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THERMAL PROPERTIES OF REFRACTORY MATERIALS

(THIRD QUARTERLY PROGRESS REPORT)

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Contract No. AF 33(616)-6794

ARPA Order No. 24-59

Project No. 4776

9 775

(Contractor's Report No. AI-6358)

April, 1961

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FOREWORD

The work reported here was performed by Atomics International, a Division of North American Aviation, under the auspices of the Department of Defense through the Advanced Research Project Agency. Contract AF 33(616)-6794, issued under ARPA Order No. 24-59, Project 4776, "Materials Thermal Properties," was administered by the Materials Central, Directorate of Advanced Systems Technology, Wright Air Development Division, with Mr. Hyman Marcus acting as project engineer. This report covers work conducted from February 1, 1961 to April 31, 1961.

The final sections of this report deal with the steady state thermal conductivity of titanium carbide and the specific heat of conductors as determined by pulse techniques. Major credit for the authorship of these sections is due Mr. R. E. Taylor, who developed the pulse techniques and performed the measurements reported in these sections. He was assisted by Mr. R.A. Finch and Mr. D. C. Robinson.

The project is indebted to Mr. R. S. Carpenter for technical assistance in the development of the transient thermal property apparatus.

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ABSTRACT

The construction of an automatic recording optical pyrometer has been completed. This completes the apparatus for measurement of transient thermal properties. Preliminary results of the testing and alignment of the complete apparatus indicate that modifications must be made on the heater radiation shields to prevent spurious light from being collected by the pyrometer.

The thermal conductivity of titanium carbide was measured over the temperature region 400°C to 1200°C. The steady state radial heat flow method was used. The conductivity varies linearly from 0.086 cal/sec cm°C at 500°C to 0.109 cal/sec cm°C at 1100°C. These results are in marked contrast to values reported in the literature.

The techniques and apparatus for measuring the specific heat of brittle conductors by pulse heating are described. Resistivity and specific heat data for uranium silicide of several compositions are reported. The resistivity and specific heat increased with increasing silicon content. For uranium silicide containing 3.8% silicon, the resistivity increased from 56 microhm-cm at 0°C to 75 microhm-cm at 750°C and for uranium silicide containing 5.9% silicon, the resistivity increased from 81 microhm-cm at 0°C to 111 microhm-cm at 800°C. The specific heat for the 3.8% material is given by $c_p = 3.16 \times 10^{-6}T + .0412$ cal/gm °C from 50 to 430°C and for the 5.8% material $c_p = 16.1 \times 10^{-6}T + 0.0455$ cal/gm °C from 50° to 715°C. T is in °C.

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I INTRODUCTION

The primary purpose of this program is to measure and understand the high temperature thermal properties of refractory materials such as the carbides, borides, and nitrides of zirconium, titanium, tantalum, and tungsten.

This quarterly progress report covers the period from February 1, 1961 to April 31, 1961.

At this writing, construction of a working model of the optical recording pyrometer to be used for transient temperature measurements has been completed. Preliminary results of the testing and alignment of the instrument are given in section II.

The thermal conductivity of titanium carbide has been measured from 400°C to 1200°C. The measurements were taken by means of well-established steady state apparatus. The data and discussion are presented in section III.

A method for the measurement of specific heats of brittle conductors has proved to be satisfactory. The method is generally applicable for materials such as the carbides, silicides, and nitrides, and can be used from near absolute zero to the melting point. The results and discussion for measurements on silicides of uranium are given in section IV.

II STATUS REPORT ON TRANSIENT THERMAL PROPERTY TECHNIQUE

The description of the transient thermal property apparatus, exclusive of the optical pyrometer, has been given in a previous report.[1] During this reporting period, a working model of the pyrometer, constructed specifically for application with the transient apparatus, has been completed. A photograph of the instrument with associated electronics, is shown in Figure 1. Detailed description of the design principals for the pyrometer have been given by Vawter[2] and Nutter.[3] The working model is presently being tested and adjusted for optimum stability and response.

For transient temperature measurements, in the present arrangement, the pyrometer is required to view the radiation emanating from a 0.046 inch hole at a distance of about 5 feet. This situation is nearly at the limit of the resolution of the pyrometer. It has been observed during testing that spurious light originating from outside the site holes in the heater cavity[1], is collected by the pyrometer. To obviate this difficulty, the heater cap and radiation shields are being redesigned. It is intended, at this writing, to mount two 0.059 inch O.D. tubes of 0.001 inch wall thickness, in the heater cap. The tubes will fit directly into the sample sight holes and project upward through the cap so that only light originating within the sight holes will emanate from the ends of the tubes and be collected by the pyrometer.

