FOREWORD

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This report covers work conducted from January 1, 1961 to January 1, 1962 and, therefore, includes the information reported in USNRDL-TR-518, "Thermal Diffusivity Measurements on Metals at High Temperatures," by R. L. Rudkin, R. J. Jenkins and W. J. Parker.

ABSTRACT

The adaption of the NRDL flash method to the measurement of the thermal diffusivity of metals and ceramics at high temperatures is described. A high intensity short duration light pulse from a xenon flash lamp is absorbed in the front surface of a thermally insulated specimen a few millimeters thick and the resultant temperature history of the rear surface is measured by a lead sulfide cell radiation detector or a thermocouple, displayed on an oscilloscope and photographed by a Polaroid Land camera. The thermal diffusivity of the material is determined from this temperature versus time curve provided the theoretical boundary conditions are experimentally satisfied. Measurements of the thermal diffusivity of Armco iron, molybdenum, titanium, zirconia, and alumina have been made up to 1200°C, 1300°C, 1700°C, 1100°C and 1100°C, respectively.

This technical documentary report has been reviewed and is approved.

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INTRODUCTION

The flash method of determining thermal diffusivity, developed at NRDL,[1] has been applied in measurements on metals up to 1700°C, and on ceramics up to 1100°C. This method consists essentially of the absorption of a very short pulse of radiant energy in the front surface of a specimen and the recording of the resultant temperature history of the rear surface.

In the ideal case of a perfectly insulated specimen with a constant absorptivity across its surface, uniformly irradiated with a pulse of thermal energy short compared with the time required for heat to flow through the material, the back surface temperature history is given by

$$T_{(L,t)}/T_m = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2\pi^2\alpha t/L^2) \tag{1}$$

where $T_{(L,t)}$ represents the instantaneous back surface temperature rise at time t, T_m is the maximum back surface temperature rise, α is the thermal diffusivity in cm /sec, L is the specimen thickness in cm and n represents successive integers. At the time, $t_{1/2}$, where $T_{(L,t)} = 0.5\ T_m$, Equation (1) reduces to

$$\alpha = \frac{1.37\ L^2}{\pi^2 t_{1/2}} = 0.139\ L^2/t_{1/2} \tag{2}$$

Hence, the thermal diffusivity of a material can be determined from the specimen thickness and the time in seconds required for the back surface temperature to reach one-half of its maximum value.

The success of the method depends upon adequately meeting the boundary conditions which lead to Equation (1). Figure 1 is a dimensionless plot of Equation (1) and represents the form that the back surface temperature history of the sample will take if these boundary conditions are satisfactorily met. A departure of the data from this curve illustrates that these conditions have not been met and invalidates the data.

A condition vital in the use of Equation (1) is that the front surface of the sample must be uniformly irradiated with a pulse of thermal energy in a time which is short compared to the rise time of the back surface temperature. To accomplish this, a xenon flash lamp is used as the source of that thermal pulse. The lamp used is a G. E. Type 524 through which 600 joules are discharged. The pulse is essentially completed in 500 microseconds while the time to one-half of the maximum of the rear surface temperature is for the most part 50 to 300 milliseconds. It should be noted in Equation (2) that for a

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given material the rise time of the rear surface temperature is a function of the square of the sample thickness. A sample thickness sufficient to satisfy this condition of a short pulse duration, compared to the rise time of the temperature at the rear surface, should be used. However, for a given amount of input energy, the maximum temperature rise attained, T_m, is an inverse function of the thickness of the sample, and in order to maximize the temperature change a thin sample should be used. These two restrictions on sample thickness have been satisfied in the cases reported here by a thickness of approximately one to two millimeters. Samples were used which varied from 0.90 to 2.63 mm in thickness without variation in the results. In addition to the time considerations of the irradiance, the distribution of that irradiance on the front surface of the sample is important as noted earlier. It is a simple procedure to obtain uniform irradiation on a small flat surface from a flash lamp but it is a boundary condition which must nevertheless be satisfied, otherwise the shape shown in Fig. 1 may be distorted. In the cases reported here the 2-inch diameter helical lamp was placed without optics only a few centimeters from the sample. Two tests were made to check for uniform irradiance. First a diffusing glass was placed between the lamp and the sample and a comparison made with data taken without the glass. There were no detectable differences in the curves thus obtained. Secondly, these curves were compared with Fig. 1, with the result that they indicated satisfactory agreement with the theoretical temperature history. The other boundary condition imposed on Equation (1) is that the specimen be perfectly insulated. The degree to which this is satisfied within the time limits of interest is indicated by the decay rate of the back surface temperature after the maximum, T_m, is attained. Because of these factors, the sample holder should be designed so as to minimize all heat losses. Conductive heat losses are minimized by supporting the sample on a small area. Provided appropriate care is exercised by the experimenter, conduction heat losses, as well as convective heat losses, are negligible because of the short times involved in the flash technique. Radiative heat losses at high temperatures cannot be eliminated and therefore could constitute the greatest problem in the satisfaction of this boundary condition.

This method of diffusivity measurements has been successful at ambient temperatures in air[1] and up to 1000°C in an argon atmosphere[2] using a resistance furnace and a thermocouple as the rear surface temperature detector. There were numerous problems which were anticipated when it was planned to carry this type of measurement to higher temperatures. Foremost among these was the question concerning the most satisfactory means of attaining temperatures above 1000°C in small samples.

