International Journal of Thermophysics, Vol. 6, No. 6, 1985

Measurement of Thermophysical Properties by a Pulse-Heating Method: Niobium in the Range 1000–2500 K[1]

F. Righini,[2] R. B. Roberts,[2,3] and A. Rosso[2]

Data for the heat capacity, electrical resistivity, hemispherical total emittance, and normal spectral emittance (at 898 nm) of niobium are reported for the temperature range 1000–2500 K. Measurements were based on a subsecond pulse-heating technique. The results are discussed and compared with the literature values. Reported uncertainties for the properties are 3% for heat capacity, 1% for electrical resistivity, 5% for hemispherical total emittance, and 4% for normal spectral emittance.

KEY WORDS: dynamic measurements; electrical resistivity; emittance; heat capacity; high temperature; niobium.

1. INTRODUCTION

Several thermophysical properties of niobium at high temperatures (above 1000 K) were recently determined at the Istituto di Metrologia "G. Colonnetti" (IMGC). The effort was complementary to the development of a new technique for the measurement of thermal expansion at high temperatures. The new technique correlates the thermal expansion of a nonuniform specimen to its temperature profile. Profile measurements are performed by a high-speed pyrometer that scans the specimen surface, collecting over 200 measurements/ms. Surface temperature measurements are transformed to true temperatures either by the knowledge of the normal spectral emittance of the sample or by knowing the resistivity versus temperature relationship.

[1] Paper presented at the Ninth Symposium on Thermophysical Properties, June 24–27, 1985, Boulder, Colorado, U.S.A.

[2] CNR Istituto di Metrologia "G. Colonnetti," Strada delle Cacce 73, 10135 Torino, Italy.

[3] Visiting scientist from the CSIRO Division of Applied Physics, Sydney 2070, Australia.

0195-928X/85/1100-0681$04.50/0

The present paper describes the results on heat capacity, electrical resistivity, hemispherical total emittance, and normal spectral emittance at 898 nm obtained on several niobium specimens. A new feature is the use of the high-speed scanning pyrometer both as a diagnostic tool and to measure the temperature profile of the central portion of the specimen.

2. MEASUREMENTS

The experiments reported here were performed with the high-speed multiproperty apparatus of the IMGC. Details of the experimental setup and of the measuring technique are reported in earlier papers [1, 2]. The true temperature was measured with a high-speed pyrometer focused on the specimen blackbody hole. The 1000–2500 K temperature range was divided into several subranges (1000–1300, 1150–1700, 1300–2100, and 1700–2500 K) with large overlapping regions. A stable and accurate programmable amplifier was inserted between the high-speed pyrometer and the data acquisition system. Gains of 50 and 5 were used for the two lower temperature subranges; a calibrated neutral-density filter was inserted in the pyrometer optical path for measurements in the highest temperature subrange. The pyrometer interference filter had an effective wavelength near 900 nm and a bandwidth of 83 nm. Measurements of the radiance temperature on the surface of the specimen were performed with another high-speed pyrometer operating near 900 nm and with a bandwidth of 82 nm. Amplification gains from 1000 to 1 were used to optimize the pyrometer performance in the various temperature ranges. This pyrometer was operated in two ways: fixed on the surface of the specimen during measurements of the normal spectral emittance [1] and as a high-speed scanning instrument to measure the temperature profile of the specimen [3]. The high-speed scanning pyrometer was used as a diagnostic tool before property measurements: the specimen was placed inside the experimental chamber and fine adjustments were performed until the longitudinal temperature profile of the specimen indicated that an adequate uniform cross section had been attained. At the end of property measurements another set of profiles was measured as a checking procedure. All the temperatures reported in the present paper are based on the International Practical Temperature Scale of 1968 [4].

