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Simultaneous Measurements of Heat Capacity, Electrical Resistivity, and Hemispherical Total Emittance by a Pulse Heating Technique: Vanadium, 1500 to 2100 K*

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Simultaneous measurements of heat capacity, electrical resistivity, and hemispherical total emittance of vanadium in the temperature range 1500 to 2100 K by a subsecond duration, pulse heating technique are described. The results are expressed by the relations:

$$c_p = 56.34 - 3.839 \times 10^{-2} T + 1.563 \times 10^{-5} T^2$$
$$\rho = 8.794 + 6.282 \times 10^{-2} T - 6.804 \times 10^{-6} T^2$$

where c_p is in $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, ρ is in $10^{-8}\ \Omega \cdot \mathrm{m}$, and T is in K. The values for the hemispherical total emittance are: 0.313 at 1900 K and 0.332 at 2000 K. Estimated inaccuracies of the measured properties are: 3 percent for heat capacity, 0.5 percent for electrical resistivity and 5 percent for hemispherical total emittance.

Key words: Electrical resistivity; emittance; heat capacity; high-speed measurements; high temperature; thermodynamics; thermophysics; vanadium.

1. Introduction

In this paper, application of a pulse heating technique to the simultaneous measurements of heat capacity, electrical resistivity, and hemispherical total emittance of vanadium in the temperature range 1500 to 2100 K is described.

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 new approach—tabular format—is adopted in presenting information on the specimen, measurements, system characteristics, results, and errors.

The reasons for adopting this format are: (1) to facilitate the preparation of manuscripts, (2) to standardize the contents of the papers on measurements using the present or similar systems in other laboratories, (3) to facilitate information retrieval by the reader, (4) to provide a means for efficient and accurate identification, coding, characterization, and data reduction by scientific and technical information centers, and (5) to ultimately lead to the computerized preparation of papers.

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

2. Measurements

The details regarding the vanadium specimen 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 are given in table 3. The final values on properties at 100 degree temperature intervals computed using the functions are given 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. 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.

TABLE 1. Specimen information

No.	Item	Unit	Explanation
1	Substance		Vanadium (polycrystalline)
2	Source*		Materials Research Corporation
3	Purity		99.9^{+}%
4	Impurities		Listed in table 1a
5	Geometry		Tube made from rod by electro-erosion
6	Dimensions		
	total length	mm	76.26
	effective** length	mm	25.53
	outside diameter	mm	6.3
	wall thickness	mm	0.5
	blackbody hole	mm	0.5 × 1 (rectangular)
7	Weight		
	total weight	g	4.319
	effective** weight	g	1.438
8	Characteristics		
	atomic weight		50.942
	density	g · cm^{-3}	6.1
	resistivity at 293 K	$10^{-8}\Omega \cdot$ m	21.7
9	Special treatment		Heat treated by pulse heating before the experiments (30 pulses to 1900 K)

*The 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.

**Effective refers to the portion of the specimen between the voltage probes.

TABLE 1a. Impurities in the specimen*

(according to the manufacturer's analysis)

Element	C	Fe	Nb	N	O	P
ppm	120	20	60	10	15	15
Element	Si	Ta	Ti	W	Zr	
ppm	50	70	10	30	15	

*The total amount of all other detected elements is less than 50 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 (14series-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	Date of measurements		August 1973
12	Number of experiments		4
13	Temperature range	K	1500–2100
14	Temperature subranges	K	I (1480–1710) II (1690–1890) III (1810–2050) IV (2000–2130)
15	Experiment duration	ms	600–620
16	Current pulse length	ms	400–420
17	Imparted power	W	4000–5200
18	Current	A	1300–1600
19	Rate of current change	A·ms^{-1}	0.3–0.6
20	Heating rate	K·ms^{-1}	3.9–4.5
21	Cooling rate	K·ms^{-1}	0.04–0.15
22	Radiative heat loss (% of input power)		1% at 1500 K 4% at 2100 K

TABLE 3. Functional representation of results on vanadium

Heat capacity ($J \cdot mol^{-1} \cdot K^{-1}$)	Resistivity ($10^{-8}\Omega \cdot m$)	Hemispherical total emittance
$c_p = A + BT + CT^2$	$\rho = A + BT + CT^2$	$\epsilon = A + BT$
$A = 56.34$ $B = -3.839 \times 10^{-2}$ $C = 1.563 \times 10^{-5}$	$A = 8.794$ $B = 6.282 \times 10^{-2}$ $C = -6.804 \times 10^{-6}$	$A = -5.413 \times 10^{-2}$ $B = 1.930 \times 10^{-4}$
$1500\ K < T < 2100\ K$	$1500\ K < T < 2100\ K$	$1880\ K < T < 2050\ K$
$\sigma^* = 1.1\%$	$\sigma^* = 0.06\%$	$\sigma^* = 0.05\%$

*Standard deviation.

