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A COMPARATIVE METHOD APPARATUS AND STANDARDS FOR MEASUREMENT OF THERMAL CONDUCTIVITY

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A COMPARATIVE METHOD APPARATUS AND STANDARDS FOR MEASUREMENT OF THERMAL CONDUCTIVITY

by

V.V. Mirkovich*

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SYNOPSIS

A comparative method thermal conductivity apparatus was designed. The precision of measurements was determined by measuring the conductivity of alumina with standards made of the same alumina. The accuracy of measurements was determined by cross-checking the conductivities of alumina, forsterite, Pyroceram Code 9606 and titanium carbide. The thermal stabilities of Pyroceram Code 9606 and zirconia were examined in order to establish their values as thermal conductivity reference materials. It was concluded that: 1) with this apparatus, accurate thermal conductivity data can be obtained; and 2) Pyroceram Code 9606 can be recommended for use as a primary standard for the low thermal conductivity range.

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Direction des mines

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APPAREIL À MÉTHODE COMPARATIVE ET NORMES POUR MESURER LA CONDUCTIVITÉ THERMIQUE

par

V. V. Mirkovich*

RÉSUMÉ

On a mis au point un appareil utilisant la méthode comparative pour mesurer la conductivité thermique. On a déterminé la précision des mesures en mesurant la conductivité de l'alumine en regard de normes établies pour la même alumine. La précision des mesures a été confirmée en vérifiant les conductivités de l'alumine, de la forsterite, du Pyroceram Code 9606 et du carbure de titane. La stabilité thermique du Pyroceram Code 9606 et de la zircone a été étudiée afin d'établir leur valeur comme matériaux de référence en conductivité thermique. L'auteur a conclu 1) qu'avec l'appareil en question on peut en arriver à des données précises sur la conductivité thermique et 2) que l'on peut utiliser le Pyroceram Code 9606 comme norme primaire dans l'échelle des faibles conductivités thermiques.

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INTRODUCTION

There are three distinct ways by which heat is transferred between hot and cold bodies. These are conduction, convection, and radiation. In almost any system the heat is transferred by a combination of two or three of these methods. The overall objective may be the maximum heat transfer rate in one instance, or a minimum heat flux for the other case. But in order to attain the desired condition, the knowledge of each mode of heat transfer must be established. This work is concerned with heat transfer by conduction only. Its purpose is to study a comparative method for measurement of thermal conductivity of solids.

Thermal conductivity can be measured by the steady state or the transient methods. In the latter, a pulsating heat source is commonly used and the temperature of the specimen is measured as a function of time and position. Steady state methods, as the name implies, require that the temperature gradient between the heat source and heat sink become independent of time. If the heat flux and temperature gradient are measured for a sample of given geometrical shape, the method is absolute. On the other hand, if only the temperature gradient is measured and then compared with a temperature gradient obtained under the same conditions in material of known conductivity, the method is said to be comparative.

The principle of the comparative method is simple. In a column formed by several samples, the necessary condition is that the linear heat flow q_1 (per unit time) through the first sample equal that of the second, q_2, and so on. Thus

$$q_1 = q_2 = q_3 = \ldots. \qquad \text{Eq(1)}$$

By applying to Equation(1) the fundamental equation of thermal conductivity,

$$q = kA\frac{dt}{dx}, \qquad \text{Eq(2)}$$

where q is the heat flow per unit time through an area A, dt/dx is the temperature gradient normal to A, and k is the thermal conductivity, one obtains:

$$k_1A_1\left(\frac{dt}{dx}\right)_1 = k_2A_2\left(\frac{dt}{dx}\right)_2 = k_3A_3\left(\frac{dt}{dx}\right)_3 = \ldots. \qquad \text{Eq(3)}$$

or, if expressing in finite differences and postulating that $A_1=A_2=A_3= \ldots.$ and $\Delta x_1 = \Delta x_2 = \Delta x_3 = \ldots,$ and simplifying, the resulting relation becomes:

$$k_1\Delta t_1 = k_2\Delta t_2 = k_3\Delta t_3 = \ldots \qquad \text{Eq(4)}$$

The difficulty arises, however, when the condition described by Equation(1) is duplicated experimentally. It is virtually impossible to maintain the linear heat flow through the specimens by the use of insulation alone, for in some cases the specimens themselves may be insulating materials. In principle this difficulty can be overcome by the use of heat guards. By this method, heating elements are strategically placed about the hollow cylinder surrounding the specimens, so that isothermal planes are maintained perpendicular to the direction of the desired heat flow through the samples.

Unfortunately, the measure that may be taken to prevent radial heat flow introduces new difficulties. In order to control the power input to the heat guards, the temperature of the inner surface of the cylinder must be measured and matched with the temperature in the specimens. However, with the exception of radiation pyrometry, no direct methods exist for measuring surface temperature. In practice this means that hot joints of the thermocouples must be somehow placed in good contact with the inner surface of the cylinder guard, with the hope that the resulting readings represent the true temperature of the wall surface. Incorrect readings of this temperature cause improper heat guarding and this in turn leads to erroneous results.

It is the purpose of the present work to devise an apparatus for measurement of thermal conductivity by the comparative method. It is to be used on homogeneous ceramics, rocks and minerals at temperatures from 100° to about 1000°C. Most of these materials have low thermal conductivities and specimens may be limited in size because of cracks. In addition, selection of proper standards must be made and the stabilities of the thermal properties of these standards must be examined.

The thermal conductivity unit used in this work is watt $cm^{-1} {}^{o}C^{-1}$. This unit was proposed at the First Thermal Conductivity Conference, held at the Battelle Memorial Institute, Columbus, Ohio, in 1961. The unit was generally accepted by the attendants of the subsequent meetings, for use in scientific papers.

EXPERIMENTAL METHODS

A. Experimental Equipment Used in Past Investigations

One of the earlier applications of the comparative method can be found in the equipment described by Van Dusen and Shelton(1). The thermal conductivity of metals was determined by soldering the unknown to the nickel secondary standard and then placing the assembly into the stainless-steel cylinder guard. The conductivity of the nickel standard was determined from the melting point lead, which was used as the primary standard. The space between the sample and the guard was filled with insulation. The temperatures of the cylinder guard and of the samples were measured in the same plane and their differences adjusted, by means of heaters on the cylinder guard, to about ±2.5°C.

