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THERMAL CONDUCTIVITY AND ELECTRICAL RESISTIVITY OF ZIRCALOY-4

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ABSTRACT

The thermal conductivity of Zircaloy-4 was measured in a radial heat flow device. Results of these measurements indicate that the conductivity of this material increases with temperature from 0.16 w/cm°C at 400°C to 0.425 w/cm°C at 1500°C. A platinum-platinum +10% rhodium thermocouple was used as a probe for temperature measurements up to about 1150°C whereas an optical pyrometer was used above this temperature.

Electrical resistivity measurements were made from room temperature to 920°C using a rod specimen which was fabricated from the same raw material as the thermal conductivity specimens. Results of this study show that the electrical resistivity of Zircaloy-4 is considerably higher than essentially pure zirconium. The data indicate a maximum in resistivity of of 140.0×10^{-6} ohm-cm at 810°C with a sharp decrease in resistivity as the material undergoes a phase change from hexagonal close packed (α) to the body centered cubic (β) phase at ~860°C.

INTRODUCTION

Alloys of zirconium have proven to be valuable for structural and fuel cladding applications in nuclear reactors for many years due to their corrosion resistance in the heat transfer medium and their relatively low neutron absorption cross section. Thermal property data have been reported(1) for pure zirconium and some of its alloys to 780°C; however, very little, if any data exist above this temperature. The data described in this report are the results of our efforts to determine the thermal conductivity of Zircaloy-4 up to temperatures approaching its melting point (~1830°-1845°C). This work was performed for the AEC High Temperature Materials Program in support of LOFT.

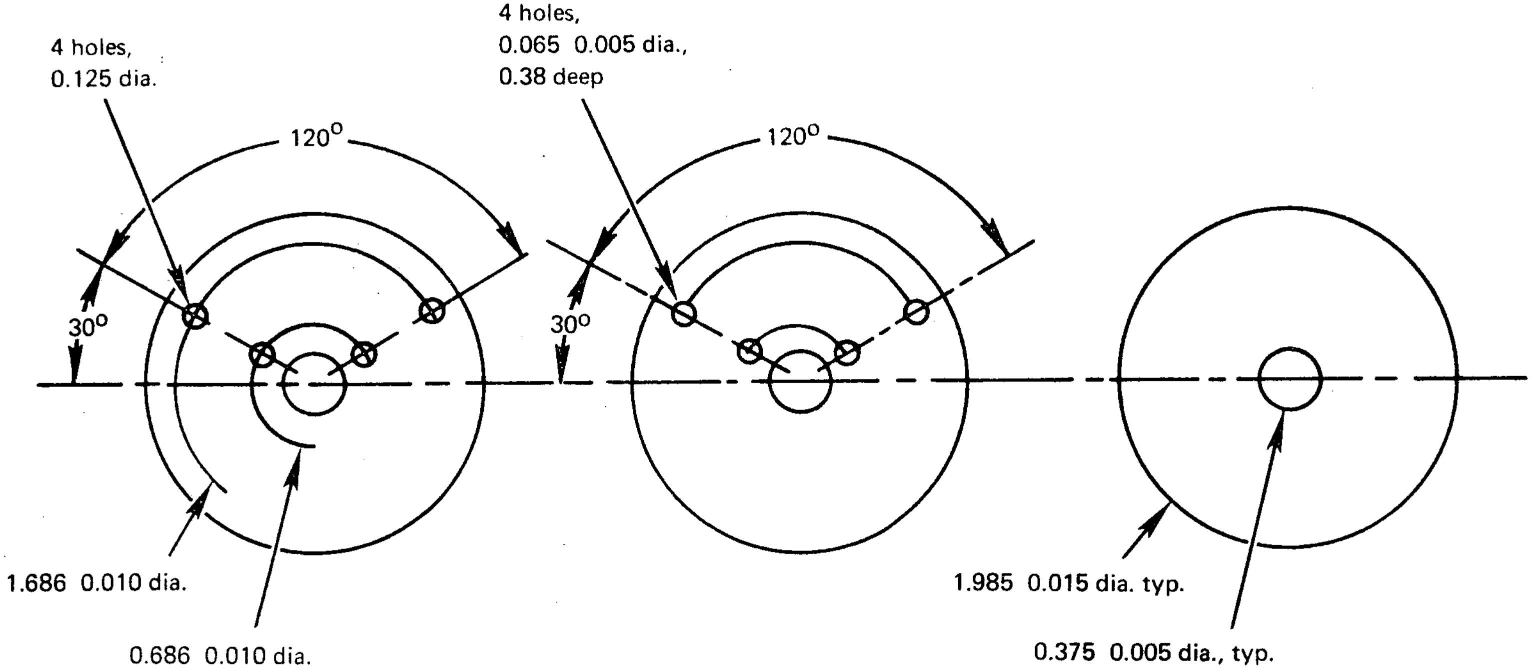
Although zirconium and its alloys exhibit excellent corrosion resistance and stability in the presence of other materials below 1000°C, it reacts readily with most other materials at temperatures above ~1200°C. Its "gettering" properties for oxygen, nitrogen, hydrogen, etc., have been exploited in electronic component applications where it is employed as a getter in vacuum tubes to absorb small traces of these elements which may outgas from other components in the tube enclosure(1). Absorption of, and reactions with gases and other elements cause changes in the thermal and electrical properties of the material; therefore, property measurements on this material are very difficult. Zirconium also forms eutectics with refractory metals, i.e., molybdenum at 1520°C(1) and tungsten at 1650°C(1), which further increase the difficulties in making property measurements at high temperatures.

