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EVALUATION OF SELECTED REFRACTORIES AS HIGH TEMPERATURE THERMOPHYSICAL PROPERTY CALIBRATION MATERIALS

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Abstract—Twenty-two materials were screened as candidates for high temperature thermophysical property reference standards. Of these five (alumina, thoria, tungsten and two graphites) were selected for an initial field test program involving six laboratories in the U.S. Thermal conductivity and thermal diffusivity data and physical-chemical stability results on these materials in the temperature range from 500 to 2700°K are presented. Two of the materials, tungsten and an isotropic graphite, were selected for more detailed evaluation in an expanded international measurement program which involved 18 laboratories, 9 in Europe and 9 in the U.S. It was concluded with some qualifications which are described that the thermal conductivity and thermal diffusivity of the graphite were known within ±10 per cent and ± 6 per cent respectively while for the tungsten the corresponding inaccuracy bound for both properties was ±5 per cent. Although greater data scatter was observed among the tungsten results, the uncertainty estimates in the thermophysical properties were reduced using high precision electrical resistivity data. The experimental results on graphite and tungsten were found to be consistent based on theoretical considerations. Specific recommendations are given for further experimental and analytical studies with these two calibration materials.

NOMENCLATURE

A, B, C, D,	empirical constants, equation (1);
Cp,	heat capacity [J/g-°K];
Lo,	Lorenz number, $2{\cdot}443 \times 10^{-8}$ [$V^2/°K^2$];
L_∞,	empirical constant, equation (2);
RRR,	residual resistivity ratio ($\equiv \rho_{273°}/\rho_{4°}$);
T,	temperature [°K];
α,	thermal diffusivity [cm^2/s];
α,	thermal expansion coefficient [°K^{-1}];
β,	material purity parameter ($\equiv \rho_0/Lo$) [cm °K^2/W^2];
η_1, η_2, θ,	empirical constants, equation (2);
θ_D,	Debye temperature [°K];
λ,	thermal conductivity [w/cm-°K];
ρ,	density [g/cm^3];
ρ,	electrical resistivity [$\mu\Omega$-cm].

1. INTRODUCTION

THE MEASUREMENT of properties involving energy fluxes (transport properties) especially at high temperatures is very difficult experimentally. In designing high temperature aerospace systems where transport property information is nearly always required this is particularly troublesome since these measurement difficulties are manifested as a paucity of important design data with acceptable engineering accuracy (around ±10 per cent). In evaluating different thermophysical property measurement techniques, particularly those for determining thermal conductivity and thermal diffusivity of solids above about 1000°C it became clear that reference standards or calibration materials were not available for improving or even demonstrating accuracy limits with any confidence or for intercomparing the numerous measurement methods available. For temperatures below 1000°C and into the cryogenic range development work on standards has been extensive [1–3]. Some of these studies have been successful to the extent that reference specimens and reference transport property data as a function of temperature are available. In the U.S. some of these materials are available through the Office of Standard Reference Materials, National Bureau of Standards [4].

However because no systematic effort had been made in the high temperature range a program was begun to select and evaluate calibration materials with the aim of defining and eventually improving the accuracy of high temperature thermophysical property measurements. The initial search for candidate materials was broadly based and from a condensed list of twenty-two materials, five were selected for detailed evaluation with two in this latter group receiving particular emphasis.

Since no general accepted reference standard for the high temperature range was available at the start of this program it was necessary throughout to balance two objectives with some mutually exclusive features: (1) selection and evaluation of several materials (i.e. "materials variable" features) and (2) evaluation of error sources in the various measurement equipment (i.e. "technique variable" features). This was accomplished basically by carefully selecting, characterizing and controlling the test specimens, by round-robin measurements using in some cases the same sample in different apparatus and by employing a number of fundamentally dissimilar measurement techniques to help isolate systematic error sources.

2. MATERIALS SELECTION

In launching the systematized search for materials which had favorable characteristics as potential high temperature calibration standards, the initial criterion was two dimensional: (1) the general level of thermal conductivity: low, medium, high, and (2) test environment compatibility: vacuum, inert, graphitic. Once placed in these categories which were dictated by requirements of the different high temperature experimental apparatus, the materials were rated along more conventional scales of physical and chemical stability. The twenty-two materials isolated in this exercise [5] were then evaluated as to: (1) timely availability from qualified vendors, (2) effects of temperature cycling (to 2500°K and above) and time-at-temperature (24 h) in vacuum, inert and graphitic furnace environments, (3) physical and chemical stability (as observed microstructurally and through chemical analysis), (4) macroscopic physical stability (absence of distortion and cracking), and (5) low temperature thermal and electrical conductivity stability as inferred from measurement in pre- and post-heat treat condition.

Two of the five ceramic materials evaluated were selected for further study in the "field-test" program. The three remaining ceramics were rejected based on excessive high temperature vaporization or physical-chemical instability in contact with refractory metals. None of the intermetallics were carried forward into the measurement program because all exhibited substantial vaporization and stoichiometric instability through preferential loss of one constituent.

Among the several metals evaluated tungsten in arc-cast form was selected because of its relatively high melting point, its physical stability, and because it did not exhibit volatilization instability characteristic of molybdenum and molybdenum alloys. The chemical reactivity of tantalum and its alloys eliminated them from further consideration.

Distinguishing among the several graphites evaluated was quite difficult since no real differentiation developed among the candidates during preliminary screening. AXM-5Q Grade material from Poco Graphite Corp. was selected based on its high degree of isotropy relative to the more conventional commercial materials. RVD Grade material from Union Carbide Corp. was also chosen for evaluation because of its well established production history and reproducibility. Table 1 summarizes the initial specifications of these candidate calibration materials.

Table 1. Summary specification of calibration materials

Material and supplier	Purity (%)	Density (g/cm³)	Grain size	Other
Aluminum oxide (Alpha) Grade: AD 995 Coors Porcelain Co.	99·5 {0·23 ± 0·005% chromium}	3·84 (3% porosity)	25 μ	Water absorption: 0·0%
Thorium oxide (Cubic) Grade: Thorox National Beryllia Corp.	99·9	9·20 (8% porosity)	30 μ	Water absorption: 0·1–1·0%
Tungsten Grade: Arc Cast Climax Molybdenum Co.	99·87	19·21–19·25 (0·4% porosity)	4 mils	Heat treatment: Recrystallized at 1650°C
Graphite (2-Fold Anisotropic) Grade: RVD Union Carbide Corp.	0·4% ash content	1·86–1·92	Medium: 15 mils	Compressive strength: 7000 psi Process temperature: 2800°C
Graphite (Isotropic) Grade: AXM-5Q1 Poco Graphite Corp.	0·002% ash content	1·74–1·76	Fine: 1 mil	Compressive strength: $\geqslant$ 14 000 psi Process temperature: 2500°C

3. INITIAL FIELD TEST PROGRAM RESULTS

The initial thermophysical property measurement program involved six laboratories in the U.S. active in measurements on essentially a routine basis. The purposes of this round-robin sequence included: (1) verification of the expected physical and chemical stability of the materials under field test conditions, (2) obtaining an estimate of the data scatter among different laboratories active in such measurements, with controlled specimens to reduce the "materials-variability" parameter, and (3) establishing thermal conductivity–thermal diffusivity curves for the several materials with a clearly definable degree of precision and hopefully accuracy. Detailed results are presented in [6]; only a summary is presented here.

(A) *Aluminum oxide*

Thermal conductivity measurements were performed by Feith and by Hedge using relatively massive cylindrical specimens (Table 2). Thermal diffusivity measurements were performed by Nakata and by Springer *et al.*, using the laser flash technique (Table 3).

