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AND THERMAL CONDUCTIVITY OF GRAPHITE
BETWEEN 300° AND 3300°K

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LASER-PULSE METHOD OF DETERMINING THERMAL DIFFUSIVITY
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Abstract

The laser-pulse method is used to determine thermal diffusivity and thermal conductivity of graphite over a continuous temperature range of 300° to 3300°K. A thin-disk specimen is pulsed with a neodymium laser, and the transient temperature rise is detected with a photovoltaic indium antimonide device. The InSb detector, normally used in the low temperature region, was extended to also include measurements at high temperatures.

The method was tested with OFHC copper and Armco iron of various thicknesses at low temperatures; the results of the measured thermal diffusivities agreed within an experimental error of approximately 5% with reported values. At high temperatures, the technique was tested with H 327 graphite. The thermal conductivity of the graphite computed from the measured thermal diffusivity was in good agreement with results from other methods.

1. INTRODUCTION

The High Temperature Gas Cooled Reactor, using graphite as a moderator, is one of the major developments at Gulf General Atomic Incorporated. As the operating power level and the size of the reactor are increased, the thermal conductivity K of the graphite becomes increasingly more important in the calculations of thermal stresses and heat transfer in case of loss of coolant. It is therefore desirable to have a knowledge of K over as wide a temperature range as possible, generally from 300° to over 3300°K. The measurement of K over such a temperature range by steady-state techniques is difficult and time consuming because it usually requires two or more methods with sufficient overlap to produce a

continuous curve. Additionally, each method usually requires a different sample geometry so that cross calibration between samples and methods is necessary.

The experimental technique is greatly simplified by the heat-pulse (flash) method of measuring thermal diffusivity. The advantages of this method are the small sample size required and the possibility of employing this single method over the entire temperature range. The heat-pulse technique was first reported by Parker *et al.*,⁽¹⁾ who used a xenon flash lamp as the source of radiant energy. For measurements at high temperatures, however, the radiant energy from the xenon flash lamp is usually

too low; thus, the flash lamp has been replaced with a laser. Deem and Wood⁽²⁾ were the first to report the use of a laser as a source of radiant energy. A laser is ideally suited for such measurements because its output beam is uniform and well collimated for simple entry into the furnace. In recent years the laser has been applied to the heat-pulse technique by other investigators: Moser and Kruger⁽³⁻⁴⁾ studied the properties of uranium and plutonium compounds; Lagedrost *et al.*,⁽⁵⁾ the properties of PuO_2 ; Gibby,⁽⁶⁾ the properties of $(\text{U}_{0.8}\text{Pu}_{0.2})\text{O}_2$; Bates,⁽⁷⁾ the properties of UO_2 , and Taylor,^(8,9) the properties of graphitic materials. However, none have reported the capability of making measurements from 300° to 3300°K with a single temperature detection system. In the past, two or more techniques have been used to detect the temperature rise of the back surface of the sample: intrinsic thermocouples in the temperature range below 1200°K and lead sulfide and multiplier phototubes in the medium and high temperature ranges. The high sensitivity InSb detector can be used over the entire temperature range, eliminating the need for changing detectors during the measurement. Gibby⁽¹⁰⁾ and Bates⁽¹¹⁾ are among the few investigators who have been using the InSb detector in place of the thermocouple; however, the upper temperature limit of their measurements has been about 2000°K.