APPARATUS

The radial heat flow apparatus in which the thermal conductivity work was performed has been previously described in detail(2). A description of the four probe method for measuring electrical resistivity has also been reported(3).

SPECIMENS

The thermal conductivity specimen and guard discs, as shown in Figure 1, were fabricated from Zircaloy-4 plate, 0.75 inch thick and 9 inches square, which was purchased from Carborundum Metals Climax, Inc. as Zircaloy-4, Grade 34 Zirconium (ASTM-B352-64T Grade RA2). Cylindrical rods (0.635 cm diameter by 10.16 cm long) were machined from the same raw material and were used as electrical resistivity specimens. The rods had small holes through the diameter at a 7.5 cm spacing for voltage probes. Grooves near the ends of the rods accommodated the power leads. Small cubes (approximately 0.6 cm on a side) of Zircaloy-4 were placed in the furnace with the thermal conductivity specimens to monitor changes in composition due to high temperature exposure. The chemical composition of the material in the as-received condition is shown in Table 1 along with the composition after exposure in argon at high temperatures. It will be observed in Table 1 that the alloying constituents are very small in quantity; including impurities the additives total 1.14%.



Upper guard

Specimen

Lower guard

Note: All dimensions are in inches. Thickness may
be variable, however not less than 0.5 inch.

Figure 1 – Design of thermal conductivity specimens

TABLE 1. COMPOSITION OF ZIRCALOY-4 THERMAL CONDUCTIVITY SPECIMENS
(ppm except as noted)

	As-Received	Exposed 100 Hrs 400-800°C	Exposed 200 Hrs 400-1500°C
C	38	37	52
N_2	43	42	210
Al	24	27	87
B	<1	<1	<1
Cd	<1	<1	<1
Co	<10	<10	<10
Cu	176	216	153
Hf	<100	130	<100
Mg	1600	1500	<10
Mn	24	32	13
Ni	12	7	7
Si	24	28	46
Ti	18	19	<10
W	<100	<100	<100
Sn*	0.61%	1.16%	0.37%
Fe*	2300	2400	1900
Cr*	860	870	815

*Alloying Constituents.

EXPERIMENTAL RESULTS

Thermal Conductivity

The results of the thermal conductivity measurements on Zircaloy-4 are shown in Figure 2 along with the least squares line reported by D. B. Scott(4). Scott estimates the accuracy of his method to be within 5 percent; however, the data from which his line was derived show scatter as high as ±10 percent. The spread in data presented herein is shown by the length of the bar at each point. The poorer precision at the higher temperatures is largely due to the small temperature gradient obtained ($\sim 15^{o}C$) and the difficulty in making small ΔT determinations to high precision with an optical pyrometer; refractory metal thermocouples could not be considered due to the probable reactions of the specimen with the thermoelements and insulators at the higher temperatures. Data presented herein are reproducible since they represent measurements on two different specimens. Figure 2A shows the deviation in conductivity between the average measured values and the smoothed line of Figure 2.

Repeated measurements were made below $860^{o}C$, the α to β phase transformation temperature, before going to higher temperatures in an attempt to determine the effect of the phase change on the thermal conductivity. If an effect exists it is probably within the scatter of these results. Table 2 is a complete list of measured values of thermal conductivity for several cycles of two different specimens. An examination of this table will reveal that the values are reproducible.

Electrical Resistivity

Measurements of electrical resistivity are normally more routine than are those of thermal conductivity. However, considerable difficulty was experienced with this material. Initially, the power leads and the voltage leads of pure zirconium wire were attached in a manner to insure good mechanical contact; measurements were made in argon at room temperature and at increasing temperatures to $920^{o}C$ with small temperature intervals near the phase change. After the reading at $920^{o}C$ was obtained, the voltage signal became very erratic and difficult to obtain. Upon shutdown and disassembly it was observed that a non-conducting film had formed on the voltage leads and on the thermocouple wires. This film was identified by radiographic techniques as ZrO_2. The oxidation of the specimen was attributed to trace impurities of O_2 or water vapor in the argon gas. These data are recorded in Table 3 as cycles 1, 2 and 3.

A second test was made after cleaning the specimen to remove loose surface contamination. The emf, thermocouple, and voltage leads were welded to the sample to assure a metallurgical bond and an uninterrupted signal if further contamination should occur. Measurements were made at room temperature in argon and helium and found to agree within one percent although about 2 percent higher than the initial measurements. The measurements at increasing temperatures followed the initial curve up to about $500^{o}C$ where the second curve crosses the first (Figure 3). The maximum value was about 135×10^{-6} Ω-cm at $808^{o}C$ during the second run whereas it was about 140×10^{-6} Ω-cm at $810^{o}C$ during the first test. Data at $1150^{o}C$ were considerably higher than anticipated when compared

