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Thermal Diffusivity Measurements of Thermographite

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This paper presents results of measurements of a graphite proposed to serve as a thermophysical property reference or standard reference material. The reported measurements contribute to a program launched in 1999 by Anter Corp. with the objective to provide a replacement for the NIST thermal property reference material RM AXM-5Q graphite whose supplies were being exhausted. Measurements of the thermal diffusivity performed on five specimens taken from different positions within a large graphite block between room temperature and 1300 K were in good mutual agreement. Measurements of NIST reference AXM-5Q graphite sample supplied to minimize effects of different contributors to a common base were also in good agreement, both with the NBS reference function established by Hust in 1984 and contributions to the NBS project from the Vinča Institute of Nuclear Sciences carried out in 1979. The influence of different data reduction techniques on the measured thermal diffusivity values is illustrated and discussed.

KEY WORDS: AXM-5Q graphite; standard reference materials; thermal diffusivity; thermographite; thermophysical property SRMs.

1. INTRODUCTION

In the spring of 1999, P. S. Gaal,[3] Chairman of the 24th International Thermal Conductivity Conference (ITCC, Pittsburgh, Pennsylvania, 1997) invited selected thermophysical properties laboratories to participate in cooperative measurements aimed at renewal, replacement, or supplementing existing transport property reference materials (SRMs) with new materials, in particular, a new type of graphite [1]. This action was in line with conclusions of the workshop on thermophysical property reference

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materials at the 24th ITCC, which surveyed the current status of RMs, their property and range coverage, stocks of certified RMs and plans for future provision of new materials. Discussion revealed a pessimistic outlook worldwide: stocks of available SRMs have been generally depleted or were nearing exhaustion, and new national or international projects for their replacement or supplementing were neither in existence nor known to be planned.

Our laboratory joined in, like it did in most similar international co-operative measurements organized since the mid-1970s. Moreover, it took part in the measurements of AXM-5Q graphite within the NBS program of establishing it as a thermophysical property RM [2], whose replacement was intended in this new project. Results of our contribution were published in Ref. 3.

In the present round-robin project, measurements had to be carried out on one sample of the NIST traceable AXM-5Q graphite, and five samples of the new candidate material designated HM-1. A few years later, HM-1 was identified to be Thermographite [4]. Interesting and stimulating results obtained for this SRM candidate, supported by good agreement between our present values for AXM-5Q graphite and the ones reported in Ref. 3, suggested their early publication, as was done with the results for AXM-5Q graphite in 1980 [3].

2. EXPERIMENTAL

2.1. Apparatus

Our flash diffusivity apparatus is essentially the same as was described in Ref. 5, only at the time of reported measurements its upper operating temperature was restricted to 1350 K.

2.2. Samples

The reference AXM-5Q graphite used in the tests came from a rod 12.7 mm in diameter designated NIST RM 8425, whose location in the original NIST block of AXM-5Q has been identified; its room temperature density was 1.722 $g \cdot cm^{-3}$ and its electrical resistivity was 13.95 $\mu\Omega \cdot m$ [6]. The sample used in our measurements was 2 mm thick and 10 mm in diameter.

According to Program organizer [4], the original block of Thermographite from which samples were prepared was about $200 \times 200 \times 500$ mm in size, and test samples were randomly taken from different locations within it. Axes of all discs were parallel to its 500 mm dimension.

Anisotropy of Thermographite in other dimensions was not indicated. The samples we measured were designated 13 A2; 18 A2; 24 A2; 55 A2, and 70 A2. Their diameter was 10 mm and their thickness varied between 2.05 and 2.06 mm.

2.3. Measurement Procedure

The samples were mounted in a graphite holder in an arrangement described in Ref. 5. Transients below 550 K were detected with an InSb photovoltaic detector with built-in preamplifier (Judson EG&G), above this temperature a PbS photoresistor (Philips) served the same purpose. Measurements were carried out at eleven to twelve reference temperatures between room temperature and about 1300 K. At each reference temperature at least three measurements were performed, and averaged values of these measurements are presented in Figs. 1 to 3, as well as in data tables supplied to the Program organizer. The largest difference between averaged data points never exceeded $\pm 1\%$ limits. Obtained thermal diffusivity results have been corrected for thermal expansion. The sample reference temperature was measured with an Inconel sheathed K-type thermocouple (sheath diameter of 1 mm) tightly fitting in a hole axially positioned in the sample holder body, with the thermocouple junction being close to the sample perimeter. After thermal diffusivity measurements were completed, the