III THERMAL CONDUCTIVITY OF TITANIUM CARBIDE

The thermal conductivity of titanium carbide was measured by the steady state radial heat flow method. The technique has been described in detail in the literature.[4] In the present case, the sample is in the form of a right circular cylinder, three inches in length. The outside diameter is two inches and the inside diameter 1/2 inch. By means of a graphite helix. heat is supplied to the outer surface of the sample. Through the center of the sample, along its axis. is mounted a water flow heat sink so that heat flows inwardly through the sample along a radial temperature gradient of circular isotherms. Only the radial heat flow through a small portion at the longitudinal center of the specimen is measured. In the present case, the section is one inch in length. This heat flow, q, is determined by measuring the temperature rise and flow rate of the cooling water in the coorespsonding section of the heat sink. The radial temperature gradient ΔT, is determined by measuring the temperature at two different radii through holes penetrating to the longitudinal center of the sample from the upper end. Longitudinal heat flow and end effects in the sample are minimized by using guard rings and thermal insulation at the ends of the sample. The thermal conductivity at any temperature is then given by the relation:

$$k = q \ \ln(\frac{r_2}{r_1}) \ \Big/ \ 2\pi L \Delta T \tag{1}$$

where r_1 and r_2 are the radii of the inside and outside sight holes respectively, and L is the length of the section (one inch) in which the heat flow was measured. Temperature measurements were made at three locations on each radius to detect any departure of the isotherms from circular symmetry. If a serious departure was observed, the run was terminated and the sample relocated in the furnace. Slight departures were usually noted but an average of the readings at each radius minimized this effect.

The apparatus is capable of measurements up to about 2400°C. At present, measurements have been completed from 400°C to 1200°C and at this writing are being extended to higher temperatures.

The present data are shown in Figure 2. The conductivity of TiC was found to increase from 0.088 at 500°C to 0.109 cal/sec cm °C (curve 1). These results are in marked contrast to values reported by Vasilos and Kingery[5] (curve 3), which shows the conductivity of TiC decreasing from 0.028 to 0.010 cal/sec cm °C over the same temperature interval.

Shown also in Figure 2, is the electronic contribution to the thermal conductivity (curve 2). This has been calculated from the Wiedeman-Franz relationship. As may be seen in Figure 2, the electronic conductivity, at the higher temperatures, exceeds the values reported by Vasilos and Kingery.

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One may regard the calculated electronic contribution to the thermal conductivity as representing a lower limit to the total conductivity. On this basis, the data of Vasilos and Kingery can not be understood. On the other hand, it is known that variations in the compositions of the refractory materials may cause variations in the observed properties. For this reason, chemical and x-ray analysis of the samples are being carried out to shed light on these discrepencies.

IV A METHOD FOR MEASURING THE SPECIFIC HEAT
OF BRITTLE CONDUCTORS: URANIUM SILICIDES

Initial studies of the feasibility of measuring the specific heat of electrical conductors by pulse heating demonstrated that accurate results can readily be obtained on metallic samples from near absolute zero to their melting temperatures.[7] In these studies wire samples of molybdenum, tantalum, and rhenium were rapidly heated to high temperatures. Heating rates varying from 1000 to 60,000°C per second were used. Expansion loops were incorporated into the sample and no thermal stress problems arose. However, attempts to use this method on brittle non-metals, such as carbides, were not successful due to sample failure during rapid heating.

The primary purpose of the present work was to investigate the reasons for failure and, if possible, to develop techniques and hardware suitable for pulsing brittle conductors. Uranium silicide was chosen as the test material because its brittleness is controlled by the percentage of silicon present. Therefore, attempts to pulse heat the material could be tried on less brittle samples and as techniques and hardware improved, the test could be conducted on samples of increased brittleness. The data obtained while developing the techniques were found to be of general interest and are incorporated as a significant portion of this report.

Uranium silicide samples were prepared by arc melting and casting weighed amounts of uranium and silicon. Chemical analysis were performed on the cast material to correct for the loss of silicon due to vaporization. Sample histories are given in Table I. Three compositions were used, 3.8% silicon (U_3Si), 5.9% silicon ($U_3Si + U_3Si_2$) and 7.3% silicon (U_3Si_2).

A. Experimental Apparatus and Procedure

The specific heat apparatus is described in detail in another report[7] and only a brief description will be presented here. The apparatus is pictured in Figure 3. The sample, which is contained in a vacuum chamber, is connected in series with a relay, a bank of batteries, a standard resistor, and a variable resistor. When the relay is closed, a surge of current flows through the circuit heating the sample. The heating rates, which may be varied from 1000° to 50,000°C per second, are determined by the number of batteries used and the value of the variable resistor. The duration of the pulse is controlled by a timing circuit and will terminate when the sample melts or at any preselected time short of melting.