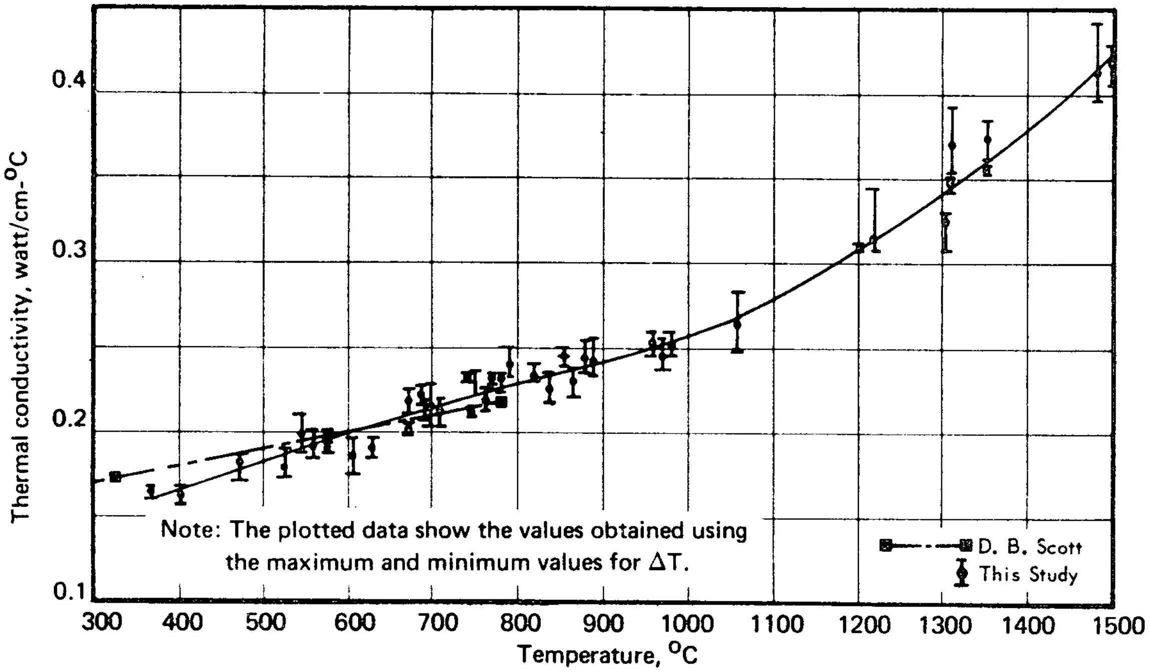


Figure 2 – Thermal conductivity vs. temperature for Zircaloy-4

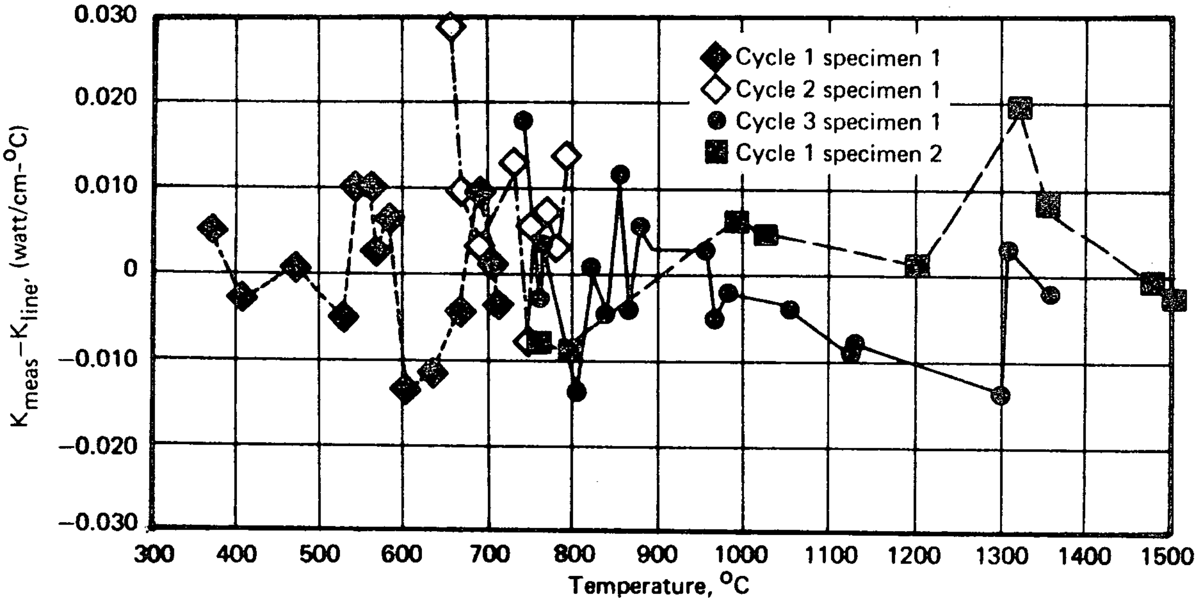


Figure 2a – Thermal conductivity of Zircaloy-4 deviation from smooth curve vs. temperature