Table 2. Thermal conductivity measurement participants

Investigator	Affiliation	Measurement technique	Temp. range (°K)
E. D. Smyly C. M. Pyron, Jr. C. D. Pears	Southern Res. Inst. Birmingham, Ala.	Comparative rod Environment: Vacuum: 10^{-3} torr Precision: ±3·5% Accuracy: +5%	500–1300°
		Radial flow Environment: Inert Precision: ±3·5% Accuracy: ±10%	1600–3100°
J. F. Lagedrost	Battelle Mem. Inst. Columbus, Ohio	Comparative rod Environment: Vacuum: 10^{-3} to 10^{-5} torr Precision: ±2 to ±4% Accuracy: ±10%	700–2800°
G. Sertour M. Canavet	SUD-Aviation Courbevoie, France	Radial flow Environment: Vacuum	500–900°
L. Binkele	Inst. for Reaktorwerkstofle Julich, Germany	Modified Kohlrausch Environment: Argon Precision: ±2% Accuracy: ±6%	400–1300°
J. Rappeneau	Centre d'Etudes Nucleaires de Saclay Gif-sur-Yvette, France	Modified Kohlrausch Environment: Vacuum: 10^{-5} torr	300–1200°
C. K. Jun, S. Ebrahim and M. Hoch	Univ. of Cincinnati Cincinnati, Ohio	Inductively heated cylinder Environment: Vacuum: 10^{-6} torr Precision: ±5% Accuracy: ±8%	1800–2700°
J. C. Hedge	IIT Research Inst. Chicago, Illinois	Radial flow Environment: Argon Precision: ±6%	1200–2500°
A. D. Feith	General Electric Co. Cincinnati, Ohio	Radial flow Environment: Argon (Hydrogen) Precision: ±6% Accuracy: ±5%	1300–2800°
R. E. Taylor, R. W. Powell, F. Davis and M. Nalbantyan	Thermophysical Properties Research Center Purdue University West Lafayett, Indiana	Direct electrical heating Environment: Vacuum: 10^{-7} torr Precision: ±3% Accuracy: ±5%	1700–2800°

Table 3. Thermal diffusivity measurement participants

Investigator	Affiliation	Measurement technique	Temp. range (°K)
G. Neuer W. Brandt	Univ. Inst. f. Kernenergetik Stuttgart, Germany	Modulated xenon light beam Environment: Vacuum: 10^{-5} torr Precision: 3–4%	1200–2300°
R. DeConinck	Centre d'Etude de L'Energ. Nucl. MOL, Belgium	Modulated electron beam Environment: Vacuum Precision: ±5%	1100–2300°
G. L. Denman	AF Materials Laboratory Dayton, Ohio	Laser pulse Environment: Vacuum: 1×10^{-5} torr Precision: ±2% Accuracy: ±5%	600–2300°
C. Ferro	Comitato Nazionale Energia Nucleare Rome, Italy	Laser pulse Environment: Argon Accuracy: ±5%	600–2700°
K. E. Gilchrist	United Kingdom Atomic Energy Authority Warrington, England	Laser pulse Environment: Vacuum Precision: ±2% Accuracy: ±5–8%	400–1000°
M. M. Nakata	Atomics International Canoga Park, Calif.	Laser pulse Environment: Vacuum: 7×10^{-5} torr Precision: 3·7% RMS Deviation Accuracy: ±7%	1400–2500°
J. Rappeneau	Centre d'Etudes Nucleaire de Saclay Gif-sur-Yvette, France	Laser pulse Environment: Vacuum: 10^{-5} torr	400–1300°
H. E. Schmidt	Instit. f. Transurane EURATOM Karlsruhe, Germany	Modulated electron beam Environment: Vacuum: 10^{-5} torr Precision: ±5%	1000–2100°
J. R. Springer J. F. Lagedrost and R. A. McCann	Battelle Memorial Institute Columbus, Ohio	Laser pulse Environment: Vacuum: 2×10^{-6} at T Precision: ±1–3% Accuracy: ±5% (to 2100°) ±8% (to 2500°)	1200–2500°
M. R. Null and W. W. Lozier	Union Carbide Corp Parma, Ohio	Modulated carbon arc Environment: Argon Precision: 2% Accuracy: ±5– ±8%	1700–2200°
R. Taylor	University of Manchester Manchester, England	Laser pulse Environment: Vacuum: 3×10^{-5} Precision: 1–2% Accuracy: +3%	300–2600°

The data scatter of the results from individual laboratories ranged from 2 to 7 per cent. Converting the diffusivity results to thermal conductivity via ρCp multiplication and least squares fitting all the data produced the equation given in Table 4. Comparison of this curve with the Thermophysical Properties Research Center (TPRC) recommendation for alumina in the same density range [7] gave good agreement (within 2 per cent) to 1800°K but substantial negative divergence (about 12 per cent) at 2100°K. Deviation from the expected temperature linearity of the thermal resistivity (λ^{-1}) began at 1400°K and amounted to 12 per cent at 2100°K indicating significant effects of high temperature radiation transport. These deviations however were significantly less than that shown in the TPRC curve most probably due to the attenuation

Table 4. Least squares equations

$[\alpha\,(\mathrm{cm}^2/\mathrm{s}),\ \lambda(\mathrm{w/cm\text{-}^\circ K})\ \text{or}\ \lambda^{-1}] = A+BT+CT^{-n},\ T(^\circ\mathrm{K})$

Dependent variable	Material	Constants				RMS deviation (%)
		A	*B*	*C*	*n*	
Thermal conductivity	Aluminum oxide	0·00839	$9{\cdot}50 \times 10^{-5}$	56·377	1	9·0
Thermal conductivity	Thorium oxide	0·00808	$-8{\cdot}207 \times 10^{-7}$	37·634	1	13·4
Thermal conductivity	RVD Graphite					
	with grain	0·1421	$1{\cdot}251 \times 10^{-5}$	351·84	1	6·6
	across grain	0·0820	$1{\cdot}858 \times 10^{-5}$	304·19	1	5·5
Thermal diffusivity (data fit, Fig. 1)	AXM-5Q Graphite	0·1279	$-2{\cdot}272 \times 10^{-5}$	68066·64	2	5·7
Thermal conductivity (data fit, Fig. 2)	AXM-5Q Graphite	0·3666	$-6{\cdot}159 \times 10^{-5}$	275·228	1	7·5
Thermal resistivity (from conductivity data curve, Fig. 2)	AXM-5Q Graphite	0·8058	$9{\cdot}136 \times 10^{-4}$	0·0	—	0·55
Thermal resistivity (from converted diffusivity curve, Fig. 3)	AXM-5Q Graphite	0·7546	$1{\cdot}073 \times 10^{-3}$	0·0	—	0·60
Thermal diffusivity (data fit, Fig. 4)	Arc-cast Tungsten	0·3863	$-5{\cdot}205 \times 10^{-5}$	93·199	1	6·7
Thermal conductivity (data fit, Fig. 5)	Arc-cast Tungsten	1·0834	$-1{\cdot}052 \times 10^{-4}$	234·199	1	13·1
Thermal conductivity (TPRC recommended curve)	Tungsten	1·0317	$-7{\cdot}688 \times 10^{-5}$	222·763	1	0·88

influences of the chromium addition to this particular alumina body. The principal difficulties encountered in the use of alumina among the field testing laboratories were: (1) occasional cracking of the samples during heating, (2) reaction and vaporization of the noble metal coatings used on the diffusivity specimens, and (3) probable radiation transport effects above 1400°K despite the use of chromium-doping.

(B) *Thorium oxide*

The same investigators measured the thermal transport properties of thoria. The data scatter was somewhat greater than observed with the alumina amounting to 4–13 per cent among the several investigators. Additionally, the thermal conductivity data were found to lie about 20 per cent above the mean curve for the converted diffusivity. Considering all data together an RMS scatter of 13·4 per cent was calculated, the form of the least squares equation being given in Table 4. Literature results were not particularly useful for comparison since there is a general paucity of data, with that available, including the TPRC recommendation, being derived from relatively low density materials. Some difficulties were encountered during the course of measurements from several sources. On heating into the 2500°K range densification on the order of 5 per cent occurred. Further, as a consequence of the very low thermal conductivity and relatively low strength of the thoria, cracking of the samples was encountered particularly in the vicinity of instrumentation holes, thus causing probable errors in temperature measurements. As with other low conductivity refractory materials, where the calorimetric heat fluxes are low, control of significant spurious heat flows is most difficult. The effects of tungsten and indium opacity coatings on the diffusivity specimens introduced the possibility of error sources due to coating reaction with the substrate specimen and loss of bond integrity on thermal cycling.

