

Simultaneous Measurements of Specific Heat, Electrical Resistivity, and Hemispherical Total Emittance by a Pulse Heating Technique: Hafnium–3 (Wt. %) Zirconium, 1500 to 2400 K*

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Simultaneous measurements of specific heat, electrical resistivity and hemispherical total emittance of hafnium containing 3.12 weight percent zirconium in the temperature range 1500 to 2400 K by a subsecond duration, pulse heating technique are described. The measurements indicate decreases in specific heat (by about 13%) and in electrical resistivity (by about 8%) as the result of the $\alpha \rightarrow \beta$ transformation. Estimated inaccuracies of the measured properties are: 3 percent for specific heat, 1 percent for electrical resistivity and 5 percent for hemispherical total emittance.

Key words: Electrical resistivity; emittance; hafnium; high-speed measurements; high temperatures; specific heat; thermodynamics.

1. Introduction

In this paper, application of a pulse heating technique to the simultaneous measurements of specific heat, electrical resistivity and hemispherical total emittance of hafnium containing 3.12 weight percent zirconium in the temperature range 1500 to 2400 K is described. For simplicity, in the paper this substance will be referred to as hafnium–3 (wt. %) zirconium. The measurements are of particular interest in view of the fact that hafnium undergoes a solid-solid phase transformation (from hexagonal close-packed to body-centered cubic) in this range.

The method is based on rapid resistive self-heating of the specimen from room temperature to high temperatures (above 1500 K) in less than one second by the passage of an electrical current pulse through it; and on measuring, with millisecond resolution, such experimental quantities as current through the specimen, potential drop across the specimen, and specimen temperature. Details regarding the construction and operation of the measurement system, the methods of measuring experimental quantities, and other pertinent information, such as the formulation of relations for properties, error analysis, etc., are given in earlier publications [1, 2].¹

In the following sections of this paper a tabular format is adopted in presenting information on the specimen, measurements, system characteristics, results and errors.

2. Measurements

The details regarding the hafnium–3 (wt. %) zirconium specimens used in the present measurements are given in table 1. A summary of the measurement technique and the operational characteristics of the system is given in table 2. The polynomial functions (obtained by the least squares method) that represent the experimental results of specific heat and electrical resistivity are given in table 3. The values of properties at 100 degree temperature intervals computed using the functions are presented in table 4. The experimental results are presented in the appendix. Each number tabulated in the appendix represents results from over 50 original data points. The results of hemispherical total emittance are given in table 7. An estimate of errors in the measured and computed quantities is given in table 5. All values reported in this paper are based on the International Practical Temperature Scale of 1968 [3]. In all computations, the geometrical quantities are based on their room temperature (298 K) dimensions.

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¹Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *Specimen information*

No.	Item	Unit	Explanation
1	Substance.....		Hafnium-3.12 (wt. %) zirconium. ^a
2	Source ^b		Materials Research Corporation.
3	Purity.....		99.97%
4	Impurities		Listed in table 1a.
5	Geometry		Tube made from rod by electro-erosion.
6	Dimensions (nominal):		
	total length	mm	89.1
	effective ^c length...	mm	38.7
	outside diameter...	mm	6.3
	wall thickness	mm	0.5
	blackbody hole	mm	0.5 × 1 (rectangular)
7	Weight:		
	total weight.....	g	10.296
	effective ^c weight...	g	4.450
8	Characteristics:		
	density.....	g · cm ⁻³	12.9
	resistivity at 293 K	10 ⁻⁸ Ω · m	33.1
9	Special treatment.....		Heat treated by pulse heating before the experiments—10 pulses to 1700 K.

^aThe analysis to determine the zirconium content was performed by the Spectrochemical Analysis Section at NBS.

^bThe supplier is identified in this paper in order to adequately characterize the specimen—Such an identification does not imply recommendation or endorsement by the National Bureau of Standards.

^cEffective refers to the portion of the specimen between the voltage probes.

