Thermal Conductivity Measurements of Pyroceram 9606 Using a High-Temperature Guarded-Hot-Plate

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ABSTRACT

The thermal conductivity of Pyroceram 9606 has been measured using a steady-state high-temperature guarded-hot-plate over a temperature range of 130 °C to 800 °C. The measurements were performed as part of an international round-robin to determine the suitability of Pyroceram 9606 as a high-temperature, medium-range, thermal conductivity and thermal diffusivity reference standard. The results of the current study have shown that Pyroceram 9606 is a very stable material with good measurement repeatability. The average values of thermal conductivity, from our tests, decrease from 3.7 $W \cdot m^{-1} \cdot K^{-1}$ at 130 °C to 3.1 $W \cdot m^{-1} \cdot K^{-1}$ at 800 °C. A number of thicknesses were tested, ranging from 1.26 mm to 7.7 mm. A dependence of thermal conductivity on specimen thickness was observed, with thicker specimens yielding higher values of thermal conductivity. This effect is discussed in terms of possible radiative heat transfer, along with a description of the measurements and data analysis method. An absorption coefficient of 19 cm^{-1} was derived from the data, based on the assumptions that Pyroceram 9606 is a translucent glass/ceramic oxide and that no parasitic heat loss occurs in the system.

INTRODUCTION

The availability of standards for thermal conductivity and thermal diffusivity has always been of importance to industry and national standards laboratories. Without these benchmarks it would be impossible to reliably calibrate comparative instruments or validate the operation of absolute instruments. Due to the wide range of new materials that are currently being developed, standards that cover a larger range of both temperature and thermal conductivity are needed. One of the most likely candidates for a mid-range thermal conductivity material that is stable to moderately-high temperatures is Pyroceram 9606.

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Pyroceram 9606 is made from a high temperature melt of alumina, silica, magnesia, and small amounts of titania. The initially transparent glass is processed to produce a polycrystalline material composed of 10 nm to 1 μm diameter, randomly oriented crystals of cordierite ($2\ MgO \cdot 2\ Al_2O_3 \cdot 5\ SiO_2$), cristobalite (SiO_2), and rutile (TiO_2). The resulting cream-colored optically-opaque solid is homogeneous, isotropic, stiff and strong enough for measurement purposes, and chemically stable over the required temperature range.

In the early 1960's, the National Bureau of Standards began making measurements on Pyroceram 9606 to determine its suitability as a thermal conductivity standard reference material. Density, linear thermal expansion, thermal diffusivity, and thermal conductivity measurements were made. Thermal conductivity was measured using an absolute cut-bar apparatus and a long-bar apparatus for metals [1, 2]. With promising results from these tests, seven 46 cm. diameter by 5.7 cm. thick disks were ordered from Corning Glass Works. To assure uniformity, all the disks were fabricated from a single melt and the transparent material was carefully inspected for defects before the material was cerammed. This quantity was chosen to provide a sufficient number of specimens for testing and still leave enough material to distribute as thermal conductivity reference samples. The Office of Standard Reference Materials (OSRM) is currently sponsoring an international round-robin [3], using this material, to determine the suitability of Pyroceram 9606 as a standard reference material. The thermal conductivity results presented here are part of that study.

APPARATUS DESCRIPTION AND MEASUREMENT METHOD

A very-high-temperature guarded-hot-plate apparatus (VHTGHP) [4, 5] was used in this study to measure thermal conductivity. It is a steady-state absolute-measurement device based on the ASTM C 177-85 standard test procedure [6]. Although similar in many respects to a standard guarded-hot-plate device, this one-sided, heat-flow-up apparatus incorporates several unique design features that allow high temperature operation with specimens of low to moderately high thermal conductivity. Figure 1 shows a schematic drawing of the essential features of the apparatus.