Linear temperature dependence of the thermal resistivity as derived from the least squares equation was observed, however, within 1 per cent to the highest test temperature, 2500°K. In addition recent lower temperature results with this particular thoria material from Oak Ridge National Laboratories [8] indicate that linearity of measured thermal resistivity is obeyed from 1400°K down to 400°K.

(C) *RVD grade graphite*

Thermal conductivity of RVD was measured by Smyly *et al.*, using two different experimental techniques since the twofold anisotropy of the material prevented the measurement of across-grain conductivity in the radial flow type of apparatus. Thermal diffusivity was determined by Nakata and by Springer *et al.*, with the laser flash technique and by Null and Lozier with the modulated carbon arc technique. Generally the with-grain results were about 25 per cent above the across-grain data as would be expected. The data scatter for the graphite was considerably less than for the refractory oxides studied, ranging from 0·5 to 4 per cent individually and amounting to 6 per cent when considering all the data collectively. Least squares curve fit coefficients are included in Table 4. Very few difficulties were encountered with the material during measurement. The most significant item of concern was the selection of test specimens from the graphite billets supplied by the manufacturer. In the process of radiographic inspecting these billets, regions of higher density (on the order of 2 per cent) were found near the ends. These scans revealed, however, that the central regions were uniform and thus specimens were cut from there.

4. INTERNATIONAL TEST PROGRAM

The scope of the evaluations on tungsten and the isotropic grade AXM-5Q graphite was expanded compared with the studies on alumina, thoria and RVD grade graphite both as regards the property measurement program and the extent of materials characterizations. As a result of the initial field testing, it was concluded that a broader data base was necessary to bring any of the five selected materials to a state of general usefulness as engineering-accuracy calibration materials. The isotropic graphite and the tungsten were chosen for more extensive study [6] for several reasons: (1) relatively few pressing requirements existed at least in our work in the very low conductivity range where the oxides would be especially useful, (2) the physical integrity difficulties and relatively high cost of obtaining the oxide materials in proper specimen configurations, and (3) the more general utility of the isotropic vis-a-vis the anisotropic graphite.

The formation of the Advisory Group for Aerospace Research and Development (AGARD) project TX44 on thermophysical properties of solid materials presented a unique opportunity for international evaluation of these materials in developing a broader experimental basis encompassing a wider spectrum of measurement techniques. The following sections present results from both European and U.S. investigators.

(A) *Isotropic graphite as a calibration material*

(i) *Material characterization.* For graphite the notion of establishing a procurement specification which would be applicable from lot to lot was not judged to be practical in view of the complex character of polycrystalline graphites generally. Thus a large lot of material was obtained sufficient for the measurement program as well as providing a reserve for future use. After verifying the physical stability of the AXM-5Q material lot through heat treatment a stock of cylindrical billets (4 in. dia. × 12 in. long) and blocks (2 in. × 4 in. × 6 in.) was obtained. As a result of processing, graphite materials generally exhibit density variations in billet form, thus radiographic examinations were conducted on the POCO stock. The density was determined from the measured attenuation of a gamma-ray source beam aligned along three orthogonal planes of the individual billets. Maximum variations of up to $\pm 1{\cdot}3$ per cent from the average gravimetric density of 1·757 were observed while the average deviation was 0·4 per cent. However, regions of abnormal density tended to be localized and any material which deviated substantially from this average was not used.

The microstructure showed the fine grain character of this material relative to more typical commercial graphites such as RVD. Micrographs of post-test specimens revealed no observable changes during heat treating or during the field testing program. Thus the summary specifications in Table 1 used to procure the lot of material together with radiographic determination of specimen selection sites within the various billets in the lot served as the principal methods of assuring specimen homogeneity for the test program.

(ii) *Measurement results.* Thermal diffusivity measurements were performed by nine investigators, three in the United States and six in Europe with Belgium, Britain, France, Germany and Italy represented. Several different measurement techniques were used as indicated in Table 3, all United States investigators and three Europeans using the flash technique, while the remainder used either modulated thermal or electron beams. Typical measurements results as a function of temperature are shown in Fig. 1. Only a few data points for each investigator are shown to give a general indication of the precision and interrelationship of the results. The form of the least-squares equation curve fit and its coefficients are given in Table 4. Deviation plots of individual results relative to the least-squares curve fits of all data are given in [6].

It is significant to note that specimens taken from orthogonal locations within the same and within different graphite billets yielded the same diffusivity values within the precision of individual measurements. Further there were no differences in results on heating or cooling cycles within the precision of the data.

The spread of the diffusivity data shows no definite temperature trend, averaging about ±6 per cent over the wide temperature range covered in the program. This is particularly noteworthy in view of (1) the large number of independent investigators who contributed, (2) the wide lower temperature scatter in the direct AXM-5Q thermal conductivity measurements men-

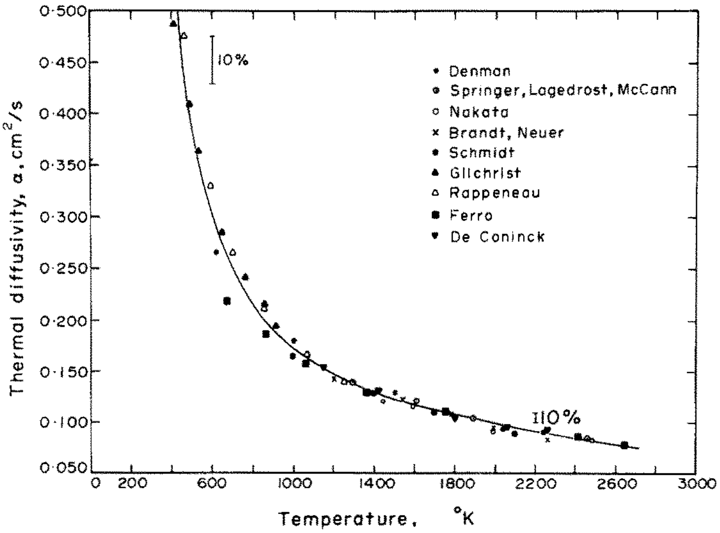

FIG. 1. Thermal diffusivity of AXM-5Q grade graphite.

tioned below which traditionally were thought to be more precise in this range particularly for higher conductivity materials, and (3) the wider scatter in diffusivity results on tungsten discussed in the next section. Systematic differences between the laser flash and modulated beam technique results were not evident except that the flash technique data are on the average 1–2 per cent above the modulated beam, a difference too small to be considered significant.

The high i.r. emittance and absorptance of graphite makes it particularly well suited for transient technique measurements especially at higher temperatures. The scatter in measurement results does not decrease at lower temperatures due in large measure to the diminished sensitivity of the optical temperature measurements or because the temperatures were determined with relatively low sensitivity thermocouples.

Five investigators measured the thermal conductivity of the graphite, Fig. 2, using a total of five different measurement methods which really fall into three categories: comparative techniques, direct heating techniques, and radial flow techniques. The radial flow method used widely in the United States for high

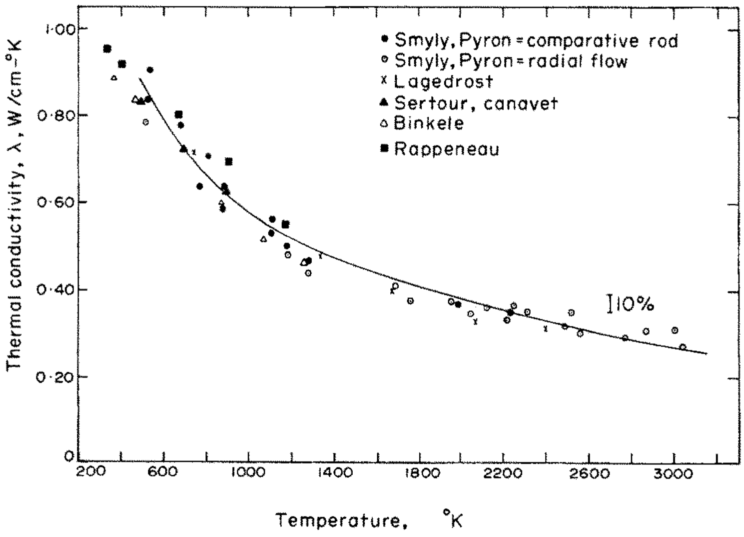

FIG. 2. Thermal conductivity of AXM-5Q grade graphite.

