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Specific Heat and Electrical Resistivity of Niobium Measured by Subsecond Calorimetric Technique

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This paper presents results of measurements of specific heat and electrical resistivity of niobium from ambient temperature to the experimental limit of the equipment which is close to 2500 K. The study used a contact thermometry variant of the millisecond resolution pulse calorimetry developed at the Institute of Nuclear Sciences VINČA. In the experiments exceeding 1000 K, thermocouple thermometry was supplemented with parallel pyrometric temperature measurements. This, together with application of tungsten/rhenium thermocouple thermometry, increased the temperature range of measurements to 2500 K. In the range where two thermometries overlap, data on the specimen emittance were also generated. Novelties in the method, the results on electrical resistivity, specific heat, hemispherical total emittance and normal spectral emittance of niobium, and accuracies attained in different property measurements are discussed.

KEY WORDS: electrical resistivity; niobium; normal spectral emittance; pulse heating; specific heat; subsecond calorimetry; hemispherical total emittance.

1. INTRODUCTION

The present study on niobium is a part of a study of thermal and electrical properties of refractory metals at the Thermophysical Properties Laboratory of the Institute of Nuclear Sciences VINČA. This study will, beside niobium, involve molybdenum and tungsten. In addition to providing data on specific heat and electrical resistivity of the investigated metal, research described in this paper has increased the upper temperature limit of the measurements to 2500 K and has, in the range above 1000 K, enabled generation of data on both hemispherical total emittance and normal

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spectral emittance. As the subsecond pulse calorimetry based on pyrometric temperature measurements [1–3] provides good and reliable data above 1500 K, this extension of the subsecond pulse calorimetry using contact thermometry to 2500 K has provided an overlap between the two calorimetric techniques.

In the study of niobium, the temperature limit was increased to 2500 K by employing a combination of platinum/rhodium (Pt-Rh) and tungsten/rhenium (W-Re) thermocouple thermometry, in contrast to previously used combination of base metal and noble metal thermocouples, which limited its application to 1800 K. Accurate and reliable measurements using Pt Rh thermocouples to 1800 K, provided an *in situ* calibration of the high-temperature W Re thermocouples. Simultaneous pyrometric measurements provided information which allowed computation of normal spectral emittance from the same set of experimental data.

2. MEASUREMENTS

2.1. Specimen

The niobium specimen was manufactured by Goodfellow (England) in the shape of a rod 1.982 mm in diameter and 200 mm in length, which was

Table I. Typical Analysis of the Goodfellow NB007910 2.0-mm Rod

Al	< 10
B	2
Ca	< 10
Co	< 10
Cr	< 10
Cu	< 10
Fe	< 10
Mg	< 10
Mn	< 10
Mo	< 10
Ni	< 10
Si	< 10
Sn	< 10
Ta	255
Ti	20
W	100
Zr	< 10
C	25
H	< 10
N	35
O	230

directly used in the measurements. Typical analysis of the sample supplied by the manufacturer is given in Table I. Specimen was in original geometry and was not thermally treated prior to the pulse experiments.

After the last pulse, in which the ultimate temperature of 2500 K was reached, certain elongation of the specimen caused by the weight of the lower electrode clamp with its heavy-current attachments (made of massive copper) was observed. Change in the length of the measured section amounted to about 5%, with the corresponding reduction of the specimen diameter. This change in the specimen geometry was accounted for in subsequent computations. At the end of the entire set of measurements specimen surface showed a visible change of its structure, obviously caused by grain growth.

2.2. Procedure

The specific heat and electrical resistivity of the niobium specimen were measured simultaneously by a pulse heating method [4], which involved fast-resistive heating of the specimen from room temperature to a predetermined maximum temperature, which simultaneous measurement of its temperature, voltage drop, and the current through the specimen. Direct current pulses from two heavy-duty 12-V batteries connected in series or in parallel, supplied 250–500 A and 500–900 A, respectively, enabling heating rates of about 1500 and about 4000 $K \cdot s^{-1}$ to be achieved.

Three thermocouples 0.1 mm in diameter (both for Pt Rh and W Re combinations) were welded intrinsically to the central zone of the specimen, at 20-mm separations. The central thermocouple measured the specimen temperature. The other two monitored the temperature uniformity within the measurement zone (40 mm long), with their P legs serving as potential leads in the voltage drop measurements. The measurements were performed in vacuum (10^{-3} Pa).

A PC controlled the experiment and was used for real-time data acquisition and their subsequent processing. Data on the current, voltage drop across the measurement zone, the thermocouple emf, and pyrometer output were collected during specimen heating lasting 500–1500 ms, and during the initial part of the cooling period. Several thousand data points were collected per run, yielding 500–1000 values of specific heat and electrical resistivity in the temperature range studied.