TABLE 2. THERMAL CONDUCTIVITY VALUES OF ZIRCALOY-4

	Conductivity, w/cm °C(a)				Conductivity, w/cm °C(a)		
Temperature, °C	Data	Curve(b) Figure 2	Deviation	Temperature, °C	Data	Curve(b) Figure 2	Deviation
SPECIMEN NO. 1							
Cycle 1				Cycle 2			
369	0.163	0.158	+0.005	652	0.231	0.202	+0.029
405	0.161	0.164	-0.003	670	0.218	0.208	+0.010
473	0.176	0.175	+0.001	690	0.215	0.212	+0.003
527	0.177	0.183	-0.006	732	0.229	0.216	+0.013
546	0.198	0.188	+0.010	746	0.211	0.220	-0.009
560	0.201	0.191	+0.010	750	0.226	0.220	+0.006
574	0.196	0.193	+0.003	767	0.229	0.222	+0.007
577	0.200		+0.007	781	0.227	0.224	+0.003
607	0.184	0.198	-0.014	790	0.240	0.226	+0.014
629	0.190	0.202	-0.012				
673	0.204	0.208	-0.004				
687	0.221	0.211	+0.010				
696	0.214	0.213	+0.001				
708	0.212	0.215	-0.003				

(a) Each Conductivity Value is Calculated Using an Average of 5 Values for ΔT.

(b) Values From Smoothed Line in Figure 2.

(Table Continued on Page 9.)

TABLE 2. THERMAL CONDUCTIVITY VALUES OF ZIRCALOY-4 (Cont'd)

Temperature, °C	Conductivity, w/cm °C(a) Data	 Curve(b) Figure 2	 Deviation
SPECIMEN NO. 1			
	Cycle 3		
739	0.236	0.218	+0.018
762	0.218	0.221	-0.003
764	0.225	0.221	+0.004
806	0.214	0.228	-0.014
820	0.233	0.232	+0.001
839	0.225	0.230	-0.005
855	0.245	0.233	+0.012
866	0.231	0.236	-0.005
879	0.244	0.238	+0.006
888	0.242	0.239	+0.003
959	0.253	0.250	+0.003
970	0.247	0.252	-0.005
980	0.252	0.254	-0.002
1058	0.264	0.268	-0.004
1128	0.278	0.287	-0.009
1131	0.279		-0.008
1303	0.326	0.342	-0.014
1308	0.346		+0.004
1351	0.363	0.365	-0.002

Temperature, °C	Conductivity, w/cm °C(a) Data	 Curve(b) Figure 2	 Deviation
SPECIMEN NO. 2			
	Cycle 1		
748	0.212	0.220	-0.008
793	0.217	0.226	-0.009
996	0.262	0.255	+0.007
1016	0.265	0.260	+0.005
1211	0.311	0.310	+0.001
1321	0.368	0.348	+0.020
1352	0.373	0.365	+0.008
1482	0.414	0.415	-0.001
1498	0.418	0.420	-0.002
	Cycle 2		
752	0.232	0.220	+0.012
1235	0.317	0.320	-0.003

TABLE 3. ELECTRICAL RESISTIVITY VALUES FOR ZIRCALOY-4

Temperature, °C	Resistivity x 10^6, Ohm-cm	Temperature, °C	Resistivity x 10^6, Ohm-cm
Cycle 1		Cycle 4(a)	
30	70.53	30	74.05
78	80.50	62	79.58
146	87.80	100	84.05
		177	93.14
		378	115.04
Cycle 2		Cycle 5	
28	73.15	27	72.07
186	89.73	155	93.01
455	123.55	350	115.03
540	129.26	513	127.61
543	129.62	808	135.00
662	135.59	970	122.12
742	137.75	975	123.31
740	139.80	1151	128.88
846	135.47	1160	130.1
859	134.34	910	137.60
		730	145.35
		Post Test	
		27	84.65
Cycle 3			
694	137.47		
810	140.47		
814	136.45		
920	116.36		

As Received		Exposed(b)	
T, °C	Resistivity x 10^6, Ohm-cm	T, °C	Resistivity x 10^6, Ohm-cm
19.6	70.24	24.6	85.25
-196	37.65	-196	48.75

(a)NOTE: The Specimen was Removed and Cleaned Prior to Cycle 4.

(b)Measurements After Cycle 5.