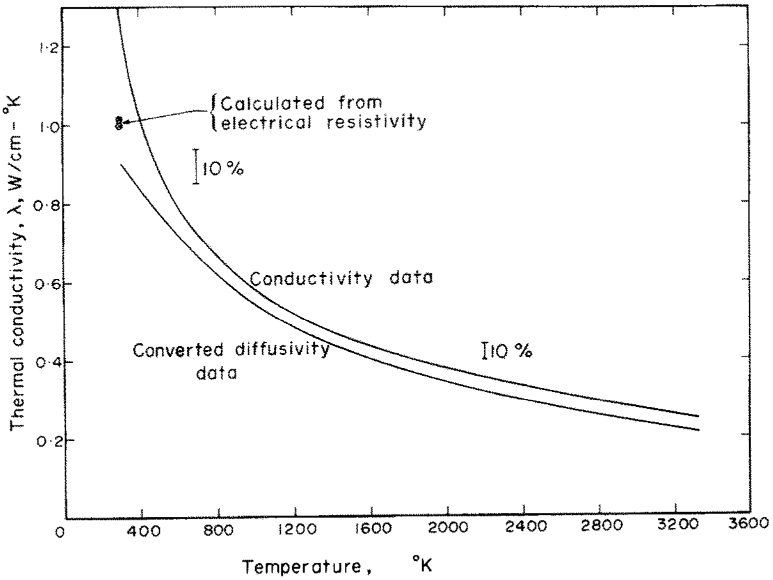

FIG. 3. Least squares thermal conductivity curves for AXM-5Q grade graphite.

temperature measurements on graphite was employed by two investigators in this program, one extending to the 3000°K range. Variations of the results relative to the least-square curve fit amounted to 7·5 per cent, c.f. Table 4. Consistent with the diffusivity results, no differences in experimental values were found in the measurements along the three orthogonal planes through the material within the precision of the data confirming the isotropic nature of this graphite. Neither were effects of temperature cycling observed.

At high temperatures the differences in mean conductivity of about 4–10 per cent between investigators, Fig. 2, are not surprising in view of the ±10 per cent accuracy quoted which is typical for the technique in this range. The divergence of up to 12 per cent in directly measured conductivity at lower temperatures is surprising in view of the expected measurement accuracy, typically about ±5 per cent for higher conductivity materials in this range.

Thermal expansion data for the conversion of measured thermal diffusivity to thermal conductivity was derived from linear curve fitting the results obtained on this graphite under the AGARD program [9, 10]. The scatter in the thermal expansion data reported by 10 investigators was within 1–2 per cent while the estimated uncertainty in the coefficients was no more than 5 per cent.

Heat capacity was estimated from the literature using the equation of West and Ishihara [11] which was developed by differentiating the least-squares curve fit of measured enthalpy data obtained over the range from 1200 to 2600°K. Recent direct heat capacity measurements on the AXM-5Q by Cezirliyan at the National Bureau of Standards [12] are within 0·8–1·7 per cent of the West–Ishihara results. Considering a number of additional literature sources collectively [13–15] it is estimated that the uncertainties in the heat capacity data used here are on the order of ±3 per cent or less.

A comparison between the least-squares conductivity curve fit, Fig. 2, and the converted least-squares diffusivity curve, from Fig. 1, is given in Fig. 3. Combining the uncertainties in density and heat capacity and the estimated inaccuracies of the diffusivity results gives an uncertainty of about ±7·5 per cent for the converted diffusivity curve. The average 6–8 per cent difference between the curves in Fig. 3 is thus within the spread of the several sets of measured data.

(iii) *Theoretical consistency.* Thermal energy transport in graphite is modelled either (1) as pure lattice conduction where the acoustic vibrational spectrum is calculated assuming the simplified but apparently successful semicontinuum model, or (2) using the model applied to metallic alloys and some pure metals where significant electronic as well as lattice contributions are assumed. In the former instance, application of the theoretical results to other than basal plane pyrolytic graphite conductivity involves large, basically empirical corrections, for porosity (density effects) and tortuosity (crystallite orientation/conduction path effect) effects. In the latter instance uncertainties in modelling of electronic conduction mechanisms lead to substantial differences in apparent Lorenz ratio at high temperatures where this component is relatively more significant. Excellent recent reviews of the theoretical analyses pertinent to graphite are available [e.g. 15 and 16] and thus will not be elaborated upon here.

The consistency of measured electrical resistivity results due to Binkele [17] was determined by applying two semi-empirical relationships between thermal and electrical conductivities of graphite [18] which assume that around room temperature the flow of both thermal and electrical energy is controlled by crystal boundary scattering. The calculated points are shown in Fig. 3. Over most of the range of the present study three phonon scattering would predominate and thus the thermal resistivity would be expected to be linear in temperature. Examining the least squares representations of the measured conductivity and converted diffusivity results, Fig. 3, plots of $\lambda^{-1} = A+BT$ show an RMS deviation of only 0·6 per cent between 800 and 2500°K. Numerical values of these constants are included in Table 4. Deviations from linearity below 800°K, amounting to 7 per cent around 400°K, are expected since other scattering mechanisms become important. Reasons for the deviations from a linear thermal resistivity above 2500°K, amounting to about 5 per cent at 3000°K are more difficult to explain since the measured thermal conductivities lie below the T^{-1} equation. Invoking the possibilities of additional transport mechanisms such as ambipoler diffusion [19] or optical phonons [20] lead to increases rather than decreases in expected thermal conductivity.

If a slightly altered form of the lattice conduction equation is applied the disagreement is eliminated. Expanding the thermal resistivity equation in a binomial series retaining the significant terms yields,

$$\lambda = (A+BT)^{-1} = C/T+D/T^2. \qquad (1)$$

This form of the lattice conduction equation was suggested by Williams and Fulkerson in evaluating results on other phonon conductors [21]. This temperature functionality is also suggested if Taylor's theoretical exponential expression for the basal plane conductivity of graphite [22] is expanded in series form. If this equation is applied, the thermal resistivity is essentially linear from about 1200 to 3000°K, the highest test temperature in this study.

The temperature linearity of the total thermal resistivity over a wide range and the excellent curve fits with functions of the form given in equation (1) indicates consistency with a pure lattice conduction model. However with electrical resistivity data available on this material [17] the results were evaluated alternately in terms of possible combined electronic/lattice conduction modes. There are basically two methods of approach here: (1) calculation of the effective Lorenz number based on measured electrical resistivity and on the difference between total conductivity and inferred lattice conductivity (assuming $\lambda^{-1} \propto T$); the result can then be compared with Sommerfield and/or ambipolar diffusion values (e.g. [23]), and (2) calculations of the Lorenz function theoretically based on an assumed mechanism of electron transport, the difference between measured and predicted thermal conductivity than being attributed to either lattice conduction ($\propto T^{-1}$) and/or inaccuracies in the assumed energy transport model. The first approach is not particularly attractive for graphite at high temperatures since the differences between measured and inferred conductivities are small and the calculation of electronic contributions very uncertain (on the order of ± 100 per cent) due to the inaccuracies in measured conductivity, typically ± 10 per cent. Using this approach effective electronic contributions in the case of the AXM-5Q data were found to be negligible. Using the second, Kaspar concludes that the general temperature independence of polycrystalline graphite conductivity above 2000°K is the result of substantial ambipolor diffusion [19]. The results presented here, however, show a distinct temperature dependence even at 2000°K. Depending on the form of the energy band model used [15] effective Lorenz ratios from 4·0 to $\sim 9\ (k/e)^2$ are anticipated. Using the measured electrical resistivity data of Binkele and Brandstaedter [17] and the two conductivity curves, Fig. 3, total Lorenz functions were calculated. Only very near 3000°K does the Lorenz function approach the range suggested by Kaspar for ambipolor diffusion; at 2500°K the apparent lattice contribution still amounts to over 40 per cent of the total which is not anticipated based on his model. In addition the apparent lattice thermal resistivity, $(\lambda_{\text{Total}} - \lambda_e)^{-1}$ did not exhibit the expected linearity with temperature.