Four specimens (S–1, S-2, S-3, and S-4) were used for the measurements. For some properties five sets of values are reported: the first four sets were obtained on the various specimens using niobium knife-edge probes. The probes had a tendency to weld inside the grooves and to become sources of heat leaks at very high temperatures: to assess the importance of this phenomenon an additional set of measurements (labeled

S-4/2) was performed on specimen S-4 using niobium wire probes (diameter, 0.05 mm) spot welded on the specimen. The high-purity niobium (99.9%) was obtained in tube form; the impurities in the specimens, according to the manufacturer's typical analysis, were as follows (ppm): Ta, 500; O, 100; Fe, 30; C, 25; N, 20; Mo and Si, 10 each; and B, Ti, W, Zr, and H, <10 each. The nominal dimensions of the tubular specimens were as follows: total length, 76 mm; effective length (the central portion of the specimen where properties are measured), 25 mm; outside diameter, 6.3 mm; and wall thickness, 0.5 mm. The machining to obtain a rectangular blackbody hole (0.7×1 mm) and a uniform cross section was performed at the IMGC.

The electrical resistivity at room temperature was measured on two additional specimens in the "as-received" condition. The specimens were placed in a thermostated environment and measurements were performed with a potentiometric technique. The average of the electrical resistivity determination referred to 293 K was $15.36 \times 10^{-8}\ \Omega \cdot \mathrm{m}$ and the temperature derivative was

$$\alpha = \frac{1}{\rho_{293}} \left(\frac{d\rho}{dT} \right)_{293\ \mathrm{K}} = 0.00321\ \mathrm{K}^{-1}$$

Additional measurements of ρ_{293} performed on all the specimens in the experimental chamber before and after the pulse experiments seemed to indicate lower resistivity values (15.0–$15.3 \times 10^{-8}\ \Omega \cdot \mathrm{m}$). The difference was attributed to the oxygen content of as-received specimens: gases evolved from the specimens during pulse heating, but this fact caused no measurable difference in the properties.

The density of the specimens was measured at the Mass Section of the IMGC. Four 10-mm-long pieces were cut from two of the specimens before the experiments: their density was determined to be $8.572\ \mathrm{g \cdot cm^{-3}}$. The mass of the specimens was measured before and after the experiments. No variations were noticed within the repeatibility of the measurements (better than 0.01%), indicating a negligible evaporation of material during measurements. Also, frequent checks of the transmission of the chamber windows indicated no coating due to evaporation.

All measurements were performed in vacuum (10^{-3} Pa or better) and experiments on all specimens were performed at three different heating rates. Operational conditions for "fast," "medium," and "slow" heating rates are reported in Table I. No significant differences arising from different heating rates were found for any property; accordingly the experimental results are presented for the individual specimens, without distinguishing among the heating rates.

Table I. Operational Conditions in Fast, Medium, and Slow Experiments

Item	Fast expts.	Medium expts.	Slow expts.
Experiment duration (s)	0.2–0.3	0.4–0.5	0.8–0.9
Power supply (V)	20	16	12
Input power (W)	4000–4800	2500–3200	1400–1800
Current (A)	1400–1700	1100–1500	800–1100
Heating rate ($K \cdot s^{-1}$)	5500–7500	3500–5500	1700–2800
Cooling rate ($K \cdot s^{-1}$)	50–500	50–500	50–500
Radiative heat loss (% of input power)	0.7% at 1500 K 2.4% at 2400 K 6.5% at 2500 K	1.2% at 1500 K 3.8% at 2000 K 10% at 2500 K	2.0% at 1500 K 7.0% at 2000 K 17% at 2500 K

3. EXPERIMENTAL RESULTS

The properties of niobium were determined from measurements taken on the central portion of the specimens. The typical temperature profiles of the specimens around 2350 K are presented in Fig. 1. Valleys observed in the profiles of S-1, S-3, and S-4/1 are a clear indication of where the knife-edge probes were located. Differences between profile S-4/1 and profile S-4/2 (same specimen) clearly indicate the heat-sink effect at high temperatures of the knife-edge probes with respect to the spot-welded wire probes. The measured properties (with the exception of normal spectral emittance) depend on the integral of the temperature distribution between the probes. Experimental results presented in this section do not show any dependence on the shape of the corresponding temperature profile, indicating that temperature distributions such as those in Fig. 1 do not affect significantly the precision of the measurements.

3.1. Heat Capacity

The value 92.91 $g \cdot mol^{-1}$ was used for the atomic mass of niobium [5]. The experimental results are adequately represented by a third-degree polynomial (Table II) and the values obtained from the smooth function are presented in Table III. The deviation of the heat capacity of each set of experimental values from the fitting polynomial is shown in Fig. 2. Except for some values at high temperatures, all deviations are within $\pm 0.5\%$.