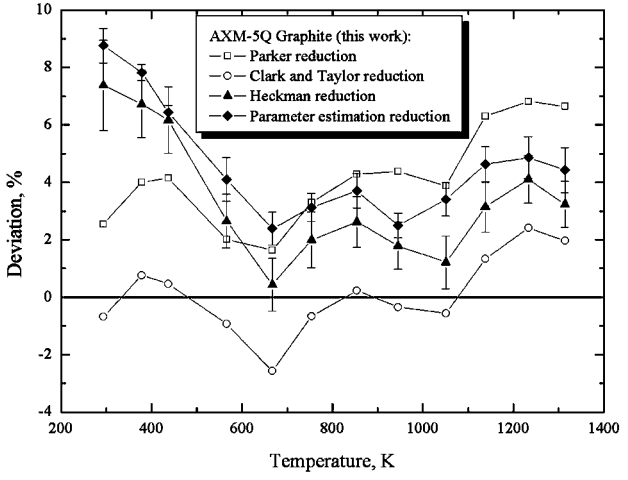

Fig. 1. Effect of different data reduction techniques applied on Graphite AXM-5Q thermal diffusivity measurements in comparison to reference values [2].

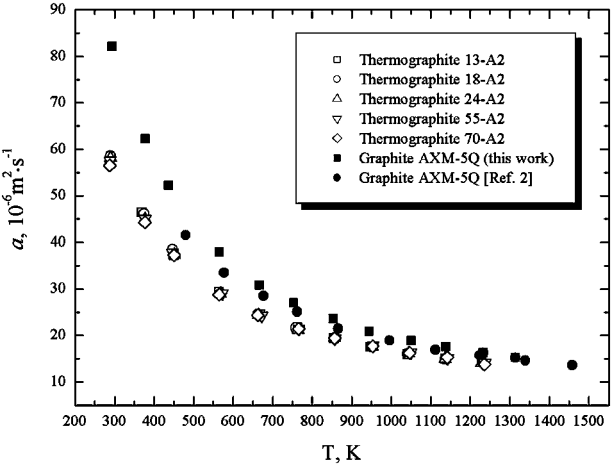

Fig. 2. Measured thermal diffusivities on Thermographite and Graphite AXM-5Q.

sample was replaced with a graphite dummy sample having same dimensions and similar density, at whose center, in a 1 mm deep hole of 0.9 mm diameter a miniature K-type thermocouple within twin-bore alumina tube with 0.9 mm outside diameter was cemented. Then the whole temperature range was traversed in approximately 50 K steps, recording under stationary temperature conditions the readings of both thermocouples, in the

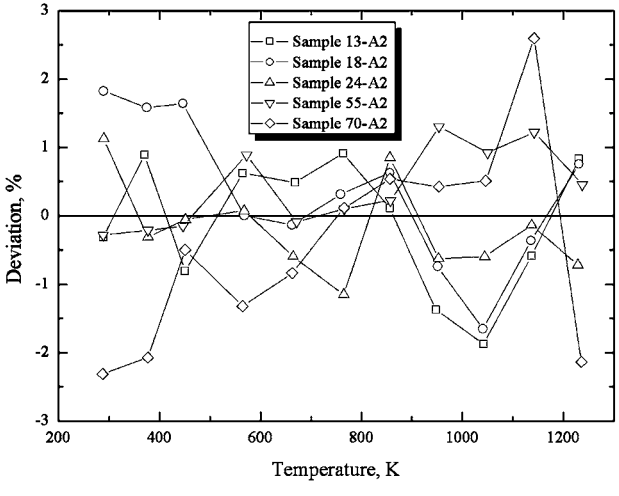

Fig. 3. Thermal diffusivity deviations from the mean fit of five Thermographite samples.

sample holder and at the dummy sample center. The relation between these enabled defining a true reference temperature. Both thermocouples were calibrated against ITS-90.

2.4. Data Reduction

The Program organizer requested application of as many reduction procedures as feasible, and specifically that the Clark and Taylor [7] method should be one of them. We applied four: Parker et al. [8], Clark and Taylor [7], Heckman [9], and the parameter estimation method (Miloševič et al. [10]). Since the last reference might not be easily accessible, the essence of this procedure is given in the Appendix.

In presenting results of our laboratory in Figs. 1 to 3 generally those obtained by parameter estimation are given, as this procedure takes advantage of the whole transient response, providing information not only on thermal diffusivity but also on some other parameters such as the Biot number and laser pulse duration. This increases exactness of the procedure and reliability of data reduction. As a result, the uncertainty of a single thermal diffusivity measurement is estimated to be between 1 and 2%.

