FOREWORD

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This report covers work conducted from December 1962 to February 1964.

ABSTRACT

The ratio of thermal conductivities (k_z/k_r) and of thermal conductivities to total emissivities (k_z/ε and k_r/ε) have been measured for anisotropic ZT-type graphite in the temperature range 1000-2000°C. The emissivity of a sample changes even if it is stored at room temperature for a long time. To obtain the total emissivity of a material, the ratio of specific heat to total emissivity is determined for tantalum, tungsten, molybdenum, and niobium in the temperature range 1000-2000°C. In all cases, it is found that C_p/ε is a constant, independent of temperature. This permits an easy and accurate determination of the total emissivity of any material.

This technical documentary report has been reviewed and is approved.

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LIST OF SYMBOLS

a	radius of specimen (cm).
A	area of sample at temperature T, cm^2.
A_o	area of sample at room temperature.
α, β	first and second coefficients of linear thermal expansion
C_p	specific heat, cal/g/°K.
k_r	thermal conductivity in r direction (cal/cm-sec-°K).
k_z	thermal conductivity in z direction (cal/cm-sec-°K).
L	half height of specimen (cm).
m	mass of sample in gr.
r	independent variable for radius in cylindrical coordinates.
T	dependent variable for temperature (°K).
T'	T - 300
T_a	temperature T(a,L)(°K).
T_o	temperature T(0,L)(°K).
T_s	constant surface temperature (°K).
ΔT	temperature difference T(a,L) - T(0,L)(°K).
w	$\sqrt{k_z/k_r}$.
z	independent variable for distance in cylindrical coordinates.
ε	total emissivity.
σ	Stefan-Boltzmann radiation constant.

INTRODUCTION

A new method to determine the thermal conductivity of solid materials at high temperatures had been developed earlier in this laboratory.[1,2] Later, this method was applied to anisotropic solids.[3]

The advantages of the method are that very small samples (discs 1/4" diameter and 1/32" high) can be used, the samples are heated in vacuum, and the only connection to them are three tungsten points on which the samples rest; thus, the danger of contamination is eliminated and no instrumentation has to be connected to the sample. The disadvantages of the method are that it can be used only above 900°C, and that the total emissivity of the material has to be known to determine the thermal conductivity.

In the present paper, further measurements on ZT-type graphite are reported and the method developed to measure the total emissivity[4] applied to the refractory metals tantalum, tungsten, molybdenum, and niobium. Experimental and mathematical procedures are covered in detail in the references.

A. Thermal Conductivity Measurements

1. Experimental Procedure, Materials.

When a sample is heated by high-frequency induction in vacuum, the temperature distribution is on the top and side surfaces respectively,

$$T(r,L) = T_o + T\left(\frac{r}{a}\right)^2 \qquad (1)$$

$$T(a,z) = T_s \qquad (2)$$

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from which we obtain

$$k_z = \frac{\sigma \varepsilon T_o^4}{\frac{4\Delta T}{aw} \cdot \Psi_o} \tag{3}$$

Using $w = \sqrt{k_z/k_r}$, Equation 3 yields

$$\frac{\Delta T}{a} \Psi_o = \sigma \varepsilon T_o^4 / 4 \sqrt{k_r k_z} \tag{4}$$

All quantities in Equation 4 are known or measurable experimentally except the thermal conductivities k_r and k_z. Two equations of the form of Equation 4 are sufficient to solve for k_z and k_r; such equations are obtained by taking experimental data at a temperature T_o for two different specimens of the same material with different L/a (preferentially same a). The right side of Equation 4 is the same for both specimens; thus if the left side is plotted against w for each specimen, the point of intersection of the two curves determines w ($= \sqrt{k_z/k_r}$) and the ordinate the value of the quantity $\sigma \varepsilon T_o^4 / 4 \sqrt{k_r k_z}$. Values of the function Ψ_o are identical with the value of the constant K_o calculated earlier[1] if the abscissa is changed from L/a to the variable L/aw.

The molded (z axis parallel to pressing direction) graphite, ZT-type, was obtained from the National Carbon Company. Its properties, as determined by the company, are as follows:

Specimen	Density (g/cm^3)	Anisotropy ratio of electrical resistivity (z direction over r direction) at room temperature	Dimensions cm	
			2L	2a
G-3A	1.980	2.50	1.126	2.537
G-7	1.978	2.50	0.287	2.539
G-5	2.000	2.86	0.622	2.537
G-9	2.000	2.86	0.289	2.539