EXPERIMENTAL - METALS

Radio frequency induction heating is the most convenient means of heating small metal samples to high steady state temperatures. In addition to satisfying the requirement of producing high temperatures in metals, this form of heating is very fast and temperature equilibrium is reached quite rapidly. Induction heating has another advantage in that by using ceramic supports, only the metal sample itself attains the high temperature. The radiating surface area is therefore less and consequently the walls of the vacuum chamber are easier to keep cool, thereby facilitating the use of rubber seals.

The experimental apparatus used in these measurements is shown schematically in Fig. 2 and photographically in Fig. 3. The induction heater coil leads are fed into the vacuum chamber and form a coil with an inside diameter of about one inch. The sample is held in position in the coil by a mount machined from lava and baked to a ceramic. Shields of baked lava prevent heating of the chamber walls by radiation from the sample. Fused quartz is used for the top window because the large thermal gradients close to the hot sample would crack glass windows. The steady state temperature at which measurements are made is indicated by thermocouple leads which are fastened to the edge of the sample and fed out of the vacuum system. An optical pyrometer is used at temperatures above which platinum/platinum-rhodium thermocouples will perform. A glass lens below the sample focuses the center portion of the rear of the sample on an uncooled lead sulfide cell which measures the surface temperature history over a range from 300°C to 1800°C. The lower temperature cut-off was caused by the fall off in spectral sensitivity of the cell to radiation from lower temperature bodies while the upper temperature limit was caused in the cases reported by the evaporation of the sample material, which reduced the transmission of the quartz window and lowered the intensity of the pulse of energy falling on the front of the sample. In any detection system the linearity of the response must be considered over the range of interest. The linearity of the lead sulfide cell is adequate since the temperature change of the sample due to the pulse is not more than a few degrees. It should be noted that a knowledge of the detector sensitivity or the thermal input to the sample is not required because only $t_{1/2}$ is involved in Equation (2) and this time can be obtained from the data curve which is proportional to the temperature rise and the calibrated sweep of the oscilloscope.

The detector is connected differentially through a load selector and balance control unit to the differential preamp of an oscilloscope. The use of differential detector circuitry is necessary to minimize the effects of the extremely high magnetic field which surrounds induction heating coils. One very great advantage of the lead sulfide cell for sensing the rear surface temperature history is the elimination of the high gain D.C. preamplifier which is necessary ahead of the oscilloscope if a thermocouple is used for this purpose. A trigger delay circuit is used to fire the flash lamp after the oscilloscope sweep has been triggered. This is necessary in order to have a base line on the print from which to measure the change in the detector output voltage.

RESULTS - METALS

Figure 4 is a Polaroid Land print of the oscilloscopic display of the detector output. When the shape of the temperature rise is compared with Fig. 1, the agreement indicates the boundary requirements have been satisfied by the samples reported here. Since heat losses from the sample would show up as a decay in the detector output after the initial rise, it is evident from this print that the thermal pulse travels through the sample in a time which is extremely short compared with the time required for the sample to return by heat losses to the equilibrium temperature at which the measurement is made. Non-uniform illumination of the front surface would distort the knee of the curve.

A print similar to Fig. 4 is made for each temperature at which a measurement is desired. The output from the detector section ranged between 2 and 50 millivolts. The time base on the prints used in these measurements was either 20 milliseconds/cm or 50 milliseconds/cm. This time is determined, as was previously mentioned, by the thickness of the sample and by the thermal diffusivity of the material. The time, $t_{1/2}$ is obtained with the aid of a reading device which divides the distance between the steady state temperature, T_o, and the maximum temperature, T_m, in half and which has a calibrated scale to read the distance from the time the lamp is fired, which shows up as a transient on the print as is seen in Fig. 4.

Measurements have been made with this system on Armco iron, molybdenum, and titanium. Figure 5 is a plot of the thermal diffusivity of Armco iron versus temperature. Data obtained with the resistance furnace and the argon atmosphere[2] are shown along with the data obtained as reported here. It is noted that the Curie Point and the β-γ transition temperatures are 30 degrees lower than those published for pure iron. These data essentially agree with results obtained by Sidles and Danielson[3] except for the temperature shifts noted above. Because of this difference, considerable care was taken in the measurement of these temperatures. A Leeds and Northrup type K potentiometer was used to check the thermocouple output. All data obtained in this set of experiments were internally consistent so the reasons for the differences with other measurements are still unknown.

Figure 6 presents the thermal diffusivity of molybdenum versus temperature and again includes data obtained in the resistance furnace.[2] These data are presented to illustrate that this method of diffusivity measurement is independent of the type of heating or the kind of temperature sensing method employed as long as the boundary conditions for Equation (1) are maintained.

The results obtained for titanium are given in Fig. 7. The break in the curve corresponds to the transformation to the β phase which has been reported to occur at 883°C.[4] The estimated accuracy of these measurements is ± 5 percent.

EXPERIMENTAL - CERAMICS

The best means of heating ceramics to high temperatures for these measurements is not nearly as obvious as that for metals. There are several means available, none of which is as convenient as induction heating. Perhaps the most obvious means is heating by conduction. Because of the theoretical boundary conditions imposed by the flash technique the front and the rear surfaces near the center of the sample must not be in contact with the supporting structure. In order to reduce the effect of lateral conductive heat losses the sample diameter should be approximately an order of magnitude greater than the thickness. A disc of low thermal conductivity material heated by conduction from the edges will have a serious temperature depression in the center of the sample at temperatures where radiant heat losses start to become an important consideration.