The radiative loss term needed in the computation of heat capacity was obtained from the hemispherical total emittance values reported in Table II and III. At temperatures below 1700 K extrapolated values were used. At high temperatures the correction term for radiative heat loss

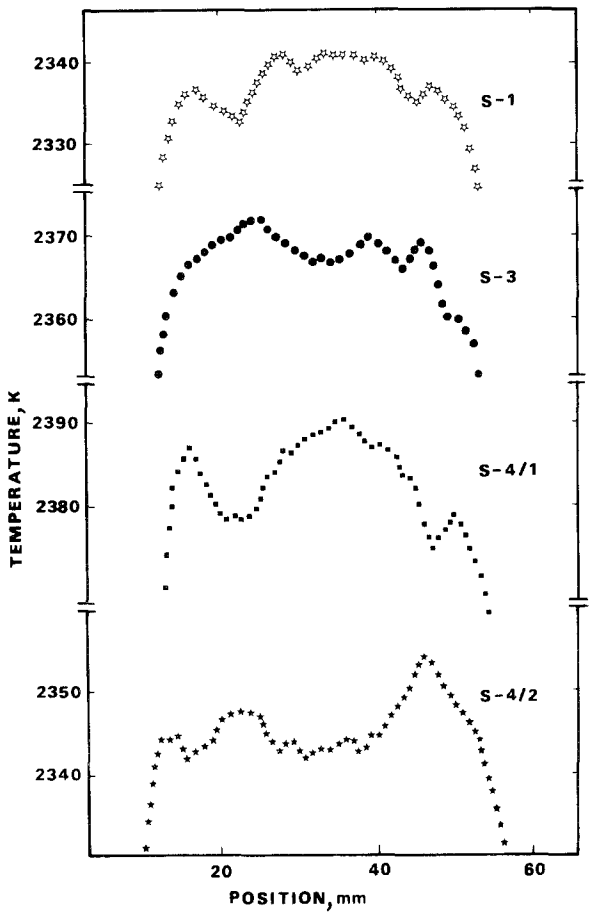

Fig. 1. Typical temperature profiles of the niobium specimens measured after the experiments (medium heating rate). One of three experimental points is plotted.

varied from 6% of the input power for fast experiments to approximately 20% for slow experiments, with no significant differences in the heat capacity results.

3.2. Electrical Resistivity

The experimental values of electrical resistivity are based on geometric dimensions at room temperature (293 K): no thermal expansion correction was applied. The coefficients of the least-squares fitting polynomial are presented in Table II and the values obtained from the smooth function are in Table III. The deviation of each set of experimental values from the

Table II. Functional Representation of the Results for Niobium by Fitted Polynomials

	C_p ($J \cdot mol^{-1} \cdot K^{-1}$), $a+bT+cT^2+dT^3$	ρ ($10^{-8}\ \Omega \cdot m$), $a+bT+cT^2+dT^3$
a	19.007	7.7924
b	0.14155×10^{-1}	0.37945×10^{-1}
c	-0.77868×10^{-5}	-0.37218×10^{-5}
d	0.21745×10^{-8}	0.32391×10^{-9}
Temp. range (K)	1000 – 2500	1000 – 2600
S^a (%)	0.34	0.12
	ε_{ht}, $a+bT$	ε_{sn} at 898 nm, $a+bT+cT^2$
a	0.7214×10^{-1}	0.29845
b	0.8211×10^{-4}	-0.78377×10^{-5}
c		0.45658×10^{-8}
Temp. range (K)	1700–2650	1400–2500
S^a (%)	1.3	0.20

[a] Relative standard deviation as computed from the difference between an experimental value and that from the smooth functions reported above.

Table III. Smoothed Properties of Niobium Calculated from the Functions Listed in Table II

Temp. (K)	C_p ($J \cdot mol^{-1} \cdot K^{-1}$)	ρ ($10^{-8}\ \Omega \cdot m$)	ε_{ht}	ε_{sn}
1000	27.55	42.34	0.154[a]	
1100	28.05	45.46	0.162[a]	
1200	28.54	48.53	0.171[a]	
1300	29.03	51.54	0.179[a]	
1400	29.53	43.51	0.187[a]	0.296
1500	30.06	57.43	0.195[a]	0.297
1600	30.63	60.30	0.204[a]	0.298
1700	31.25	63.13	0.212	0.298
1800	31.94	65.92	0.220	0.299
1900	32.71	68.67	0.228	0.300
2000	33.57	71.39	0.236	0.301
2100	34.53	74.06	0.245	0.302
2200	35.61	76.71	0.253	0.303
2300	36.83	79.32	0.261	0.305
2400	38.19	81.90	0.269	0.306
2500	39.70	84.45	0.277	0.307
2600	41.39[a]	86.98	0.286	0.309[a]

[a] Extrapolated value.