TABLE 4. Results on properties of vanadium

T (K)	c_p ($J \cdot mol^{-1} \cdot K^{-1}$)	ρ ($10^{-8}\Omega \cdot m$)	ϵ
1500	33.92	87.72	– – –
1600	34.93	91.89	– – –
1700	36.25	95.92	– – –
1800	37.88	99.83	– – –
1900	39.82	103.59	0.313
2000	42.08	107.22	0.332
2100	44.65	110.71	– – –

TABLE 5. Error analysis (at 2000 K)

Quantity	Imprecision*	Inaccuracy**
Temperature..........................	0.5 K	4 K
Voltage..................................	0.03%	0.1%
Current..................................	0.03%	0.1%
Heat capacity..........................	1%	3%
Electrical resistivity..................	0.1%	0.5%
Hemispherical total emittance.....	0.1%	5%

*Imprecision refers to the standard deviation of an individual point as computed from the difference between measured value and that from the smooth function obtained by the least squares method.

**Inaccuracy refers to the estimated total error (random and systematic).

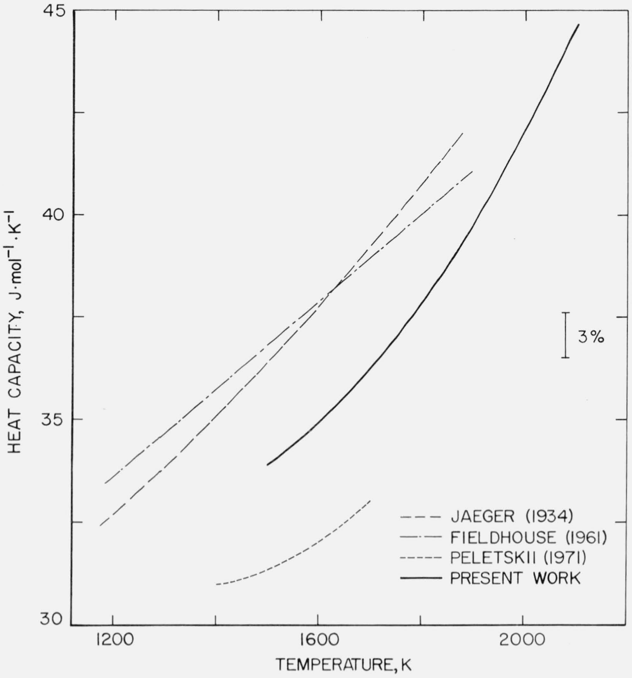

FIGURE 1. *Heat capacity of vanadium reported in the literature.*

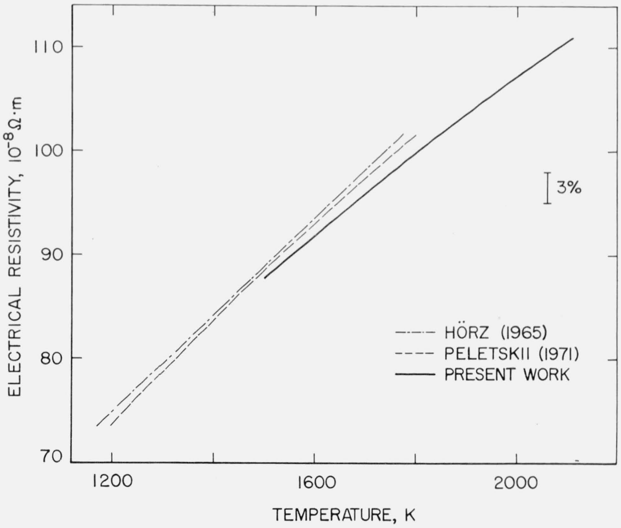

FIGURE 2. *Electrical resistivity of vanadium reported in the literature.*

3. Discussion

The heat capacity, electrical resistivity, and hemispherical total emittance of vanadium measured in this work are presented and compared graphically with those reported in the literature in figures 1, 2 and 3, respectively.

The heat capacity results of this work are approximately 6–8 percent lower than those of Jaeger and Veenstra [5] and Fieldhouse and Land [6], and are approximately 8 percent higher than those of Peletskii et al. [7] over the respective overlapping regions. The results reported in the literature were for temperatures below 1900 K. In this work, the measurements are extended to 2100 K, which is approximately 90 K below the melting point of vanadium.

The electrical resistivity results are in reasonably good agreement (maximum differences about 2%) with those reported by Hörz et al. [8] and Peletskii et al. [7]. At 293 K, the observed electrical resistivity is approximately 3 percent higher than the value ($21.02 \times 10^{-8}\Omega \cdot m$) reported by Peletskii et al. [7]. In the range of the present measurements, vanadium showed a negative departure from linearity in the

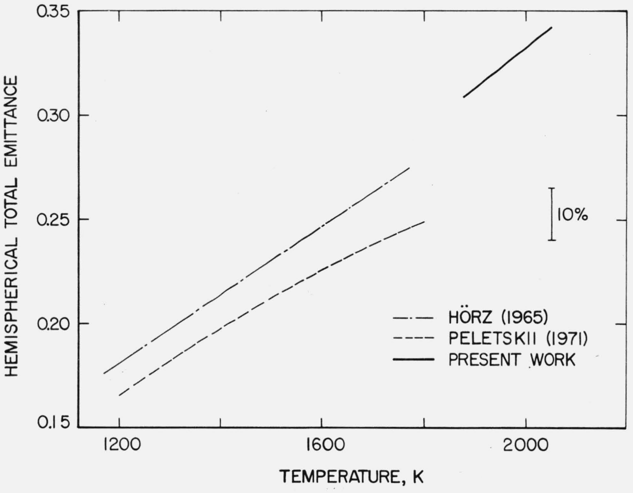

FIGURE 3. *Hemispherical total emittance of vanadium reported in the literature.*

temperature dependence of electrical resistivity. A similar behavior was previously noted for niobium [9] and tantalum [10], which belong to the same group (V) on the periodic table.