Because of the ease with which these measurements were made on metals using the induction furnace, the same facility was initially tried in the measurements on ceramics. Several configurations of graphite heating rings were tried in an effort to heat the sample uniformly. The most successful sample holder, from the standpoint of a uniform specimen temperature, was a long cylindrical one with the sample at the midpoint. The temperature depression was minimized in this case by radiant heating from the cylinder walls. However, the irradiance level produced by the flash lamp at the surface of the specimen is seriously reduced with this arrangement. The radiation emitted by the heating cylinder was avoided in the detection system by focusing the photoconductive cell onto a small area at the rear surface of the specimen.

It appeared from this effort that a more direct means of heating could be superior to an indirect means. On this basis considerable effort was put into the setting up of an apparatus wherein the sample was heated in air by an oxy-hydrogen flame. This type of heating is attractive because extremely high temperatures can be attained in air quite easily. The sample was supported between two ceramic rods and held at the short focal point of an ellipical mirror. The flash lamp was placed at the long focal point with an occulter near the sample to block the direct radiation from the lamp. It was necessary to place the lamp at a distance from the sample because of the heat from the flame. The torch was aimed through a two-inch hole in the twelve-inch diameter mirror. A variety of torch tips and flames was used in attempting to get an even distribution of temperature across the face of the sample. It was found that with more than one flame there was a low temperature line on the sample at the boundary between the two gas flows. For this reason it was necessary to use only one flame to heat the sample. Various gas pressures and flame characteristics were tried and it was found necessary to use a low pressure, slow velocity flame in order to heat the sample uniformly.

The lead sulfide detector was again used to give the rear surface temperature rise. In the arrangement of components as described above it was necessary to place the detector about 20 degrees from the normal to the sample. Since the rear surface temperature rise is of the order of one degree the temperature variations of the sample must be considerably less in order to give a reasonable signal to noise ratio. This proved to be the limiting factor in this setup. Even after variations due to air currents were minimized there remained random variations in signal which were traced to the burning of impurities in the hydrogen flame. These variations constituted an insufficient signal to noise ratio to give satisfactory results.

In order to demonstrate the feasibility of this technique as applied to ceramics, it was decided to make some measurements in the temperature range available by the use of resistance heaters. The resistance furnace used earlier[2] was used in these measurements with a new sample holder and with a tungsten heater. The sample holder was designed so as to minimize any temperature depression in the center of the sample as discussed earlier. The rear surface temperature detector used with this apparatus was a chromel-alumel thermocouple. The thermocouple wires were of sufficient size to be rigid and were filed to a point. The junction was formed at the rear of the sample by pressing these pointed wires, which were separated by about two millimeters, against a one mil silver or platinum foil. The thermocouple output was amplified by a Burr-Brown differential amplifier (model 1303) and fed into a Tektronix type 53/54D preamp on the 531 oscilloscope.

It became obvious in these initial measurements on ceramics that the boundary conditions necessary for valid results were not satisfied. This was most pronounced in the case of a very dense alumina sample. The detector output was nearly what would be expected without the presence of a sample at all, that is, an abrupt rise and then a rapid decay. In ceramics the pulse of thermal energy is not absorbed in the front surface of the sample but rather is absorbed throughout the sample. This transparency in ceramics varies tremendously with the type of ceramic and with the density of the particular sample. Consequently, in order to use the flash technique on ceramics they must be coated with a material which will absorb the energy from the flash and will transmit this thermal pulse to the ceramic. This coating must be thin so that the transit time of the pulse through the coating is negligible with respect to that through the sample. This coating must be well bonded to the sample in order to transmit the pulse. The most promising approach seemed to be the vacuum evaporation of a metal onto the sample face. Platinum was chosen because its melting point is well above the temperature at which the furnace would operate and because of its inertness. Platinum is a very difficult metal to evaporate and consequently the coatings obtained had sufficient holes to prevent the satisfaction of the boundary condition of total front surface absorption. The most complete surface coverage was obtained by plating the ceramics with Hanovia Platinum Bright (No. 05). By repeated applications a coating was obtained that satisfied the requirements. One precaution which must be taken when using this technique is to be certain that the Hanovia liquid is not absorbed into the ceramic before it is fired. (This does occur except in the densest of the ceramics and constitutes a probable source of error for many samples.) Although this method of coating has worked satisfactorily for these samples in the limited temperature range, it is by no means the answer to the general problem of ceramic transparency.

RESULTS - CERAMICS

Figure 8 presents the thermal diffusivity as a function of temperature of a high purity magnesia-stabilized zirconia which was furnished by the Norton Company. To verify that this material was completely stabilized x-ray diffraction patterns were taken on the material as it was received and after it had been heated to above 2000°C. There were no detectable changes in the structure indicating complete stabilization. Figure 9 is a plot of the thermal diffusivity versus temperature for an extruded alumina sample whose density is 3.834 gm/cm^3. Figure 10 shows this type of data for a pressed specimen of alumina with a density of 3.914 gm/cm^3.