For measuring the thermal conductivity of ceramics, a comparative method apparatus was used by Knapp(2). A one-centimetre-cube specimen and a stainless-steel standard were placed in a separately heated stainless-steel cylinder guard. Thermocouples were placed only into the stainless-steel standard and the heating plate. Although tin foil was placed between the sample and the standard to improve thermal contact, the temperature drop in the sample could only have been estimated, since the contact resistance was unknown.

Francl and Kingery(3) constructed an improved version of Knapp's apparatus. They placed the unknown between two one-inch-cube standards. To attain good thermal contact, silver or platinum foils were inserted between the samples. In order to eliminate the effect of contact resistance, the temperature gradient in each sample was determined by locating the thermocouples in small holes, which were drilled some 1-3 mm away from the interface. The specimen and the standards were placed in an Alundum cylinder guard and the space in between filled with insulation. The temperature of the guard was controlled by means of five heaters wound on the outside. Dense alumina was used as a standard. The conductivity of this alumina above 550°C was determined by absolute methods. Below 550°C it was determined by extrapolation and by comparison with melting point lead.

A characteristic feature for the above described equipment is the temperature-matched cylindrical heat guard. Laubitz(4,5) took a somewhat different approach. He deliberately mismatched the temperature of the guard to the sample column and calculated the resulting radial and longitudinal temperature distribution in the system. In principle, the only unknown was assumed to be the conductivity of the specimen. Therefore, by measuring the steady state temperature in strategic positions of the furnace, Laubitz considers that it is possible to evaluate this conductivity.

B. The Apparatus

1. Prototype of the Final Apparatus

The prototype of the final apparatus was virtually the same as the equipment used by Francl and Kingery. Details of the apparatus were acquired by Brady(6) at the College of Ceramics at Alfred University, Alfred, N. Y., and its construction initiated. The assembly was completed by Bell, who also made some preliminary measurements(7). The measurements, however, did not yield satisfactory results.

Under present work, for preliminary experiments with this prototype, alumina Al-300* was used for all three samples. The results confirmed Bell's findings. They indicated that even when the temperatures between the cylinder guard and the samples appeared to be matched, the longitudinal heat flux varied from sample to sample. Because the conductivity of alumina decreases with increasing temperature, one would expect that the temperature gradient through the samples would become successively smaller from the heat source to the heat sink. In these experiments the hottest sample frequently had the smallest Δt of all. And while it was logical to conclude that improper thermal balance must be ultimately responsible for this anomaly, it was not apparent where and why the thermal imbalance occurred.

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* Al-300 is a 97.6% alumina supplied by the Western Gold and Platinum Company, of Belmont, Calif., U.S.A. Its properties are described under "Materials".

Gradually, however, from the information gained through the experimental work, it was concluded that:

(1) the design of the heat source was not suitable;

(2) the portion of the heat guard surrounding the heat sink was not necessary and was detrimental at low temperatures;

(3) samples should be of cylindrical form to attain better symmetry with respect to the heat guard;

(4) the thermal conductivity of the heat guard should be similar to that of the samples, or, alternatively, the conductivity of the heat guard should be low;

(5) the temperature measurements of the heat guard cannot be relied upon, and consequently the temperature matching between the samples and the cylinder guard should not be used as a sole criterion for establishing the thermal balance of the system; and

(6) the principle expressed in Equation(4) should always be satisfied.

The apparatus constructed as a result of these observations and conclusions is described in the next section.

2. The Final Apparatus

The principal improvements in the final apparatus are achieved by introducing a heat stabilizer, by making all samples cylindrical, by making the heat guard of low thermal conductivity zirconia, and by using better insulation between the sample column and the heat guard.

In this apparatus three major sections can be distinguished: the furnace assembly, the power supply, and the temperature measurement system.

a) The Furnace Assembly

The furnace is shown in Figure 1. It consists of a stainless-steel shell, 9 inches in diameter and 9.5 inches high, closed at the top and bottom with stainless-steel covers. Each cover is insulated from the inside with a one-inch-thick Transite plate. Both covers and the insulation attached to them have a concentric hole, 2.25 inches in diameter. By means of a groove in the hole of each insulation plate, a zirconia tube 7.75 inches long and 2.25 inches inside diameter is held concentrically. The wall thickness of this tube is 0.25 inch. Its purpose is to serve as a heat guard. The annual space between the heat guard and the stainless-steel shell is filled with Fiberfrax insulation. The shell is provided with suitable brackets that fit over three guide rods. The guide rods are bolted to the horizontal, 0.5-inch-thick, Transite support. The furnace is counterbalanced to facilitate its raising and lowering.