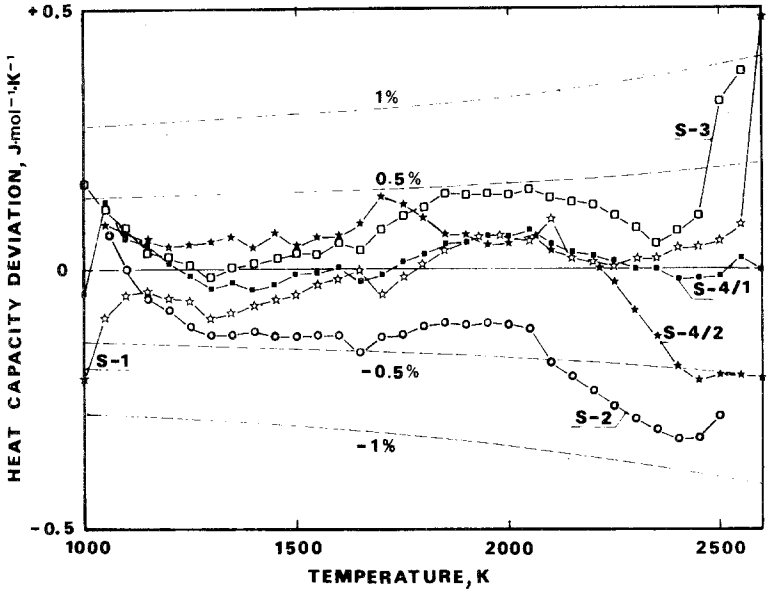

Fig. 2. Deviation of the experimental results on heat capacity from the least-squares fitting.

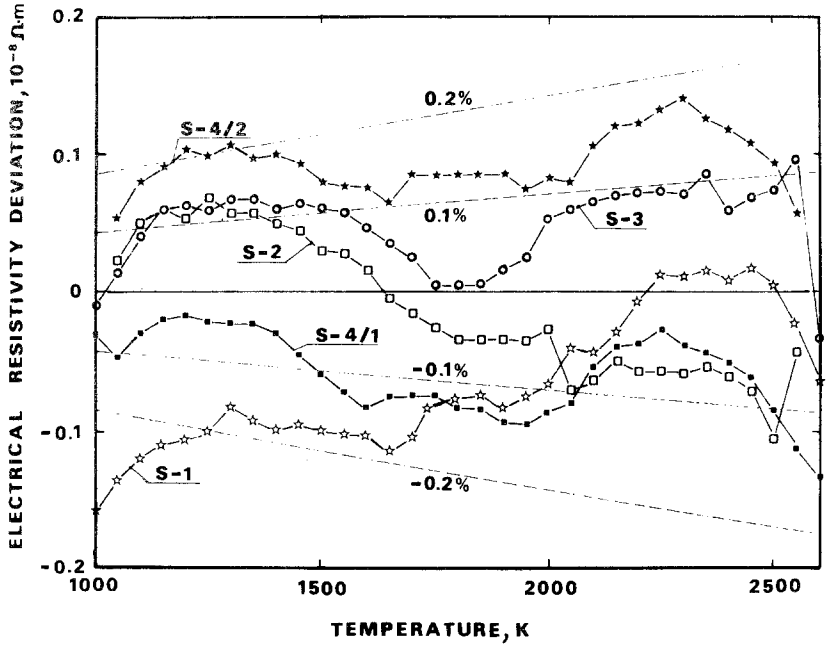

Fig. 3. Deviation of the experimental results on electrical resistivity from the least-squares fitting.

fitting polynomial is shown in Fig. 3. Practically all deviations are within $\pm 0.2\%$.