DISCUSSION AND CONCLUSIONS

The NRDL flash technique for measuring thermal diffusivity can be extended to metals and ceramics at high temperatures. In the case of metals, or other materials with a sufficiently low electrical resistivity, a straightforward procedure has been devised. Radio frequency induction heating provides a rapid and convenient method of attaining high equilibrium temperatures in these thermally insulated test specimens. The upper temperature limit in a vacuum is determined by the evaporation of the test material onto the window of the vacuum chamber. Radiation detectors, such as lead sulfide photoconductive cells, provide a very simple and accurate means of sensing the rear surface temperature history at high temperatures without interacting with the surface they are measuring. They also provide adequate sensitivity so that the low level, high gain d.c. preamplifier normally used for thermocouples is not required. Radiation detectors located a considerable distance away from the flash lamp and the electrical fields associated with heating the sample are relatively free from stray voltage pickup. The ratio of increased power received on the detector per degree surface temperature rise to the total power received is approximately inversely proportional to the absolute temperature. This means that an increasing large bucking voltage must be used to balance out the steady signal voltage prior to the flash. Also the increased heat dissipation in the photoconductive cell will cause its temperature to rise and its sensitivity to drop unless effective cooling of the cell is provided. It would probably be desirable at the very high temperatures to use a phototube or a photomultiplier with its response limited to the short wavelength tail of the spectral distribution curve to monitor the rear surface temperature.

Ceramics are inherently more difficult to measure by this technique. Their low electrical conductivity precludes the use of induction heating. If they are heated by conduction from the edges their low thermal conductivity and high emittance make it impossible to obtain a uniform equilibrium temperature across the face of the thin test specimen. Direct heating of the whole surface by a gas flame fluctuates too much to permit an accurate measurement of the small signals induced by the flash. It has yet to be determined whether direct radiation heating of the whole surface by a high intensity carbon arc source will be steady enough for this purpose.

The most successful method of heating of those tried has been the argon filled wire-wound resistance furnace. The sample is placed far enough back into the holder that it is heated by radiation and convection across the surfaces as well as by conduction from the edges. The wire-wound resistance furnace has a practical upper limit around 1500°C. Above this temperature the best results might be obtained by inserting the specimen in a silicon carbide tube and heating the tube directly by resistance heating or by placing it in an induction furnace. In either case the specimen should be located deep enough to provide good surface heating. However, this is done at the expense of sensitivity due to the decrease in the amount of light from the flash lamp that can be intercepted by the specimen.

The second problem with ceramic materials is that they are often semi-transparent. One boundary condition that must be met with this technique is that the energy is absorbed in a very small depth at the surface. This requires that an opaque coating be applied that will hold up at the required temperature and will not diffuse into the specimen. Although an opaque front surface coating was obtained using Hanovia Platinum Bright (No. 05), this material contains sufficient gold so as to limit its temperature range of usefulness to about 900°C. Hanovia Platinum Paste (No. 6082) contains only platinum with a binding material and will operate up to 1500°C. This paste is also less apt to cause errors due to diffusion into the ceramic because of its thick consistency.

Yet another problem is the transparency of the material at long wavelengths where the front surface due to its initially high temperature rise may radiate through the specimen. This is minimized by lowering the peak power input to the specimen. If there is a large enough radiation transfer within the specimen at the equilibrium temperature that the mean free path for the photons is greater than the dimensions of the specimen the thermal diffusivity is no longer a meaningful term. The thermal conductivity will then depend on the thickness of the specimen.

It was anticipated that radiation cooling might be sufficiently high to make it impossible to achieve a flat region at the top of the rear surface temperature history curve. There was no problem on any of the tests made so far including the molybdenum at 1700°C.

As mentioned in previous adaptations of the flash technique, the method has several advantages which should be mentioned, e.g., cooling losses can be neglected, very small size specimens can be utilized and the data reduction is quite simple.

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3. P. H. Sidles and G. C. Danielson, "Thermal Diffusivity Measurements at High Temperature," Thermoelectricity, P. N. Egli, Editor, p. 270-288, Wiley, New York (1960).

4. A. Goldsmith and T. E. Watermann, "Thermophysical Properties of Solid Materials," Armour Research Foundation, WADC TR 58-476, January 1959.