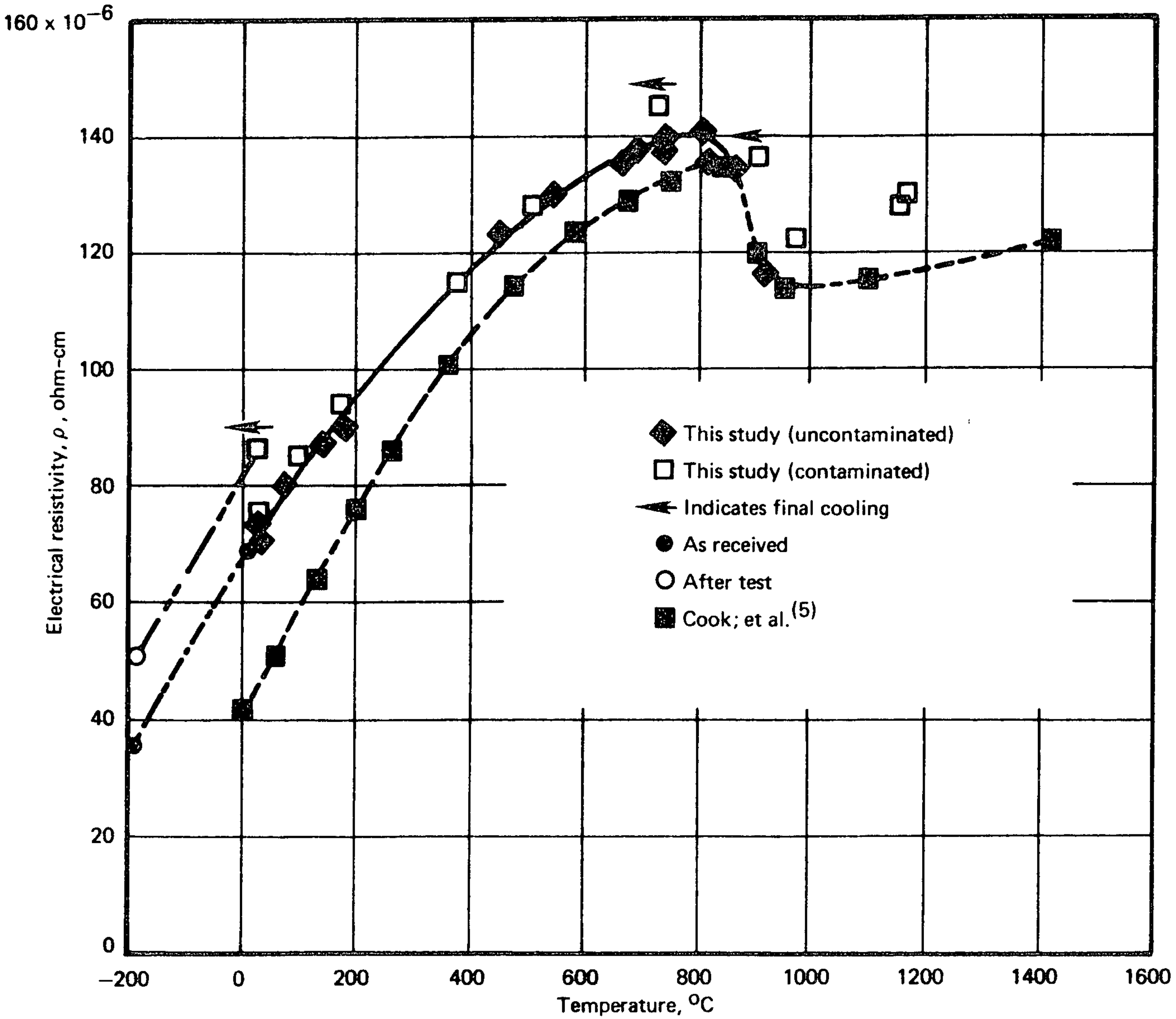
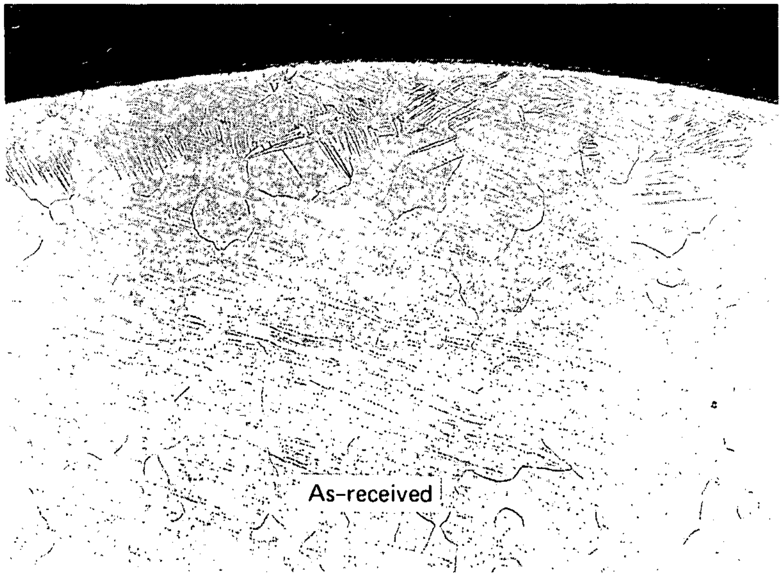
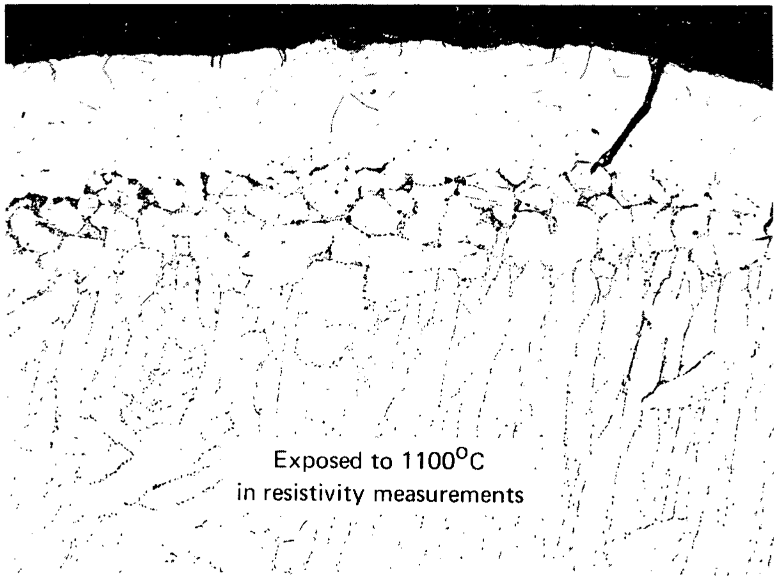


