International Journal of Thermophysics, Vol. 4, No. 2, 1983

Heat Capacity and Electrical Resistivity of SRM Molybdenum (1300–2500 K)

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Received April 18, 1983

Data for the heat capacity and electrical resistivity of the National Bureau of Standards (NBS) molybdenum standard reference material 781 are reported for the temperature range 1300–2500 K. The specimen was one of the three specimens previously used at NBS for similar measurements. Measurements of both properties agree within $\pm 0.5\%$ in the overlapping temperature range (1500–2500 K).

KEY WORDS: dynamic measurements; electrical resistivity; heat capacity; high temperature; molybdenum; standard reference material.

1. INTRODUCTION

Several thermophysical properties of molybdenum at high temperatures (above 1300 K) were recently determined at the Istituto di Metrologia "G. Colonnetti" (IMGC). One of the specimens used in these measurements was loaned by the Dynamic Measurements Group of the National Bureau of Standards (NBS). This specimen was machined and prepared at NBS from molybdenum SRM 781.[2] This specimen was one of the three specimens used previously by the Dynamic Measurements Group at NBS for measurements of heat capacity [1] above 1500 K, which led to the establishment of molybdenum as a standard reference material for heat capacity. Measurements at NBS of the electrical resistivity of SRM molybdenum above 1500 K were also reported in the literature [2]. The present paper reports the results of heat capacity and electrical resistivity in the

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[2] Standard Reference Material 781, Molybdenum—Enthalpy and Heat Capacity, Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234. The certified values of the properties for the range 273–2800 K are given in the literature [12].

temperature range 1300–2500 K obtained at IMGC for this particular specimen and compares the data with those obtained at NBS. The use of the same specimen permits a direct comparison of the results obtained in the two laboratories. Both groups use a subsecond pulse heating method developed at the National Bureau of Standards [3, 4], with important differences in the technique of high speed temperature measurements. The NBS pyrometer [5] uses a photomultiplier tube as a detector and operates in the chopped mode near 0.65 μm. The IMGC pyrometer [6] makes use of a silicon detector in the dc mode working in the near infrared.

2. MEASUREMENTS

The experiments reported here were performed with the high speed multiproperty apparatus of IMGC. Details of the experimental setup and of the measurement technique may be found elsewhere [7]. The 1300–2500 K temperature range was divided into two subranges (1300–2100 and 1700–2500 K) with a large overlapping region [8]. A calibrated neutral density filter was inserted in the pyrometer optical path for measurements in the higher temperature subrange. The pryometer interference filter had an effective wavelength near 900 nm and a bandwidth of 83 nm. All the temperatures reported in the present paper are based on the International Practical Temperature Scale of 1968 [9].

The nominal dimensions of the tubular specimen were: length, 76 mm; outside diameter, 6.3 mm; and wall thickness, 0.5 mm. Since the specimen had been previously used at NBS for similar measurements [1, 2], no additional heat treatment was applied. A total of 10 experiments were performed, 6 of them in the lower temperature subrange and 4 of them in the higher temperature subrange. The typical heating rates ranged from 3600 to 5400 $K \cdot s^{-1}$ with the current pulses lasting from 470 to 710 ms. Currents in the range 1500–2100 A were used; and in all the measurements the specimen was in a vacuum environment at approximately 4×10^{-3} Pa ($\sim 3 \times 10^{-5}$ torr). An additional set of 5 experiments with lower heating rates (1600–2400 $K \cdot s^{-1}$) was performed in the lower temperature subrange. The heat capacity results of these experiments were compatible with those obtained with faster heating rates, while the electrical resistivity results were lower (by approximately 0.5%) indicating a possible temperature nonuniformity of the specimen on account of the low heating rate. Data from this additional set of measurements are not included in the results. All the specimen parameters (geometrical dimensions, mass, blackbody cavity emissivity, resistivity at room temperature, etc.) were measured or computed at IMGC without any knowledge of the data previously used at NBS.

The mass and geometrical dimensions were measured three times during the experiments: no difference was found within the precision of the measurements. The electrical resistivity at room temperature was measured with a voltamperometric (potentiometric) method five times under different conditions (specimen in vacuum or in air at atmospheric pressure). Since the measurements were performed at different temperatures in the range 285–292 K, a least squares fit (standard deviation 0.1%) provided the temperature coefficient of the electrical resistivity near room temperature ($0.022 \times 10^{-8}\ \Omega \cdot m \cdot K^{-1}$) and permitted the referral of all the measurements to 293 K. The average of the electrical resistivity determinations referred to 293 K was $5.459 \times 10^{-8}\ \Omega \cdot m$; the maximum difference of these measurements being 0.3%.