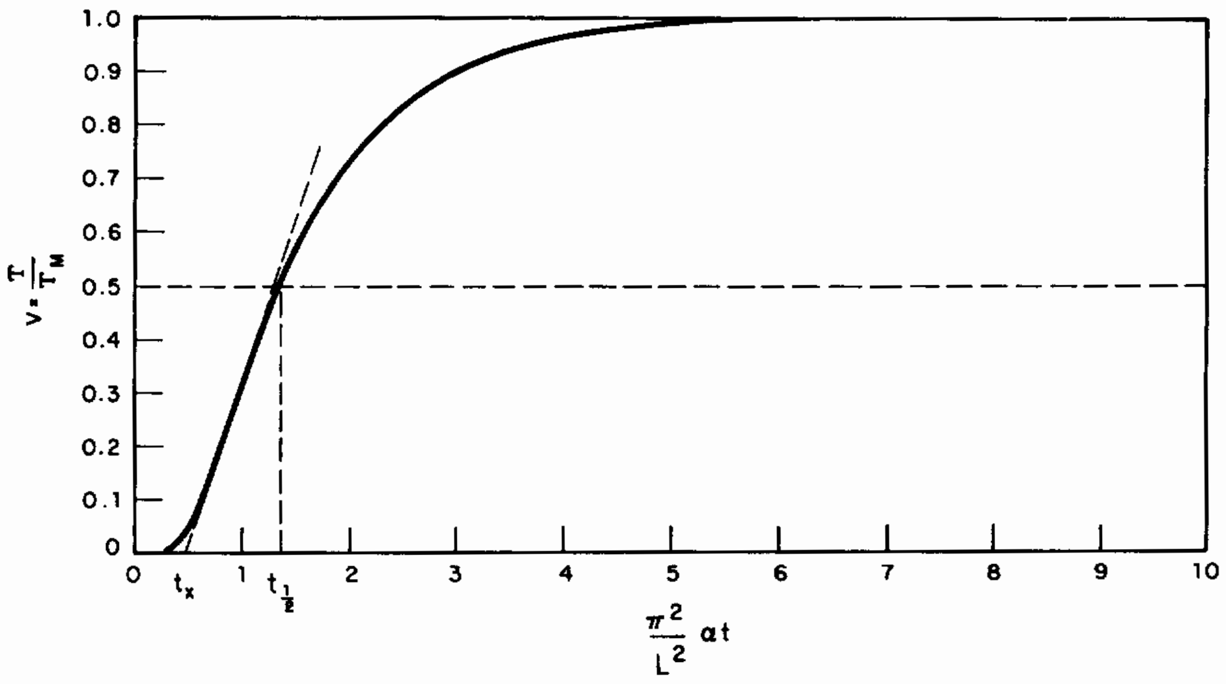

Fig. 1 Dimensionless plot of rear surface temperature history

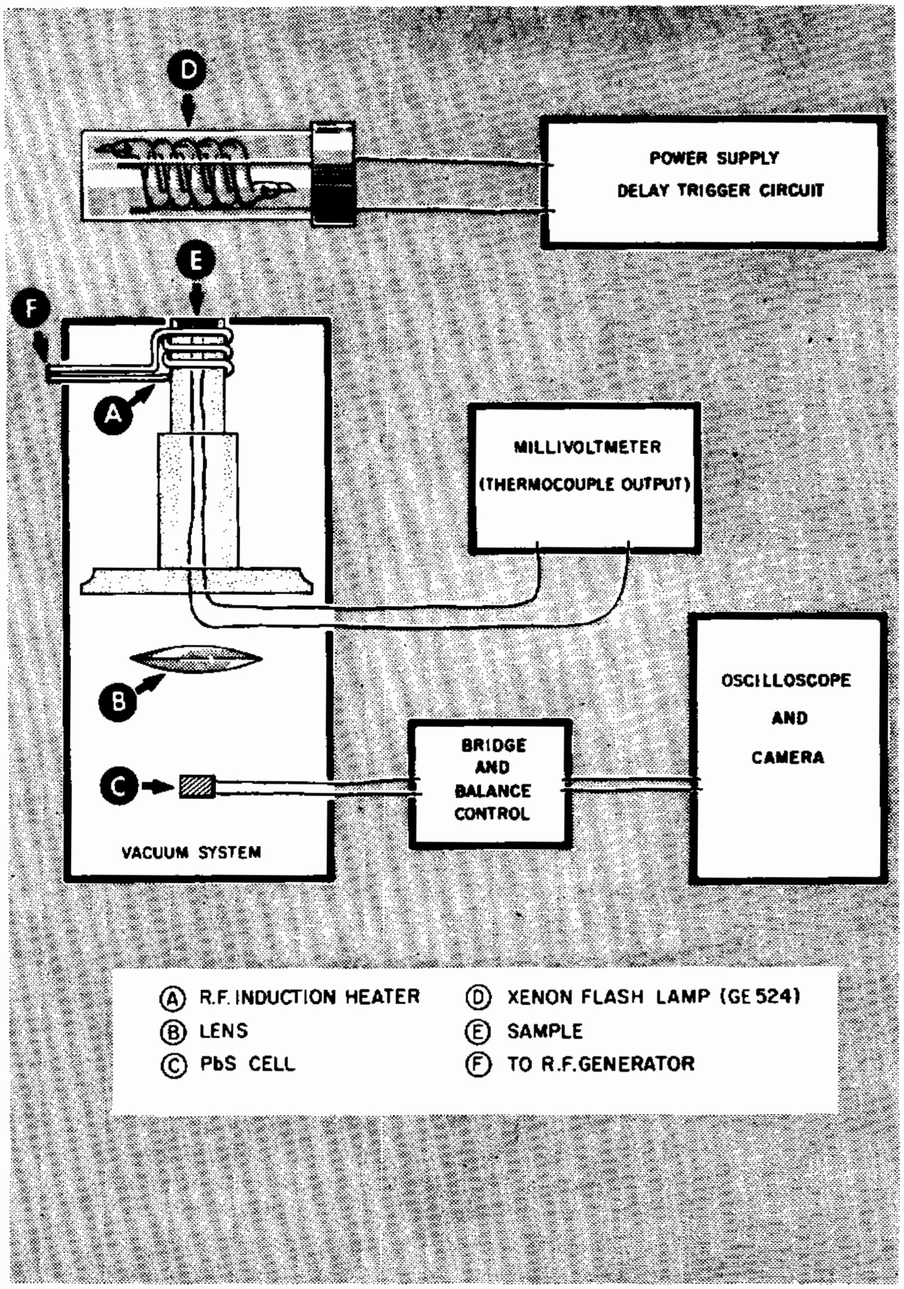

Fig. 2 Schematic diagram of experimental arrangement for metals

Fig. 3 Photograph of experimental arrangement for metals

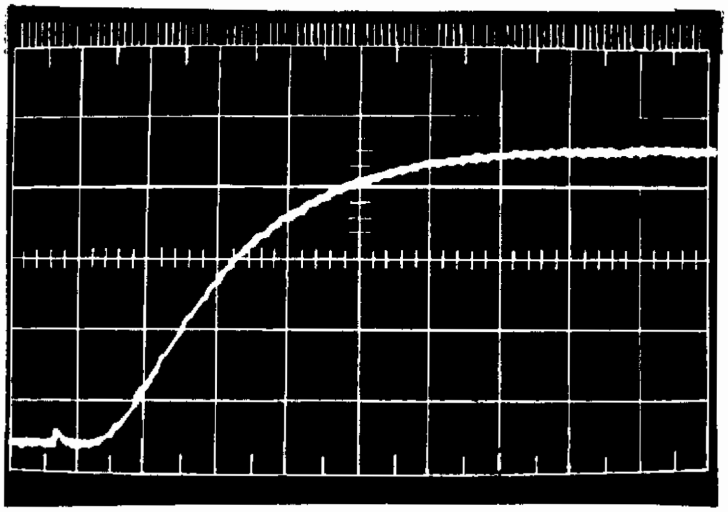