Figure 3 – Electrical resistivity as a function of temperature for Zircaloy-4

to literature values of Cook, et al.(5) for his high hafnium (1.8% Hf) sample. During cool down, measurements were made at 910°C, 730°C and room temperature. These data are considerably higher than the data on heating having a maximum of about 145 x 10^{-6} Ω-cm at 730°C; the room temperature value was increased by more than 10 percent over the initial value. The data are tabulated in Table 3 as cycles 4 and 5 and shown in Figure 3 with those of the previously cited literature(5). Suspecting that either additional contamination or diffusion of the oxygen from the outer surface through the diameter (or both) caused the change in resistivity, new measurements were made at room temperature and at liquid nitrogen temperature on this specimen and one which had not been exposed to high temperatures. These data, obtained in a different four probe apparatus, are also shown in Figure 3 and tabulated at the bottom of Table 3 and show a similar change in resistivity of the exposed material compared to the as-received specimen. This type of measurement is used routinely to identify changes in composition and effects of reactor environments on structural materials. Metallographic specimens were prepared and are shown in Figure 4. The as-received material is a homogeneous structure with the major phase believed to be basically zirconium containing a fine metallic appearing precipitate uniformly dispersed throughout the matrix. The photomicrograph of the exposed specimen indicates that considerable changes have taken place in this material. A dense layer, approximately 0.006 inch thick, which appears to be oxygen rich α zirconium surround a uniform 2 or 3 phase structure similar to the as-received material but containing large "islands" rather than finely dispersed particles of the precipitate. A diamond point hardness of 572 was measured in the outer layer compared to 300 in the core. This large difference in hardness is attributed to oxygen absorption into the surface layer. X-ray powder patterns revealed no change in the lattice parameters as a result of the exposure during measurement. The 0.006 inch thick surface layer, if uniform, represents about 9.4% of the cross section area of the specimen. The change in resistivity which amounted to about 4% at 730°C and about 18% at room temperature may be due to the oxide layer if the surface layer has a considerably higher resistivity than does the Zircaloy-4. The third photomicrograph in Figure 4 shows the effect of exposure to 1500°C in argon during the thermal conductivity measurements. Although the color of the surface was blue after exposure, no oxide film can be observed.


As-received


Exposed to 1100°C in resistivity measurements

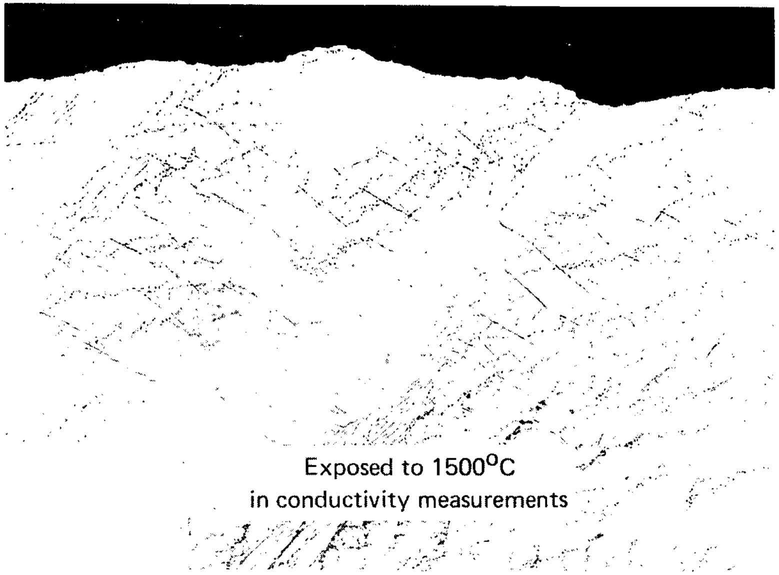

Exposed to 1500°C in conductivity measurements

Figure 4 – Photomicrographs of Zircaloy-4 specimens (100X)

DISCUSSION OF RESULTS

The thermal conductivity data for α phase (hcp) Zircaloy-4 appear to contain a lattice component on the order of 10 percent of the total conductivity. Almost 100 percent of the conductivity in the β phase (bcc) appears to be electronic. Conclusions such as these are based on the curves shown in Figure 5. The total conductivity from the smooth curve in Figure 2 has been replotted along with the calculated values of the electronic conductivity from (Table 4) the equation:

$$k_e = \frac{LT}{\rho}$$

where

k_e = electronic component of thermal conductivity (watt/cm $^{\circ}$K)

L = Lorenz number = 2.45×10^{-8} watt ohm/$^{\circ}K^2$

T = absolute temperature, $^{\circ}$K

ρ = electrical resistivity, ohm-cm

The values above 920°C were obtained by using the resistivity data of Cook(5); however, its use may lead to an erroneous comparison since the composition is different. It has been shown generally that the electrical resistivity of an element increases as impurities or alloying constituents are increased. It is quite possible that the resistivity of β phase Zircaloy-4 may be higher than that reported by Cook for the high hafnium sample; therefore, some displacement between these two curves may occur in the β phase regions. The rise in the electronic component between 850° and 900°C is due to the sharp decrease in electrical resistivity as the material transforms from the hexagonal close packed α structure to the body centered cubic structure of the β phase.