In the experiments, where pyrometric measurements were performed, a fast monochromatic optical pyrometer operating at the wavelength of 0.9 μm was sighted at the center of the specimen close to the position of the central thermocouple. The pyrometer spot covered about 1 mm^2 of the specimen surface.

The specific heat capacity, c_p, was computed from

$$c_p = \frac{UI - P_r}{m(dT/dt)_h} \tag{1}$$

and the electrical resistivity, ρ, was computed from

$$\rho = \frac{U}{I}\frac{S}{L_c} \tag{2}$$

where U is the voltage drop across the effective specimen length between the potential leads, L_c; I is the current; P_r is the radiative power loss from the measurement zone; m is the mass of the effective specimen; $(dT/dt)_h$ is the heating rate at a given temperature; and S is the specimen cross section.

The radiative power loss, P_r, in Eq. (1) is expressed by

$$P_r = \varepsilon_t \sigma A(T^4 - T_0^4) \tag{3}$$

where T_0 and T are the absolute temperatures of the ambient and the specimen respectively, A is the specimen surface area, σ is the Stefan–Boltzmann constant, and ε_t is the hemispherical total emittance.

The latter is computed at different temperatures from the experimental data obtained in the heating and the initial part of the cooling period of experiments ending at these temperatures from expression

$$\varepsilon_t = \frac{UI}{\sigma A(T^4 - T_0^4)[1 - ((dT/dt)_h/(dT/dt)_c)]} \tag{4}$$

Data collected during experiments with simultaneous pyrometric measurements enabled determination of normal spectral emittance. The latter was computed from

$$\varepsilon_\lambda = e^{\frac{c_2}{\lambda}\left(\frac{1}{T_b} - \frac{1}{T}\right)} \tag{5}$$

where T is the absolute specimen temperature (measured either by a Pt Rh or a W Re thermocouple), T_b is the specimen brightness temperature, and c_2 is the second radiation constant.

3. RESULTS

A total of 32 experiments was performed, in which experimental conditions, such as heating rates, thermocouple types, and wire dimensions, including parallel pyrometric measurements were varied. The greatest number of experiments (24) were confined to the range below 1800 K, using

Pt Rh (Pt 10%Rh/Pt) thermocouple. Above 1800 K, 8 experiments with W Re (W5%Re/W26%Re) thermocouple were made. Sixteen experiments were supplemented with pyrometric measurements. Use of the pyrometer provided data about the normal spectral emittance of the specimen surface over a significant temperature range.

For the final processing, six experimental data sets obtained with the Pt Rh and three with the W Re thermocouple were taken, selection being based on the quality of the primary information contained in the temperature records (low noise, etc.).

3.1. Specific Heat

For specific heat calculations, nine individual data sets covering intervals between 1000 and 2200 K were averaged by a cubic spline fit, resulting in an interpolated specific heat function

$$c_p = 267.099 + 2.69165 \times 10^{-2} T - 6.72079 \times 10^{-7} T^2 + 7.28962 \times 10^{-9} T^3 \tag{6}$$

which is presented in Fig. 1. All the individual data sets which are not shown in the diagram were contained within a zone $\pm 1.7\%$ at its widest,

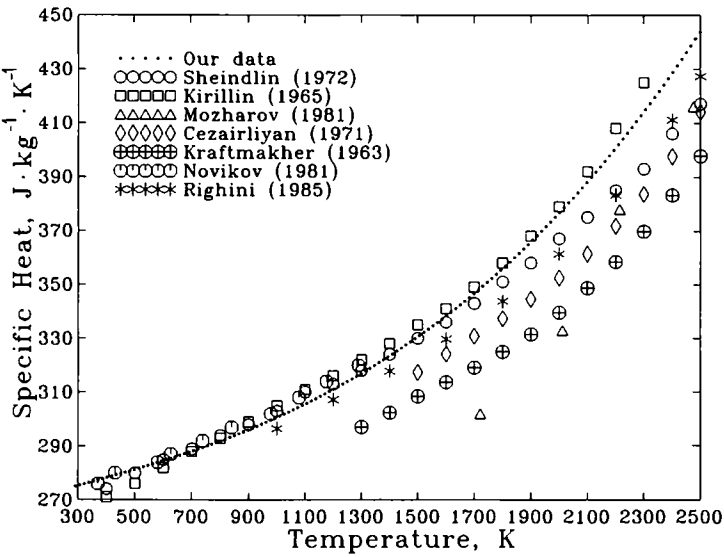

Fig. 1. Specific heat of niobium.