TABLE 1a. *Impurities in the specimen*^a

(According to the manufacturer's analysis)

Element.....	C	O	N	Al	Ca	Cu	Fe
ppm.....	15	10	10	20	10	10	< 50
Element.....	Mn	Mo	Nb	Si	Ta	Ti	W
ppm.....	20	10	30	20	30	10	10

^aThe total amount of all other detected elements is less than 70 ppm, each element being below 10 ppm limit.

TABLE 2. Measurement technique and system characteristics

No.	Item	Unit	Explanation and data
1.....	General technique.....		Pulse heating (subsecond).
2.....	Voltage measurement.....		Across tungsten knife-edge probes.
3.....	Current measurement.....		Across standard resistor (0.001 Ω) in series with the specimen.
4.....	Temperature measurement.....		High-speed photoelectric pyrometer [4].
5.....	Specimen environment.....		Vacuum ~ 1.3 × 10 ⁻³ N·m ⁻² (~10 ⁻⁵ torr).
6.....	Power source.....		Battery bank (14 series-connected 2V batteries, capacity 1100 A·h each).
7.....	Recording.....		Digital data acquisition system.
8.....	Signal resolution.....		~0.01% (at full scale).
9.....	Time resolution.....	ms	0.4
10.....	Data processing.....		Time-sharing computer.
11.....	Number of specimens.....		2
12.....	Number of experiments.....		11
13.....	Temperature range.....	K	1500–2400
14.....	Experiment duration.....	ms	500–660
15.....	Current pulse length.....	ms	300–460
16.....	Imparted power.....	W	3400–7900
17.....	Current.....	A	700–1000
18.....	Rate of current change.....	A·ms ⁻¹	0.1–0.2
19.....	Heating rate.....	K·ms ⁻¹	3.7–8.1
20.....	Cooling rate.....	K·ms ⁻¹	0.08–0.55
21.....	Radiative heat loss (% of input power).....		2% at 1500 K 8% at 2400 K

TABLE 3. Functional representation of the results on hafnium-3 (wt. %) zirconium

Phase	Specific heat (J·g ⁻¹ ·K ⁻¹)	Electrical resistivity (10 ⁻⁸ Ω·m)
α	1500 < T < 1850 K $c_p = A + BT$ A = 1.431 × 10 ⁻¹ B = 3.830 × 10 ⁻⁵ σ ^a = 0.3%	1500 < T < 2000 K $\rho = A + BT + CT^2$ A = 46.936 B = 1.1967 × 10 ⁻¹ C = -3.0002 × 10 ⁻⁵ σ ^a = 0.2%
	2150 < T < 2400 K $c_p = A + BT + CT^2$ A = 0.4544 B = -2.771 × 10 ⁻⁴ C = 7.286 × 10 ⁻⁸ σ ^a = 0.5%	2050 < T < 2400 K $\rho = A + BT$ A = 130.47 B = 1.1276 × 10 ⁻² σ ^a = 0.2%

^aStandard deviation as computed from the difference between the value of an experimental result (as tabulated in the appendix) and that from the smooth functions reported above.

TABLE 4. Results on properties of hafnium-3 (wt. %) zirconium

Phase	T (K)	c _p (J·g ⁻¹ ·K ⁻¹)	ρ (10 ⁻⁸ Ω·m)
α	1500	0.2006	158.94
	1600	.2044	161.60
	1700	.2082	163.67
	1800	.2120	165.14
	1900	—	166.00
	2000	—	166.27
β	2100	—	154.15
	2200	0.1974	155.28
	2300	.2025	156.41
	2400	.2090	157.53

TABLE 5. Error analysis

Quantity	Imprecision ^a	Inaccuracy ^b
Temperature (at 2000 K).....	0.5K	4K
Voltage.....	.03%	0.1%
Current.....	.03%	0.1%
Specific heat.....	.5	3%
Electrical resistivity.....	.2	1%
Hemispherical total emittance.....	—	5%

^aImprecision refers to the standard deviation of a quantity as computed from the difference between the value of the quantity and that from the smooth function obtained by the least squares method. The quantities in the case of temperature, voltage, and current are the individual points measured in a single experiment, and in the case of specific heat and electrical resistivity are the results from all experiments as tabulated in the appendix.