The experimental procedure followed in these experiments does not allow any long-term annealing of the specimens. After several experiments at very high temperatures (above 2600 K), large grains were observed on the central portion of the specimens and the normal spectral emittance stabilized to its final value. All experimental results were obtained after the specimen was conditioned as described above. The specimen freely cooled down to room temperature after each experiment in approximately 1 min.

3.3. Hemispherical Total Emittance

Hemispherical total emittance depends on a combination of data obtained during heating and cooling. The results obtained on the same

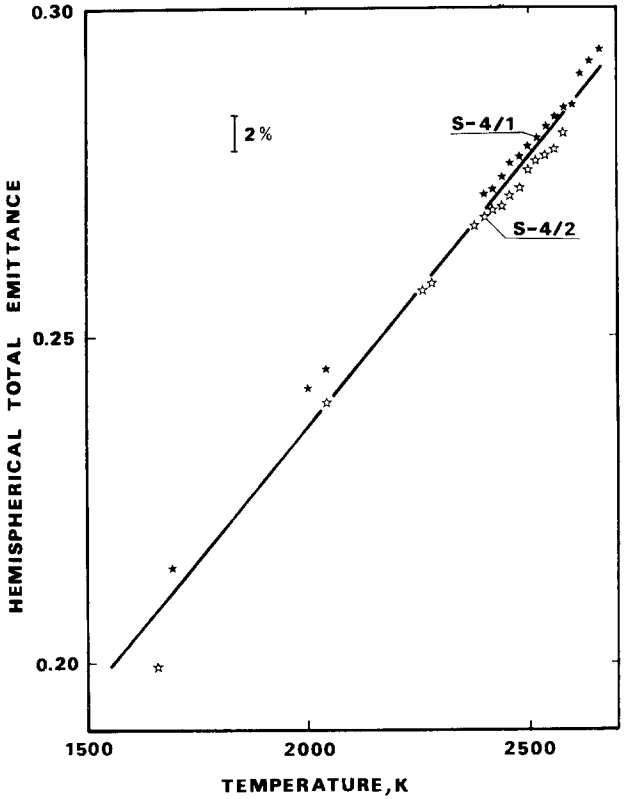

Fig. 4. Experimental results on the hemispherical total emittance of niobium. The solid line represents the least-squares fitting to all the data.

specimen with knife-edge probes (set S-4/1) and with spot-welded wire probes (set S-4/2) are presented in Fig. 4. The straight line in Fig. 4 is the fitting polynomial in Table II, with the smoothed values in Table III.

A clear difference of 1-2% is noticeable between the two sets of experimental values (Fig. 4). This does not affect significantly the radiation loss term in the heat capacity computation, and the straight line between the two sets is an adequate representation of the results. The most likely explanation of the difference may be found in the profiles in Fig. 1. No significant blackbody temperature difference is present during heating, because no evidence of this fact may be found in the heat capacity and electrical resistivity results. But when the current stops and the specimen starts to cool freely, the thermal conduction will quickly smooth the temperature differences in the profiles and the entire specimen will cool down with profiles that tend to become round with time (on account of heat conduction losses toward the clamps). The smoothing of profiles S-4/1 and S-4/2 will clearly take place in different ways and is probably responsible for the difference in cooling rates that leads to the hemispherical total emittance differences in Fig. 4.

3.4. Normal Spectral Emittance at 898 nm

Experimental results obtained on specimen S-4/2 in slow, medium, and fast experiments are reported in Fig. 5. The continuous line in the same figure is the least-squares fit of the data (see Table II) with the smoothed values in Table III.

The normal spectral emittance of niobium at 898 nm is a very weak function of temperature, and thus the temperature differences in the profile do not affect significantly the blackbody radiance or the true temperature with which the measurement is associated. But the surface radiance strongly depends on the particular point on the surface of the specimen where the pyrometer is focused. An irregular temperature profile (Fig. 1) is an indication of the lack of a uniform cross section, which will produce slightly different profiles with changing heating rates (in general, peaks and valleys will be enhanced by fast heating rates). This was very noticeable with the raw data of spcimen S-4/2. The knowledge of the profiles for slow, medium, and fast heating rates allowed a correction in which the difference between the temperature of the focused point and that of the blackbody (assumed to be made of all points between the voltage probes) was taken into account to compute the data in Fig. 5. The remaining difference is of the order of $\pm 0.5\%$ and well within the precision of the measurement.