Inside the zirconia heat guard are two main heaters. Both are

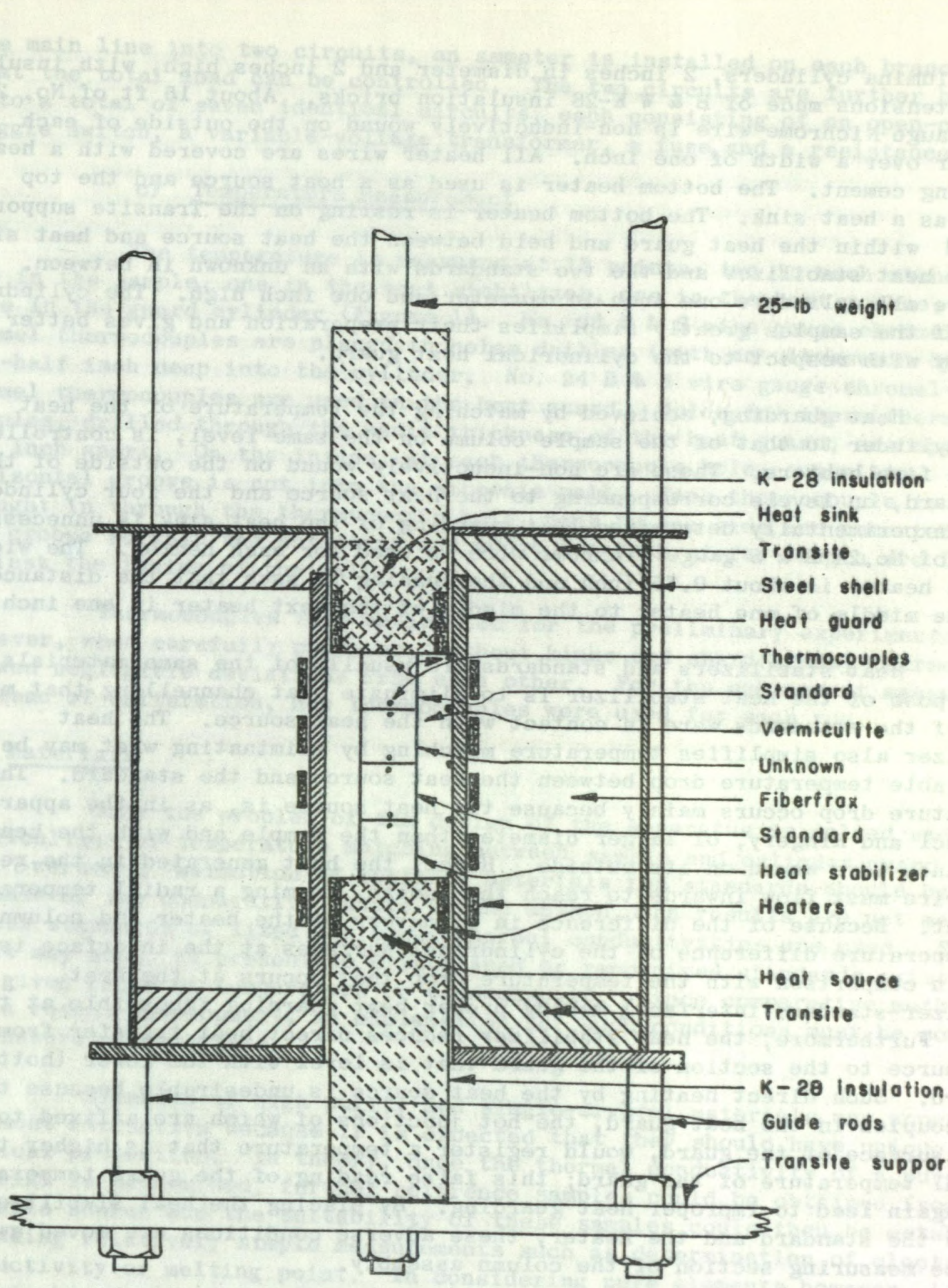

FIGURE I. THE THERMAL CONDUCTIVITY APPARATUS
(APPROXIMATE SCALE : 1:3)

solid alumina cylinders, 2 inches in diameter and 2 inches high, with insulating extensions made of B & W K-28 insulation bricks. About 15 ft of No. 24 B & S gauge Nichrome wire is non-inductively wound on the outside of each cylinder over a width of one inch. All heater wires are covered with a heat-resisting cement. The bottom heater is used as a heat source and the top heater as a heat sink. The bottom heater is resting on the Transite support. Centred within the heat guard and held between the heat source and heat sink are the heat stabilizer and the two standards with an unknown in between. They are all cylinders one inch in diameter and one inch high. The cylindrical shape of the samples greatly simplifies their preparation and gives better symmetry with respect to the cylindrical heat guard.

Heat guarding, achieved by matching the temperature of the heat guard cylinder to that of the sample column on the same level, is controlled through five heaters. These are non-inductively wound on the outside of the heat guard, on levels corresponding to the heat source and the four cylinders. It was experimentally determined that guarding of the heat sink is unnecessary. 15 ft. of No.24 B & S gauge Nichrome wire is used for each heater. The width of each heater is about 0.75 inch and the spacing is such that the distance from the middle of one heater to the middle of the next heater is one inch.

Heat stabilizers and standards are usually of the same materials. The purpose of the heat stabilizer is to eliminate heat channelling that might occur if the standards were in contact with the heat source. The heat stabilizer also simplifies temperature matching by eliminating what may be an appreciable temperature drop between the heat source and the standard. This temperature drop occurs mainly because the heat source is, as in the apparatus of Francl and Kingery, of larger diameter than the sample and with the heating resistance wire wound on its outside. Hence, the heat generated in the resistance wire must flow inwards to reach the sample, forming a radial temperature gradient. Because of the difference in diameters of the heater and column, the temperature difference of the cylindrical surfaces at the interface is high (in comparison with the temperature drop that occurs at the heat stabilizer-standard interface), making proper heat guarding impossible at this level. Furthermore, the heat stabilizer reduces direct heat transfer from the heat source to the section of the guard that is level with the lower (hotter) standard. Such direct heating by the heat source is undesirable because the thermocouples in the heat guard, the hot junctions of which are affixed to the inside surface of the guard, would register a temperature that is higher than the real temperature of the guard; this false reading of the guard temperature would again lead to improper heat guarding. By placing the heat stabilizer between the standard and the heater, these adverse conditions are moved away from the measuring section of the column assembly.

To reduce errors which may be caused by insufficient heat guarding or possible longitudinal displacement of guard to Specimen(5), the space between the sample column and the guard is filled with minus 6-, plus 10-mesh (Tyler) exfoliated vermiculite. As an example, the ratio of conductivities for vermiculite to Pyroceram 9606 is of the order of 1 to 100.

b) Power Supply

Power is obtained from the 110-volt AC mains. To eliminate voltage fluctuations, a constant voltage transformer is used. After the branching of the main line into two circuits, an ammeter is installed on each branch so that the total load can be controlled. The two circuits are further branched into a total of seven identical circuits, each consisting of an open-close toggle switch, a variable-voltage transformer, a fuse, and a resistance heater.

c) Temperature Measurement

The temperature is measured at 13 points: two in each standard, two in the sample, one in the heat stabilizer, one in the heat source, and five in the guard cylinder (Figure 1). No. 28 B & S wire gauge chromel-alumel thermocouples are placed in holes drilled (with an ultrasonic drill) one-half inch deep into the cylinder. No. 24 B & S wire gauge chromel-alumel thermocouples are used in the heat guard. Holes for these thermocouples, drilled through the whole thickness of the heat guard, are spaced one inch apart. On the inside, at each thermocouple hole, a shallow horizontal groove is cut into the zirconia wall. Each thermocouple is then brought in through the thermocouple hole, bent to one side, and cemented into the groove so that the hot joint and about 1/4 inch of its length are flat against the inside of the wall.

Thermocouples were calibrated for the preliminary experiments. However, when carefully prepared, without kinks and sharp bends, thermocouples showed negligible deviations from each other. For the subsequent measurements, instead of calibration, new thermocouples were used for each run.