^bInaccuracy refers to the estimated total error (random and systematic).

3. Discussion

The specific heat and electrical resistivity of hafnium-3 (wt. %) zirconium measured in this work are presented in figures 1 and 2, respectively, and are compared graphically with the results reported in the literature on hafnium containing varying amounts of zirconium. The results reported in the literature were for temperatures below 2200 K. In this work, the measurements were extended to 2400 K, which is approximately 100 K below the melting point of hafnium.

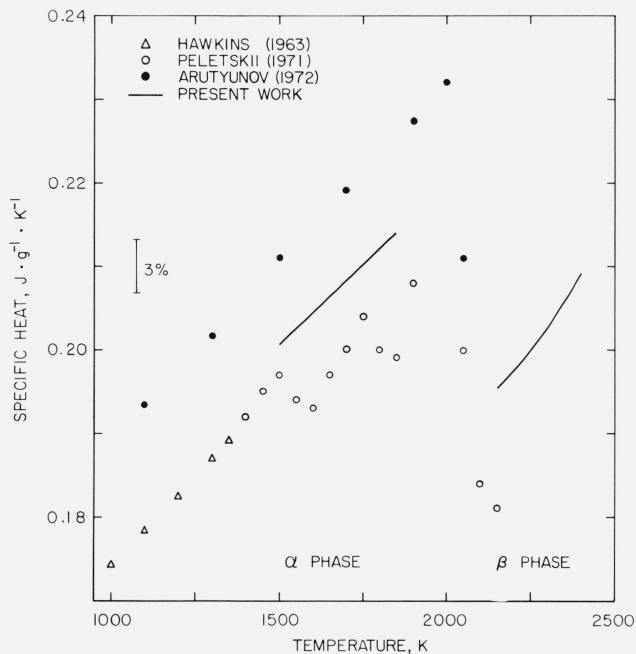


FIGURE 1. Specific heat of hafnium reported in the literature.

Zirconium content in weight percent is: 2.8, Hawkins et al [7]; 0.66, Peletskii and Druzhinin [6]; 0.65, Arutyunov et al [5]; and 3.12 present work.

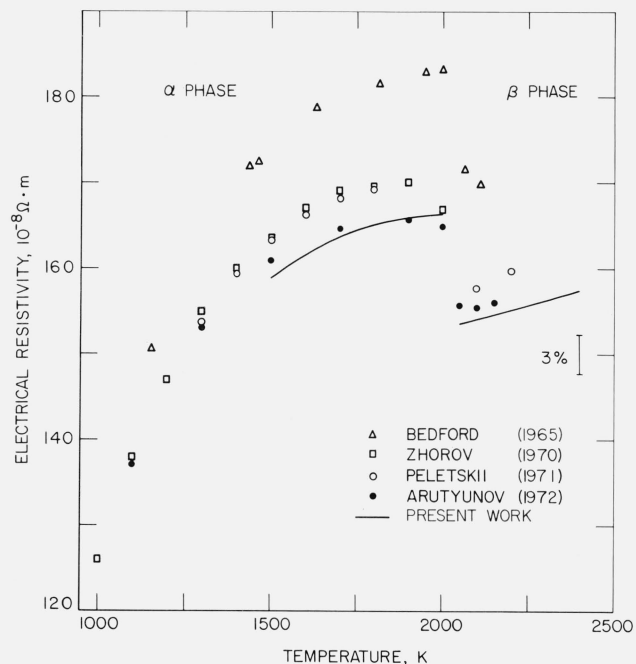


FIGURE 2. Electrical resistivity of hafnium reported in the literature.