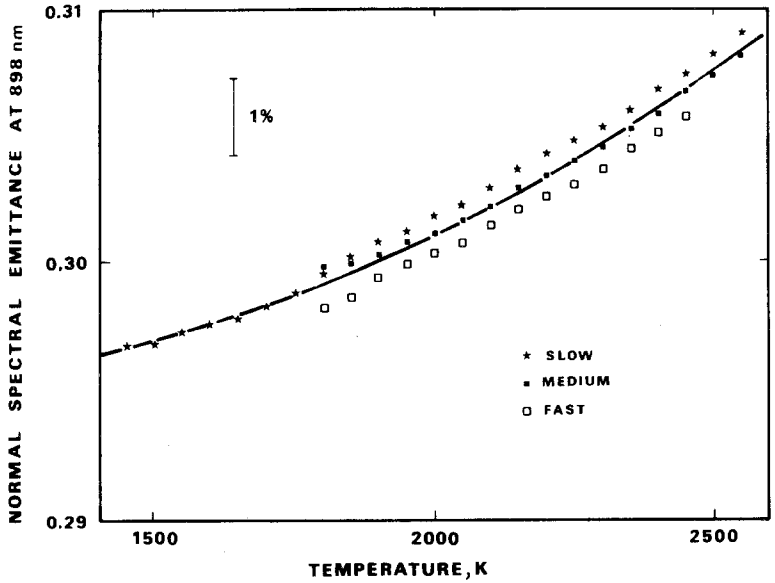

Fig. 5. Experimental results on the normal spectral emittance at 898 nm of niobium (specimen S-4/2). The solid line represents the least-squares fitting to all the data.

4. DISCUSSION

The results of the uncertainty analysis expressed according to BIPM suggestions [15] are presented in Table IV. The second column takes into account only statistical considerations. The third column also includes estimated contributions of various sources: uncertainties after calibrations, combined effects of measured quantities on computed properties, etc. Details of the method used in preparing the uncertainty analysis are given in an earlier publication [1].

Results on the heat capacity of niobium performed at the NBS with the same technique are reported in the literature [6]. The same paper reports most of the literature values that appeared before 1970. Measurements performed after that date (with the inclusion of the classical work of Jaeger and Veenstra [7]) are compared with the results of the present work in Fig. 6. Whenever possible, measurements were converted to IPTS-68, but in some cases this was not possible due to insufficient information in the original papers. The agreement among the various measurements is always within the combined accuracy of results; and in general terms, the situation for niobium is satisfactory and much better than that found for most high-temperature metals.

Table IV. Uncertainty of Measured and Computed Quantities

Quantity	Uncertainty[a]	
	Type A	Type B
Temperature		
At 1000 K	0.4 K	3 K
At 1500 K	0.2 K	2 K
At 2000 K	0.1 K	3 K
At 2500 K	0.2 K	5 K
Voltage	0.02%	0.1%
Current	0.02%	0.1%
Length	0.01%	0.05%
Mass	0.01%	0.1%
Density	0.03%	0.1%
Time	0.001%	0.01%
Heat capacity	0.34%	3%
Electrical resistivity	0.12%	1%
Hemispherical total emittance	1.3%	5%
Normal spectral emittance at 898 nm	0.2%	4%

[a] See text for the designations of Type A and Type B uncertainties.