C. Materials

Once the problem of the design of the apparatus is solved and the difficulties of temperature matching between sample and cylinder guard are overcome, selection of suitable materials for standards should be made. Because of the comparative nature of the method, the results are not meaningful unless standards of fixed and known thermal conductivities are used. Surprising as it may seem, at present no established or recognized standards exist for any given range of temperature or conductivity. Since comparative methods are not a recent development, an explanation for such conditions must be sought in the nature of materials.

Elements of high purity and single-crystal materials may appear as the most attractive because it is expected that they should have unique physical properties. In theory, once the thermal conductivity of a pure material is determined, further reference samples could be obtained from any suitable source and the suitability of these samples could then be established by making relatively simple measurements such as determination of electrical conductivity or melting point. In considering pure elements, however, it must be remembered that they are, especially at high temperatures, chemically quite reactive and that it is difficult to provide suitable protection even in inert atmosphere or in vacuum. This is important because traces of impurities may considerably affect the thermal conductivity of a pure material. Also, the relatively high thermal conductivities of pure materials impose some limitations on their use as standards for low-conductivity (below 0.1 watt/cm°C) materials.

Multi-component structures and materials of no particular purity represent the other possibility. They are not sensitive to moderate changes in composition and, of course, quite a number of them are chemically stable even at high temperatures. However, their thermal properties may be considerably affected by methods of fabrication and heat treatments. A number of multi-component materials, such as ceramics, are not continuous structures but are composed of agglomerates of crystals or grains that are sintered together. Under changing temperatures they undergo thermal expansion, and may suffer crystal changes or gradual phase transformations, phenomena that may radically change the thermal properties and may also, on repeated heating and cooling, cause cracks and render the materials unusable as standards.

One of the major tasks of this work is to study and select materials that can be used as reference standards for thermal conductivity measurements in the range of 0.02 to 0.10 watt/cm°C. Structural, chemical and thermal properties of these substances should be stable and, if possible, independent of temperature. The samples should be rigid, hard, and capable of attaining and retaining polished surfaces. They should not react with thermocouple wires or insulation, and should be substantially nonconducting to simplify the electrical insulation of thermocouples. Furthermore, materials for reference standards must be opaque to thermal radiant energy so that transfer of heat will be by conduction alone. And, finally, they should be readily available through commercial outlets or easily fabricated by standard methods.

In all, five materials were selected as candidates for thermal conductivity reference materials:

(1) Alumina, grade AL-300, a standard product manufactured by the Western Gold and Platinum Company, of California. A typical chemical analysis of the fired AL-300, supplied by the manufacturer, is as follows: 97.55% Al_2O_3, 1.35% SiO_2, 1.05% CaO, 0.03% Fe_2O_3, 0.02% Na_2O. The grain size(8) of this material is in the range 10 to 150 microns, with 80% less than 100 microns. Its bulk density is 3.75 g/cm^3 and true density is 3.92 g/cm^3. The porosity therefore is about 5% of the total volume, but the material is not permeable. The thermal conductivity of AL-300 was determined at Alfred University by an absolute method(9).

(2) Titanium carbide, fabricated by the Norton Company, Worcester, Massachusetts, and supplied by Atomics International, Canoga Park, California. The batch analysis of the powder used for making TiC samples is as follows: 79.2% Ti, 20.2% C, and 0.02% Fe. The sample density is in excess of 97% of the theoretical density.

(3) Pyroceram Code 9606, made by Corning Glass Works, Corning, New York. This is a microcrystalline glass structure, made by the addition of a nucleating agent to a homogeneous glass melt, which is then subjected to a special heat treatment during which the glass article, substantially unchanged in shape and size, is converted to a fine-grained product. The properties of the product can be closely controlled. The thermal conductivity of this material was determined at the National Bureau of Standards, Washington, D.C.(10).

(4) Forsterite "L", a standard product made by Harbison-Walker Refractories Company, Pittsburgh, Pennsylvania. This refractory material is produced in the form of a standard brick. The average chemical analysis supplied by the Company, is as follows: 29.5% SiO_2, 10.9% Al_2O_3, 7.6% Fe_2O_3, 0.7% CaO, 50.3% MgO, and 1.0% Cr_2O_3. The bulk density is 2.6 g/cm^3 and the

apparent porosity 21%. The principal reasons for using this material were its low, nearly temperature-independent thermal conductivity and the relatively large size of samples. Because of the suitable size, it was possible to determine its thermal conductivity in this laboratory by an absolute ASTM method (11), thus making the sample valuable for checking the absolute thermal conductivity of other specimens and the accuracy of the measuring apparatus in general.

(5) Type C, lime-stabilized zirconia, fabricated by the Zirconium Corporation of America, Solon, Ohio. The bulk density is 5.4 g/cm^3, the true density is 5.7 g/cm^3, and the true porosity amounts to 5% of the total volume. The samples are composed of polygonal grains of anisotropic material, with most grains in the 100 to 150 micron range. The chemical analysis(12) is as follows: 93.7% ZrO_2, 3.35% CaO, 1.38% HfO_2, 0.30% SiO_2, 1.07% Al_2O_3, 0.17% Fe_2O_3, 0.03% TiO_2.

All samples were prepared to a tolerance of ±0.001 inch in the form of cylinders, one inch in diameter and one inch high. The flat plan parallel surfaces of the cylinders were polished. The cylinders were provided with two thermocouple holes, 0.03 inch in diameter, 0.5 inch deep, extending radially from the axis to the outside of the cylinder. The holes were drilled 0.90 inch apart, so that each hole was 0.05 inch from the end of the cylinder.

D. Experimental Procedure

The general procedure for thermal conductivity experiments was as follows: The heat source (i.e. the bottom heater) was placed on the horizontal Transite support so that the furnace could be freely lowered about it. The heat stabilizer and the standards with the unknown sample in between were centred with respect to the heat guard, on top of the heat source. To secure good thermal contact, samples were conjoined by platinum foil 0.001 in. thick. A load of some 10 lb was then applied from the top to hold them firmly to allow placement of thermocouples in the samples and in the heat source.

With thermocouples positioned, the furnace was lowered and fixed into such a position that the thermocouples of the cylinder guard were level with the interfaces between the samples. The space between the sample column and the cylindrical heat guard was filled with expanded vermiculite insulation, the weight removed, a platinum disc placed on the top of the sample column (for better thermal contact), and the furnace closed from the top with the heat sink. To insure good thermal contact between the heaters and the sample column, and also between the individual samples, a 25-lb weight was applied on the heat sink.