Table II. Interpolated Experimental Values of Specific Heat, Electrical Resistivity, Hemispherical Total Emittance, and Normal Spectral Emittance of Niobium

Temperature (K)	Specific heat ($J \cdot kg^{-1} \cdot K^{-1}$)	Electrical resistivity ($\mu\Omega \cdot m$)	Hemispherical total emittance	Normal spectral emittance
293	—	0.1506[a]	—	—
293	275.1	0.1496	—	—
300	275.3	0.1528	—	—
400	278.2	0.1975	—	—
500	281.3	0.2395	—	—
600	284.6	0.2792	—	—
700	288.1	0.3169	—	—
800	291.9	0.3528	—	—
900	296.1	0.3872	—	—
1000	300.6	0.4202	—	—
1100	305.6	0.4521	0.158	—
1200	311.0	0.4831	0.174	—
1300	317.0	0.5132	0.189	0.300
1400	323.5	0.5427	0.203	0.306
1500	330.6	0.5718	0.215	0.311
1600	338.3	0.6004	0.228	0.315
1700	346.7	0.6287	0.239	0.318
1800	355.9	0.6567	0.249	0.321
1900	365.8	0.6846	0.258	0.323
2000	376.6	0.7123	0.267	0.324
2100	388.2	0.7399	0.274	0.324
2200	400.7	0.7673	0.281	0.323
2300	414.1	0.7945	0.287	0.322
2400	428.6	0.8216	0.292	—
2500	444.1	0.8484	0.296	—

[a] Determined at 290 K using the four-probe method (with current reversal).

the biggest difference being at lowest temperatures. Between 1000 and 2000 K, the margins were reduced to about $\pm 1\%$. Numerical values at 100 K intervals are given in Table II.

Figure 1 also shows experimental results of Novikov et al. [5] obtained in the medium temperature range, Kirillin et al. [6] and Sheindlin et al. [7] covering a wide temperature range, and the high temperature results of Kraftmakher [8], Mozharov and Savvatimskii [9], and Cezairliyan [10], whose lowest-temperature portion lies in the range covered by this investigation. Results of Righini et al. [11], using the pulse heating method employing high-speed scanning pyrometry, cover the range between 1000 and 2500 K. In the range 500 to 1800 K, our results show good agreement with the results of Novikov et al. [5], Kirillin et al. [6], and Sheindlin

et al. [7], of which the first used adiabatic calorimetry, and the other two drop calorimetry. In the range above 1800 K, our results lie between those of Kirillin et al. and Sheindlin et al., lying somewhat closer to the former. The data of Righini et al. [11], start at 1000 K, about 1.5% below this common set, to run in parallel with the data of Cezairliyan [10], lying above the latter from 1.6 to 3.1% in the 1500 to 2500 K range. Lowest are the data of Kraftmakher [8], using equivalent-impedance modulation technique, and the data of Mozharov and Savvatimskii [9], obtained by the exploding wire technique. The two lowest temperature points of the latter evidently represent the extreme of the measurement range, and should not be taken with full significance. Above 2200 K, they join the high-temperature pulse data of Cezairliyan [10], both sets meeting the function of Sheindlin et al. [7] at about 2500 K.

According to a recent communication from Kraftmakher [12], the relatively low position of his specific heat function [8] results from the literature data [13] on the temperature derivative of resistivity, $d\rho/dT$, used in the computation of his data, as in the equivalent-impedance technique he applied, only $(d\rho/dT)$ values are measured directly. Using recent $C_p/(d\rho/dT)$ data of Righini et al. [11], his specific heat values would be shifted about 4–6% higher, conforming with the data of Cezairliyan [10] to within 1%.

It seems that most of the specific heat data presented in this paper could contribute toward defining a recommended function for niobium, in the range between the ambient and the melting temperature, taking into account advantages of particular measurement techniques for particular temperature ranges and giving more weight to their results. Obviously, the boundary portions of measurement ranges, particularly the lowest ones, represent regions of increasing uncertainty. This certainly could apply to the results obtained with our method [4] in the range below 500 K, where they deviate as much as 3% from the adiabatic calorimetry data, and are not able to follow the theoretical model.