Specimens used in this apparatus are 70 mm diameter disks that can range in thickness from 1 mm to 8 mm. A micrometer with an uncertainty of 12 μm is used to measure the specimen thickness. The specimen diameter is measured using calipers with an uncertainty of 25 μm. The specimen surfaces are ground flat to within 10 μm, with parallelity tolerance of less than 1% of the thickness. A uniform surface finish is required on all specimens. The finish roughness on all of the Pyroceram 9606 specimens was 0.25 μm ± 0.02 μm. This is critical for our measurements, because the surfaces cannot be made uniform and opaque by blackening, due to the sensitivity of the system to chemical contamination.

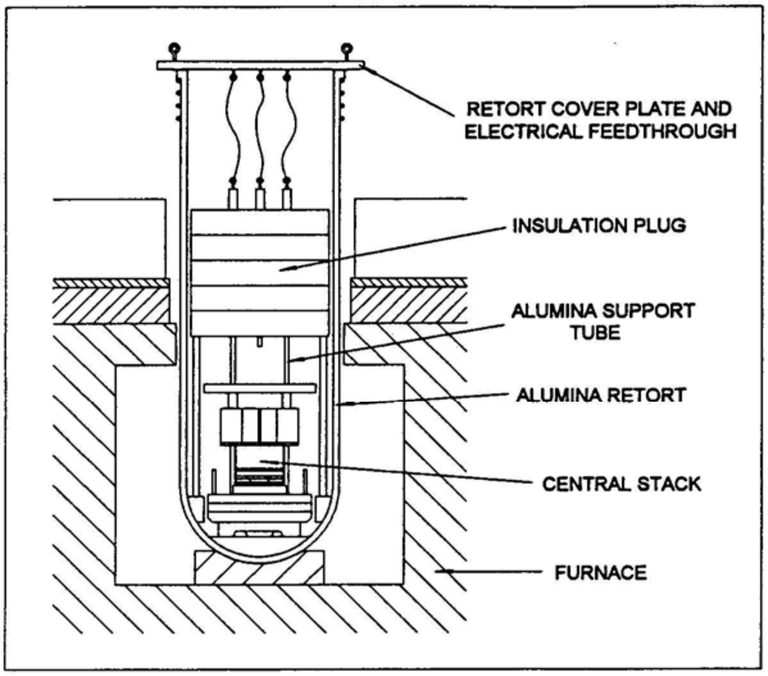

FIGURE 1. OVERALL SCHEMATIC DIAGRAM OF THE VHTGHP SYSTEM SHOWING THE RELATIVE POSITIONS OF THE CENTRAL STACK, CERAMIC RETORT, AND THE HIGH-TEMPERATURE FURNACE.

The apparatus operates within a sealed ceramic retort filled with pure helium at a pressure of 47 kPa. The retort assembly is placed within a 1500°C crucible furnace, which defines the low temperature of the system and acts as a heat sink. Figure 2 shows a detail of the main stack assembly. One of the unique features of this system is the use of a radiative heat sink instead of a temperature-controlled plate for the low temperature side. The heat sink radiates heat away from the main stack to the inner walls of the retort. It's 2 kilogram mass also provides a small compressive force on the plates in the main stack, enhancing thermal contact between the plates. Since the temperature of the radiative heat sink is open-loop controlled, the temperature difference across the specimen cannot be explicitly set. Nevertheless, the critical experimental value, the ratio of temperature difference to heat flux, shows better than 99% repeatability for repeat testing of a given specimen. This measurement precision has been verified with a number of different specimens, including monolithic ceramics such as MgO [5, 7] and ceramic coated metals such as ZrO_2 coated stainless steel [5, 8], with thermal conductivities ranging from 30 W $m^{-1} K^{-1}$ to 0.5 W $m^{-1} K^{-1}$, respectively.