Additional measurements of AXM-5Q electrical resistivity across the full temperature range would be useful to allow more quantitative treatment of the postulated electronic conduction contributions, particularly the validity of the implicit assumption that intercrystalline contacts and crystal boundaries impede electron transport in the same manner as thermal energy transport.

(B) *Arc cast tungsten as a calibration material*

(i) *Material characterization.* Tungsten from several different sources was evaluated in the preliminary phases of the program. These materials were produced by one or two basic techniques: pressing and sintering or arc-melt casting. Most commercially available tungsten is of the former type. Temperature cycling at low rates (150°K/h) produced intergranular cracking in the pressed and sintered material while the arc cast stock was unaffected. Preliminary thermal conductivity measurements on the sintered materials near room temperature were lower than on the arc cast by about 10 per cent despite the fact that the densities were within 1 per cent. Very high temperature measurements (2000–2800°K) on a number of arc cast and sintered specimens by Jun *et al.* [24] including one of the arc-cast heats from this program showed that the latter averaged about 13 per cent lower in conductivity despite the fact that specimen densities were in the same range. Based on these tests especially the differences in physical integrity, the pressed and sintered materials were eliminated from further consideration. Similar physical stability difficulties particularly on exposure above 2100°K were encountered in the AGARD program [17] where a pressed and sintered tungsten was used initially. These experiences supported the rationale for selection of the arc cast material.

The fact that the pressed and sintered materials gave consistently lower thermal conductivities than the arc cast materials even with comparable densities indicates that there are basic differences in structure, most probably the persistence of intergranular interfaces, in the sintered material despite high temperature processing. Thus it appeared that density was not a sufficiently sensitive measure of material quality with respect to energy transport to be a primary index in the material specification.

With regard to impurity criteria, stock of commercial purity (that is, on the order of 99·9 per cent), was used rather than very high purity material to mitigate the contamination susceptibility of test specimens in the various measurement facilities. Several different heats of material were obtained from Climax Molybdenum Company, all within the initial specification (Table 1).

As the principle materials characterization index the residual resistivity ($RRR = \rho_{273°}/\rho_{4°}$) was used as suggested by Powell, Hust *et al.* [25, 26]. This technique is based on the Matthiessen rule approximation. That is, the residual resistivity is nearly temperature independent, its magnitude being determined by electron interaction with physical and chemical impurities in the metal while the intrinsic resistivity, determined by phonon–electron interaction, decreases rapidly with decreasing temperature, its magnitude being negligible relative to the residual resistivity at liquid helium temperatures (4°K). Thus for a given metal the ratio of room temperature electrical resistivity to liquid helium temperature resistivity is a direct measure of what Hust and Clark term "electrical purity" [25]. To assure that measured *RRR* values were most sensitive to chemical impurities rather than physical defects, annealing or heat treating was used to reduce physical imperfections in the specimens.

Measurements of *RRR* were performed by Hust and Sparks of the National Bureau of Standards [27] on the several heats of arc cast tungsten used in this program. The accuracy of individual *RRR* measurements was on the order of ±0·7 per cent or better. These several heats of material showed an "as received" range of *RRR* from about 60 to 100 and β [28] from 2 to 3 which is typical of a metallic element with 99·9 per cent purity. *RRR* values obtained after return of the specimens from high temperature thermophysical property measurements were considerably increased. Microstructural evaluation and chemical analysis of the post-test specimens showed that grain size had increased greatly from the pre-test condition while the concentration of all impurity elements was less than that of the pre-test specimens. Volatilization of molybdenum, the principle refractory impurity, was noted in some cases. The higher post-test *RRR* values were consistent with these results since the level of both physical imperfections and chemical impurities had been reduced.

(ii) *Measurement results.* The thermal diffusivity of arc cast tungsten (Heat 8577) was measured by five investigators, three in Europe and two in the United States with Great Britain, Belgium and Germany being represented. As shown in Table 3, four different measurement techniques were represented among these investigators. Typical measurement results are shown in Fig. 4 where a least squares curve fit of the form shown in Table 4 has been drawn along with the TPRC recommended curve [28]. The RMS deviation of the various results is higher than for the graphite diffusivity results averaging 6·7 per cent; in some instances differences of over ±12 per cent from the least squares curve are noted. Disagreement with the TRPC curve is as high as 16 per cent at 1400°K. Further, the temperature functionality of the several sets of diffusivity results are considerably different. The magnitude of these variations is difficult to reconcile with the reported accuracy bounds for the measurement techniques used (Table 3).

With respect to physical integrity, performance of the material was reported to be excellent with complete stability to the highest test temperature, 2400°K. This was an encouraging contrast to results with sintered material where these same investigators noted cracking and densification. Further, no effects of temperature cycling were noted within the ±2 per cent precision typified in the heating/cooling curve data of Springer *et al.* (Fig. 4).

In conducting the experimental measurements, tungsten presents unique difficulties. Most important among these are traceable to the surface character of the metal. Since heat energy from the pulsed or modulated source is transported to the specimen surface via irradiation in most diffusivity measurement techniques, the high surface reflectivity and specularity

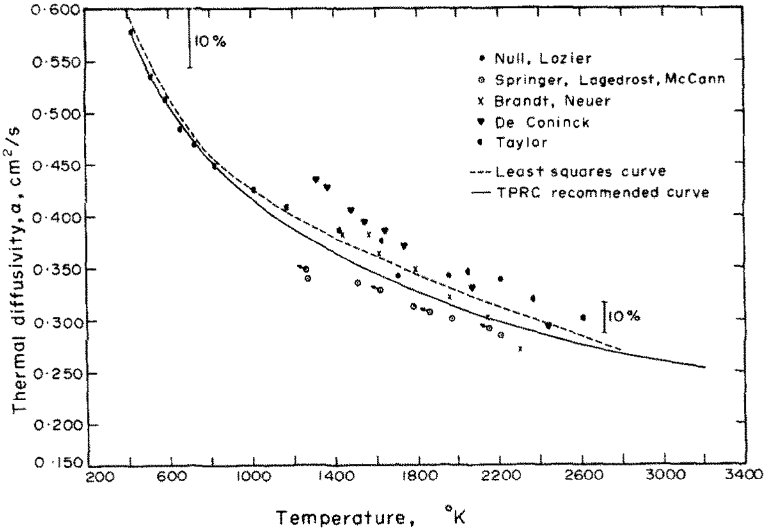

FIG. 4. Thermal diffusivity of arc-cast tungsten (heat 8577).

of tungsten is a distinct disadvantage. Similarly, since the specimen response is measured optically except at lower temperatures, the magnitude of the signal to the detector is attenuated greatly by the high reflectivity surface causing signal to noise ratio problems and reduced sensitivity. To overcome these difficulties the specimen surface can be roughened (e.g. sandblasting by Null and Lozier) or coated (e.g. graphite coating by Taylor). Lack of roughness stability on high temperature exposure, lack of coating integrity or reaction of the coating with the substrate specimen at high temperatures are possible sources of systematic error. The TPRC diffusivity curve (Fig. 4), is based on the conductivity recommendation and the Hultgren *et al.* [30] heat capacity results. Hence, the differences between the least squares and recommended curves in Fig. 4 are indicative of differences between diffusivity and conductivity results (and/or specific heat uncertainties which enter into the conversion) not internal differences between literature and measured diffusivity data.