The voltage drop across the central portion of the sample and the current, measured as the voltage drop across the standard resistor, are recorded as a function of time by photographing the traces on a dual beam oscilloscope. At any instant the voltage and current may be determined from the photograph. A vernier-microscope is used to measure the voltage and current at definite

TABLE I

SAMPLE HISTORIES

Number	% U	% Si	Density gm/cc	Composition
533	96.2	3.8	14.5	U_3Si^+
535	96.2	3.8	14.3	U_3Si^+
539	94.1	5.9	12.9	$U_3Si_2^\bullet + U_3Si^+$
7-806	92.7	7.3	12.1	U_3Si_2

+ U_3Si tetragonal

• U_3Si_2 body centered tetragonal

time intervals and the specific resistance at each time interval is calculated from the relationship $\rho = \frac{A}{L}\frac{E}{I}$ where A is the cross-sectional area of the wire, L is the distance between voltage probes and E and I are the voltage and current respectively. The specific heat at any temperature T is given by the expression:

$$c_p = \frac{EI}{J} \quad \frac{4\frac{d\rho}{dT}}{\pi D^2 \; Ld\frac{d\rho}{dt}} \; --$$

where c_i is in cal/gm sec, J is 4.186 watts/cal sec, D is the diameter of the specimen, d is the density, $\frac{d\rho}{dT}$ is the temperature dependence of the resistivity at temperature T and $\frac{d\rho}{dt}$ is the rate of change of the resistivity at the resistance corresponding to T. This approach presupposes knowledge of the resistance as a function of temperature which was obtained by the standard potential drop method. An IBM 709 computor was used to smooth the measured voltages and currents and to calculate the resistivity, its derivative and the specific heat.

Although this method proved very satisfactory for metal wires, brittle samples failed during the pulse heating. Studies indicated that sample failures were caused by three mechanisms; stresses arising from thermal expansion, stresses arising from torque caused by the surge of current, and arcing from the current contacts to the sample. The use of flexible leads allowed for thermal expansion but increased the torque problem. Consequently, it was necessary to employ rigidly mounted pistons which permitted the sample to expand and contract freely in one direction while

maintaining a current path suitable for carrying the several thousand amperes required to heat the specimens. The use of these pistons eliminated thermal stress and torque problems. However, arcing at the sample-to-piston contacts proved to be a severe problem which could not be overcome by various clamping techniques. Arcing occurred at or near the end of the clamps, especially if tight tolerances between the sample and contact were not maintained. Although precise machining apparently would overcome this difficulty, this is very difficult to accomplish on brittle materials and alternate approaches were sought. The method which proved most satisfactory involved nickle-plating the ends of the specimen and soft soldering the sample to the holders. The solder melts during pulse heating to high temperatures but this causes no difficulty except to plate the walls of the vacuum chamber with a metallic film. A photograph of a mounted sample and an exploded view of a piston is shown in Figure 4. With this arrangement is was possible to pulse heat uranium silicide samples repeatedly. Runs were also made successfully on the carbides of zirconium and titanium.

B. Experimental Results and Discussion

1. Electrical Resistivity

Initial attempts to measure the electrical resistivity proved unfruitful because of the marked tendency of the resistance to change with temperature. After several cyclings to 600°C and a 24 hour anneal to 800°C the resistivity of the 3.8 and 5.9% samples stabilized. However, the resistivity of 7.3% material continued to drift.

The final values for 3.8% and 5.9% samples and the last measurements on the 7.3% sample are shown in Figure 5. From this figure it may be seen that the resistivity of uranium silicide increases with increasing silicon content and that the resistivity tends to become constant at the higher temperatures. As presently conceived, it is necessary that the resistivity change with temperature in order to obtain specific heat results. Therefore, the specific heat of the 3.8% material should not be accurately obtained above 500°C.

2. Specific Heat

The data from three runs on sample 533 and one run on sample 535 (both 3.8% Si) were reduced and calculated. The specific heats of both specimens increased lineally with temperature and are given by:

$$c_p = 3.16 \times 10^{-6}T + 0.0412 \text{ cal/gm °C from 50 to 430°C}$$

where T is in °C.

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A total of 118 data points were obtained and all were within 5% of the curve shown. The data from two runs on sample 53⁰ were reduced and computed. The specific heat of this specimen was found to increase lineally with temperature and to be expressed as $c_p = 16.1 \times 10^{-6} T + 0.0455$ cal/gm °C from 50 to 715°C. A total of 70 data points were obtained and all were within 6% of the curve shown in Figure 6.

The specific heat of uranium silicide increases with increasing silicon content as expected from simple considerations based on the Dulong-Petit law. Values of the specific heat of various uranium silicides calculated from this law are presented in Table II. The 3.8% material corresponds to $U_3 Si$, the 7.3% material corresponds to $U_3 Si_2$, and the 5.9% material represents a two-phase system of $U_3 Si_2$ and $U Si_3$. Based on the phase diagram for the uranium-silicon system[8] the specific heats of these materials should show no anomalies up to 930°C, which is beyond the range that the measurements were made. The temperature region was limited by restrictions on the resistivity furnace. Although only minor modifications were necessary to extend the range, the major objective of the present work was the development of specific heat techniques and therefore, no efforts were undertaken to obtain resistivity data at high temperatures.

