obtained from $D = (D_a^* D_p^*)^{1/2}$.

3. VALIDATION MEASUREMENTS

Two series of measurements were carried out in air at room temperature (25 ± 0.5°C), the first to illustrate the range of materials for which the technique is suitable and the second to compare the results obtained by this technique with those by the traditional modified ac calorimetry method.

For the first study this included a number of materials having accepted recommended thermal diffusivities [12] or measured values by acceptable techniques used at national standard laboratories [13, 14]. These include three metals, a ceramic, and a glassy carbon. These covered a thermal diffusivity range of approximately 0.05 to 1 $cm^2 \cdot s^{-1}$. Details of the materials are given in Table I. Measurements were undertaken on these materials using the normal slow scanning movement technique over a distance of 3 mm some 15 to 18 mm from one end.

For the second series of measurements the three $50 \times 4 \times 0.3$ to 0.4-mm "rectangular bar" specimens of CVD diamond films that had been used in the earlier first round-robin study [15] were used. In the overall round robin a number of different configurations of the same materials had been measured by 10 international organizations using a variety of methods. The rectangular bars chosen to have thermal diffusivities in the range 2 to 10 $cm^2 \cdot s^{-1}$ were among those measured by several methods. However, the traditional modified ac calorimeter technique was the only one where more than two organizations, including Sinku Riko, used the same experimental method and procedure. The three specimens were measured in the present apparatus using the two-point long-time interval technique.

Table I. Description of Materials Used in this Study

Material	Material source	Size (mm)	Data source
99.99% O_2-free copper	Nilaco	$30 \times 5 \times 0.05$	CINDAS recommended
99.99% Ni	Goodfellow	$30 \times 5 \times 0.05$	CINDAS [12]
304 stainless steel	Nilaco	$30 \times 5 \times 0.05$	CINDAS [12]
Referceram AL-1	Japan Fine Ceramics Centre	$30 \times 5 \times 0.5$	NRLM [13]
Glassy carbon GC-20	Tokai Carbon Co.	$30 \times 5 \times 0.7$	NRLM [14]

Table II. Thermal Diffusivity of Various Materials

Material	Thermal diffusivity ($cm^2 \cdot s^{-1}$)	
	Present work	Comparative data
99.99% O_2-free copper	$1.174 \pm 3\%$	1.17
99.99% Ni	$0.225 \pm 3\%$	0.229
304 stainless steel	$0.034 \pm 3\%$	0.035
Referceram AL-1	$0.103 \pm 3\%$	$0.104 \pm 3\%$
Glassy carbon GC-20	$0.0608 \pm 3\%$	$0.0603 \pm 4\%$

4. RESULTS AND DISCUSSION

The results for the two series of measurements are presented in Tables II and III. Figure 4 shows the experimental data illustrating the expected linear relationship of amplitude decay and phase shift with distance from which D_a^* and D_p^* are obtained. Figures 5 and 6 show the value of D obtained from curves such as those shown in Fig. 4 for copper and glassy carbon, respectively. The results obtained on the three metals and the CVD diamond samples using the 0.1-mm-diameter thermocouples are in very good agreement with those originally obtained by the traditional method using 0.025-mm-diameter wires. Thicker wires were used in the present technique rather than the 0.025-mm diameter used in the conventional method in order to have a sufficiently low electrical resistance to provide more reliable measurable signals by using a 1 : 1000 ratio of input transformer and for ease of handling. Furthermore, it has been shown analytically and experimentally that the size of the sensor does not affect the result [16].

The results on the first series of materials indicate that the technique is suitable for measurements on a wide range of materials having bulk

Table III. Thermal Diffusivity of First Round-Robin CVD Diamond

Material	Thermal diffusivity by modified ac calorimetry ($cm^2 \cdot s^{-1}$)		
	Laser scanning	Traditional	
	Sinku Riko	Sinku Riko	Range for 3 organizations [13]
LB-X (high)	8.56	8.36	8.36–9.97
LB-T (Intermediate)	6.75	6.57	6.57–8.2
LB-E (low)	2.25	2.28	2.28–2.5