By means of variable transformers the power input to the heat source and heat sink was adjusted to form a temperature gradient through the sample column. Then the power to the guard heaters was adjusted to establish the same temperature profile in the guard. After attaining a satisfactory temperature match between the guard and the column, the uniformity of the heat flux through the column was checked. This was done by comparing the product of thermal conductivity and temperature gradient in one standard with the same product in the other standard. When the two products were equal (within ±4% of the average), it was assumed that no radial heat exchange existed and that the system was in good thermal balance. If this was not the case, further adjustments of power input to the guard were made, even at the expense of causing an apparent temperature mismatch between the guard and the column. Such a temperature mismatch was considered "apparent" because it was presumed that an error of temperature measurement would be due to the location of the thermocouples at the inner surface of the guard. A surface temperature cannot be measured with thermocouples as accurately as that of a body.

The greatest difficulty arises when conductivities of the unknown and the standard are considerably different. Figure 2 illustrates graphically a case in which alumina standards were used to measure the conductivity of forsterite. The conductivity of forsterite is substantially lower than that of alumina. As a result, the temperature gradients for alumina are about 7 or 8 times smaller than that of the forsterite. The heat guard, on the other hand, is of the same material throughout its length and such sharp changes in the temperature gradients cannot be achieved. A possible temperature gradient, shown by the dotted line, is, of course, only a compromise. Under such severe conditions, shunting of heat flow may become appreciable and, even though the products for the two standards are equal, the resulting conductivity of the unknown could be incorrect. Not only is the scatter of points greater, but, also, the average may be displaced.

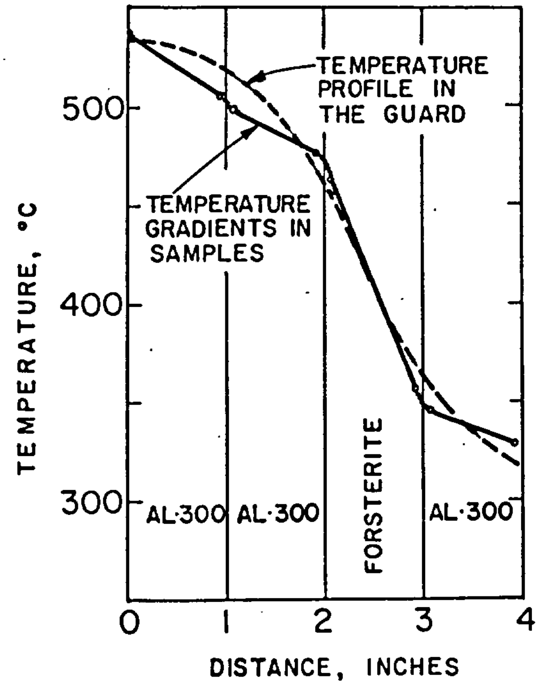

FIGURE 2. TEMPERATURE DISTRIBUTION IN THE GUARD AND FORSTERITE-ALUMINA SAMPLE COLUMN

The measurements were always started at the lowest temperature, and as the experiment progressed, the temperature was successively increased. In principle it would not really matter whether the steady state was achieved from a rising or a decreasing temperature. However, since thermocouples at higher temperatures deteriorate faster than at lower ones, it was considered to be better to start the measurements at a low temperature.

From the scatter of the experimental results, the precision of measurements was established to be 3 to 5%, depending mainly on the difference between the thermal conductivities of the unknown and the standard. Good agreement, obtained from cross-checking the conductivities of materials (with the exception of TiC) used in this work, places the accuracy of measurements in the same range.

RESULTS

Thermal conductivities of alumina AL-300, Forsterite "L", Pyroceram 9606, titanium carbide and zirconia were measured at temperatures ranging from 100° to about 1000°C. Two types of measurements were made: one dealt with the precision of measurements, and, in the other, conductivity of individual samples was established. The results are given in Tables 1-3 and Figures 3-6 (diagrams).

In Tables 1 to 3, t_1, t_2, and t_3 are the arithmetical averages of measured temperatures in the hotter standard, the unknown sample and the cooler standard, respectively; Δt_1, Δt_2 and Δt_3 are the mean temperature gradients in the same samples at their respective average temperatures. Measured conductivity represents the average value of the conductivities obtained from each standard. The percentage in this column indicates the spread of the conductivities (from the average) as obtained from each standard for a given temperature. Table 1 contains two additional columns. The purpose of these measurements was to determine the experimental error by comparing the measured conductivity with the actual* conductivity of AL-300. Hence, the actual conductivity of AL-300 at temperature t_2 is given in one additional column. The last column shows the percentage difference between the measured and actual conductivities of alumina AL-300.

In Figures 3, 4, 5 and 6, thermal conductivities of alumina, forsterite, Pyroceram, titanium carbide and zirconia are plotted against temperature.

The upper, dotted curve in Figure 3 represents the actual conductivity of alumina AL-300. The points show the conductivity of AL-300, measured by using standards made of the same alumina. The lower curve gives the thermal conductivity of Forsterite "L", measured by an absolute method(11). The points denote the conductivity of Forsterite "L", measured by comparison with alumina standards. The agreement between the data obtained by the two methods is very good. Unfortunately, on repeated heating and cooling the

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* It should be noted that the term "actual" is used here not rigorously and the term "accepted" might be better. However, so long as the conductivities of AL-300, as obtained at Alfred University, are reasonably accurate, it matters little since the standards and the unknown are the same material. The resultant "measured" conductivity gives only the experimental precision of the apparatus, not the absolute conductivity values for AL-300. The use of the term "actual" was therefore considered justified, especially in view of the later results in which the thermal conductivity obtained at Alfred University was confirmed with an accuracy limited only by the precision of the apparatus.