TABLE II

CALCULATED SPECIFIC HEATS OF URANIUM SILICIDES

Compound	Formula Weight	Number of Atoms	Specific Heats [*]
U	238	1	0.0269
U_3Si	742	4	0.0359
U_3Si_2	770	5	0.0416
U Si	266	2	0.0482
U Si_2	294	3	0.0653

[*] Calculated from $C_s = \dfrac{6.4 \times \text{number of atoms}}{\text{Formula weight}}$

The chief difficulties in obtaining specific heat results
on uranium silicide by the present approach are connected with
its resistivity. In the case of the 7.3% material the resistivity
did not stabilize and in the case of the 3.8% material, the
change in resistivity with temperature approaches zero at the
higher temperature. Therefore, the specific heat of the 7.3%
material could not be measured at any temperature and the specific
heat of the 3.8% samples could not be measured above 500°C.
During the initial work on metals a method of directly measuring
the rate of change of temperature was explored and found to be
feasable.[7] When this quantity is measured directly, the
requirements that the resistivity as a function of temperature
be known, that it be reproducible, and that it not approach
zero are no longer applicable. Therefore, the use of this method,
which is based on the sample acting as the thermocouple junction,
may allow the measurement of the specific heat in those cases
where it cannot be determined by the present procedure.

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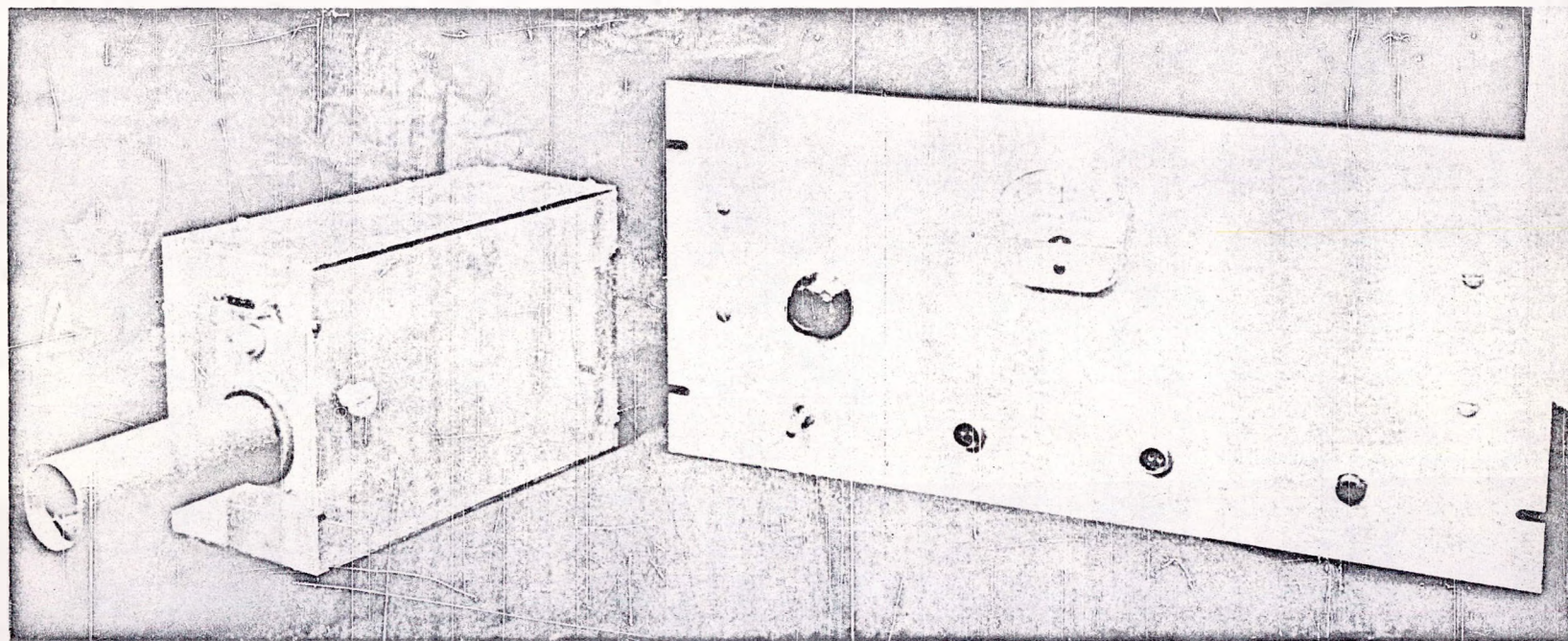
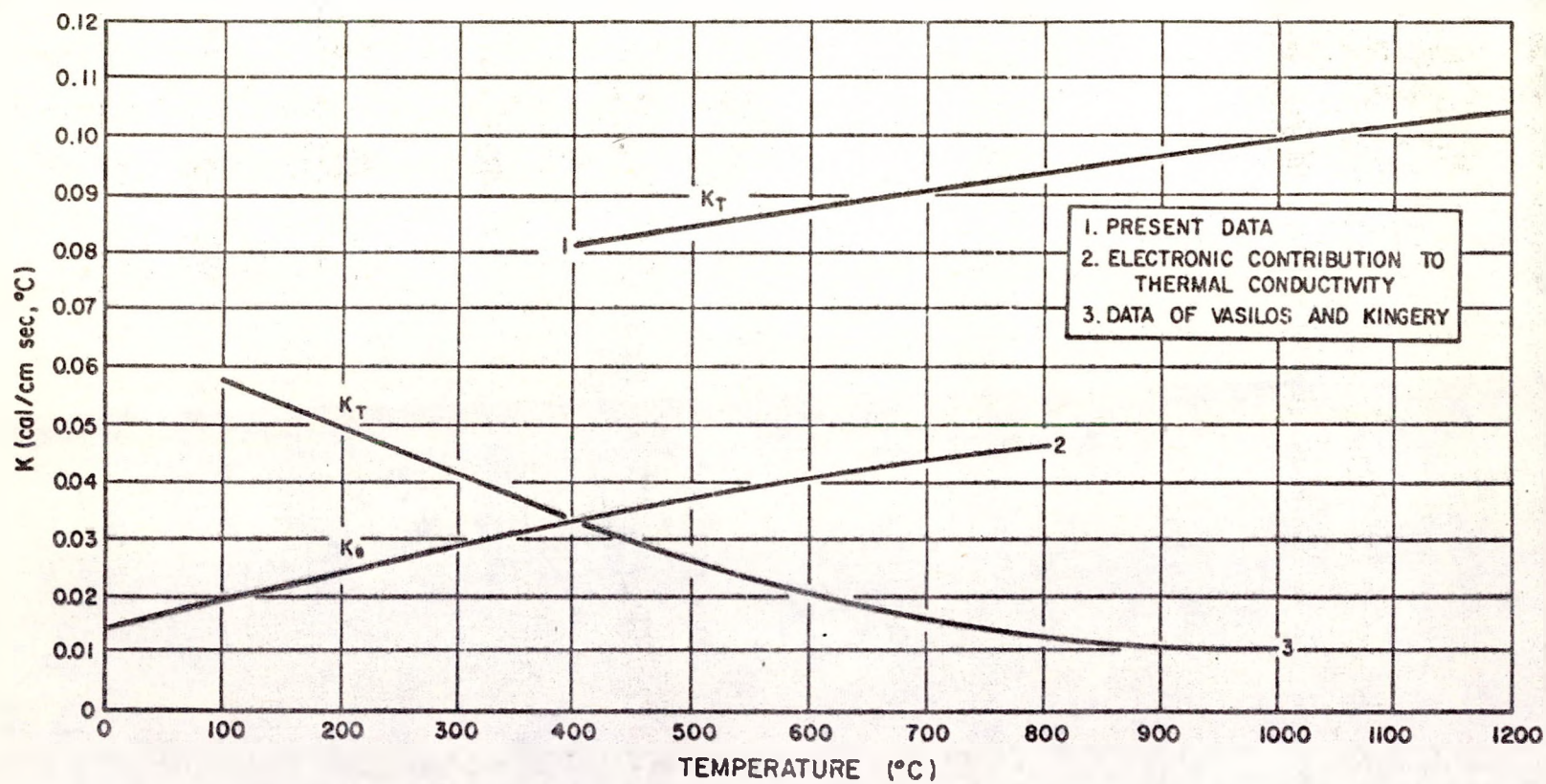Figure 1. Automatic Recording Pyrometer