Fig. 4 Photographic trace of the rear surface temperature rise. Trigger transient and reference baseline are at the left.

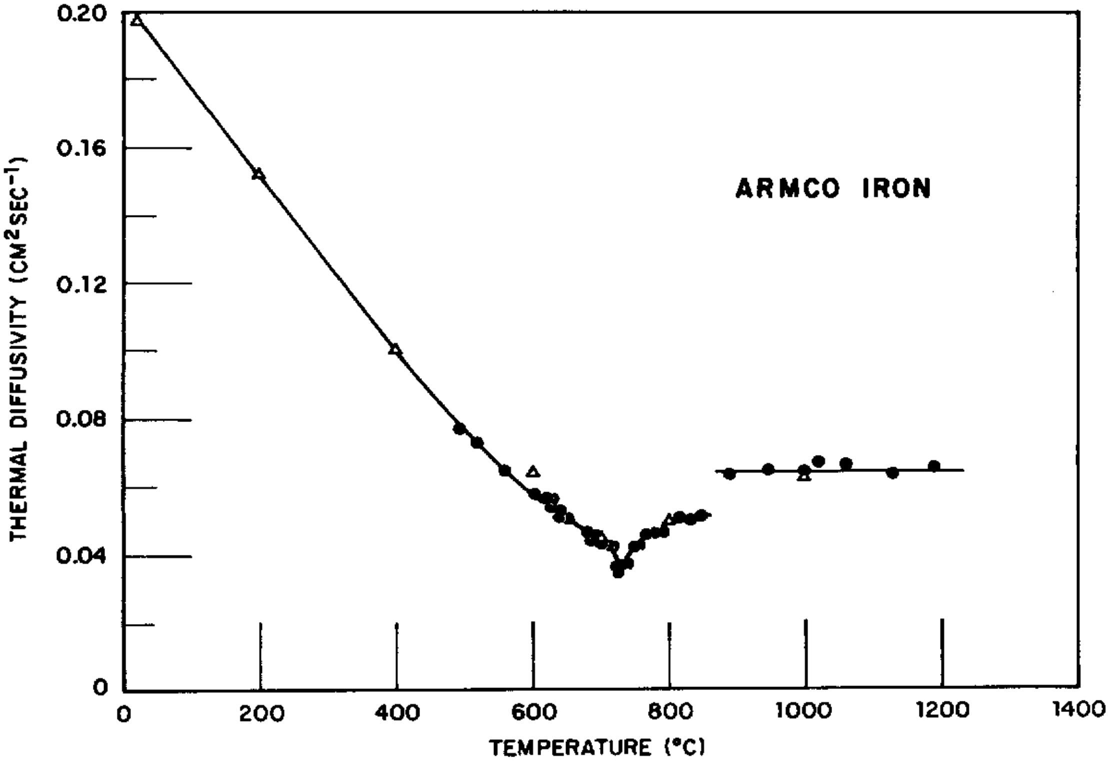

Fig. 5 Thermal diffusivity of Armco iron versus temperature (data points shown by triangles were obtained in the resistance furnace).