2.5. Experimental Results

The first set of experiments was devoted to AXM-5Q, and the other five to Thermographite. Figure 1 illustrates the effect of different data reduction techniques, presented as deviations from the thermal diffusivity function of AXM-5Q graphite computed from the reference thermal conductivity, and specific heat and density functions established within the NBS study (Hust, 1983 [2]). Figure 2 presents in a joint diagram thermal diffusivity data of AXM-5Q graphite and Thermographite, including our data for AXM-5Q graphite [3], which were our contribution to the NBS study [2], and were obtained with the Clark and Taylor reduction technique. All other data in the diagram resulted from parameter estimation. The new values ranged from 288 to 1237 K, and the old ones [3] between 480 and 1713 K. It should be kept in mind that although the studies were carried out on the same material, AXM-5Q graphite, present and old samples had different basic physical properties, such as density and electrical resistivity. Those of the new sample were $1.722\,g\cdot cm^{-3}$ and $13.95\,\mu\Omega\cdot m$, respectively, while for the one whose measurements were reported in 1980, they were $1.755\,g\cdot cm^{-3}$ and $14.59\,\mu\Omega\cdot m$, respectively. In Fig. 3 are given variations of the thermal diffusivity of five Thermographite samples presented as deviations from the corresponding mean fit. The numerical data of present measurements on Thermographite and graphite

Table I. Thermal Diffusivity Values of Thermographite, Graphite AXM-5Q from This Work and from Ref. 2

Thermographite[a]		Graphite AXM-5Q (this work)		Graphite AXM-5Q (from Ref. 2)	
T (K)	a (10^{-6} m$^2 \cdot$ s^{-1})	T (K)	a (10^{-6} m$^2 \cdot$ s^{-1})	T (K)	a (10^{-6} m$^2 \cdot$ s^{-1})
288.7	57.7	294	82.1	480	41.5
375.4	45.4	378.4	62.3	577	33.5
449.1	37.6	437.2	52.2	677	28.5
567.7	29.0	565.9	37.9	762	25.1
665.9	24.4	667.4	30.8	866	21.5
763.7	21.4	753.9	27.0	996	18.9
856.7	19.4	853.8	23.6	1112	16.9
951.6	17.6	945.2	20.9	1224	15.7
1044.5	16.1	1050.9	18.8	1233	16.2
1138.6	15.0	1138.3	17.5	1314	15.2
1232.4	14.1	1233.2	16.2	1339	14.6
		1313.9	15.2	1458	13.6

[a] Values averaged from the data on five different samples.

AXM-5Q and previous measurements on graphite AXM-5Q are given in Table I. Each value for a single temperature point represents the mean of three of four measurements, while the values of Thermographite are averaged from the data on five different Thermographite samples.

2.6. Discussion of Results

In the late 1970s NBS undertook a comprehensive study of different high-density graphite materials looking for a possible transport property SRM, and from a range of materials AXM-5Q graphite was accepted for NBS thermal conductivity and electrical resistivity RM. This study reported by Hust [2] pointed out deficiencies of the AXM-5Q graphite with respect to variation of its density and electrical resistivity throughout the block, but showed that it was the best material among the candidates studied, and that, within specified uncertainty limits, its thermal conductivity could be related to two other physical properties, density and electrical resistivity. So when the density and electrical resistivity of a particular AXM-5Q sample are known, its recommended thermal conductivity can be computed, leading with the aid of established specific heat and thermal expansion functions to thermal diffusivity. From relations given in Ref. 2, thermal properties of the particular RM 8425 used as a reference in the present study were found, showing that the thermal diffusivity of RM 8425 was 3.3% higher than that of the AXM-5Q measured in 1980.

Consequences of application of various reduction techniques are demonstrated in Fig. 1 using AXM-5Q graphite as an example. Four reduction techniques give results, which fall within a band widest at room temperature (about 10%) whose width is reduced to about 5% over most of the higher temperature region. As can be seen, most deviations are positive with respect to the reference function computed from the recommended equation [2] (full line in Fig. 1). Data reduction according to Parker et al. [8] results in values, which vary between 1 and 4.3% above this zero function. The values using the Clark and Taylor reduction method [7] follow those of Parker et al. lying about 4% lower; over most of their range, their deviation is negative. Except for the initial part below 700 K, the Heckman [9] and parameter estimation [10] reduction values fall between the former two, differing between themselves generally between 1 and 1.5%.