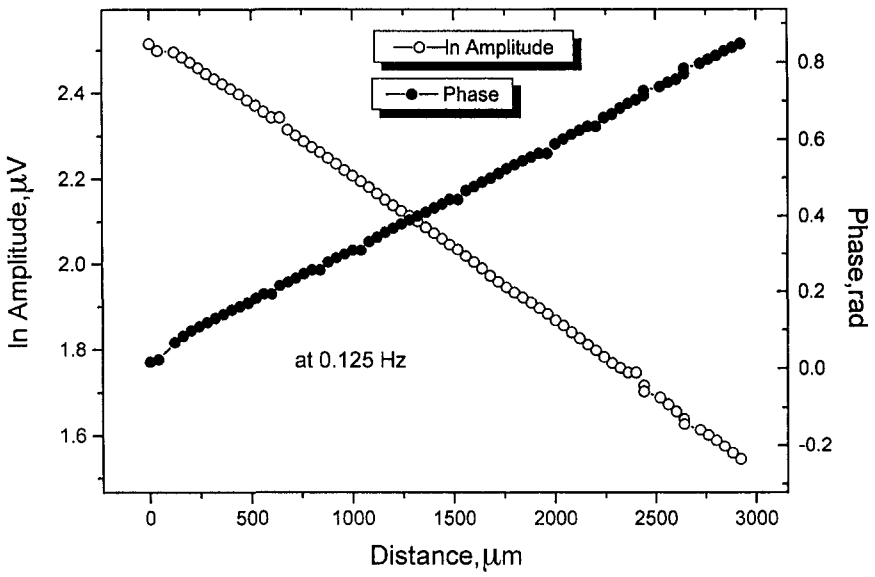

Fig. 4. Results for stainless steel (SU 304): ln amplitude and phase shift versus distance.

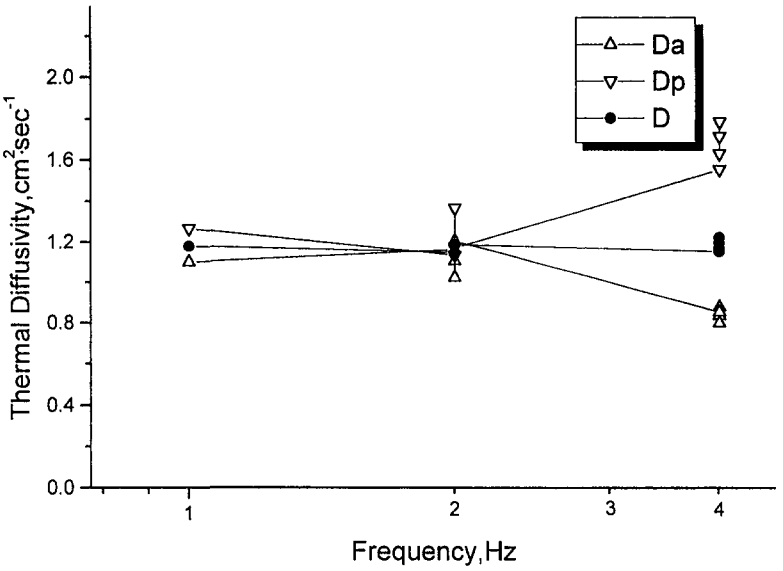

Fig. 5. Thermal diffusivity of 99.99% oxygen free copper.

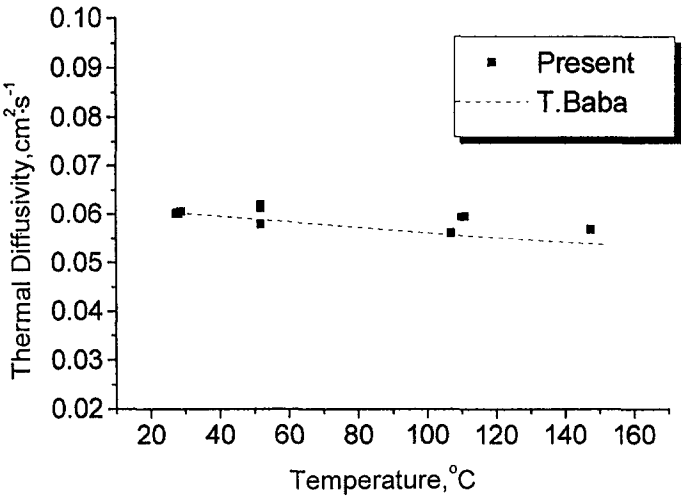

Fig. 6. Thermal diffusivity of a glassy carbon.

thermal diffusivity values in the approximate range 0.05 to 1 $cm^2 \cdot s^{-1}$. All values agree to within 5% or better with recommended values or measured values obtained at national standards laboratories. The system is now being modified in order to undertake measurements in vacuum, thus extending its application to materials of lower thermal diffusivity and also to smaller thicknesses. The variation of D with temperature up to approximately 500°C is also being investigated.

The results for the diamond films are in very good agreement with these measured by the same authors using the traditional technique. It is believed that, in addition to possible experimental errors in the various techniques, some specimens could have been inhomogeneous. For example, in the modified ac calorimeter technique, results of the three laboratories differed by more than the stated experimental error for the method, ranging from over 10 to less than 5%. However, in the overall study, the differences ranged up to $\pm 40\%$ for some of the samples. As a result of these uncertainties, a second round robin has just been concluded on various CVD diamond films and other ceramic and metal samples. The results are being analyzed and will be published shortly.

One of the most interesting observations concerns the apparent divergence between D_a^* and D_p^* as the frequency increases, especially for the case of thin samples of the high-thermal diffusivity metals. This phenomenon does not appear to affect the final value of D. Currently this issue is being studied further both analytically and experimentally.

5. SUMMARY

A modification of the ac calorimetric method for measuring in-plane thermal properties of thin samples has been developed and its performance validated with the use of a variety of materials covering a wide range of thermal diffusivity. Further work is in progress to extend the ranges of thermal diffusivity and temperature for thinner and smaller specimen configurations.

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