Zirconium content in weight percent is: 2.4, Bedford [9]; 0.96, Zhorov [8]; 0.66, Peletskii and Druzhinin [6]; 0.65 Arutyunov et al [5]; and 3.12 present work.

3.1. Specific Heat

Zirconium content (2.8 wt. %) of the specimen used by Hawkins et al. [7] was comparable to that of the specimen used in the present work. Extrapolation of the results of Hawkins et al. from 1350 K to 1500 K yields a value which is approximately 2.5 percent lower than the present work result. Arutyunov et al. [5] and Peletskii and Druzhinin [6] have reported measurements using specimens with lower zirconium content—approximately 0.65 (wt. %) zirconium. However, their results are in considerable disagreement with each other (6 to 10 %). The results (after correcting for zirconium content) of the present work are about 5 percent lower than those of Arutyunov et al., and on the average about 4 percent higher than those of Peletskii and Druzhinin in the overlapping temperature regions below the transformation point. Above the transformation point, only a few measurements (all below 2200 K) were reported by the above investigators. Because of the insufficient data, it was not possible for them to establish the trend of specific heat versus temperature in the range between the transformation and the melting points.

The results of the present work indicate the following trend for specific heat as a function of temperature: (1) before transformation—increases nearly linearly, (2) at the transformation point—decreases sharply, and (3) above the transformation point—increases with an increasing rate of change. Extrapolation of the results to the transformation temperature, 2012 K [10], indicates a change in specific heat of 12.9 percent² (0.0283 J · g⁻¹ · K⁻¹) during the transformation. A similar procedure applied to the results reported in the literature yields the following approximate values for the change in specific heat during transformation: 13.0 percent (Peletskii and Druzhinin [6]) and 9.1 percent (Arutyunov et al. [5]). The latter is likely to be low since data did not extend beyond the initial transformation period.

Table 6 gives estimated results of the heat capacity of pure hafnium obtained from the present work data after making a correction for the zirconium content

TABLE 6. Heat capacity of pure hafnium

Phase	Temperature (K)	Heat capacity (J · mol ⁻¹ · K ⁻¹)
α	1500	35.0
	1600	35.7
	1700	36.4
	1800	37.0
β	2200	34.1
	2300	35.0
	2400	36.3

² Computed according to the relation:

$$\Delta c_p = 100[(c_p)_{\text{before}} - (c_p)_{\text{after}}]/(c_p)_{\text{before}}$$

(using Kopp's additivity law). Heat capacity of zirconium needed for this correction is obtained from an earlier publication [11]. The atomic weight of hafnium was taken as 178.49 [13]. It may be seen that at 2400 K (about 100 K below its melting point), heat capacity of hafnium reaches a value of $36.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, which is considerably higher than the Dulong and Petit value of $3R$ ($24.943 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$).

3.2. Electrical Resistivity

Electrical resistivity results for hafnium reported in the recent literature [5, 6, 8, 9], with one exception [9], are in agreement with those of the present work within 3 percent. The results of Bedford [9] are 5 to 10 percent higher than those of the other investigators. This difference cannot be attributed to the high value of zirconium content in the specimen (about 2.4 percent by weight), since the present work results, which were obtained on specimens of comparable composition, were lower than those of the other investigators. The zirconium content of specimens used by Arutyunov et al. [5] and Peletskii and Druzhinin [6] was about 0.65 percent by weight, while the specimen used by Zhorov [8] contained about 1 percent zirconium. The results of all the investigators show a decrease in electrical resistivity as the result of the $\alpha \rightarrow \beta$ transformation. However, because of the insufficient data, it was not possible to establish the trend of resistivity versus temperature in the range between the transformation and the melting points.