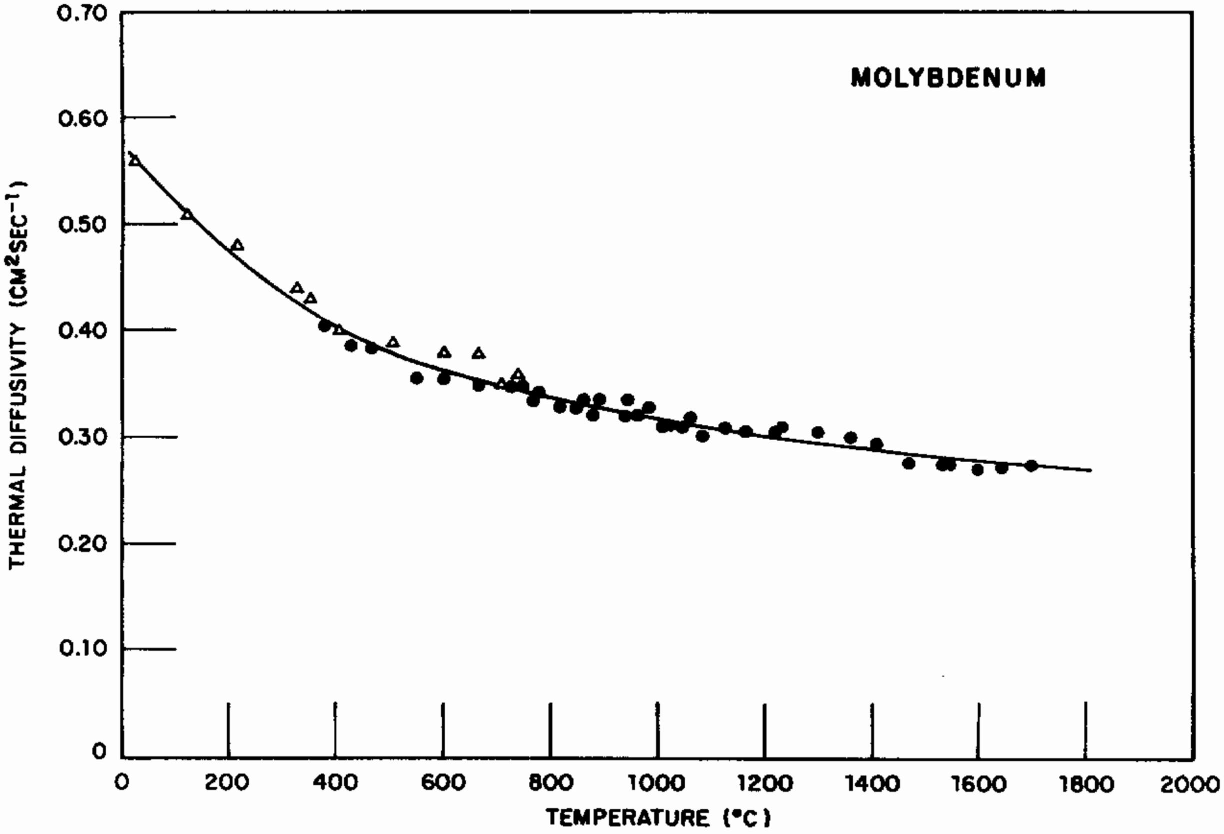

Fig. 6 Thermal diffusivity of molybdenum versus temperature (data points shown by triangles were obtained in the resistance furnace).