2 THEORY

Thermal diffusivity is measured by the heat-pulse method initially developed by Parker *et al.*⁽¹⁾ In this method, a short pulse of radiant energy from the laser is used to irradiate the front surface of a thin disk-shaped specimen positioned in the isothermal zone of a furnace, and the subsequent temperature rise of the rear surface is recorded as a function of time. The thermal diffusivity α is calculated from the half-rise time $\tau_{1/2}$ for the temperature at the back face by the relation

$$\alpha = \psi \frac{\ell^2}{\tau_{1/2}} \quad (1)$$

where ℓ is the specimen thickness and ψ is a dimensionless half-rise time. The constant ψ is equal to 0.139 when the heat loss and finite pulse-time effect are negligible.⁽¹²⁾ Cape and Lehman⁽¹³⁾ have shown that, although radiation effects are decreased by reducing the sample thickness, the finite pulse-time effect is made smaller by increasing the sample thickness. For a given material and pulse duration, there is an optimum sample thickness for which the use of the analysis by Parker *et al.*⁽¹⁾ will result in minimum error. Of the two types of corrections, the use of thin samples to reduce heat losses, but correcting for the finite pulse-time effect, is the simpler approach to use. Larson and Koyama⁽¹²⁾ developed a mathematical model approximating the output of a xenon flash tube and found that the heat pulse function

$$\phi(t) = \frac{t}{t_p} \exp\left(1 - \frac{t}{t_p}\right), \quad t > 0 \quad (2)$$

(where t is time and t_p is peak-pulse time) gave a proper correction to the experimental values, even for high values of $t_p/\tau_{1/2}$. The pulse shape from the Nd laser (Fig. 1) very closely fits the heat-pulse function of Eq. 2, as shown in Fig. 2. Using a peak-pulse time of 150 μsec gave agreement to less than $\pm 5\%$.

3 EXPERIMENTAL

Thermal diffusivity measurements were made with the laser heat-pulse apparatus shown schematically in Fig. 3. The apparatus consists of an Nd laser, a graphite tube furnace, and an InSb detector. The laser used to heat the specimen with a pulse of energy was the Korad Model K2Q system with the Nd glass laser rod operated in the conventional mode without Q-switching at a wavelength of 1.06 μm . The Nd laser gives a shorter pulse width and higher beam intensities than the ruby laser. The laser output was monitored by a photodiode and calorimeter. The output of the photodiode was integrated with a time constant of 20 μsec and was displayed on an oscilloscope, giving the time shape of the heat pulse. A typical pulse is

shown in Fig. 1. Although the laser output could be varied from 5 to 35 joules, it was operated at approximately 20 joules to maintain a reproducible pulse shape. Neutral density filters were used to limit the heat pulse to the sample, so that the change in ambient temperature of the sample was less than approximately 10^{-2} K. The specimen was heated in a resistance-heated graphite tube furnace situated in a removable vacuum enclosure. Several layers of Grafoil served as radiation shields on the ends and around the graphite tube to give a central isothermal zone of approximately 2 in. The sample disks, nominally 1.25 cm diam by 0.1 cm thick, were held in a graphite sample holder and placed at the center of this zone. Windows were installed on the enclosure in line with the furnace tube: quartz on the laser side and calcium fluoride on the detector side of the sample. Another quartz window was located on the side of the furnace to allow the pyrometer controller to focus onto the sample holder for effective automatic control of the ambient sample temperature to $\pm 0.5^\circ\text{K}$. The pyrometer was calibrated at low temperatures with a Pt/Pt10%Rh thermocouple attached to the sample and at high temperatures with a calibrated Micro-Optical pyrometer. The measurements were made in vacuo up to about 1200°K and in 1 atm helium at the higher temperatures. The detector for sensing the temperature rise at the back surface of the sample was an InSb infrared cell made by the American Electronics Laboratories. The detector, with an element of 0.090 in. diam, was operated at 77°K for optimum signal-to-noise ratio and maximum sensitivity. The sensitivity extends from less than 1 to $6\text{-}\mu\text{m}$ wavelength. Although the wavelength of the maximum energy radiation from a blackbody is $9.6\text{ }\mu\text{m}$ at 300°K , there is sufficient radiation at $6\text{ }\mu\text{m}$ to be detected by the InSb cell when coupled with a high-gain, low-noise amplifier. For this detector, the highest $(D^*)^{**}$ is obtained at zero bias,

^{**}The D^* is the signal-to-noise ratio at a given chopping frequency with an amplifier band width of 1 Hz for a photoconductor of 1 sq cm sensitive area when irradiated by 1 W of flux.

however, the responsivity is increased when a negative bias is applied. For our measurements, the bias was held at -10 mV, giving a D^* of approximately 9×10^9 and a responsivity of approximately 10^4 V/W. The thermal radiation from the back surface of the specimen was focused on the detector, although not perfectly, with a concave first surface mirror, as shown in Fig. 3. The output of the detector was connected to a Tektronix 545 oscilloscope with a high-gain Type E differential amplifier.