The results of the present work indicate the following trend for electrical resistivity as a function of temperature: (1) before transformation increases with a decreasing rate of change, (2) during transformation decreases sharply, and (3) after transformation increases with an increasing rate of change. Extrapolation of the results to the transformation temperature³ indicate a change in electrical resistivity of 7.9 percent ($13.1 \times 10^{-8} \Omega \cdot \text{m}$) during the transformation. The data reported in the literature yield the following results for the change in electrical resistivity during the transformation: 6.4 percent (Arutyunov et al. [5]), 6.9 percent (Peletskii and Druzhinin [6]), and 7.3 percent (Bedford [9]). Zhorov's measurements did not extend beyond the initial transformation period, thus it was not possible to obtain a meaningful result on resistivity change. Earlier measurements by Fast [12] of the resistance change in a hafnium specimen containing 3 weight percent zirconium during transformation yielded a value of 7.5 percent.

A distinct advantage of the method employed in this work is that it provides resistivity data during the

entire transformation period. This allows the accurate determination of the variation of electrical resistivity as a function of time and temperature near and at the transformation point. The results of a typical experiment are shown in figures 3 and 4.

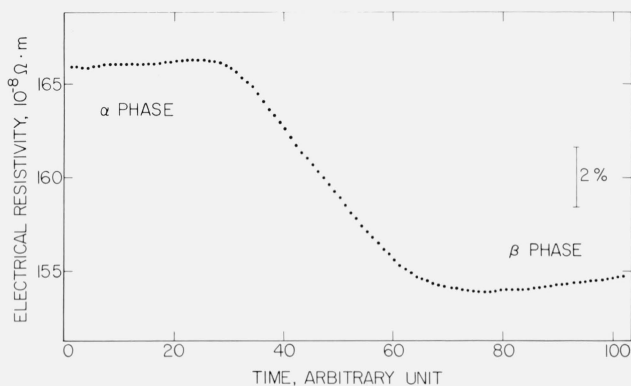


FIGURE 3. Variation of electrical resistivity as a function of time near and at the $\alpha \rightarrow \beta$ transformation point of hafnium-3 (wt %) zirconium.

(The curve refers to specimen 1; 1 time unit = 0.833 ms).

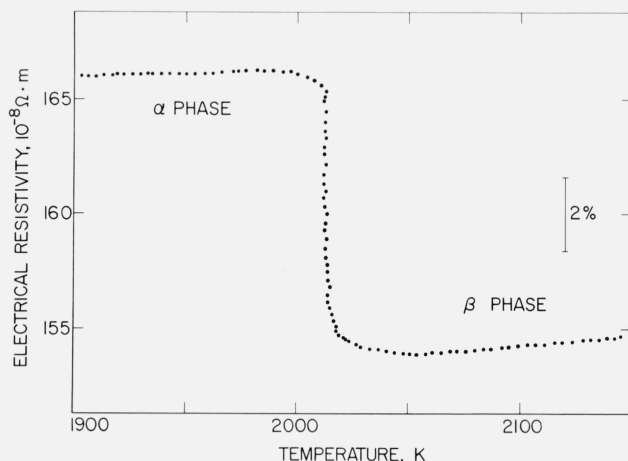


FIGURE 4. Variation of electrical resistivity as a function of temperature near and at the $\alpha \rightarrow \beta$ transformation point of hafnium-3 (wt %) zirconium.

(The curve refers to specimen 1).

³ Computed according to the relation:

$$\Delta\rho = 100 (\rho_{\text{before}} - \rho_{\text{after}}) / \rho_{\text{before}}$$

3.3. Hemispherical Total Emittance

Hemispherical total emittance was measured at three temperatures, two below and one above the transformation point. A comparison of the present work results with those reported in the literature (table 7) shows a general agreement in the range 0 to 5 percent at temperatures 1700 and 1870 K. No data was located in the literature for temperatures above 2200 K. From the available data no satisfactory conclusion could be drawn regarding the effect of zirconium on the hemispherical total emittance of hafnium.