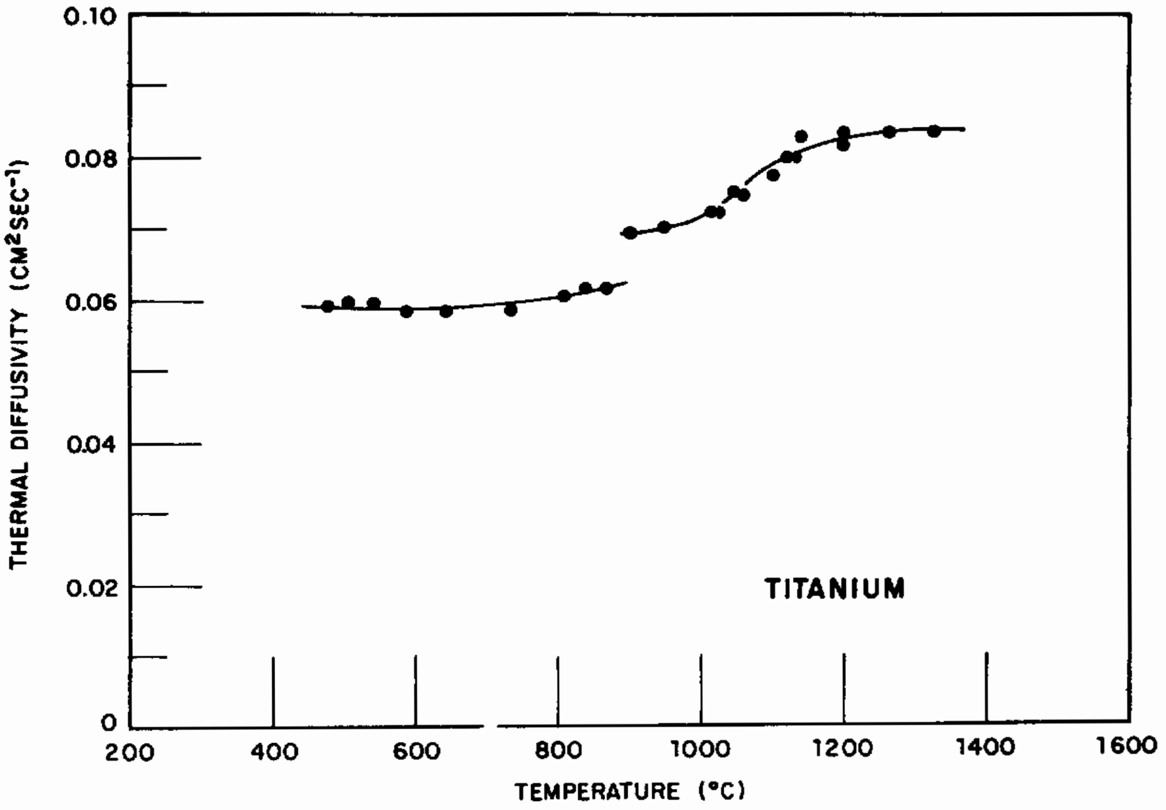

Fig. 7 Thermal diffusivity of titanium versus temperature

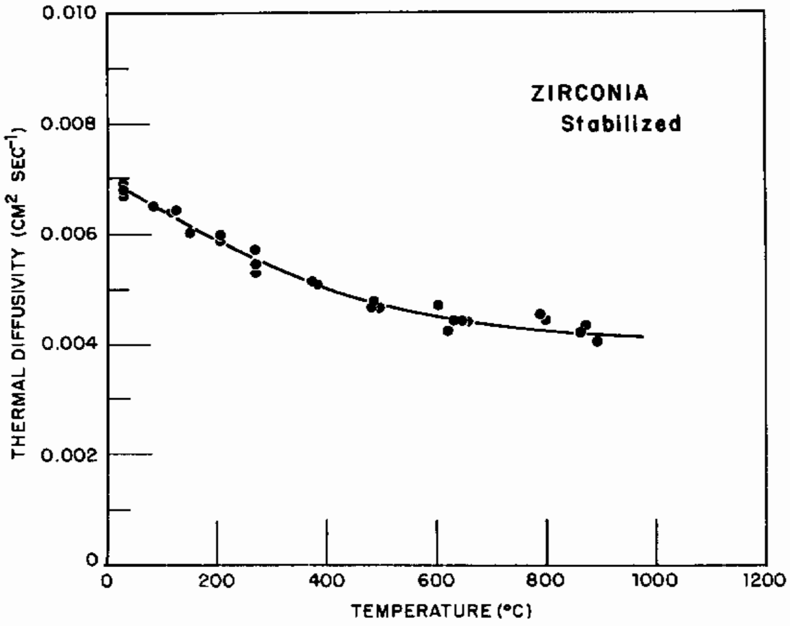

Fig. 8 Thermal diffusivity of zirconia versus temperature (Norton mix 302, magnesia-stabilized)

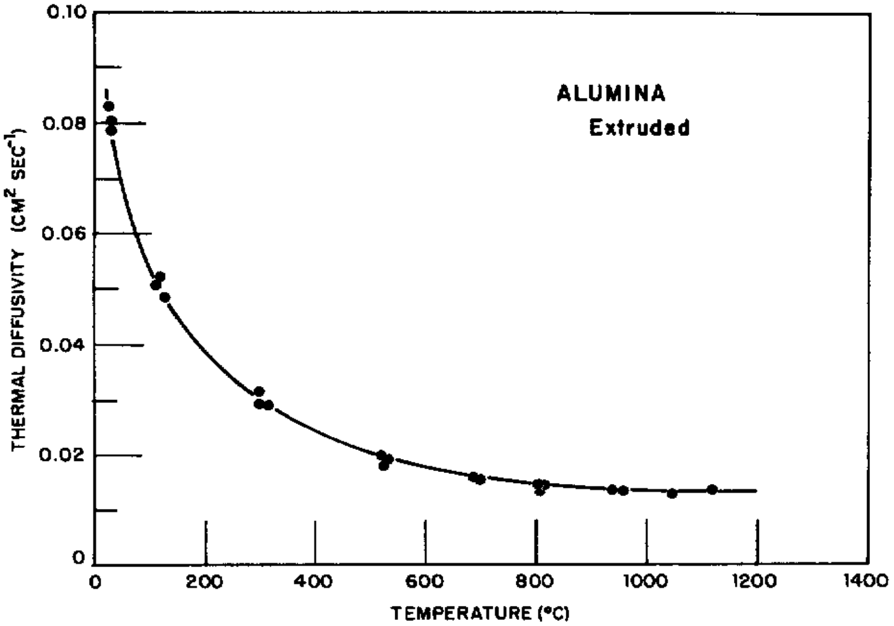

Fig. 9 Thermal diffusivity of "pure", extruded alumina (density = 3.834 gm/cm^3)

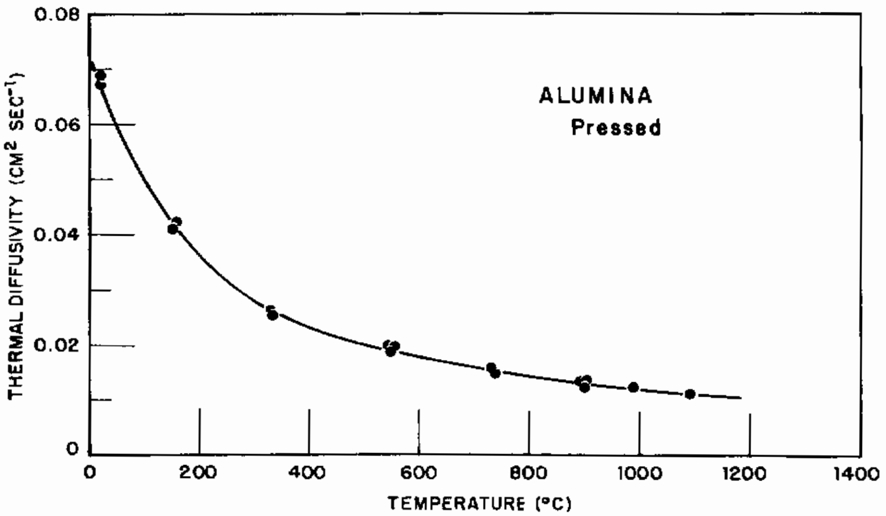

Fig. 10 Thermal diffusivity of "pure" pressed alumina (density = 3.914 gm/cm^3)