As stated earlier, it is highly possible that the scatter in the thermal conductivity data may have obscured a change in conductivity at the phase change unless the phonon contribution from the body centered cubic structure is considerably less than that of the hexagonal close packed structure. At this time it is difficult to draw any conclusions from the data above 1200°C due to the difficulties in measurements of conductivity and the lack of electrical resistivity data for this particular material.

Calculation of the Lorenz number at various temperatures from the thermal conductivity and the electrical resistivity data gives the results shown in Figure 6 and Table 5. These values again indicate a phonon contribution in the α phase since the calculated Lorenz number is greater than the theoretical constant but virtually no phonon contribution in the β phase (above 862°C).

Changes in chemical composition during the thermal conductivity measurements which are shown in Table 1 are significant only in the increase in nitrogen, decrease in tin, and the loss of virtually all of the magnesium. It is felt that these small changes in composition did not

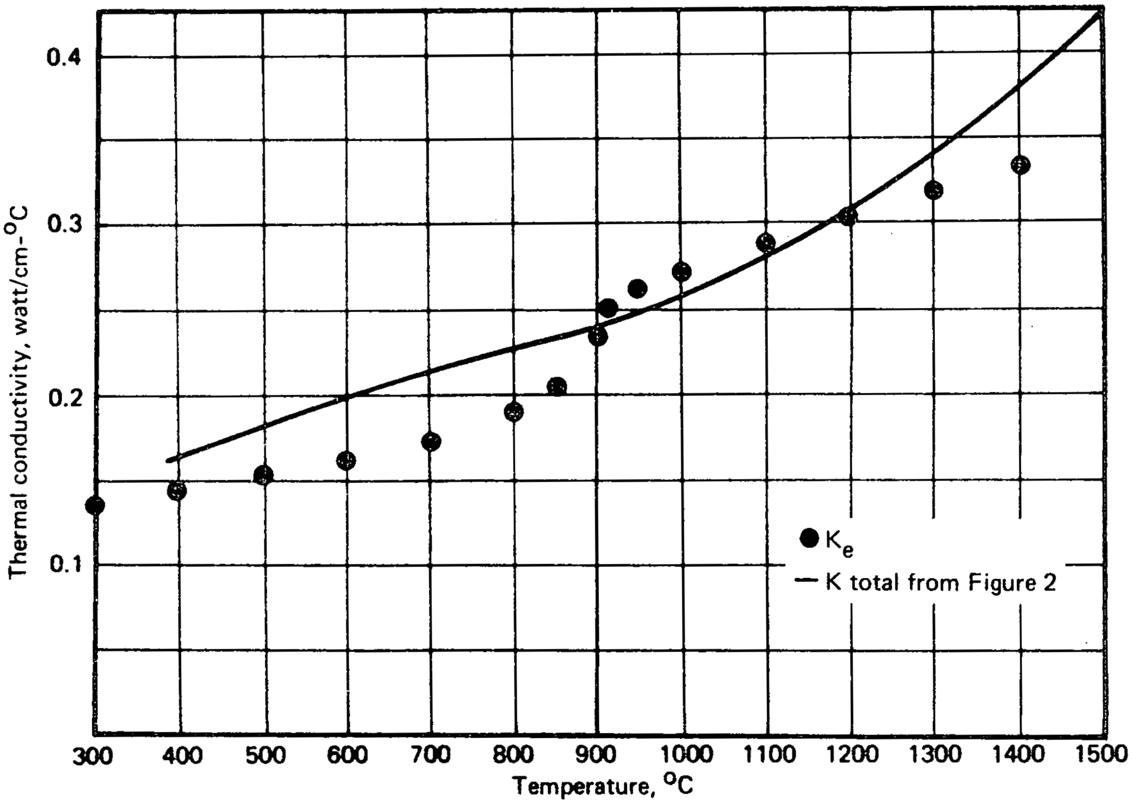


Figure 5 – Total thermal conductivity and electronic conductivity as a function of temperature for Zircaloy-4