TABLE 1

Determination of the Experimental Error, Using Alumina AL-300 Sample with Alumina AL-300 Standards

Average Temperature Of Samples, °C			Temp. Gradient In Samples, °C			Measured Conductivity, watt $cm^{-1} °C^{-1}$	Actual Conductivity of the Unknown Sample, watt $cm^{-1} °C^{-1}$	% Deviation from the Actual Conductivity
t_1	t_2	t_3	Δt_1	Δt_2	Δt_3			
164	146	138	14.0	13.0	13.0	0.169±1%	0.173	-2.5
209	188	169	17.3	16.3	15.5	.156±0%	.155	0
200	180	162	16.3	15.8	14.7	.155±0%	.159	-2
397	377	359	16.7	16.0	15.7	.109±2%	.108	+1
543	516	488	23.8	23.5	23.3	.092±2%	.092	0
543	513	484	26.5	25.7	24.0	.091±1%	.092	-1
760	641	530	109.0	98.0	89.0	.081±2%	.082	-1
771	648	535	111.5	100.7	91.2	.081±1%	.080	+1
795	669	551	113.0	105.0	96.0	.078±5%	.079	-1
790	662	543	115.0	108.0	94.0	.079±5%	.079	0

TABLE 2

Measured Thermal Conductivity of Forsterite "L" Titanium Carbide and Zirconia with Alumina AL-300 Standards

Sample	Average Temp. of Sample, °C			Temp. Gradient in Samples, °C			Measured Conductivity,
	t_1	t_2	t_3	Δt_1	Δt_2	Δt_3	watt cm^{-1} $^oC^{-1}$
Forsterite	271	210	151	13.7	89.2	11.5	0.0208± 4%
	303	252	202	12.5	72.2	8.3	.0189± 8%
	345	310	275	8.3	53.2	7.3	.0178± 0%
	435	334	234	26.0	149.0	21.3	.0187± 6%
	487	409	335	21.8	107.8	14.4	.0174±11%
	521	449	376	19.6	101.0	14.5	.0167± 6%
	532	457	384	19.2	106.0	15.4	.0161± 3%
	553	472	393	19.7	113.7	17.6	.0159± 2%
	597	549	488	13.2	71.0	12.6	.0163± 3%
	614	563	512	14.7	71.7	12.2	.0163± 4%
	816	750	684	20.2	93.2	16.7	.0143± 3%
Titanium Carbide	125	113	104	9.5	6.8	9.0	.258± 0%
	156	138	116	10.0	5.7	8.3	.285± 4%
	263	229	190	22.7	10.0	19.2	.298± 0%
	288	271	256	17.4	7.8	16.3	.278± 0%
	290	273	258	18.3	8.1	17.0	.290± 0%
	379	354	322	20.0	7.5	18.4	.288± 0%
	400	384	369	19.0	6.5	17.8	.305± 1%
	444	418	395	25.0	8.6	23.0	.297± 1%
	445	420	396	24.5	8.2	22.8	.298± 1%
	616	585	556	34.2	9.3	34.0	.320± 3%
	606	587	568	26.2	6.3	25.0	.349± 0%
	748	680	618	76.2	18.0	73.5	.323± 5%
	779	759	740	26.8	5.5	26.0	.345± 0%
	811	782	753	40.5	8.0	38.8	.352± 1%
	815	785	755	42.0	8.2	40.3	.356± 0%
	946	912	877	50.0	8.7	47.0	.556± 0%
Zirconia	1103	1040	980	27.8	83.5	24.5	.0180± 0%
	1160	1100	-	25.3	86.0	-	.016

TABLE 3

Measured Thermal Conductivity of Zirconia and Alumina AL-300 with Pyroceram 9606 Standards

Sample	Average Temp. of Samples, °C			Temp. Gradient in Samples, °C			Measured Conductivity, Watt cm^{-1} °C^{-1}
	t_1	t_2	t_3	Δt_1	Δt_2	Δt_3	
Zirconia (c)	167	144	120	16.2	24.0	14.7	0.0230±4%
	416	373	329	28.5	44.8	29.2	.0215±1%
	604	555	507	33.7	48.8	32.8	.0210±1%
	880	805	729	49.3	77.3	49.7	.0188±3%
	914	843	772	47.0	71.8	45.7	.0184±1%
Zirconia (b)	430	388	347	28.8	40.5	28.3	.0229±1%
	430	389	350	28.2	41.5	27.0	.0216±1%
	426	392	360	24.0	34.5	22.0	.0216±3%
	549	490	433	40.0	56.5	38.8	.0221±0%
	624	581	540	29.3	43.5	28.5	.0203±0%
	667	616	566	36.2	48.5	35.0	.0224±0%
	673	622	571	37.0	49.5	36.0	.0225±0%
	757	712	667	32.2	44.0	31.0	.0214±1%
	794	762	729	23.0	33.3	22.5	.0200±0%
	931	853	777	57.5	76.5	55.2	.0210±0%
Zirconia (a)	167	147	126	28.5	41.0	27.0	.0240±1%
	420	392	364	37.2	56.3	37.5	.0216±2%
	641	600	559	55.8	82.5	53.3	.0204±0%
	662	621	580	56.4	81.5	55.0	.0209±2%
	872	833	795	57.6	77.2	50.7	.0195±2%
Alumina AL-300	185	169	153	19.5	4.2	18.8	.1610±0%
	441	406	372	41.0	12.5	39.8	.1049±0%
	766	730	696	42.0	16.2	39.5	.0748±2%
	769	734	699	41.0	16.3	39.7	.0735±0%
	975	953	929	25.5	11.3	25.0	.0624±1%

(a) Unknown and Standard used for the first time.

(b) Unknown used first time, Standard used several times up to 1000°C.

(c) Unknown used several times up to 1100°C, Standard for the first time.