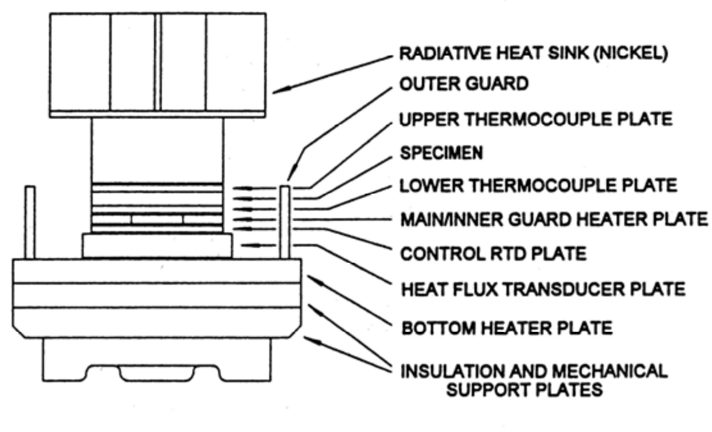

FIGURE 2. HIGH-TEMPERATURE GUARDED-HOT-PLATE APPARATUS MAIN STACK.

To obtain the thermal conductivity, we start with the one-dimensional Fourier conduction equation

$$Q=-\lambda \cdot A \cdot \frac{dT}{dx} \qquad (1)$$

where Q is heat flow rate(W), λ is thermal conductivity (W m^{-1} K^{-1}), A is area (m^2), and dT/dx is the temperature gradient (°C m^{-1}). As a steady-state approximation, the temperature difference, ΔT (°C), replaces dT and specimen thickness, Δx (m), replaces dx. However, because of the high temperatures achieved in this apparatus and the large thermal resistances that exist between the temperature sensor plates and the specimen, Equation (1) cannot be directly used. Since the temperature difference, ΔT, represents not only the temperature drop across the specimen, but also the temperature drop across the specimen/sensor plate contact interface, additional measurements and a modified data analysis procedure are required. The one-dimensional steady-state form of the Fourier conduction equation is expanded to represent the series of thermal resistances present in the VHTGHP apparatus. The functional equation is :

$$\frac{\Delta T \cdot A}{Q}=\frac{\Delta x}{\lambda}+2R_T\ , \qquad (2)$$

where the first term on the right side of Equation (2) represents the specimen resistance, and R_T ($m^2\,K\,W^{-1}$) represents the sum of the specific thermal resistances between the specimen and one of the sensor plates. The resistance is doubled, based on the assumption that the resistances on each side of the specimen are equal. With this equation, data from two specimens of different thickness, run at the same absolute temperature, are used to generate two independent equations with two unknowns, λ and R_T. The resulting equations are then simultaneously solved to determine both the specific interfacial thermal resistance between the sensor plate and specimen, and the apparent thermal conductivity of the specimen.

After a specimen was mounted, the first step in the measurement procedure was to perform a conditioning run, from 200 °C up to 800 °C in 100 °C steps. This procedure was necessary to stabilize the sensor plate/specimen interface. The apparatus was then cooled to 100 °C. Data points were then taken from 130 °C to 800 °C, in 50 K steps. Three specimen thicknesses, 1.26 mm, 2.50 mm, and 7.71 mm, were measured. All combination pairs of the thicknesses were then analyzed using Equation (2) to determine average thermal conductivity and average specific interfacial thermal resistance.

A fixed-point compression-probe (FPCP) thermal conductivity apparatus [9,10] was also used in this study. The FPCP is a modified, unguarded, fixed-point device that is used to make absolute thermal conductivity measurements at temperatures from liquid helium to room temperature. The specimen is clamped between two isothermal, copper sensor blocks, with one block heated with an electrical coil, and the other block thermally anchored to a constant temperature bath. Room temperature tests using an ice/water bath were performed on a 13 mm diameter, 25.4 mm long specimen of Pyroceram 9606. Since the fixed-point apparatus runs at low temperature, indium foil and thermal grease are used between the specimen and sensor plates, effectively eliminating any interfacial thermal resistance. This allowed us to assess, at least at low temperatures, the methods used to remove the interface effects from the VHTGHP results.

