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Thermophysical and Thermal Optical Properties of Vanadium by Millisecond Calorimetry Between 300 and 1900 K[1]

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A variant of millisecond-resolution pulse calorimetry in use at the Institute of Nuclear Sciences "Vinča" since 1983 involves measuring the specific heat and electrical resistivity of electrical conductors from room temperature to 2500 K and the hemispherical total emissivity and normal spectral emissivity from about 1300 K to the same maximum operating temperature. The method was applied successfully to different materials: pure metals, ferrous and nickel-base alloys, reactor materials, and refractory metals in thermal characterization of candidates for thermophysical property standard reference materials. This paper presents and discusses new data obtained in the study of thermophysical and thermal optical properties of vanadium.

KEY WORDS: electrical conductors; electrical resistivity; hemispherical total emissivity; high temperatures; normal spectral emissivity; refractory metals; specific heat; vanadium.

1. INTRODUCTION

Vanadium is the last in the group of refractory metals whose thermophysical and thermal optical properties have been studied at the Institute of Nuclear Sciences "Vinča" by millisecond resolution pulse calorimetry. Other metals, tungsten [1], niobium [2], molybdenum [3], and tantalum (not yet published), were investigated previously. Vanadium is a metal important in metallurgical processes. Its study was also interesting, as very few recent

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data could be found either in data reference books or in the THERSYST[4] data bank.

2. EXPERIMENTAL

A sample of vanadium in the form of a rod 2 mm in diameter and 200 mm in length, with a nominal purity of 99.8 + % (Goodfellow),[5] was used in the millisecond-resolution pulse calorimetry experiments as received, without further thermal treatment. The method, apparatus, and measurement uncertainties have been described previously [4, 5].

The specific heat and electrical resistivity were measured using 0.05-mm PtRh 10%/Pt thermocouples. DC pulses ranging from 300 to 600 A delivered by two heavy duty 12-V batteries connected in series resulted in heating rates of 2000 to 2800 $K \cdot s^{-1}$.

Experiments with parallel pyrometric temperature measurements gave the hemispherical total emissivity and normal spectral emissivity, in addition to the specific heat and electrical resistivity. The experimental procedure is described in detail in Ref. 5.

3. RESULTS

In order to increase the statistical significance of the final functions, the specific heat and electrical resistivity were measured in seven experiments, with the maximum temperatures of different experiments ranging between 1898 and 1933 K. These seven experiments are represented by smooth interpolated functions of specific heat and electrical resistivity, whose values are reported in Table I at 50 K increments. Deviations of individual specific heats from the final fit are about $\pm 1\%$ at 400 and 1700 K and about $\pm 0.5\%$ in the middle of the range. Similar, somewhat smaller, deviations were observed for the electrical resistivities.

3.1. Specific Heat

Figure 1 presents our specific heat data, together with low-temperature data of Bieganski and Stalinski [6] and Anderson [7], the data above room temperature of Jaeger and Veenstra [8], Fieldhouse and Lang [9], Golutvin and Kozlovskaya [10], and Bendick and Pepperhoff [11],

[4] THERSYST is a name of a thermophysical properties data bank for solid materials developed and operated by the University of Stuttgart-IKE, Stuttgart, Germany.

[5] Typical analysis given by the manufacturer is as follows: Ag, 1; Al, 2; Ca, < 1; Cr, 15; Cu, < 1; Fe, 70; Mg, < 1; Mn, 1; Si, 300 (ppm).

Table I. Numerical Values of Interpolated Functions of the Specific Heat, Electrical Resistivity, and Hemispherical Total and Normal Spectral Emissivity of Vanadium at 50 K Intervals

T (K)	C_p ($J \cdot kg^{-1} \cdot K^{-1}$)	ρ ($\mu\Omega \cdot m$)	ε_h	ε_λ
293.15	—	0.2198[a]	—	—
293.15	—	0.2133[b]	—	—
350	513.5	0.2592	—	—
400	518.6	0.2929	—	—
450	523.6	0.3258	—	—
500	528.4	0.3580	—	—
550	533.1	0.3894	—	—
600	537.6	0.4200	—	—
650	542.2	0.4500	—	—
700	546.7	0.4793	—	—
750	551.2	0.5080	—	—
800	555.8	0.5360	—	—
850	560.5	0.5634	—	—
900	565.3	0.5903	—	—
950	570.3	0.6166	—	—
1000	575.5	0.6424	—	—
1050	581.0	0.6678	—	—
1100	586.8	0.6926	—	—
1150	592.9	0.7170	—	—
1200	599.5	0.7410	—	—
1250	606.4	0.7646	—	—
1300	613.8	0.7879	0.193	0.280
1350	621.7	0.8107	0.198	0.281
1400	630.1	0.8333	0.203	0.282
1450	639.2	0.8556	0.207	0.283
1500	648.8	0.8776	0.212	0.283
1550	659.1	0.8994	0.217	0.284
1600	670.1	0.9210	0.222	0.285
1650	681.9	0.9424	0.227	0.286
1700	694.4	0.9636	0.231	0.287
1750	707.7	0.9847	0.236	0.287
1800	721.9	1.0057	0.241	0.288
1850	737.0	1.0266	0.251	0.289
1900	753.1	1.0475	0.255	0.290