Direct thermal conductivity measurements on five heats of arc cast tungsten were performed by four teams of investigators in the United States. Three different measurement techniques were involved as seen in Table 2 and Fig. 5. The operational characteristics

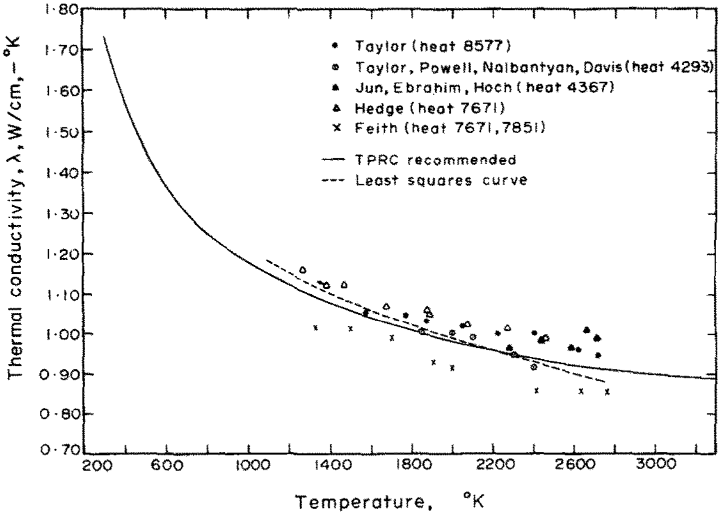

FIG. 5. Thermal conductivity of arc-cast tungsten.

of the various apparatus were such that only high temperature results could be obtained conveniently. As during the diffusivity measurements no adverse effects of temperature cycling on specimen physical integrity were noted. Within the precision of the measurement no differences were observed in measured properties on heating and cooling. No differences in measured conductivity resulted when using different specimens from within a given heat. Heat to heat variations were evaluated directly in a given measurement apparatus by Taylor and Feith. Taylor found that heat to heat variations were within 2 per cent or essentially negligible considering the precision of the measurements [31]. Feith studied two heats of material in a radial flow apparatus and observed differences of about 3 per cent again within the ±6 per cent precision of his measurements [5]. Effects of lot-to-lot variation in the arc cast tungsten results could not be evaluated quantitatively since systematic error seemed to obscure the possible small differences expected.

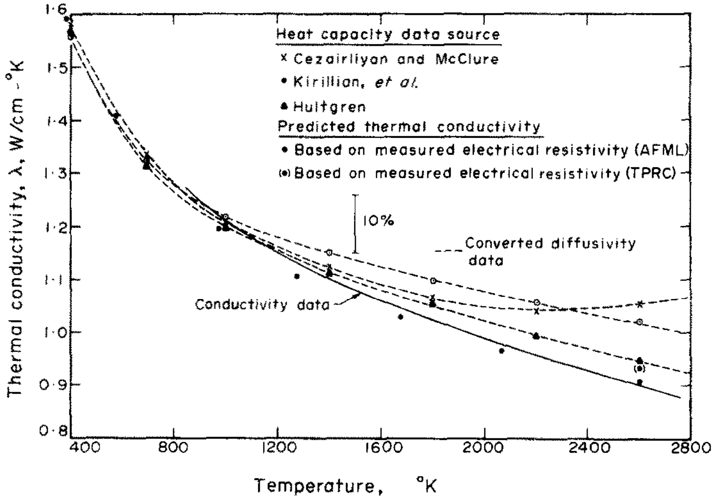

FIG. 6. Least squares thermal conductivity curves for arc-cast tungsten.

As with thermal diffusivity, a pure metal such as tungsten poses special difficulties in thermal conductivity measurement; in this instance the difficulties relate principally to the high conductivity of the material. Especially in the radial flow equipment, generating a reasonably high temperature drop across the specimen to improve gradient measurement is difficult at practical power levels. Further, the high temperature grain growth of the specimens tends generally to increase embrittlement making handling and instrumentation difficult.

The thermal expansion data used to apply the density correction in the conversion of thermal diffusivity to thermal conductivity was the mean curve obtained directly on the arc cast tungsten under the AGARD program [10]. The maximum scatter in the results was ±1 per cent at 1600°K, the highest test temperature.

Heat capacity has not yet been measured on the arc cast tungsten thus literature data were used. The recent results of Cezairliyan and McClure [32] were first applied since their material was very similar to the arc cast tungsten. The estimated inaccuracy in heat capacity was given by these authors to be 2–3 per cent while the individual data points were within 0·2 per cent of the curve fit equation given (equation 6 [32]). Comparing the results with literature data obtained by more conventional calorimetric techniques, Cezairliyan and McClure found general agreement to about 2000°K but considerable disagreement above 2500°K. At 2800° their results lie 6·6 per cent above the recent Russian results of Kirillin *et al.* [33] and 13·7 per cent above the Hultgren recommendation mentioned earlier [30], even though individually, all these investigators suggest inaccuracies in the range of 1–5 per cent.

Due to these differences in tungsten heat capacity at higher temperatures, and the absence of full theoretical rationalization of the temperature dependency, the thermal diffusivity was converted to thermal conductivity using three sets of C_p data as shown in Fig. 6. The solid curve in Fig. 6 is the least squares curve fit of the measured conductivity results (Fig. 5 and Table 4). Data points representing predicted thermal conductivities based on measured electrical resistivity are also shown and are discussed later. At 2800°K, the differences in the converted diffusivity curves amount exactly to the differences in the heat capacity data noted above. From

400° to 1400°K which includes some overlap of the converted diffusivity data with measured conductivity the average results as well as the TPRC curve are within about 6 per cent although the converted diffusivity curves begin to show a distinct positive deviation independent of the heat capacity data source. At 2600° this positive deviation of the converted diffusivity curves from the average conductivity curve ranges from 5 to 15 per cent and represents a distinct trend of disagreement even considering the data scatter. Additionally, a positive temperature coefficient for the high temperature conductivity is most unlikely based on the electrical resistivity results as discussed further below. The relative contributions to the observed differences from error sources in the diffusivity measurements and from uncertainties in the heat capacity measurements could not be determined.

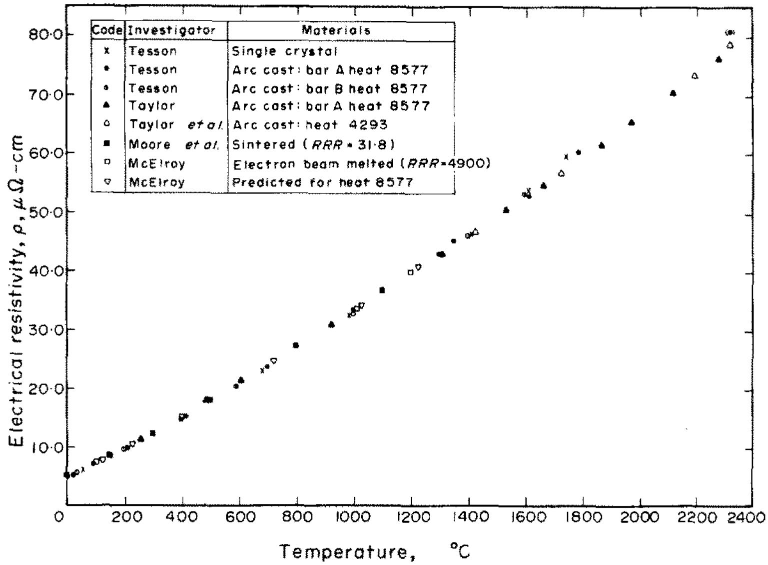

FIG. 7. Electrical resistivity of tungsten: experimental results and literature data.

Because of the predominantly electronic character of the conduction processes in a metal such as tungsten, high temperature electrical resistivity measurements are an important and really essential adjunct to thermal transport property evaluations; as noted earlier low temperature electrical resistivity measurements are essential in homogeneity assessment. These data form the basis of important consistency assessments between thermal and electrical transport measurement results. This was a particularly important point in this study due to the apparent difficulties encountered in measuring the thermal properties of tungsten at high temperatures as evidenced by the data scatter (Figs. 4 and 5). Further, essentially all of the more successful predictive schemes for estimating the thermal conductivity of tungsten involve the use of electrical resistivity data (and *RRR* measurements) as will be discussed below.