Calibration of the system for finite pulse-time effects was carried out with specimens of OFHC copper and Armco iron at 300°K , where the pulse-time correction is the greatest. The specimen thicknesses varied from 0.05 to 0.2 cm. These runs were made with a pulse shape as shown in Fig. 1, which is of the type described by Larson and Koyama⁽¹²⁾ with a peak pulse time t_p of 0.15 msec. The calibration results calculated from Eq. 1 are plotted in Fig. 4 in terms of the dimensionless ψ values. The mean of the measured thermal diffusivities for these specimens are compared with reported values⁽¹⁴⁾ in Table 1. The agreement is good, considering a pulse-time correction of greater than 50% was needed for the specimen with a half-rise time shorter than 1.0 msec. For $\tau_{1/2}$ greater than 30 msec, the signal was weak and the effects of heat loss were becoming apparent. A specimen thickness of about 0.1 cm was selected to give an approximate range of half-times of 1 to 30 msec. All calibration values and results on the graphite were corrected for finite pulse time, according to Larson and Koyama.⁽¹²⁾

4. DISCUSSION AND RESULTS

The thermal diffusivity of grade H-327 graphite was determined for temperatures up to approximately 3300°K . This upper limit was imposed because of changes in physical properties of the sample, such as expansion, sublimation, etc. Thermal conductivity K was computed from the measured diffusivity using the relation

$$K = \alpha \rho C_p, \quad (3)$$

where ρ is the density and C_p is the heat capacity. The density for H-327 graphite of $\rho = 1.78 \times 10^3 \text{ kg/m}^3$ was determined from the weight and dimensions of the material measured at room temperature. The C_p of graphite to 3300°K, shown in Fig. 5, was from two sources. Up to 1200°K, C_p in J/(kg)(°K) was obtained from the relation

$$C_p = (-0.103 + 1.165 \times 10^{-3} T - 8.64 \times 10^{-7} T^2 + 2.32 \times 10^{-10} T^3) (4.184 \times 10^3) \quad (4)$$

reported by Rossini *et al.*⁽¹⁵⁾ and successfully used in similar calculations by Baker.⁽¹⁶⁾ Above 1200°K, the values recorded in Ref. 17 for commercial graphite were used after extrapolation to 3300°K.

The derived thermal conductivity of H-327 graphite in a direction across grain or perpendicular to the extrusion direction is shown in Fig. 6. The values ranged from over 130 W/(m)(°K) at 300°K to about 22 W/(m)(°K) at 3300°K.

The accuracy of the laser-pulse method was established by comparing thermal diffusivity measurements as a function of temperature with values reported by Shanks *et al.*⁽¹⁸⁾ as shown in Fig. 7. The measured and reported values agree to within $\pm 5\%$. The accuracy of the laser heat-pulse method was further established by comparing the results with those from independent measurements on separate samples. As shown in Fig. 6, the agreement of the results from the various methods is good. The applied pulse-time corrections were approximately 20% near room temperature and approximately 3% at 1000°K, with a gradual decrease to relatively small values at higher temperature. The overall estimated error of the laser-pulse method is $\pm 5\%$. The independent methods, which have been used routinely for the past few years, consist of the xenon flash^(1,16) for below 1200°K and the Longmire⁽¹⁹⁾ steady-state technique for the higher temperatures. In the xenon flash method, an intrinsic Chromel-Alumel thermocouple was used to detect the temperature rise at the back face of the specimen. The