[a] The room-temperature value obtained using the four-probe method with current reversal, measured before the first experiment.

[b] The room-temperature value obtained using the four-probe method with current reversal, measured after the final experiment.

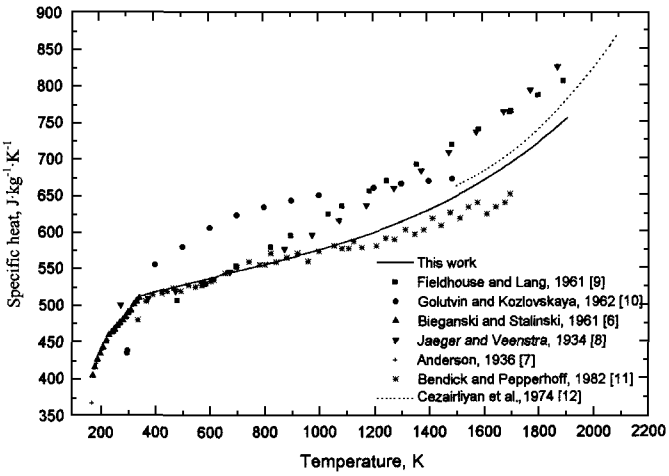

Fig. 1. Specific heat of vanadium.

and the high-temperature data of Cezairliyan et al. [12]. The two low-temperature data sets extending above room temperature obtained by adiabatic calorimetry are in perfect agreement with each other. For this paper, only data above 160 K are shown. Our results join smoothly with these data at their maximum temperature (340 K), also being in good agreement with the high-temperature data of Cezairliyan et al. [12] obtained with high-temperature pulse calorimetry. The Bendick and Pepperhoff [11] data obtained by high-temperature adiabatic calorimetry, which are somewhat lower than the current results at 335 K, are in close agreement with the present results from 367 to 1125 K. Above that temperature they start to fall below the data from this study, the difference reaching 6.3% at their maximum temperature of 1690 K. For readability of the diagram in Fig. 1, all of the Bendick and Pepperhoff data [11] are not shown; the interval between the individual data points was increased to approximately 20 to 30 K.

The data sets of Jaeger and Veenstra [8] and by Fieldhouse and Lang [9], computed from measured enthalpy data obtained by method of mixtures (metal-block calorimetry), agree with the present results at lower temperatures but show increasing differences at higher temperatures, following either linear [9] or mild parabolic functions [8]. They reach their maximum values at 1880 K, some 10% above our results. The data of Golutvin and Kozlovskaya [10], also obtained by metal-block drop calorimetry, differ substantially from the others.

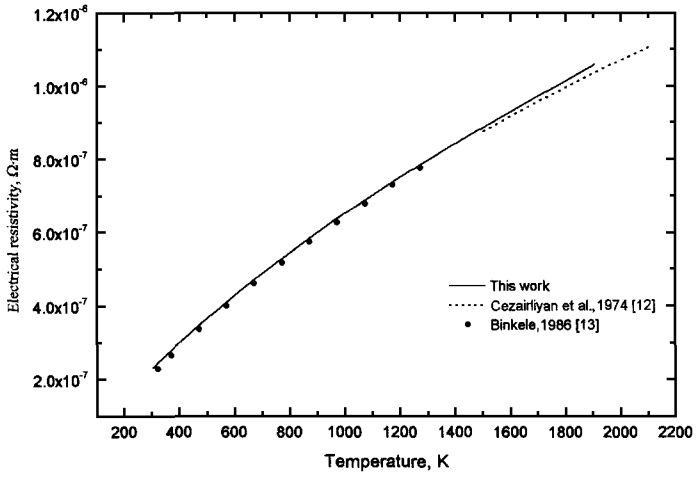

Fig. 2. Electrical resistivity of vanadium.