MEASUREMENTS AND RESULTS

The first issue addressed during the measurement of Pyroceram 9606 was its stability during heating and after repeated thermal cycling. All of the specimens exhibited a color change from a pale yellow to a dull gray during the first heating. Sectioning one of the specimens revealed that the discoloration was a surface, not a bulk effect. This surface discoloration was also observed by Flynn, et al. [2], presumed to be caused by the reduction of some component within the Pyroceram 9606. For thicker specimens, this surface discoloration had no effect on the apparent thermal conductivity, as measured during the experimental runs. The thinnest specimen, however, exhibited an apparent thermal conductivity that was higher during the first run than in any subsequent run. After completion of this initial thermal conditioning, measurements for each specimen were repeatable within 1%.

The raw data taken during a single experiment are displayed as total stack thermal conductivity, calculated using Equation (1). The total stack thermal conductivity therefore represents the inverse of the sum of the specimen and interfacial thermal resistances. The thickest and thinnest specimens were measured several times to verify experimental repeatability. Typical results are shown in Figure 3 . Three separate curves are obtained because the interfacial thermal resistance is approximately constant from specimen to specimen; therefore the percentage contribution to the total stack conductivity varies inversely with specimen thickness. The interfacial thermal resistance is considered constant from specimen to specimen since the surface finish of all of the specimens is substantially the same and there are no chemical changes at the interface after the first run of a given specimen. Figure 3 shows that the raw data are smooth and well-behaved.

All combination pairs of the three specimen thicknesses are analyzed using Equation (2). The analyzed data from the three specimen thicknesses yield three thermal conductivity curves, shown in Figure 4 and Table I. The VHTGHP data show a dependence of thermal conductivity on specimen thickness. At any given temperature, thicker specimens yield higher values of apparent thermal conductivity. Although the average curve for all the data falls within the overall 5% accuracy of the apparatus [5], the thickness-dependent apparent thermal conductivity results are consistent and repeatable. Tests on magnesium oxide [5, 7] and low temperature tests on plasma-sprayed yttria-stabilized zirconia coatings on stainless steel [5, 8]

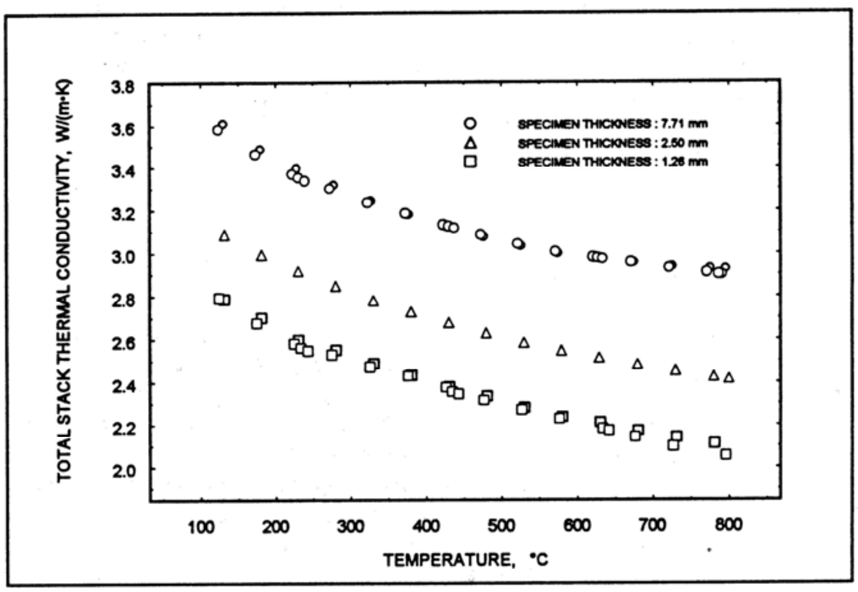

FIGURE 3. TOTAL STACK THERMAL CONDUCTIVITY FOR THREE DIFFERENT THICKNESSES OF PYROCERAM AS A FUNCTION OF TEMPERATURE.