The Parker analysis [8], which is based on ideal conditions, i.e., instantaneous pulse, uniform heating, and no heat losses, gives results with largest calculated uncertainties. The procedure of Clark and Taylor [7] takes into account heat losses resulting in lower thermal diffusivity values, but with respect to the former measurement, uncertainties are lower. The Heckman analysis [9], which accounts for both heat losses and finite pulse duration, leads to even more accurate results. Its values are higher than these of the Clark and Taylor reduction, as the effect of finite pulse duration on calculated thermal diffusivity values is opposite to that of heat losses. Finally, the parameter estimation procedure [10] includes the same effects as the Heckman analysis, but the thermal diffusivity computation takes into account the influence of the whole set of experimental data, resulting consequently in the lowest calculated uncertainties. Its deficiency lies in sensitivity to possible deformations of transient response caused by non-uniformity of distribution of the laser pulse energy, which may influence the resulting thermal diffusivity. In Fig. 1 are indicated limits of maximum uncertainties for values obtained by Heckman and parameter estimation procedures.

Figure 2 shows obtained experimental data of present and old measurements [3] of AXM-5Q graphite, and those of Thermographite. Taking into account the difference between thermal diffusivities of the two AXM-5Q samples due to their different densities and electrical resistivities, recent and old results are in good agreement over the whole range of their overlap. Naturally, those from Ref. 2 had to be compared with the new values from Clark and Taylor reduction, as the former were obtained using this technique.

Comparing the general character of thermal diffusivity functions of the two graphites, the AXM-5Q has a steeper change in the range of lower 500 K, which is generally desirable for calibrating an apparatus against a

SRM. However, since above about 800 K both graphites follow a similar tendency this advantage is not very significant. In the range to 1300 K more suitable thermal conductivity/thermal diffusivity SRMs are available, for example, electrolytic iron.

Figure 3 shows variations of thermal diffusivity values of five Thermographite samples relative to an interpolated mean function. Virtually all of them fall within $\pm 2\%$ limits, and their scatter does not indicate any systematic trend. These limits are in agreement with the results of measurements at the Anter Laboratory performed at 573 K [4] in checking the homogeneity of the block.

3. CONCLUSIONS

Results of reported measurements indicate accurate transport properties of investigated Thermographite samples, suggesting a benefit from potential use of this material as a wide temperature range thermal property RM or SRM. If results of the whole program should be similar, it is likely that the life of Thermographite as a thermophysical property RM might be longer than initially expected, which was a four to six-year period [1]. Keeping in mind the important relation between thermal transport properties and electrical resistivity and density discussed in the NBS study of AXM-5Q [2], other than density, which has been found to vary within 0.1% throughout the block [4], possible variations of electrical resistivity should be also systematically examined.

This work has again opened the question of the path of reaching recommended transport property functions of solids, which has been during the past twenty years frequently discussed among experimenters in this area. The classical approach was starting from thermal conductivity, and ending with thermal diffusivity, in the same way as was done in the study of AXM-5Q [2]. However, the thermal diffusivity can be presently measured much faster than thermal conductivity, with more ease and better accuracy, from very low to very high temperatures. Independent of the level of temperature measurement, the resulting thermal diffusivity data apply to very narrow temperature limits, particularly in the flash method, while thermal conductivity measurements with an increase of temperature level nearly inevitably involve averaging of obtained property over an ever increasing temperature range. Moreover, direct measurements of the thermal conductivity at high temperatures are also scarcely conducted anywhere, so if the classical approach is used, possible actions toward establishing new SRMs will be impeded by the procedure.

APPENDIX: DATA REDUCTION PROCEDURE BASED ON PARAMETER ESTIMATION

The parameter estimation used in foregoing measurements enables simultaneous estimation of more than one parameter from the same temperature response. It is described in detail in Ref. 10, and the next few paragraphs contain some basic details of applied estimation procedure.

Sensitivity coefficients give information about estimation possibilities. Their reduced forms are compared to indicate which parameters might be simultaneously or separately estimated with the desired accuracy. The criterion is that these coefficients should be as much as possible linearly independent, and have high and mutually comparable values. In the theoretical model that corresponds to the laser flash method, sensitivity coefficients are very complex functions of parameters. In such a case, their values must be numerically calculated using an approximate formula.