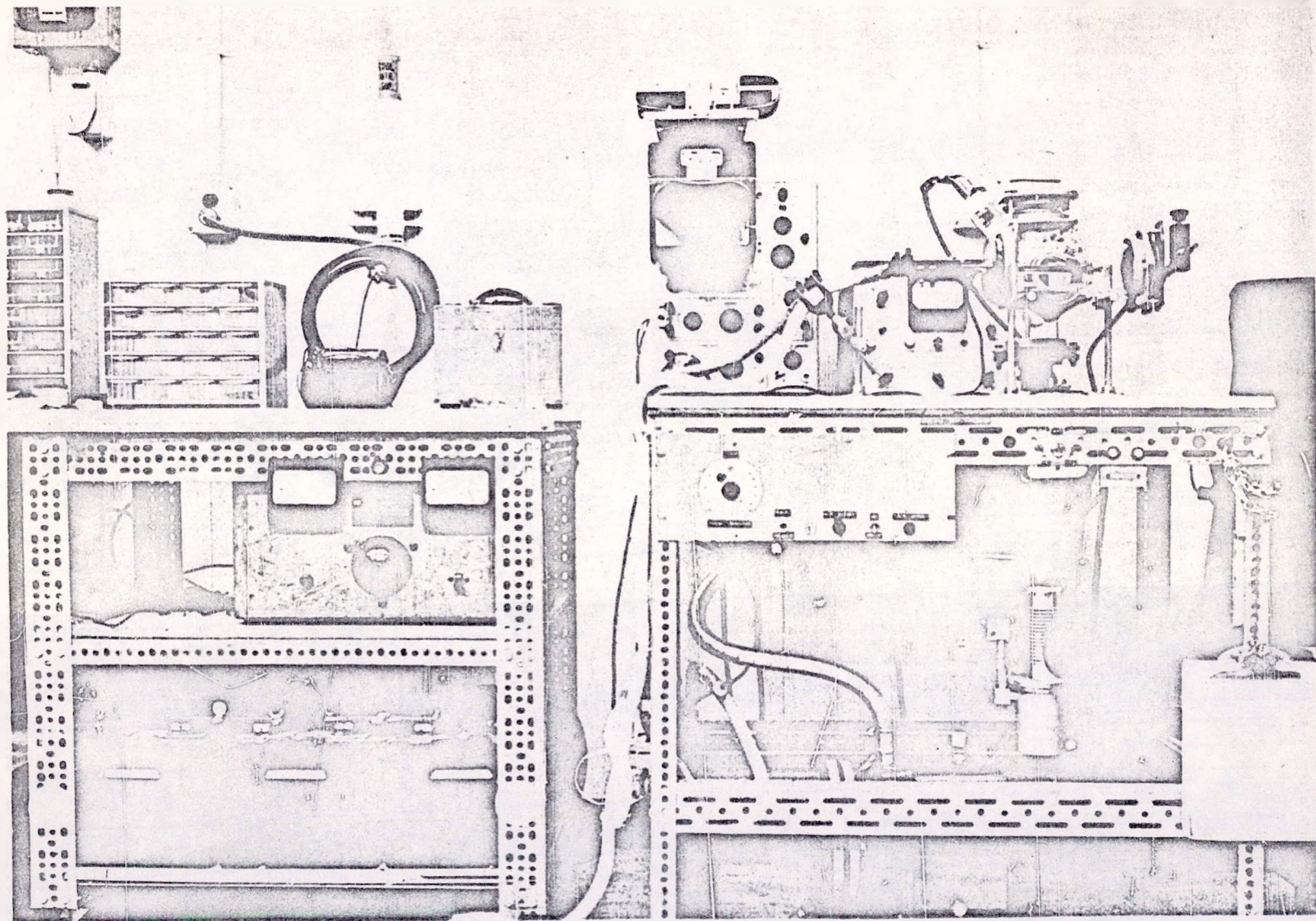
Figure 2. Thermal Conductivity of TiC
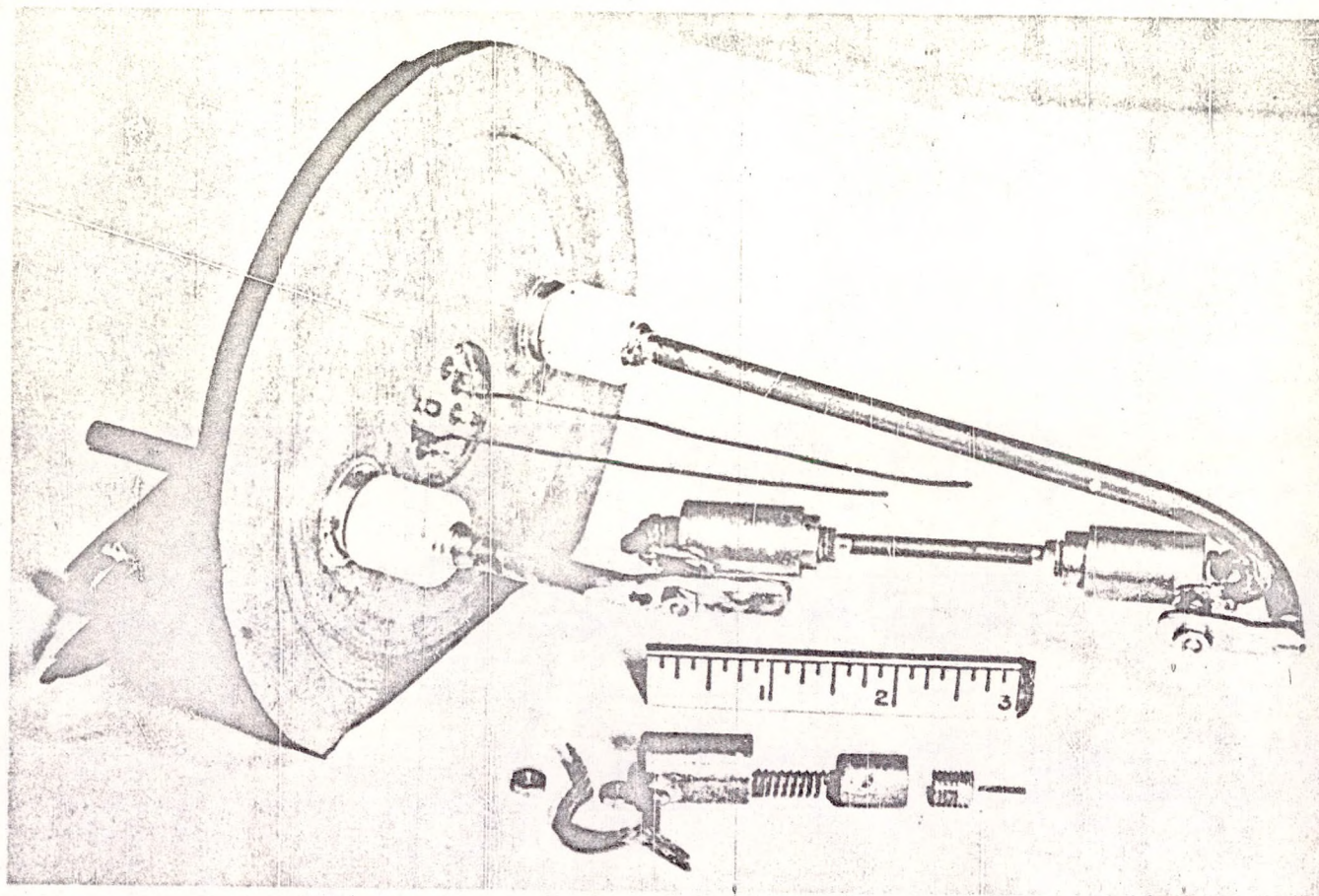
Figure 3. Specific Heat Apparatus
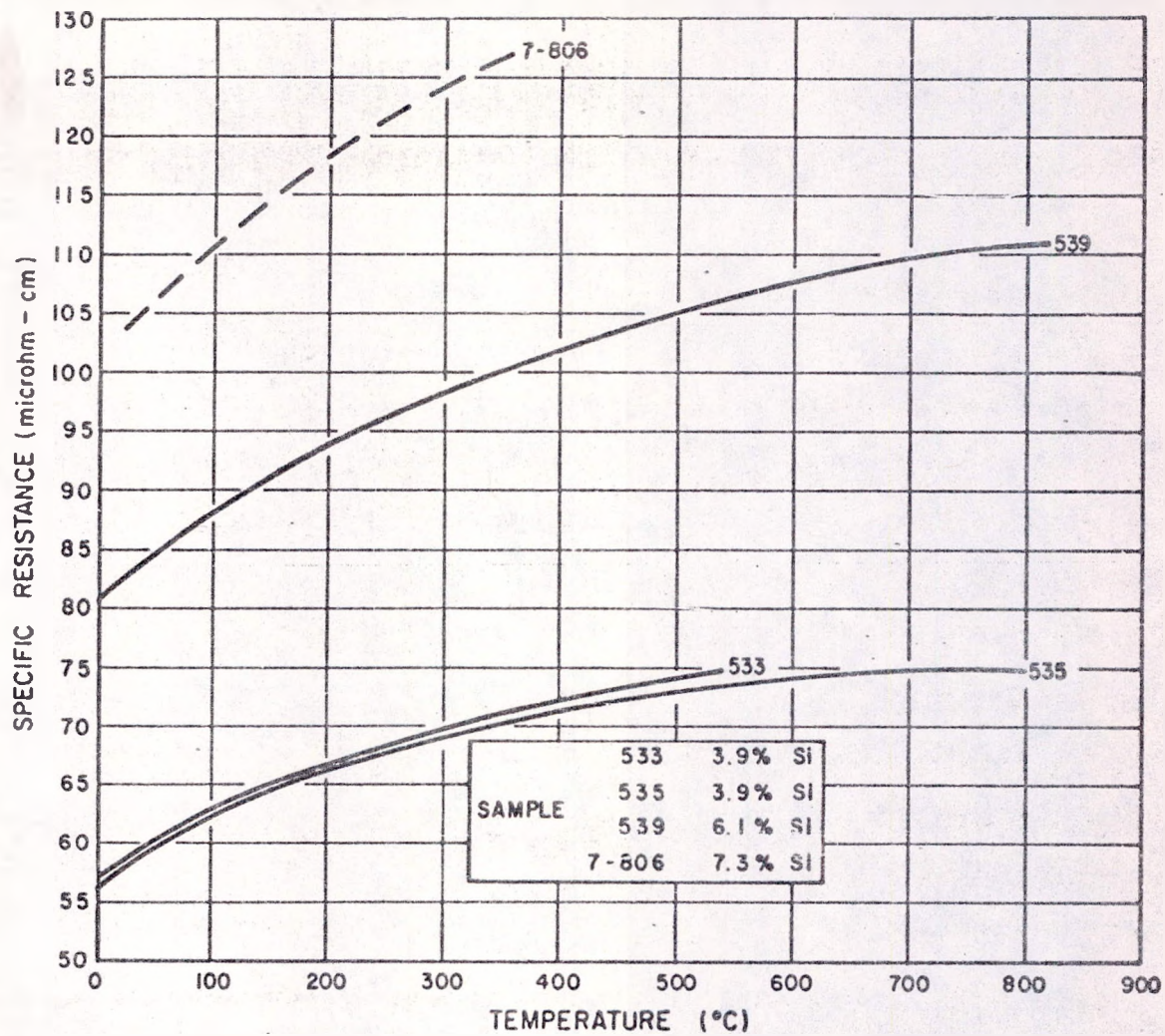
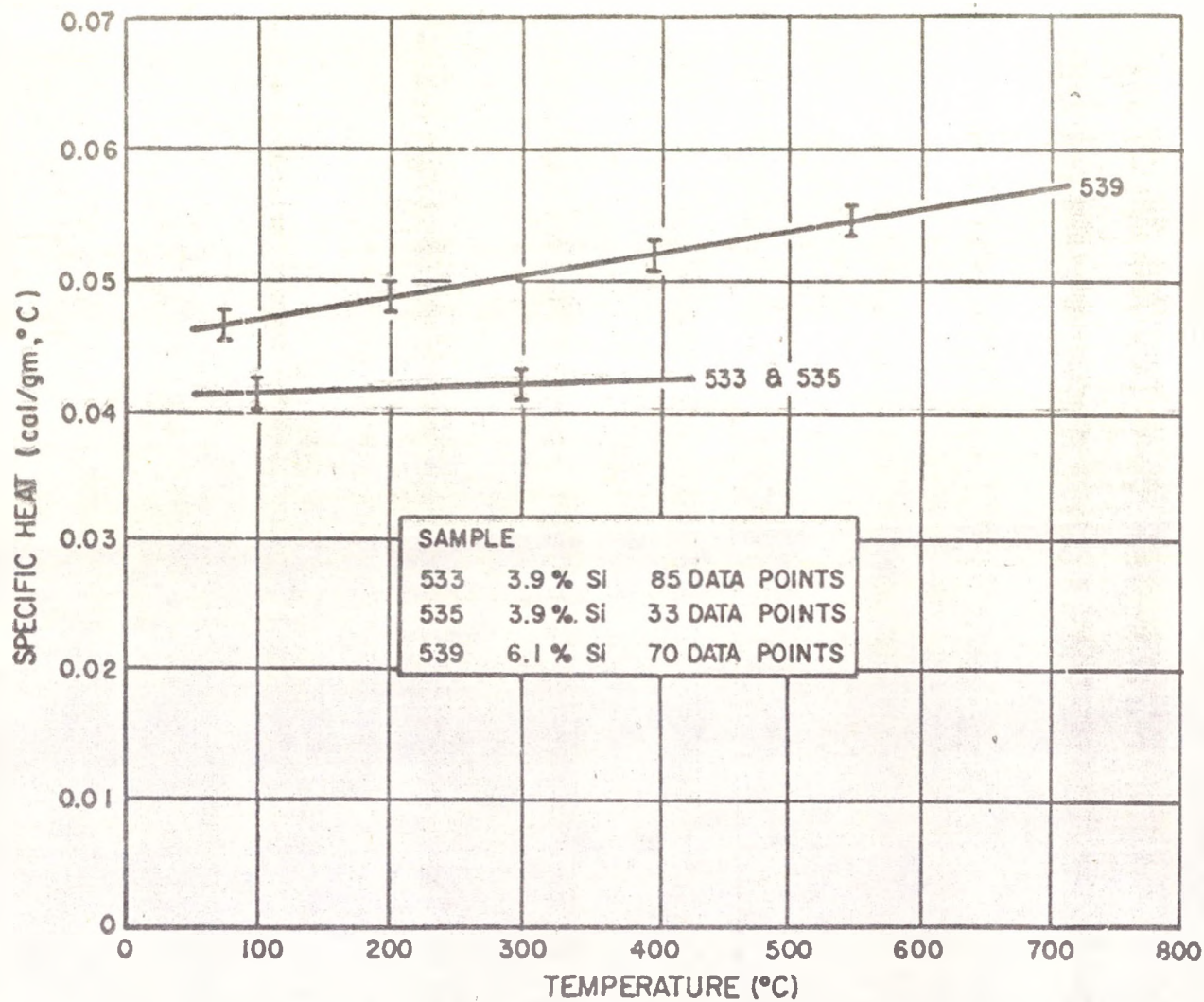Figure 4. Close-up of Mounted Sample

Figure 5. Resistivity of Uranium Silicide

Figure 6. Specific Heat Capacity of Uranium Silicide