TABLE I. THERMAL CONDUCTIVITY AND SPECIFIC INTERFACIAL RESISTANCE VALUES OBTAINED USING THE TWO FILE METHOD OF ANALYSIS FOR THREE THICKNESSES OF PYROCERAM 9606

TEMP.(°C)	7.71 mm AND 2.50 mm SPECIMENS		7.71 mm AND 1.26 mm SPECIMENS		2.50 mm AND 1.26 mm SPECIMENS	
	λ, ($W\ m^{-1}\ K^{-1}$)	R_T, ($m^2\ K/W$)	λ, ($W\ m^{-1}\ K^{-1}$)	R_T, ($m^2\ K/W$)	λ, ($W\ m^{-1}\ K^{-1}$)	R_T, ($m^2\ K/W$)
130	3.91	.000086	3.80	.000062	3.46	.000045
180	3.80	.000089	3.70	.000064	3.37	.000047
230	3.71	.000091	3.62	.000066	3.30	.000049
280	3.63	.000093	3.54	.000068	3.23	.000051
330	3.55	.000096	3.46	.000071	3.17	.000053
380	3.48	.000099	3.40	.000074	3.11	.000056
430	3.42	.000103	3.34	.000077	3.06	.000059
480	3.37	.000106	3.30	.000080	3.02	.000061
530	3.33	.000110	3.26	.000083	2.98	.000065
580	3.30	.000114	3.23	.000087	2.95	.000068
630	3.28	.000118	3.20	.000090	2.93	.000071
680	3.26	.000122	3.19	.000094	2.91	.000075
730	3.26	.000127	3.18	.000098	2.90	.000079
780	3.26	.000132	3.19	.000102	2.90	.000083
800	3.27	.000134	3.19	.000104	2.90	.000084

did not show any thickness effect . Therefore, we think that systematic bias is not responsible for the observed thickness effect.

We averaged all of the VHTGHP data and plotted the resulting curve along with the curve for the TPRC recommended literature value for Pyroceram 9606 [11], shown in Figure 4. Similar values for the thermal conductivity of Pyroceram 9606 were obtained by Cahill [12] using the 3ω method. The VHTGHP results also agree, within experimental uncertainty, with previous measurements made at the National Bureau of Standards by Flynn, et al. [2] in the early 1960's. A comparison of the data are given in Table II, with the thermal conductivity values for the Flynn data determined using the Flynn equation [1]

$$1/\lambda = 26.7 + 9.7 \cdot \left(\frac{T}{1000}\right) \qquad (3)$$

where λ is thermal conductivity ($W\ cm^{-1}\ K^{-1}$), and T is temperature (°C). Our averaged VHTGHP results are approximately 3% higher than the recommended values found in the literature. However, conductivity of the thin specimens is 3%

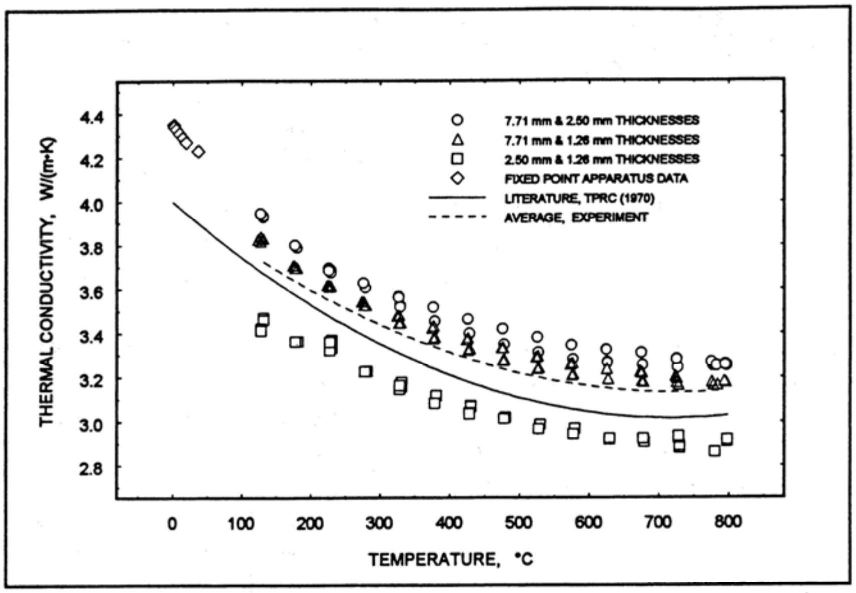

FIGURE 4. THERMAL CONDUCTIVITY USING TWO FILE DATA ANALYSIS.