TABLE 7. Hemispherical total emittance of hafnium containing various amounts of zirconium as reported in the literature

Investigator	Ref.	Zirconium content (wt. %)	Temperature, K		
			1700	1870	2280
Zhorov	[8]	0.96	0.330	0.330	—
Peletskii and Druzhinin	[6]	0.66	.306	.316	—
Arutyunov et al.	[5]	0.65	.312	.323	—
Present work		3.12	.320	.330	0.342

4. Appendix

TABLE A-1. Experimental results on specific heat of hafnium-3 (wt % zirconium)^a

Phase	Temp. (K)	Specimen-1				Specimen-2	
		First heating		Second heating			
		c_p	Δc_p	c_p	Δc_p	c_p	Δc_p
α	1500	0.2012	+0.32	0.2008	+0.12	0.2002	-0.17
	1550	0.2022	-0.13	0.2031	+0.31	0.2019	-0.28
	1600	0.2044	+0.01	0.2053	+0.45	0.2042	-0.09
	1650	0.2062	-0.04	0.2066	+0.15	0.2060	-0.14
	1700	0.2079	-0.15	0.2080	-0.10	0.2076	-0.29
	1750	0.2097	-0.20	0.2097	-0.20	0.2097	-0.20
	1800	0.2117	-0.16	0.2117	-0.16	0.2123	+0.12
	1850	0.2140	+0.02	0.2142	+0.12	0.2154	+0.67
	β	2150	0.1952	-0.13	0.1956	+0.07	0.1950
2200		0.1976	+0.07	0.1975	+0.02	0.1978	+0.18
2250		0.2002	+0.20	0.1993	-0.26	0.2007	+0.44
2300		0.2028	+0.13	0.2012	-0.66	0.2038	+0.62
2350		—	—	0.2037	-0.94	0.2055	-0.06
2400		—	—	0.2079	-0.56	0.2113	+1.06

^a Specific heat is in $J \cdot g^{-1} \cdot K^{-1}$, and the quantity Δc_p is percentage deviation of the individual results from the smooth functions represented by the pertinent eqs in table 3.

TABLE A-2. Experimental results on electrical resistivity of hafnium-3 (wt. % zirconium)^a

Phase	Temp. (K)	Specimen-1				Specimen-2	
		First heating		Second heating			
		ρ	$\Delta\rho$	ρ	$\Delta\rho$	ρ	$\Delta\rho$
α	1500	158.97	+0.02	159.52	+0.36	157.94	-0.63
	1550	160.54	+0.12	160.96	+0.38	159.61	-0.46
	1600	161.85	+0.15	162.15	+0.33	161.02	-0.36
	1650	163.02	+0.18	163.21	+0.30	162.39	-0.20
	1700	163.92	+0.15	164.02	+0.21	163.35	-0.20
	1750	164.65	+0.10	164.66	+0.11	164.15	-0.20
	1800	165.23	+0.04	165.16	+0.01	164.79	-0.21
	1850	165.65	0.00	165.54	-0.07	165.28	-0.22
	1900	166.10	+0.05	165.94	-0.04	165.82	-0.11
	1950	166.36	+0.08	166.14	-0.05	166.09	-0.08
2000	166.57	+0.17	166.30	+0.01	166.37	+0.06	
β	2050	153.93	+0.22	—	—	153.33	-0.17
	2100	154.34	+0.12	154.53	+0.25	153.68	-0.30
	2150	154.83	+0.08	154.83	+0.08	154.26	-0.29
	2200	155.44	+0.10	155.42	+0.09	154.87	-0.26
	2250	156.01	+0.11	156.02	+0.12	155.49	-0.22
	2300	156.55	+0.09	156.63	+0.14	156.13	-0.18
	2350	—	—	157.26	+0.08	156.70	-0.17
	2400	—	—	157.76	+0.14	157.30	-0.15

^a Electrical resistivity is in $10^{-8}\Omega \cdot m$, and the quantity $\Delta\rho$ is percentage deviation of the individual results from the smooth functions represented by the pertinent eqs in table 3.

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