2. Experimental Results.

First, the earlier results[3] on the ZT-type graphite were recalculated. In Reference 3, Equation 1 was evaluated by plotting the log $[T(r,L)-T_o]$ versus log r/a and passing a line of slope 2 through the points. This way ΔT was determined. This method, however, gives too large an emphasis on T_o, and therefore, the method used in [1] was applied where T_o and ΔT were determined using least square calculation with $(r/a)^2$ the independent and T(r,L) the dependent variable. The recalculated data are shown in Table 1. The difference between the two methods of evaluation is not very large; in the present one the ratio k_z/k_r does not vary between 1250 - 1650°K. As one can see from Table 1, the ratio k_z/k_r is independent of the total emissivity whereas to obtain them separately, the total emissivity has to be known. To check on the influence of the emissivity and also on the possible variation in properties of the various specimens, the thermal conductivities were remeasured in August of 1963 on the same samples on which the measurements had been carried out earlier [3]. Then the flat surfaces of the samples were repolished and again the thermal conductivities determined at one single temperature of 1250°K. Table 2 contains the data together with the recalculated data from May, 1962. First of all, the samples used are almost identical because the ratio of k_z/k_r is the same. However, looking at the value of k_r/ε we can see that last year's determination and this year's determination after repolishing are the same, but this year, before repolishing, the value of k_r/ε is small, indicating a high value for ε. This shows that the emissivity of our graphite sample which was polished in May of 1962 changed drastically just by being kept in a box at room temperature. Repolishing apparently returned the emissivity to the

previous value. This indicates that the emissivity of the sample has to be determined when thermal conductivity measurements are taken.

B. Emissivity Measurements

To determine thermal conductivity by the above-mentioned method, the total emissivity of the material is required.

Checking the literature, it was found that the total emissivity is not easy to come by, and the various values quoted for the same material vary by a factor of 2, thus a method had to be devised to obtain the total emissivity more accurately and easily than had been done heretofore.

1. Experimental Procedure.

If a sample is heated in vacuum to a certain temperature and then suddenly allowed to cool, and if the temperature of the surroundings is much lower than the temperature of the sample, then

$$m \cdot C_p \frac{dT}{d\Theta} = \sigma \varepsilon A T^4 \tag{5}$$

from which, by rearranging

$$\frac{C_p}{\varepsilon} = \frac{3\sigma A}{m} \cdot \frac{d\Theta}{d(1/T^3)} \tag{6}$$

or

$$\frac{C_p}{\varepsilon(1 + 2\alpha T' + 2\beta T'^2)} = \frac{3\sigma A_o}{m} \cdot \frac{d\Theta}{d(1/T^3)} \tag{7}$$

The relationship between time and temperature must be of the form

$$e + b\Theta = \frac{1}{T^3} + c\left(\frac{1}{T^3}\right)^2 + d\left(\frac{1}{T^3}\right)^3 + \cdots \tag{8}$$

The time must appear in the first power because replacing Θ by $(\Theta + \Theta')$ should only move the curve along the time axis parallel to itself.

The equipment is the same as that used for the thermal conductivity measurements. The cooling rate is followed by a Radiation Electronics Corporation Thermodot TD-1. The Thermodot is calibrated with a Leeds and Northrup disappearing filament optical pyrometer.

2. Experimental Results.

The properties of all samples investigated are given in Table 3. They were all obtained from the Fansteel Metallurgical Corporation.

To check the method, tantalum samples of various sizes were investigated first. The first runs made on the three tantalum samples which can be described as "as received." The data showed that the constants c and d in Equation 8 were equal to zero as a straight line between Θ and $1/T^3$ was obtained (Table 4). Thus,

$$\frac{d1/T^3}{d\Theta} = b$$

a constant, and

$$\frac{C_p}{\epsilon'} = \frac{C_p}{\epsilon(1 + 2\alpha T' + 2\beta T'^2)} = \text{constant.}$$

To get a uniform "equilibrium" surface on these tantalum samples, they and all the other samples were heated for 1/2 hour to 2350°K, also. The cooling curves were taken and the results are shown in Table 5. In the case of the tantalum samples, the treatment at 2350°K gave a uniform surface because the ratio of C_p/ϵ is the same for the three samples.

In the case of the tungsten sample, our data agrees with Rudkin et al.[5] who had $C_p/\epsilon = .124$ between 1600 - 2400°K. Their material must have been less pure than ours because as the impurities concentration increases the emissivity will also increase and thus C_p/ϵ will decrease. Table 5 shows that the

standard deviation for the molybdenum and niobium samples is larger than for the tantalum and tungsten samples. Checking the data further, it is found that the niobium and molybdenum points do not fall randomly around the straight line but indicate that the constant c in Equation 8 is not zero but positive. The present degree of accuracy of the data does not permit us to determine the constant c with any reliability.

3. Discussion.

It has been shown that the relation between C_p and ε is simple and can be determined easily, thus it is possible to determine emissivities much more accurately. The value of C_p can be determined with high accuracy (4 - 5%) in the temperature range 1000 - 3000°C[6] and thus permit the determination of the emissivity of the material. It is also important to note that C_p can be estimated easily, and thus emissivity determined by measurement of C_p/ε and estimation of C_p.

TABLE 1

Thermal Conductivity of ZT-Type Graphite

Recalculation of Previous Data

Specimen	To °K	ΔT °K	k_r/ε	k_z/ε	k_z/k_r	Gray body assumption k_r	Gray body assumption k_z
G-5	1254	12	.426	.096	.225	.328	.0740
G-9	1254	22.5					
G-5	1386	19	.410	.088	.216	.314	.0674
G-9	1379.5	34.2					
G-5	1644	46.9	.253	.060	.235	.192	.0454
G-9		86.4					
G-5	2173	168.2	.199	.074	.372	.147	.0545
G-9		353.8					

Units of k_r/ε, k_z/ε, k_r and k_z in cal/cm-sec-°K.