below and the conductivity of the thick specimens is as much as 8% above these values. Results of the low temperature measurements made with the FPCP thermal conductivity apparatus are also included in Figure 4. These results are in best agreement with the combined, analyzed VHTGHP data from the 7.71 mm and 2.5 mm specimens. The experimental uncertainty of the FPCP measurements is 5%, the same as for the VHTGHP. The uncertainty of the recommended literature values is reported as 5 to 10% [11]. All of the data represented in Figure 4 fall within the combined uncertainties, which demonstrates the reliability of our measurement and analysis methods. The measurements made on all thicknesses of Pyroceram 9606 were very repeatable and stable, and although slight discoloration occurred after heating, it did not adversely affect the data after the initial conditioning run. Although thickness may affect the absolute value of apparent thermal conductivity, measurements on any given thickness are very consistent.

The dependence of apparent thermal conductivity on thickness may be due to radiative heat transfer, which would imply that Pyroceram 9606 may be semi-transparent. Similar observations have been made with glasses and translucent ceramics. The effect was described and explained by Kingery, et al. [13] based on photon mean free paths and boundary effects. Figure 4 shows that the 7.7 mm specimen exhibits little or no radiative heat transfer effects since these data and the low-temperature fixed-point results are in good agreement. The thickness effect could also be explained by heat losses from the edge of the specimens, but this is unlikely since measurements of magnesium oxide do not show this effect, and the

TABLE II. COMPARISON OF RECOMMENDED AND MEASURED THERMAL CONDUCTIVITY VALUES FOR PYROCERAM 9606. VALUES IN PARENTHESES ARE EXTRAPOLATIONS.

TEMP. (°C)	λ, FPCP (W m^{-1} K^{-1})	λ, TPRC (W m^{-1} K^{-1})	λ, Flynn (W m^{-1} K^{-1})	λ, VHTGHP Average (W m^{-1} K^{-1})	λ, VHTGHP Trans. Corr. (W m^{-1} K^{-1})
30	4.25	3.99	(3.70)	(3.94)	(4.13)
130	—	3.64	3.58	3.73	3.91
180	—	3.53	3.52	3.63	3.81
230	—	3.44	3.46	3.54	3.72
280	—	3.37	3.40	3.47	3.64
330	—	3.30	3.34	3.40	3.56
380	—	3.25	3.29	3.33	3.50
430	—	3.20	3.24	3.28	3.44
480	—	3.15	3.19	3.23	3.39
530	—	3.11	3.14	3.20	3.35
580	—	3.07	3.09	3.17	3.32
630	—	3.03	3.05	3.15	3.30
680	—	2.99	3.00	3.14	3.29
730	—	2.96	2.96	3.13	3.28
780	—	2.93	2.92	3.14	3.28
800	—	2.92	2.90	3.14	3.29

fixed-point results, done in a vacuum-insulated environment at low temperature, fit the 7.7 mm VHTGHP results. To approximate the effect of radiative heat transport, we modify the heat input data using an absorption coefficient

$$Q = Q_t \cdot (1 - e^{-a\Delta x}) \; , \qquad (4)$$

where Q is the solid conduction heat flow rate (W), Q_t is the total, experimentally measured, heat flow rate (W), a is the absorption coefficient (cm^{-1}), and Δx is the specimen thickness (cm). Equation (4) gives the solid conductive component of heat flow by taking the total heat input and subtracting a radiative component, that affects both the interfacial thermal resistance and the specimen thermal conductivity, as given from the Beer-Lambert equation [14]. Fitting the data for all three thicknesses to Equation (4) gives an absorption coefficient of 19 cm^{-1}, which is within a reasonable range for semi-transparent ceramics [15]. This treatment is a greatly simplified view of radiative transport and assumes that the interfacial thermal resistance is constant from specimen to specimen and independent of thickness. Since there are no chemical changes at the interface during the tests and the