Longmire method consists of reading the steady-state temperatures, by optical pyrometry, of the centers of the narrow and wide faces of the electrically heated rectangular specimen. Radiation of energy from the surfaces of the specimen causes a difference in temperature between the narrow and wide faces, and this difference is related to the thermal conductivity

The method of using an intrinsic thermocouple to detect the temperature rise at the specimen back face is limited to temperatures below 1200°K, and with this method there are surface contact problems and noise. The surface contact problems are observed particularly during the measurement of graphite having large grains; in which case, the reading of the temperature rise is highly dependent on the location of the thermocouple points. This situation is not observed with photo-detectors because they are able to integrate the temperature over a larger and a more representative area; for this reason, the precision of the results for H-327 graphite in Fig. 6 from the laser-pulse method are much better than those from the xenon flash technique.

An inert gas of helium or argon is needed at temperatures above approximately 2700°K to prevent vaporization of the graphite specimen. In the Longmire method,⁽¹⁹⁾ the gas must be highly purified to prevent the reaction of trace impurities at the surface of the specimen. This situation is not encountered in the laser method because the sample is surrounded by the hot graphite heater tube, which prevents the impurities from reaching the specimen by furnishing a strong gettering action.

The bias voltage for the InSb detector was at first applied by the circuitry described by Slawek⁽²⁰⁾ who used a large current-limiting resistor that resulted in a near zero signal when a sample temperature of about 2000°K was reached. The high internal resistance of the detector near room temperature decreases to a very low value when the temperature is above about 1800°; therefore, the resistance in series with the detector must be reduced to

a low value when the sample temperature is above approximately 1800°K to obtain a readable signal. For our particular detector, at 3300°K a resistance of 50 Ω was used.

To increase the efficiency in sensing the transient temperature rise, improvements of the InSb detection system are planned. The present detector, of vertical configuration, will be replaced with a horizontal type to eliminate the need for a right-angle mirror behind the sample. The radiation emitted from the back face of the sample will be focused on the InSb element of 0.090 in. diam by a coated silicon lens with high transmittance in the near infrared. Installation of a narrow band interference filter at a wavelength of about 4 μ m in front of the detector will limit the total energy passing through the detection system at high temperatures. A significant gain in sensitivity is expected with these changes.⁽²¹⁾

5. SUMMARY

The thermal conductivity of H-327 graphite, perpendicular to the extrusion direction, in the temperature range of 300° to 3300°K by the laser-pulse method is in good agreement with values measured by other techniques. The conductivity of H-327 graphite ranged from 134 W/(m)(°K) at 300°K to 22 W/(m)(°K) at 3300°K. With the laser-pulse technique, a single method and a single temperature detection system can be used for the measurements on a single sample in the region of 300° to 3300°K. This eliminates the need for two methods, two different specimens, and the necessary cross calibration of methods.

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TABLE 1
CALIBRATION RESULTS FOR THERMAL DIFFUSIVITY
MEASUREMENTS

	OFHC copper (sq cm/sec)	Armco iron (sq cm/sec)
Measured diffusivity	1 135	0 208
Standard deviation	0 029	0 004
Value from Ref 14	1 15	0 204

Fig 1 Pulse shape of the neodymium laser
(sweep speed is 0 10 msec/cm)

Fig 2 Detector response to laser pulse Dashed line
represents functional approximation to the
pulse shape

Fig 3 Schematic diagram of the thermal diffusivity apparatus

Fig. 4 Dimensionless half-rise time ψ as a function of the half-rise time $\tau_{1/2}$. Pulse time $\tau_p = 0.15$ msec

Fig. 5. Specific heat of graphite

Fig. 6. Thermal conductivity of H-327 graphite. Comparison of results from the laser-pulse InSb detector method with those from the xenon flash-thermocouple detector and the Longmire method

Fig. 7. Thermal diffusivity of Armco iron