3.2. Electrical Resistivity

Electrical resistivity was measured in the same experiments in which specific heat was determined. Agreement between individual measurements was very good, deviations from the smoothed curve obtained by spline-fit averaging being within $\pm 0.1\%$. The final electrical resistivity function,

$$\rho = 5.63406 \times 10^{-4} T - 1.98177 \times 10^{-7} T^2 + 6.26790 \times 10^{-11} T^3 - 7.70301 \times 10^{-15} T^4 \qquad (7)$$

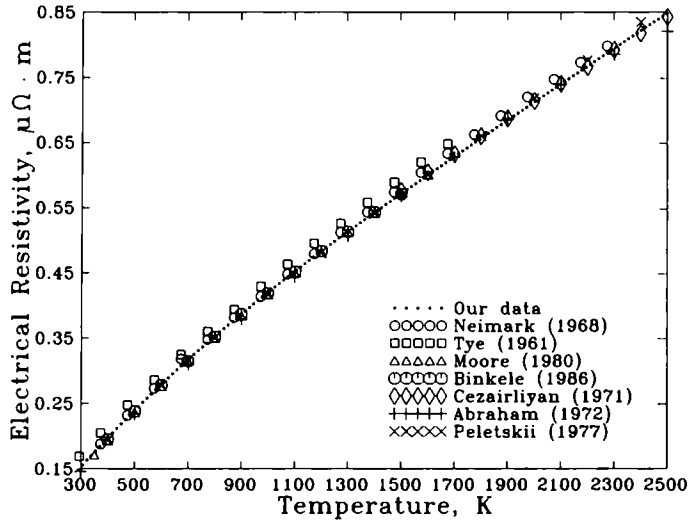

Fig. 2. Electrical resistivity of niobium.

representing an average of nine measurements within $\pm 0.67\%$ margins, is presented in Fig. 2, and the values at intervals of 100 K are given in Table II. Table II also contains a room-temperature value (293 K) measured after the final experiment using the four-probe technique with current reversal. It amounted to 0.1506 $\mu\Omega \cdot$ m, which compares with the extrapolated value from Eq. (7) for the same temperature, 0.1497 $\mu\Omega \cdot$ m (literature data corresponding to 293 K range from 0.146 to 0.169 $\mu\Omega \cdot$ m [9]).

Figure 2 also presents data reported in the literature [13–19], which include the Abraham and Deviot data for high-purity niobium [16] and the Peletskii's recommended data for niobium [17].

3.3. Measurement Uncertainties in Specific Heat and Electrical Resistivity Measurement

The maximum uncertainties in the specific heat and electrical resistivity measurements by this method using thermocouples as thermometers are given in an earlier publication [4] and were estimated to be 3 and 1%, respectively. The uncertainties increased toward the maximum values as the upper and the lowest limits of application are approached. Accuracy typically has the highest value in the region about 300 K from both ends of application range.

3.4. Emittance Measurements

Experimental data collected during each experiment enabled determination of both hemispherical total and normal spectral emittance. Hemispherical total emittance was obtained from Eq. (4). The interpolated average function is shown in Fig. 3 and is given by the following equation:

$$\varepsilon_t = -0.0718516 + 2.58276 \times 10^{-4} T - 4.44878 \times 10^{-8} T^2 \qquad (8)$$

The values of hemispherical total emittance were obtained in the temperature range 1100 to 2500 K. Maximum deviations from the average values computed from several experimental data sets did not exceed $\pm 4\%$.

From simultaneous collection of thermocouple and optical pyrometer outputs, normal spectral emittance was computed from the Eq. (5), in the temperature range 1300 to 2300 K, where these two detectors overlapped. Results of normal spectral emittance were obtained from several experimental data sets collected both during heating and cooling periods. Data, presented in Fig. 3, are represented by the following function:

$$\varepsilon_\lambda = 0.156251 + 1.60504 \times 10^{-4} T - 3.8415 \times 10^{-8} T^2 \qquad (9)$$

The maximum deviation of the data from the above function did not exceed $\pm 2.5\%$.

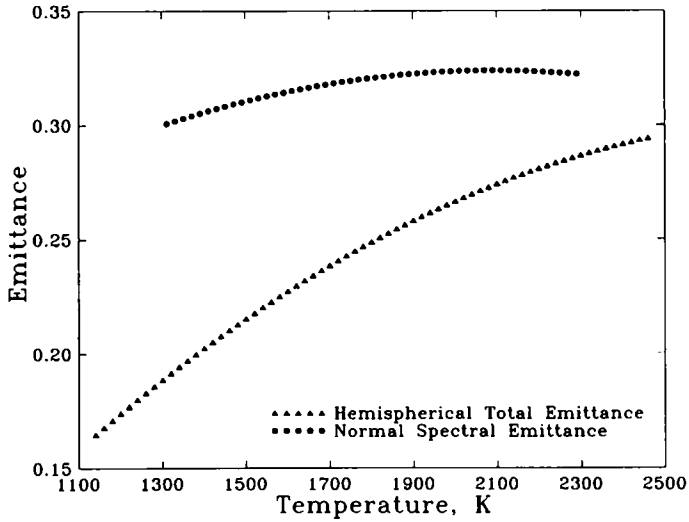

Fig. 3. Hemispherical total emittance and normal spectral emittance of niobium.

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