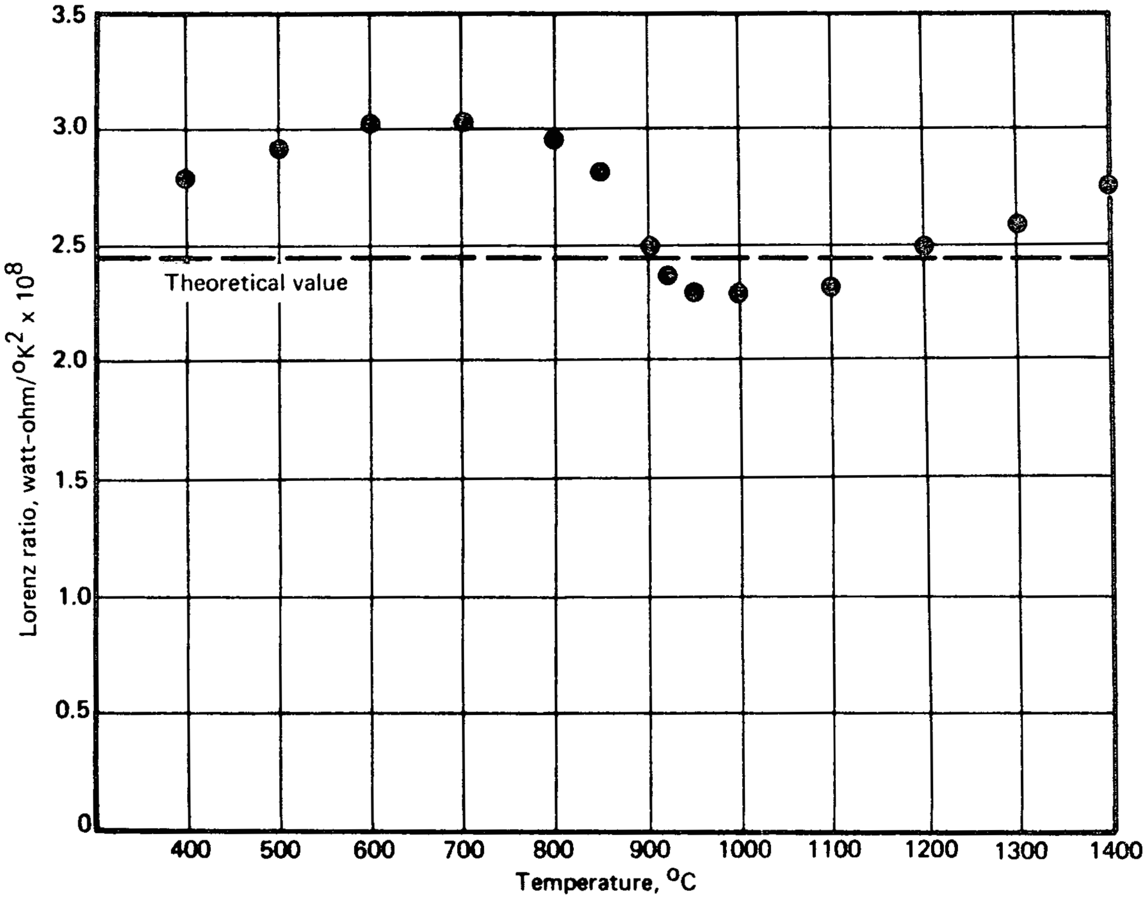


Figure 6 – Lorenz ratio $K\rho/T$ as a function of temperature for Zircaloy-4

TABLE 4. CALCULATED VALUES OF k_e FOR ZIRCALOY-4

Temperature (°C)	ρ(ohm-cm)	k_e (watt/cm °C)
20	72.0×10^{-6}	0.0997
100	84.0	0.1088
200	93.5	0.1239
300	105.0	0.1337
400	115.5	0.1428
500	125.5	0.1513
600	133.0	0.1608
700	138.0	0.1727
800	139.0	0.1891
850	134.0	0.2503
900	122.5	0.2346
920	116.5	0.2509
950	114.0	0.2628
1000*	114.0	0.2736
1100*	116.0	0.2900
1200*	118.0	0.3058
1300*	120.0	0.3211
1400*	122.0×10^{-6}	0.3360

*Values for Resistivity From Reference 5 (High Hafnium Specimen.)

TABLE 5. CALCULATED LORENZ NUMBERS FOR ZIRCALOY-4

Temperature		Thermal Conductivity	Electrical Resistivity	Lorenz Number
°C	°K	K (watt/cm °C)	ρ(ohm-cm)	L(watt-ohm/°K^2)
400	673	0.163	115.5×10^{-6}	2.797×10^{-8}
500	773	0.181	125.5	2.939
600	873	0.200	133.0	3.039
700	973	0.213	138.0	3.018
800	1073	0.228	139.0	2.947
850	1123	0.235	134.0	2.804
900	1173	0.242	122.5	2.527
920	1193	0.244	116.5	2.383
950	1223	0.248	114.0	2.312
1000*	1273	0.257	114.0	2.310
1100*	1373	0.277	116.0	2.340
1200*	1473	0.313	118.0	2.507
1300*	1573	0.342	120.0	2.609
1400*	1673	0.380	122.0×10^{-6}	2.771×10^{-8}

*Values for Resistivity From Reference 5 (High Hafnium Specimen).

affect the thermal conductivity. However, small changes in composition which may affect the α to β phase transformation may also affect the electrical resistivity. It should be noted that the chemical analyses in Table 1 were performed on samples which were exposed during the thermal conductivity measurements and that similar changes would be expected in the resistivity specimen due to the similarity in test environment. The conductivity specimens showed signs of surface oxidation in that their color changed from its normal metallic gray to shades of blue and gold typifying an oxide coating of varying thickness.

CONCLUSIONS AND RECOMMENDATIONS

Preliminary values for the thermal conductivity of Zircaloy-4 over the temperature range of 400° to $1500^{\circ}C$ have been presented. The absence of other high temperature data for this material makes it difficult to evaluate its relative accuracy; however, it has been shown to be reproducible. Electrical resistivity data for α phase Zircaloy-4 have been presented; the data for the β phase of this material is inconclusive due to contamination.

If further measurements are to be made on Zircaloy-4 on either thermal conductivity or electrical resistivity especially at high temperatures (up to $1700^{\circ}C$), problems of contamination and eutectic formations between the specimen and refractory metals of the apparatus will have to be solved or circumvented.

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