Measurements of electrical resistivity were conducted in our laboratory on single crystal tungsten and on two bars of 0·5 cm dia. arc cast tungsten. The measurements were made in vacuum (5×10^{-6} torr) by the conventional 4-probe technique. Precision of the various measurements was ±0·6 per cent while accuracy inferred by comparing results on a platinum specimen from the National Bureau of Standards with published NBS data on the same lot of material was estimated to be ±1 per cent. Details on the measurement technique are given by Tesson [34]. Because the resistivity decreased by about 1 per cent on extended exposure to high temperatures, a heat treating cycle to 2300°K for one hour was used routinely before obtaining resistivity measurements. Typical results of the measurements along with selected literature data for other well characterized tungsten material are given in Fig. 7. The resistivity based on our measurements was represented by the following equation with an RMS deviation of 0·7 per cent.

$$\rho = 4{\cdot}640 + (2{\cdot}533 \times 10^{-2})T + (3{\cdot}162 \times 10^{-6})T^2,$$
$$\text{micro-ohm-cm, } (20 \leqslant T \leqslant 1800^\circ\text{C})$$

where T is in degC.

Comparing these and the other data on materials exhibiting a wide range of *RRR*, it is noted that, as expected, variations in impurities on the order of tenths of a per cent do not significantly influence the resistivity at high temperatures. The data from a relatively wide variety of sources lie within the generally quoted resistivity measurement inaccuracy band of ±1 per cent. At lower temperatures the data scatter becomes wider for at least two reasons: (1) material inhomogeneity effects become more important, (2) individual data points may deviate significantly from the quadratic least squares equations used conventionally to express the temperature dependency of the resistivity.

Despite these factors, it was demonstrated here that high temperature electrical transport measurements on tungsten exhibit in general, better precision and accuracy than thermal transport property measurements. Further, the disagreements among different investigators were correspondingly reduced. Above 2000°K it is necessary to apply thermionic corrections to measured resistivities, however, with consequent possible reductions in measurement accuracy. Williams [35] indicates that the correction amounts to 0·1 per cent at 2500°K but rises exponentially above this level.

Actually the data of Fig. 7 include a "materials variable" as well as a "measurement technique variable" component. The former could conveniently be eliminated or at least reduced very significantly if intrinsic resistivities rather than total resistivities were compared. However residual resistivity data was not available for all the specimen materials in the figure so for consistency the correction was not applied.

(iii) *Theoretical consistency.* Theoretical treatments of thermal energy transport in metals generally and tungsten in particular have been published and will be touched upon here only briefly to summarize essential points. It is assumed basically that the lattice conduction and electronic conduction modes are independent and are thus linearly additive. Expressions for the lattice component derived for regular dielectric solids (pure lattice conductors) are then applied. Expressions for the electronic component start using basic Wiedeman–Franz–Lorenz law forms with various approaches used in explaining deviations in the Lorenz number from the classical Sommerfeld value for a degenerate electron gas, *Lo*. This is especially difficult for a "non-simple" transition metal like tungsten where inelastic electron–phonon scattering, electron–electron scattering (inelastic), band structure effects and ambipolar diffusion may be contributing to the deviations [36–39].

Relative to the lattice component, White [36] and Williams and Fulkerson [21] examined the applicability of the classical three phonon anharmonic interaction equation of Leibfried–Schlemann and modifications thereof for several metals including tungsten. From dilute alloy experimental results (where small alloy additions are assumed to perturb the electronic but not the lattice conduction component) it was concluded that the theoretical equations overpredict the lattice conductivity by as much as a factor of two. This is in agreement with earlier observations of Klemens [37] relative to use of this equation with dielectrics and semiconductors. The data of Williams and Fulkerson on tungsten and the dilute tungsten alloys do, however, indicate that the lattice thermal resistivity is approximately linear above $\theta_D/2$ ($\theta_D = 315°\mathrm{K}$). Since phonon–electron and phonon–impurity contributions to the lattice thermal resistivity are small (and nearly temperature independent) at high temperatures, the linear temperature dependence of the resistivity is expected to hold even though the theoretical predictions of absolute magnitudes are disappointing.

The uncertainties in quantitative theoretical calculations of both the lattice and electronic contributions in tungsten lead here to the use of a semi-empirical equation for thermal conductivity prediction. The equation was theoretically based, however, to the extent that the temperature functionality of the lattice component was maintained while the temperature dependency and general proportionally between electrical and thermal energy transport for the electronic component was also maintained. The relationship suggested by Williams and Fulkerson, applicable where

$$T/\theta_D > 1/3$$

was applied [21]:

$$\lambda = \lambda_e + \lambda_1 = L_\infty[1 - \exp(T/\theta + 0{\cdot}214)]T/\rho + [\eta_1/T + \eta_2/T^2] \quad (2)$$

where L_∞, η_1, θ and η_2 are empirical constants. The first term, for the electronic contribution, includes a simplified approximation describing effects of inelastic electron–phonon scattering on the Lorenz number. The second term for the lattice contribution is based on the theoretical linear dependency of the thermal resistivity on temperature and is of the same form applied to graphite (equation 1), with a temperature independent term (A) added to account for secondary impurity and electron–phonon scattering effects. Using electrical resistivity data (inaccuracy = ±0·4 per cent) and thermal conductivity data (inaccuracy = ±1·2 per cent) on a sintered tungsten of 99·98 per cent purity with $RRR = 31{\cdot}4$ Williams and Fulkerson obtained the following values of the empirical constants from their curve fit procedure:

$$L_\infty = 1{\cdot}106 L_o, \quad \theta = 77°\mathrm{K}, \quad \eta_1 = 93{\cdot}5\ \mathrm{W/cm},$$
$$\eta_2 = 4230\ \mathrm{W°K/cm}.$$

Using these numerical results and the electrical resistivity data measured directly on the arc cast tungsten, the predicted thermal conductivity was obtained. Several of the predicted data points are shown in Fig. 6, in good agreement with the directly measured conductivity data curve. The results showed a lattice contribution of 15·8 per cent at 300°K decreasing to 3·8 per cent at 2600°K.

As noted by Williams [35] a major uncertainty of the semiempirical predictive scheme used here is the validity of the essentially asymptotic limiting high temperature Lorenz function, $L_{\infty} = 1{\cdot}106Lo$. The basic empirical constants for the equation were based on experimental data that despite its high quoted accuracy extended to only 1300°K. In addition, above 2200°K the resistivity data on the arc cast material was extrapolated according to the quadratic equation given earlier. At 2600°K this extrapolation is about 4 per cent above resistivity data obtained directly by Taylor on these same lots of tungsten [31, 40]. If Taylor's very high temperature data were used to obtain a predicted conductivity value, the result would be 4 per cent higher as shown in Fig. 6 lying very close to the converted diffusivity curve.

5. CONCLUDING REMARKS

On the tungsten and the isotropic graphite where the data base was most extensive it was concluded that the variations in experimental results among the different investigators could be attributed principally to systematic measurement errors, however, with the aid of semiempirical but theoretically based transport property correlations an estimated uncertainty in the thermal transport properties of these materials has been established. Specifically the thermal diffusivity of the isotropic graphite as expressed by the least squares equation, Table 4, was estimated to be accurate within ±6 per cent. Considering the uncertainties in graphite heat capacity, the arithmetic mean of the thermal conductivity and converted diffusivity least squares curves was estimated to express the temperature dependency of the graphite conductivity within ±10 per cent. For the tungsten the scatter among experimental results was relatively large however the consistency of the predictive schemes based on electrical resistivity was sufficient to conclude that the TPRC recommended curve [41] as given by the least squares equation in Table 4 represents the thermal conductivity of tungsten within ±5 per cent. To about 1600°K the thermal diffusivity of tungsten is represented within the same inaccuracy band by converting the conductivity recommendation using the heat capacity data sources cited in the text. Above 1600°K the comparatively wide scatter in diffusivity measurement results and the uncertainty in heat capacity preclude a meaningful estimate of the true curve.