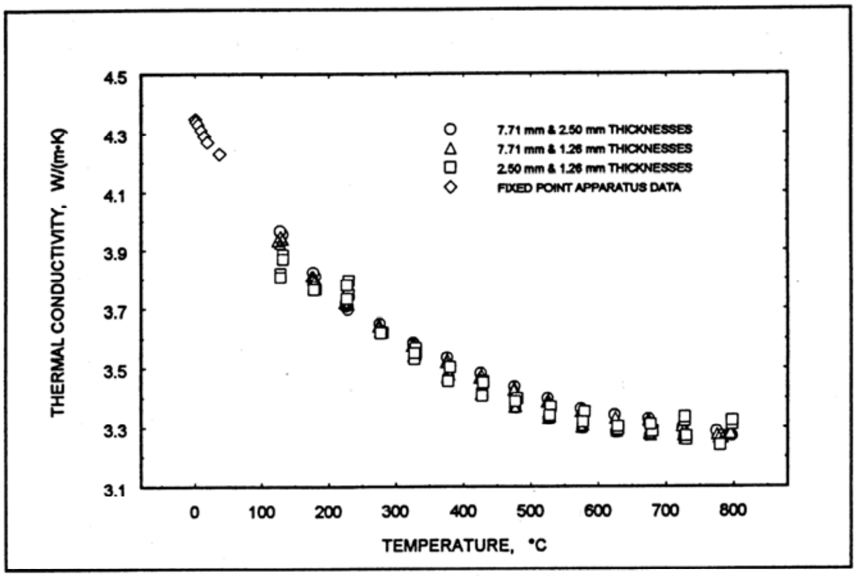

FIGURE 5. THERMAL CONDUCTIVITY ADJUSTED FOR TRANSPARENCY

emissivity of the specimens measured with an infrared scanning system does not change from test to test, following the initial test, these assumptions are probably valid. After the heat flow values are corrected for radiation, the apparent thermal conductivity and specific interfacial thermal resistance are recomputed using Equation (2). The apparent thermal conductivity due only to solid conduction is shown in Figure 5. All of the VHTGHP data converges to a single curve which correlates well with the fixed-point data. This result demonstrates that the possibility of semi-transparency in Pyroceram 9606 is not unreasonable. Note that this treatment does not include internal reflection effects due to scattering or differences in index of refraction. The curve shown in Figure 5 represents the limiting value of lattice thermal conductivity for thick specimens. Based on the fitted absorption coefficient, "infinite" optical thickness for Pyroceram 9606 is about 2 mm. Therefore, material thicknesses less than 2 mm can be expected to exhibit a significant radiative component of heat transfer which affects both the apparent thermal conductivity of the material and the specific interfacial thermal resistance.

CONCLUSIONS

We have measured the apparent thermal conductivity of Pyroceram 9606 from 130 °C to 800 °C using an absolute, steady-state measurement technique. We have found excellent measurement repeatability over the entire temperature range. Our results are within the experimental uncertainty of recommended literature values, and our average values are within 2% of those values. Even though all of the experimental data are within experimental uncertainty of the average values, it appears that the apparent thermal conductivity depends on specimen thickness. Thicker specimens repeatedly yield slightly higher values for thermal conductivity. A simplistic radiative heat-transfer correction that was applied to the data yielded convergence of the three curves for apparent thermal conductivity and also correlated with fixed-point measurements of thermal conductivity at low temperatures. We are, however, not yet confident that the question of the measurement thickness dependence has been satisfactorily answered. Nevertheless, the high temperature stability, chemical inertness, and uniformity of Pyroceram 9606 should still make it a suitable candidate for a thermal conductivity standard reference material.

DISCLAIMER

Materials are identified by trade name for technical accuracy and measurement repeatability by independent laboratories. Use of any trade names neither constitutes nor implies endorsement of products by NIST or by the U.S. Government.

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