Considerable differences in hemispherical total emittance results of various investigators may be expected due to the differences in specimen surface conditions. The difference of the present results from the extrapolated values of Hörz et al. [8] is approximately 6 percent.

Similar to the earlier results on other refractory metals [2, 9, 10, 11] obtained with the present measurement system, heat capacity of vanadium at high temperatures is considerably higher than the Dulong and Petit value of $3R$. Some of this departure is due to $c_p - c_v$ and the electronic terms. However, they do not account for the entire difference. Heat capacity above the Debye temperature may be expressed by

$$c_p = A - \frac{B}{T^2} + CT + \Delta c$$

where the constant term is $3R$ (24.943 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$), the term in T^{-2} is the first term in the expansion of the Debye function, the term in T represents $c_p - c_v$ and electronic contributions, and the quantity Δc represents excess in measured heat capacity at high temperatures, which is not accounted for by the first three terms. The coefficients B (1.50×10^5) and C (4.86×10^{-3}) were obtained from heat capacity values at 270 K [12, 13] and at 1000 K. The value at 1000 K was estimated based on the extrapolation of the present work results and the low temperature results reported in the literature [12, 13].

Using the above equation and the heat capacity results of this work, the quantity Δc was computed for temperatures above 1500 K. The results for Δc in $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ are: 1.8 at 1500 K, 4.2 at 1800 K, and 9.5 at 2100 K.

Although the mechanisms of vacancy generation become important at high temperatures, it was not possible to attribute the high heat capacity values entirely to vacancies. To demonstrate this, a crude estimate of the contribution of vacancies to heat capacity was made using the method described in a previous publication [2]. The results indicate that vacancy contribution would be small, approximately 0.03 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ at 1500 K and 0.5 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ at 2100 K, and would not account for the high heat capacity values. If the entire difference between measured and computed (using the first three terms in the above equation) heat capacities is attributed to vacancies, values of 1.1 eV for vacancy formation energy and 3.8 percent for vacancy concentration at the melting point are obtained. Both of these values, especially the concentration, seem to be unrealistic for vanadium.

The new format adopted in this paper has demonstrated the feasibility of concise yet complete and systematic documentation of measurements performed with the present system. For reasons enumerated in the Introduction, it is hoped that the approach of a standardized quasi-tabular presentation will find wide acceptance among the experimenters in the same and related fields.

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4. Appendix

TABLE A–1. Experimental results on heat capacity and electrical resistivity of vanadium

Temperature (K)	c_p (J · mol^{-1} · K^{-1})	Δc_p* (%)	ρ ($10^{-8}\Omega$ · m)	$\Delta\rho$* (%)
1500	33.48	− 1.32	87.66	− 0.06
1550	34.50	+ 0.33	89.81	− 0.01
1600	35.32	+ 1.10	91.93	+ 0.05
1650	35.88	+ 0.92	94.03	+ 0.12
1700	35.81	− 1.23	95.83	− 0.09
1750	37.20	+ 0.46	97.86	− 0.03
1800	38.26	+ 0.99	99.87	+ 0.05
1850	38.61	− 0.53	101.69	− 0.03
1900	39.71	− 0.30	103.56	− 0.02
1950	40.80	− 0.29	105.40	− 0.02
2000	41.96	− 0.30	107.20	− 0.01
2050	42.72	− 1.43	109.01	+ 0.03
2100	45.34	+ 1.51	110.70	0.00

*The quantities Δc_p and $\Delta\rho$ are percentage deviations of the individual results from the smooth functions represented by the pertinent equations in table 3.

TABLE A–2. Experimental results on hemispherical total emittance of vanadium

Temperature (K)	ϵ	$\Delta\epsilon$* (%)	Temperature (K)	ϵ	$\Delta\epsilon$* (%)
1874.5	0.307	− 0.12	2022.6	0.336	− 0.06
1878.4	0.308	− 0.03	2028.0	0.337	− 0.02
1882.4	0.309	+ 0.03	2033.4	0.338	+ 0.01
1886.4	0.310	+ 0.06	2038.9	0.339	+ 0.02
1890.5	0.311	+ 0.06	2044.5	0.341	+ 0.02
1894.7	0.312	+ 0.03	2050.1	0.342	+ 0.01

*The quantity $\Delta\epsilon$ is percentage deviation of the individual results from the smooth function represented by the pertinent equation in table 3.

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