The current state of knowledge on the transport properties of these two materials is sufficient for their use in at least two ways: (1) qualifying thermophysics apparatus in obtaining high temperature properties with engineering accuracy and (2) exploration of systematic measurement errors. With these purposes in mind the remaining stocks of the two materials studied extensively under this program have been transferred to the National Bureau of Standards for further evaluation and distribution.

One of the more important results of this study was the generation of a basis or foundation for further refinement of a small but select group of refractory materials as thermophysical property calibration references. It became clear during this program that the accuracy and even the precision of experimental results with a given apparatus are a function not only of the quantifiable error sources in the various components generally quoted but also of the type of material being tested. Specifically, the following areas for future study become evident as a result of the program:

In relation to Poco AXM-5Q graphite

Direct thermal conductivity measurements with a precision on the order of 2–3 per cent and accuracy to within at least 5 per cent are feasible to around 1200°K with the several techniques available. Such measurements are needed to clarify the conductivity relationship in this range for at least two reasons: (1) to form a basis of quantitatively isolating systematic differences in direct conductivity and converted diffusivity and (2) to form a more precise basis in determining the constants in the thermal resistivity equation particularly in the 800–1200°K range where phonon–phonon transport is clearly predominant and not perturbed by either lower temperature boundary scattering or high temperature band structure effects. Extrapolation of the lattice resistivity expressions to higher temperatures is highly sensitive to imprecisions in this mid temperature range.

Electrical resistivity measurements encompassing the above range and extending to about 3000°K within even 5–10 per cent accuracy would be a valuable adjunct to more basic theoretical analyses of high temperature electronic contributions to the thermal conductivity.

In relation to arc cast tungsten

The very encouraging high temperature electrical resistivity measurements particularly relative to the thermal transport property measurements points strongly to an analysis to reduce the principal uncertainty remaining in the predictive equation for thermal conductivity—the quantitative, theoretically based form of the high temperature Lorenz function.

Because direct thermal conductivity measurements on good conductors such as tungsten can be made with conventional techniques from about room temperature to around 1200–1500°K within an inaccuracy of 1–3 per cent, measurements on arc cast tungsten should be conducted with an attempt to extend the results to about 2000°K with a target accuracy of ±5 per cent. Even without much improvement in theoretical expressions for the high temperature Lorenz function of tungsten, confirmation of the very high temperature direct electrical heating technique results and validation of the semiempirical equations based on measured electrical resistivity should bring the probable inaccuracy in predicted conductivity into the ±3 per cent range. This range is thus narrow enough to allow exploration of systematic measurement errors with other techniques where the differences in results during this program ranged up to ±12 per cent in thermal diffusivity. The high temperature electrical resistivity coupled with post-test *RRR* characterization are particularly powerful tools in the instance of metallic conductors such as tungsten where there appear to be considerable difficulties in direct thermal transport property measurements.

If international agreement could be reached on at least the inaccuracy bounds for the very high temperature heat capacity of tungsten an additional independent consistency check would be available on thermal transport property measurements. If the heat capacity rises as rapidly as suggested by some authors, the effect would be clearly evident in the thermal diffusivity temperature dependency.

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CHOIX DE MATERIAUX REFRACTAIRES A PROPRIETES THERMOPHYSIQUES REPERES AUX HAUTES TEMPERATURES

Résumé—Vingt-deux matériaux ont été étudiés en tant que références pour les propriétés thermophysiques à haute température. Parmi eux, cinq ont été choisis pour un programme d'essai dans six laboratoires des U.S.A. (alumine, thorium, tungstène et deux graphites). On présente les valeurs de la conductivité thermique et de la diffusivité dans le domaine de température allant de 500 à 2700 K, en s'intéressant à la stabilité physico-chimique. Deux de ces matériaux, tungstène et graphite isotrope, ont été retenus pour une évaluation détaillée dans un programme international de mesure qui concerne 18 laboratoires, 9 en Europe et 9 aux U.S.A. On conclut que la conductivité et la diffusivité du graphite sont respectivement connues à ±10 et ±6 pour cent près, tandis que pour le tungstène l'imprécision sur les deux grandeurs est inférieure à ± 5 pour cent. Bien qu'une dispersion plus grande ait été observée parmi les résultats sur le tungstène, les incertitudes ont été réduites en utilisant des mesures très précises de la résistivité électrique. Les résultats expérimentaux sur le graphite et le tungstène sont en accord avec les considérations théoriques. Des recommandations spécifiques sont faites pour des études expérimentales et théoriques sur ces deux matériaux étalons.

UNTERSUCHUNG AUSGEWÄHLTER WIDERSTANDSMATERIALIEN ALS REFERENZSTOFFE FÜR THERMOPHYSIKALISCHE DATEN BEI HOHEN TEMPERATUREN

Zusammenfassung—Es wurden 22 Stoffe auf ihre Eignung als Referenzstoffe für thermophysikalische Stoffwerte bei hohen Temperaturen untersucht. Davon wurden 5 Stoffe (Tonerde, Thorium, Wolfram und zwei Graphitarten) für ein vorläufiges Untersuchungsprogramm an sechs Laboratorien in den USA ausgewählt. Die Wärmeleitfähigkeit, die Temperaturleitfähigkeit und die physikalisch-chemische Stabilität werden im Temperaturbereich von 500 K bis 2700 K angegeben. Zwei dieser Stoffe, Wolfram und isotroper Graphit, wurden für eine weitergehende Untersuchung im Rahmen eines ausgedehnten internationalen Meßprogramms an 18 Laboratorien ausgewählt, wovon sich 9 in Europa und 9 in den USA befinden. Mit einigen Einschränkungen, die beschrieben werden, sind die Wärme- und Temperaturleitfähigkeit von Graphit mit einer Genauigkeit von ±10% bzw. ±6% bekannt; bei Wolfram ergab sich für beide Transportgrößen eine Genauigkeit von ±5%. Obwohl die Meßwerte für Wolfram eine größere Streuung aufwiesen, konnten die Transportgrößen unter Verwendung sehr genauer Daten für den elektrischen Widerstand mit guter Genauigkeit angegeben werden. Es zeigte sich, daß die experimentellen Ergebnisse mit theoretischen Überlegungen in Einklang stehen. Abschließend werden einige Empfehlungen für die Fortführung der experimentellen und theoretischen Untersuchung beider Stoffe ausgesprochen.

ОЦЕНКА НЕКОТОРЫХ ЭТАЛОННЫХ ОГНЕУПОРНЫХ МАТЕРИАЛОВ В ВЫСОКОТЕМПЕРАТУРНЫХ ИССЛЕДОВАНИЯХ ТЕПЛОФИЗИЧЕСКИХ СВОЙСТВ

Аннотация — В качестве эталонов с высокотемпературными теплофизическими свойствами отобраны 22 материала. Пять материалов (алюминий, торий, вольфрам и два графита) отобраны для исследований по полупромышленной программе, проводимой в шести американских лабораториях. Представлены данные по теплопроводности, температуропроводности и физико-химической стабильности этих материалов в диапазоне температур от 500° до 2700°K. Вольфрам и изотропный графит отобраны для оценки по расширенной международной программе измерений, проводимой в 18 лабораториях: 9 в Европе и 9 в США. Установлено, что погрешность теплопроводности и температуропроводности графита составляет соответственно ±10% и ±6%, в то время как погрешность обеих величин для вольфрама составляет ±5%. Хотя наблюдается большой разброс данных по вольфраму, тем не менее снижается неопределенность теплофизических свойств за счет использования точных данных по электрической сопротивляемости. Найдено, что экспериментальные данные по графиту и вольфраму не противоречат теоретическим. Даются специальные рекомендации для дальнейших экспериментальных и аналитических исследований этих двух эталонных материалов.