The minimization of the difference between theoretical and measured values is performed using the *maximum a posteriori* (MAP) criteria (Beck and Arnold [11]). The Gauss iterative equation applied in this work is

$$\mathbf{b}^{(k+1)} = \mathbf{b}^{(k)} + [\mathbf{X}^{T(k)}\mathbf{W}\mathbf{X}^{(k)} + \mathbf{U}]^{-1} \cdot \{\mathbf{X}^{T(k)}\mathbf{W}[\mathbf{Y} - \mathbf{T}^{(k)}(\mathbf{b}^{(k)})] + \mathbf{U}[\boldsymbol{\mu} - \mathbf{b}^{(k)}]\} \tag{1}$$

where $\mathbf{T}$ is the matrix of calculated values from the model $[n \times 1]$, $\mathbf{Y}$ is the matrix of measured values $[n \times 1]$, $\mathbf{b}$ is the matrix of parameters for estimation $[p \times 1]$, μ is the matrix with *a priori* parametric values $[p \times 1]$, $\mathbf{W}$ is the variance-covariance matrix of measured values $[n \times n]$, and $\mathbf{U}$ is the variance-covariance matrix of parameters *a priori* $[p \times p]$. Diagonal elements of the matrix $\mathbf{W}$ are the function of variances of each measured value, σ, since other elements represent a correlation degree among measured values. If there is no correlation between the measured values, which is the case in the laser flash method, the characteristic diagonal element of the variance-covariance matrix $\mathbf{W}$ is $(W)_{jj} = \sigma_j^{-2}$, while those off-diagonal elements are equal to zero. The iterative procedure in Eq. (1) should be stopped when the condition of convergence is satisfied.

As the criterion of estimation accuracy, standard deviations of parameters estimated by Eq. (1) are found from the *a posteriori* variance-covariance matrix of the final iteration,

$$\mathbf{S}^{\text{final}} = [\mathbf{X}^{T(\text{final})}\mathbf{W}\mathbf{X}^{(\text{final})} + \mathbf{U}]^{-1} \tag{2}$$

whose diagonal elements represent the variances of the estimated parameters.

In the laser flash method the theoretical model is represented by the temperature response of the rear sample side (Watt [12], Yamane et al. [13]):

$$T(\tau) = \frac{8T_m}{a\tau_p} \sum_{n=1}^{+\infty} \frac{\beta_n(\beta_n \cos \beta_n + Bi_L \sin \beta_n)}{\beta_n^2 + Bi_L^2 + 2Bi_L} \times \sum_{i=1}^{+\infty} \frac{Bi_R J_1(Z_i)}{Z_i(Z_i^2 + Bi_R^2)(Z_i^2/R^2 + \beta_n^2/L^2)\, J_0(Z_i)} \times \exp\left[-\left(\frac{Z_i^2}{R^2} + \frac{\beta_n^2}{L^2}\right) a\tau \right] \left\{ \exp\left[\left(\frac{Z_i^2}{R^2} + \frac{\beta_n^2}{L^2}\right) a\tau_p \right] - 1 \right\} \quad (4)$$

where τ is time ($\tau > \tau_p$), $Bi_L = h_L L/\lambda$ and $Bi_R = h_R R/\lambda$ are Biot numbers for two base- and one lateral sample sides, respectively, h_L and h_R are radiative heat transfer coefficients (axial and lateral heat losses), L is the sample thickness, R is the sample radius, λ is the thermal conductivity, a is the thermal diffusivity, and $f(\tau, \tau_p)$ is a dimensionless function that describes the laser pulse as a function of time. As experiments are usually performed in vacuum, convective heat losses from the sample are neglected and the only important mode of heat exchange is radiative heat transfer. T_m is equal to $Q/(L\rho)$, and represents the maximum temperature rise when $h_L = h_R = 0$. Q is the absorbed laser energy per square meter, c is the specific heat of the sample material, and ρ is its density. Coefficients β_n and Z_i ($n, i = 1, 2, 3,\ldots$) are positive roots of corresponding transcendental equations (Watt [12]).

The estimation procedure was performed in three subsequent steps, as explained in Ref. 10: The first step involved the estimation of Bi from the time just before its maximum to a certain value along its descent. The second referred to estimating the pulse duration, τ_p, in the range of the signal rise, and finally, the third step presented the estimation of the thermal diffusivity, a, simultaneously with T_m, in the range from about 10% of the maximum of the response, to a certain time after the maximum has been reached.

In providing information about thermal diffusivity and parameters such as the Biot number and laser pulse duration, this procedure takes advantage of the whole transient response, which increases the reliability and exactness of data reduction.

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