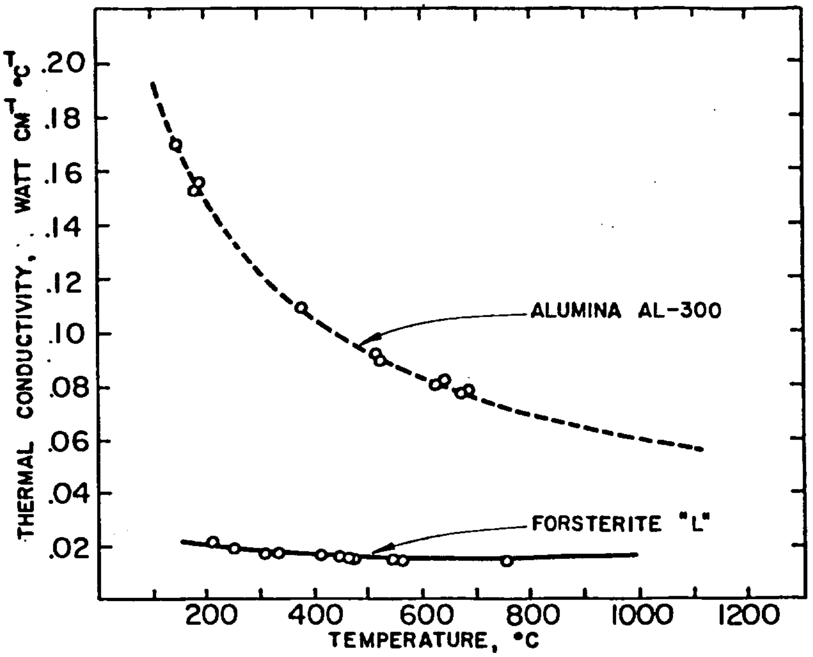

FIGURE 3. THERMAL CONDUCTIVITY OF ALUMINA AL-300 AND FORSTERITE "L", USING ALUMINA AL-300 STANDARDS

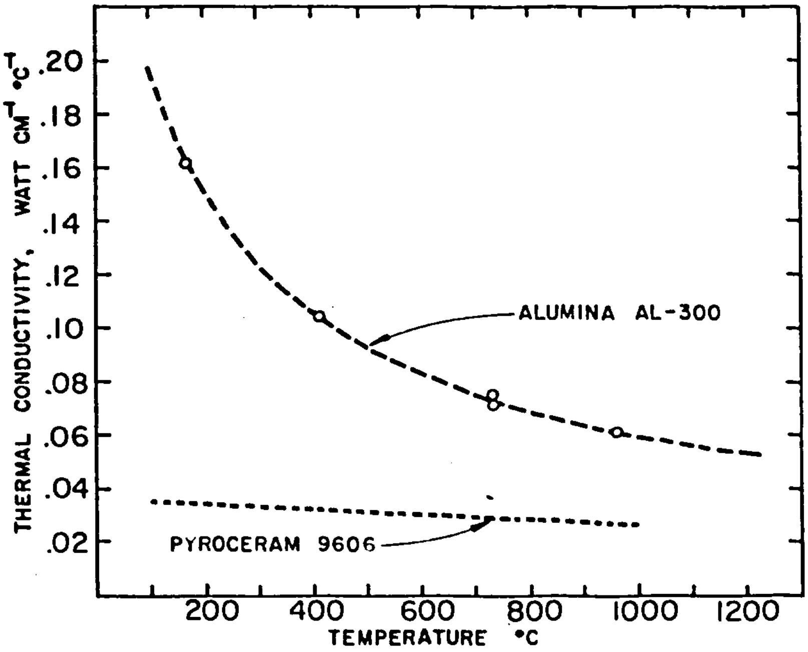

FIGURE 4. THERMAL CONDUCTIVITY OF ALUMINA AL-300, USING PYROCERAM 9606 STANDARDS

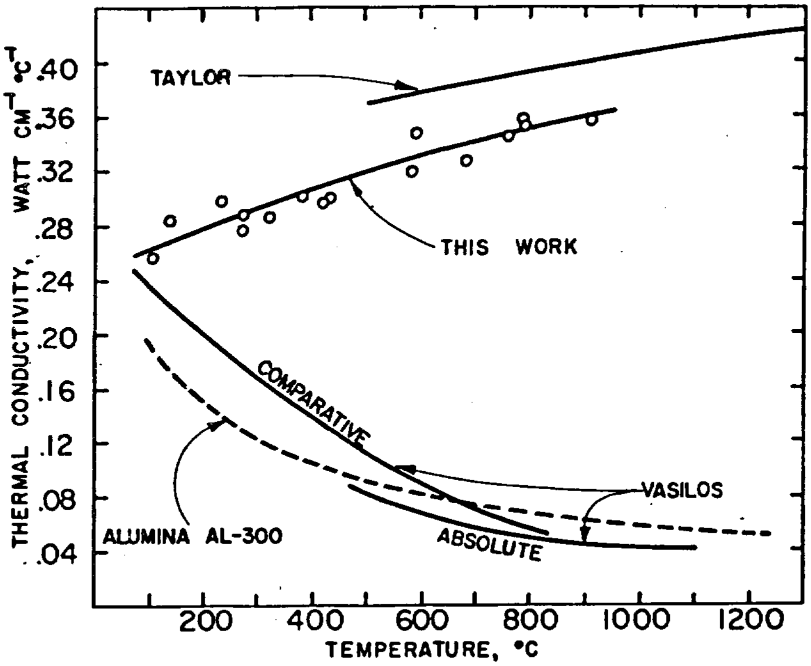

FIGURE 5. THERMAL CONDUCTIVITY OF TITANIUM CARBIDE, USING ALUMINA AL-300 STANDARDS

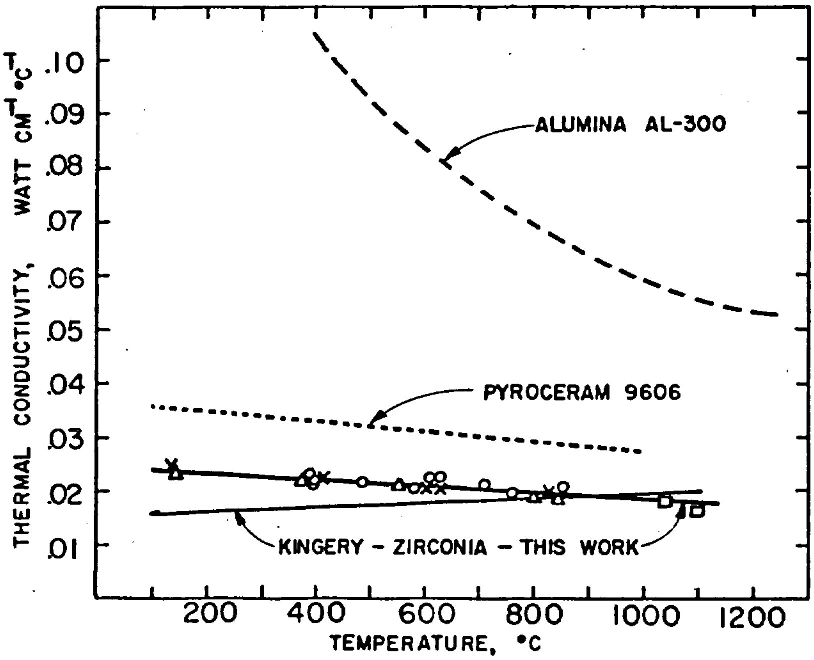

FIGURE 6. THERMAL CONDUCTIVITY OF ZIRCONIA, USING PYROCERAM 9606 AND ALUMINA AL-300 STANDARDS

forsterite samples show a certain amount of deformation and some cracking.