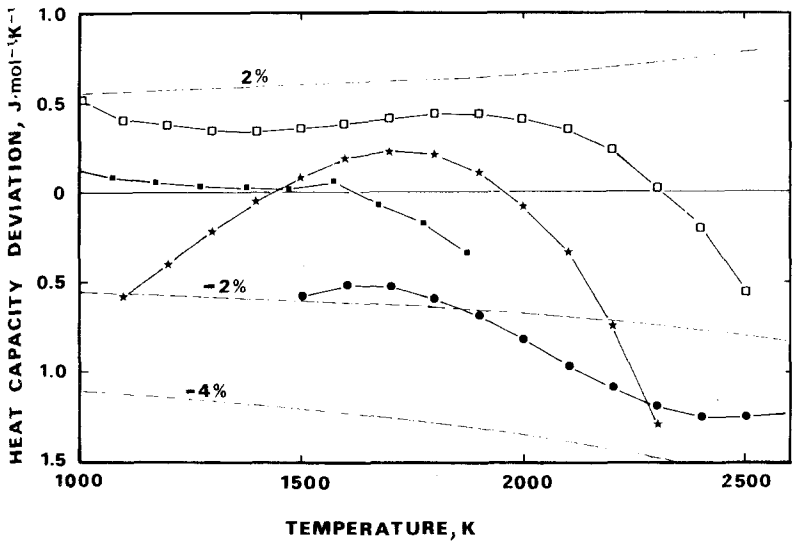

Fig. 6. Deviation of the literature values on the heat capacity of niobium published since 1970 from the resuls of the present work. (●) Ref. 6; (■) Ref. 7; (□) Ref. 8; (★) Ref. 9.

A review of the literature values of the electrical resistivity of niobium appeared in 1977 [10]. The review values and those published afterward (with the inclusion of measurements performed at the NBS with the same technique in 1971 [6]) are compared with the results of the present work in Fig. 7. The NBS data [6] agree with those of the present work within 0.3%. The results of Moore et al [11] and those of Binkele [12] are approximately 1–2% lower than those of the present work; in both cases their room-temperature resistivity was considerably lower (5–6%) than that in the present work. A disagreement exists between the recommended curve of review [10] and the results of the present work: the data are within $\pm 2\%$ in the temperature range 1000–2400 K, but the two sets seem to indicate a different temperature dependence.

Significant comparisons of emittance values are much more complicated than for other properties, on account of the strong dependence of emittance on surface conditions. The results for hemispherical total emittance obtained in the present work seem to be higher (up to 10%) than the values reported for polished samples in the TPRC compilation [13] and lower (by 2–8%) than the results obtained at the NBS [6]. No literature

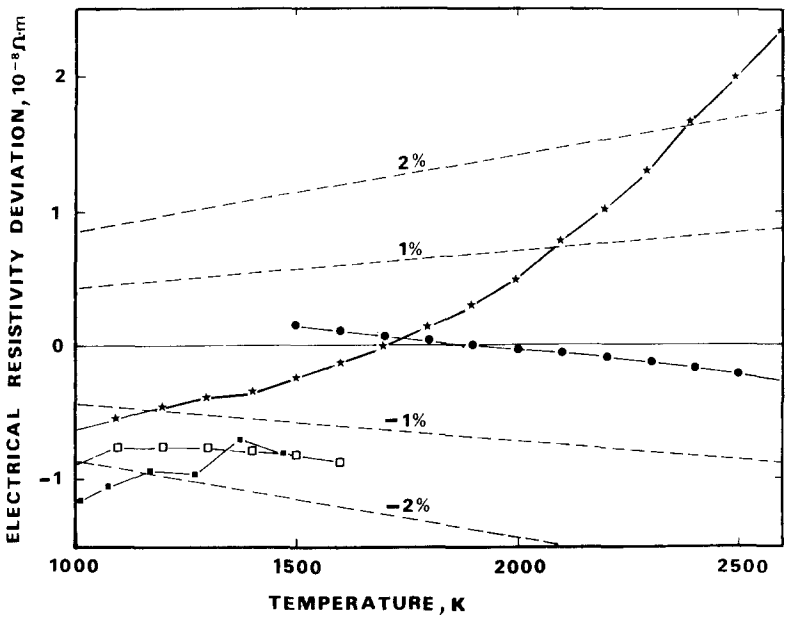

Fig. 7. Deviation of the literature values of the electrical resistivity of niobium published after 1977 from the results of the present work. (●) Ref. 6; (★) Ref. 10; (○) Ref. 11; (■) Rf. 12.

data were found for the temperature dependence of the normal spectral emittance of niobium near 900 nm. The data of the present work are in good agreement with the results of Kovalev and Muchnik [14] that investigated the wavelength dependence of the normal spectral emittance of refractory metals. Their graphical results seem to indicate, for the normal spectral emittance of niobium near 900 nm, a value close to 0.33 with a slight positive temperature dependence, which is consistent with the results of the present work.

ACKNOWLEDGMENTS

Thanks are due to A. Peuto and M. Rasetti of the Mass Section of the IMGC for the measurement of the density of the specimens.

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