TABLE 2

Thermal Conductivity of ZT-Type Graphite

Specimen	May 1962					August 1963-Before Repolishing					September 1963-After Repolishing				
	To °K	ΔT°K	k_r/ε	k_z/ε	k_z/k_r	To °K	ΔT°K	k_r/ε	k_z/ε	k_z/k_r	To°K	ΔT°K	k_r/ε	k_z/ε	k_z/k_r
G-3A						1247.5	14.5	.285	.067	.235	1250	10.5	.410	.088	.216
G-7						1244.3	32.4				1250	23			
G-3A						1247.5	14.5	.285	.067	.235	1250	10.5	.427	.082	.193
G-9						1246.8	32.2				1249	22			
G-5						1253.6	18	.291	.062	.212	1254	13	.412	.080	.195
G-7						1244.3	32.4				1250	23			
G-5	1254	12	.426	.096	.225	1253.6	18	.291	.063	.216	1254	13	.423	.075	.180
G-9	1254	22.5				1246.8	32.2				1249	22			

Units of k_r/ε, k_z/ε, k_r and k_z in cal/cm-sec-°K.

TABLE 3

Dimensions and Weights of the Samples

TANTALUM

Sample 1

length = 4.0350 in.

diameter = 0.5000 in.

A_o = 6.7339 sq. in. = 43.4444 cm^2

mass = 215.013 gm

$K = \left(\frac{3\sigma A_o}{m}\right) = 0.82199 \times 10^{-12}$ cal/sec/gm/°K^4

Sample 2

length = 3.9963 in.

diameter = 0.4945 in.

A_o = 6.5950 sq. in. = 42.5483 cm^2

mass = 208.113 gm

$K = \left(\frac{3\sigma A_o}{m}\right) = 0.83173 \times 10^{-12}$ cal/sec/gm/°K^4

Sample 3

length = 1.7440 in.

diameter = 0.2501 in.

A_o = 1.4690 sq. in. = 9.4774 cm^2

mass = 22.903 gm

$K = \left(\frac{3\sigma A_o}{m}\right) = 1.68343 \times 10^{-12}$ cal/sec/gm/°K^4

NIOBIUM

length = 4.00 in.

diameter = 0.501 in.

A_o = 6.29656 sq. in. = 40.62288 cm^2

mass = 110.886 gm

$K = \left(\frac{3\sigma A_o}{m}\right) = 1.500085 \times 10^{-12}$ cal/sec/gm/°K^4

MOLYBDENUM

length = 4.00 in.

diameter = 0.498 in.

A_o = 6.2588 sq. in. = 40.37927 cm^2

mass = 129.259 gm.

$K = \left(\frac{3\sigma A_o}{m}\right) = 1.27914 \times 10^{-12}$ cal/sec/gm/°K^4

TUNGSTEN

length = 4.00 in.

diameter = 0.502 in.

A_o = 6.30912 sq. in. = 40.70392 cm^2

mass = 248.70 gm

$K = \left(\frac{3\sigma A_o}{m}\right) = 0.670166 \times 10^{-12}$ cal/sec/gm/°K^4

TABLE 4

Evaluation of $\frac{C_p}{\varepsilon[1 + 2\alpha(T-300) + 2\beta(T-300)^2]}$

for Tantalum, Samples as Received

Sample	Temperature Range °K	Number of Points	$\frac{C_p}{\varepsilon[1 + 2\alpha(T-300) + 2\beta(T-300)^2]}$ cal/gm/°K
1	1522-1325	8	0.1231 ± 0.0028
1	1602-1326	10	0.1063 ± 0.0021
2	1784-1461	9	0.2048 ± 0.0023
2	1775-1518	10	0.2260 ± 0.0104
3	1555-1294	12	0.1216 ± 0.0017
3	1553-1382	8	0.1349 ± 0.0024

TABLE 5

Evaluation of $\frac{C_p}{\varepsilon[1 + 2\alpha(T-300) + 2\beta(T-300)^2]}$

	Temperature Range °K	Number of Points	$\frac{C_p}{\varepsilon[1 + 2\alpha(T-300) + 2\beta(T-300)^2]}$ cal/gm/°K
TANTALUM			
Sample			
1	1712-1475	9	0.2346 ± 0.0036
1	1842-1529	11	0.2233 ± 0.0029
2	1832-1570	10	0.2263 ± 0.0012
3	1741-1487	7	0.2206 ± 0.0020
3	1676-1297	11	0.2240 ± 0.0087
NIOBIUM			
	1733-2094	10	0.4157 ± 0.013
	1766-2154	9	0.3788 ± 0.0043
MOLYBDENUM			
	1698-2112	10	0.3981 ± 0.017
	1933-2165	6	0.3792 ± 0.021
TUNGSTEN			
	1589-1930	9	0.1588 ± 0.0043
	1757-2087	9	0.1543 ± 0.0056

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