Similarly, a very good agreement was obtained for the alumina-Pyroceram system, shown in Figure 4. In this case, alumina AL-300 was used as the unknown, with Pyroceram 9606 for standards. Dotted lines represent the actual conductivity of AL-300 and Pyroceram 9606. The points are the measured conductivity of AL-300.

Results for titanium carbide are shown in Figure 5. Alumina standards were used. The scatter of results is larger than in the previous cases. The top curve shows the thermal conductivity values for titanium carbide, as obtained by Taylor(13). His data are substantiated, but the agreement is not as good as before. For comparison, data by Vasilos and Kingery(14) are also shown. The solid curves on the bottom of Figure 5 represent the conductivity of titanium carbide, obtained by comparative and absolute methods.

The thermal conductivities of zirconia, shown in Figure 6, were obtained by comparison with Pyroceram and alumina standards, the conductivities of which are shown by the dotted lines. Points denoted by triangles were obtained with a new zirconia sample and new Pyroceram standards. Points marked by X's were also obtained with new Pyroceram standards, but the zirconia sample was first used in other experiments where it was repeatedly exposed to temperatures up to 1100°C. The conductivities denoted by circles were obtained by using a new zirconia sample, but the Pyroceram standards were first employed in other experiments for measurements up to 1000°C. As can be seen, the results were the same for all three cases.

Alumina standards were used for measurement of the thermal conductivity of zirconia at the temperatures above 1000°C. The conductivities thus obtained were marked by squares.

For comparison, the thermal conductivity of zirconia, by Kingery et al. (16), is also shown in Figure 6.

DISCUSSION

The experimental results of this study can be evaluated in two ways: (1) by the examination of the scatter of data, and (2) by cross-checking and comparing with values obtained in other investigations.

The thermal conductivities of alumina AL-300, shown in Table 1 and Figure 3, were measured by using standards made of AL-300. This condition of measurement is ideal. The change of the temperature gradient through the column of samples is gradual, and good heat guarding is relatively simple to attain. Because of this, the difference between the values calculated from each standard is small. Also, the scatter, as shown in the last column of Table 1, is minimal. In contrast to the above, the results for Forsterite "L" indicate that the thermal conductivity values calculated from the two alumina standards can differ appreciably from each other. For example, for t_2 of

409°C (Table 2), the low and high thermal conductivities differ by 11% from the average. Notwithstanding the unfavourable measuring conditions caused by the considerable difference in conductivity of these materials, the agreement between the conductivities of Forsterite "L" measured by the absolute method and by comparison with alumina standards is remarkably good.

The very good agreement between the alumina and Pyroceram specimens, shown in Figure 4, confirms the absolute thermal conductivities of AL-300, since now three independently measured conductivities can be cross-checked: Forsterite "L", AL-300, and Pyroceram 9606. It also demonstrates the ability of this apparatus to make accurate thermal conductivity measurements.

Results for titanium carbide (Figure 5) indicate that the scatter is somewhat larger than in the previous cases. This probably results from incomplete heat guarding, especially at high temperatures where conductivities of titanium carbide and AL-300 standards differ considerably. The data obtained by Taylor(13), although supported by the results of the present study, are not in sufficient agreement with them. Shunting of heat flow through the insulation could have been the reason why the results of this work were lower than the data of Taylor. Although the ratio of conductivities between the sample and vermiculite is very high in this case, the ratio of conductivities between the unknown and the standard is also high and good temperature matching is not possible. Some of the heat generated in the guard, or even in the heat source, could, by by-passing the first standard, enter into the unknown and again by-pass the second standard. Such a heat flow would make the temperature gradient of the unknown larger than it would be if heat came from the hotter standard only. Thus, even though the products of conductivity and temperature gradient for the two standards were equal, the measured conductivity could be different and, in this case, lower than the actual. When the reverse condition occurs, that is, when the standards are of higher conductivity than the unknown and good temperature matching is not achieved, a portion of the heat from the hotter standard may by-pass the unknown through the insulation. As before, the products for the two standards may be equal, yet the measured conductivity of the unknown could be different and, in this case, higher than the actual. Generally, heat shunting is more likely to occur when the conductivity of the standard is higher than that of the unknown. The best way to reduce its effect is to use good insulation and standards of conductivity similar to the conductivity of the unknown.

Referring again to Figure 5, the two lower (solid) curves also represent the conductivity of titanium carbide. They were obtained by comparative and absolute methods by Vasilos and Kingery(14). Such wide variations in results would imply that the conductivity of titanium carbide is considerably affected by impurities and its history of fabrication.

The thermal conductivity of zirconia samples was measured principally to examine the thermal stability of zirconia and Pyroceram. It was assumed that, if a structural change occurs in either of the samples, this change will be readily detected because it must be accompanied by a thermal conductivity change. Therefore, the thermal conductivity of a new zirconia sample was first measured with the new Pyroceram standards. The zirconia sample was then repeatedly exposed to temperatures up to 1100°C. Its thermal conductivity was measured again by using new Pyroceram standards. The resultant two sets of data are identical, demonstrating that no change occurred in the zirconia sample.

The thermal stability of Pyroceram samples was examined in the inverse manner. The thermal conductivity of a new zirconia sample was measured with standards that were used in other experiments for measurements up to 1000°C. The results are the same as those obtained in the previous two zirconia-Pyroceram measurements, indicating that. as before, no structural changes resulted from the heating of Pyroceram.

Considering that different zirconias were used, the agreement between the results of this work and that of Kingery et al.(15) is good at higher temperatures, but there is some discrepancy at lower temperatures. The agreement at higher temperatures may be significant in evaluating zirconia for use as a reference material. It indicates that small variations in composition may not have a marked effect on its thermal conductivity.

CONCLUSIONS

The results obtained by this comparative-method apparatus prove its capacity for making accurate measurements. The conductivities of Alumina AL-300, Pyroceram 9606 and zirconia have been established and confirmed.

Pyroceram 9606 has suitable properties for use as a primary standard. As a working standard it may not be suitable because of its brittleness and its tendency to chip at the surface. Alumina AL-300 is sufficiently stable to be used as a standard. Zirconia has the lowest conductivity, which is nearly independent of temperature. It is very hard, strong, and apparently structurally and thermally stable up to at least 1100°C. It can be recommended as a secondary standard, although more work will have to be done to find out the effect of changes in composition on conductivity. Forsterite "L" and titanium carbide are not suitable as reference materials.

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