3.2. Electrical Resistivity

The electrical resistivity function is shown in Fig. 2, together with the results of Cezairliyan et al. [12] and Binkele [13], the only other data sets available. In addition to the mean electrical-resistivity function obtained by averaging results of individual experiments, the electrical resistivity was measured at room temperature using the stationary state four-probe current reversal method [4, 5] before and after the end of pulse experiments. The electrical resistivity data are presented in Table I. The room-temperature electrical resistivity value provided by the manufacturer[6] is also presented in Table I. Not having measured the thermal expansion, the electrical resistivity was not corrected for this effect.

Comparison of the electrical resistivity value of $21.98\,\mu\Omega\cdot\text{cm}$ at 293.15 K, obtained in our measurement (Table I) using the stationary four-probe technique before the pulse experiments, with the value given by the manufacturer of $19.6\,\mu\Omega\cdot\text{cm}$ indicates that our sample was not initially in an annealed state. The gradual decrease in the room-temperature electrical resistivity from $21.98\,\mu\Omega\cdot\text{cm}$ before to $21.33\,\mu\Omega\cdot\text{cm}$ after the pulse experiments (also determined by the stationary four-probe technique) confirmed that pulse experiments, in spite of their relatively high heating and fast cooling rates, induce changes in the electrical resistivity.

[6] Goodfellow, Cambridge, UK.

The results of Binkele [13] cover the temperature range between 273.15 and 1273.15 K, while the results of Cezairliyan et al. [12] extend to higher temperatures, above 1500 K. Our results lie above these two sets of data, 6.8% at 323 K and 2% at 1900 K. Between these temperature extremes, the difference is smaller, amounting to 1% at the highest temperature for Binkele (1000 K) and 1.14% at the low-temperature end of the Cezairliyan et al. measurements (1500 K). It should be noted that Binkele's electrical resistivity of 19.6 $\mu\Omega \cdot$ cm at 293.15 K is equal to the value quoted by the manufacturer.

3.3. Emissivity

The data collected during the high-temperature experiments enabled the determination of both the hemispherical total emissivity and the normal spectral emissivity. The hemispherical total emissivity was determined in the range 1300 to 1900 K. The hemispherical total emissivity data is represented by the function

$$\varepsilon_h = 0.06798 + 9.6154 \times 10^{-5} T\,(\mathrm{K}) \tag{1}$$

From data collected simultaneously from a thermocouple and an optical pyrometer in the range where measurements with these two detectors overlapped, the normal spectral emissivity at 900 nm was computed according to the procedure detailed in Ref. 5. The normal spectral emissivity data are represented by

$$\varepsilon_\lambda = 0.26011 + 1.5625 \times 10^{-5} T\,(\mathrm{K}) \tag{2}$$

The hemispherical total and normal spectral emissivity data are presented in Table I.

3.4. Measurement Uncertainties

Estimation of maximum uncertainties in the specific heat and electrical resistivity measurements by this method are given in Ref. 5, and they are estimated to be 3 and 1%, respectively. The uncertainties reach their maximum values as the upper and lower limits of the measurement range are approached. The uncertainty is typically lowest in the region approximately 150 K from both ends of the measurement range.

The typical uncertainty in the hemispherical total emissivity and normal spectral emissivity is about $\pm 5\%$ [5], which can be higher as the lower temperature limit is approached.

4. DISCUSSION

The use of PtRh 10%/Pt thermocouples instead of W 5% Rh/W 25% Rh thermocouples (which are usually employed in high-temperature millisecond-resolution pulse calorimetry) improved the accuracy of obtained results, although reducing the maximum operating temperature. In considering both options, priority was given to the accuracy.

Insight into all available specific heat data sets, taking into account experimental techniques as well as their convenience or disadvantages for particular temperature regions, leads to the conclusion that present results obtained with a method suited for the whole temperature range from room temperature to 1900 K contributed to an increased knowledge of the specific heat of vanadium. Taking into account all available data, it seems that the low-temperature data of Bieganski and Stalinski [6] and Anderson [7], the data of Bendick and Pepperhoff [11] between 400 and 1100 K, the data of this work, and the data of Cezairliyan et al. [12] provide a base for establishing the specific heat of vanadium between 24 and 2100 K. Parabolic or linear specific heat functions obtained by Jaeger and Veenstra [8] and Fieldhouse and Lang [9] could result from interpretation of enthalpy data obtained by drop calorimetry.

Electrical resistivity results showed, in addition to dependence on thermal history the influence of exposing vanadium to pulse experiments. Compared with the other available data sets [12, 13], the present results confirmed the character of its temperature dependence from room temperature to 1900 K.

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