3. EXPERIMENTAL RESULTS

The experimental results of the heat capacity and electrical resistivity are reported in Tables I and II, respectively. No direct measurement of the

Table I. Experimental Results for the Heat Capacity (in $J \cdot mol^{-1} \cdot K^{-1}$) of SRM Molybdenum

Temp.	Heat capacity (exp. no.)									
(K)	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
1300	30.86		30.33	30.37	30.56	30.58				
1350	30.93		30.63	30.63	30.81	30.83				
1400	31.12		30.94	30.94	31.10	31.11				
1450	31.38		31.27	31.28	31.42	31.42				
1500	31.70	31.71	31.62	31.63	31.77	31.75				
1550	32.06	32.05	32.00	32.01	32.14	32.12				
1600	32.44	32.43	32.41	32.41	32.53	32.51				
1650	32.85	32.84	32.83	32.82	32.94	32.94				
1700	33.29	33.27	33.28	33.27	33.38	33.39	33.48	33.46	33.44	33.48
1750	33.75	33.73	33.75	33.73	33.84	33.86	33.95	33.93	33.91	33.93
1800	34.24	34.22	34.24	34.23	34.32	34.36	34.44	34.42	34.40	34.40
1850	34.76	34.73	34.75	34.75	34.84	34.87	34.94	34.92	34.89	34.89
1900	35.30	35.26	35.28	35.28	35.39	35.41	35.46	35.44	35.41	35.41
1950	35.87	35.84	35.84	35.82	35.94	35.96	35.99	35.98	35.94	35.94
2000	36.45	36.46	36.45	36.35	36.62	36.52	36.54	36.53	36.49	36.49
2050	37.04	37.14				37.09	37.11	37.09	37.06	37.07
2100	37.60	37.90				37.66	37.70	37.68	37.65	37.66
2150							38.31	38.28	38.27	38.28
2200							38.96	38.92	38.92	38.92
2250							39.64	39.59	39.59	39.59
2300							40.36	40.30	40.29	40.29
2350							41.11	41.07	41.03	41.04
2400							41.91	41.91	41.79	41.85
2450							42.75	42.85		42.75
2500							43.62	43.90		43.77

Table II. Experimental Results for the Electrical Resistivity (in $10^{-8}\ \Omega \cdot m$) of SRM Molybdenum

Temp. (K)	Electrical resistivity (exp. no.) (1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
1300	32.04		32.14	32.13	32.10	32.08				
1350	33.48		33.56	33.56	33.54	33.53				
1400	34.93		35.00	35.00	34.98	34.97				
1450	36.39		36.45	36.45	36.44	36.42				
1500	37.85	37.90	37.90	37.91	37.90	37.88				
1550	39.33	39.37	39.37	39.37	39.37	39.36				
1600	40.81	40.85	40.85	40.85	40.85	40.84				
1650	42.31	42.35	42.35	42.35	42.35	42.34				
1700	43.81	43.86	43.86	43.86	43.86	43.85	43.83	43.81	43.83	43.82
1750	45.34	45.38	45.38	45.38	45.38	45.38	45.36	45.33	45.36	45.35
1800	46.87	46.92	46.92	46.92	46.91	46.92	46.90	46.88	46.90	46.89
1850	48.42	48.47	48.47	48.47	48.46	48.47	48.46	48.44	48.45	48.45
1900	49.99	50.03	50.03	50.03	50.03	50.03	50.03	50.00	50.02	50.01
1950	51.56	51.60	51.61	51.60	51.60	51.60	51.60	51.57	51.59	51.58
2000	53.15	53.19	53.19	53.19	53.19	53.18	53.18	53.15	53.17	53.16
2050	54.74	54.78				54.77	54.77	54.73	54.75	54.74
2100	56.33	56.38				56.35	56.35	56.32	56.34	56.33
2150							57.93	57.90	57.92	57.91
2200							59.52	59.48	59.51	59.49
2250							61.10	61.06	61.09	61.07
2300							62.68	62.63	62.66	62.65
2350							64.25	64.20	64.23	64.22
2400							65.81	65.77	65.79	65.78
2450							67.36	67.33		67.33
2500							68.90	68.87		68.87

hemispherical total emittance was performed; the correction to heat capacity data for losses due to thermal radiation was computed from the hemispherical total emittance data reported in ref. 1. The power loss due to the thermal radiation in each experiment ranged from 2 to 8% of the input power. The value of 95.94 $g \cdot mol^{-1}$ [10] was used for the atomic mass of molybdenum. The density of the specimen was assumed to be 10.21 $g \cdot cm^{-3}$, as reported for NBS measurements [2].

3.1. Heat Capacity

The following function (standard deviation 0.3%) represents a least squares fit of the heat capacity data of Table I:

$$C_p = 31.479 - 6.7713\ 10^{-3}T + 4.6345\ 10^{-6}T^2 \quad (1)$$

Table III. Heat Capacity and Electrical Resistivity of SRM Molybdenum Obtained from Eqs. (1) and (2)

Temperature (K)	Heat capacity ($J \cdot mol^{-1} \cdot K^{-1}$)	Electrical resistivity ($10^{-8}\ \Omega \cdot m$)
1300	30.51	32.12
1400	31.08	34.96
1500	31.75	37.86
1600	32.51	40.83
1700	33.36	43.86
1800	34.31	46.93
1900	35.34	50.03
2000	36.47	53.16
2100	37.70	56.31
2200	39.01	59.48
2300	40.42	62.64
2400	41.92	65.79
2500	43.52	68.93

in the temperature range 1300–2500 K, where C_p is in $J \cdot mol^{-1} \cdot K^{-1}$ and T is in K. Tabulated values of this equation are reported in Table III.

The data obtained at NBS on the same material may be found in ref. 1. A subset of these data [11], containing the results of the measurements performed at NBS on the same specimen used at IMGC, was fitted to a

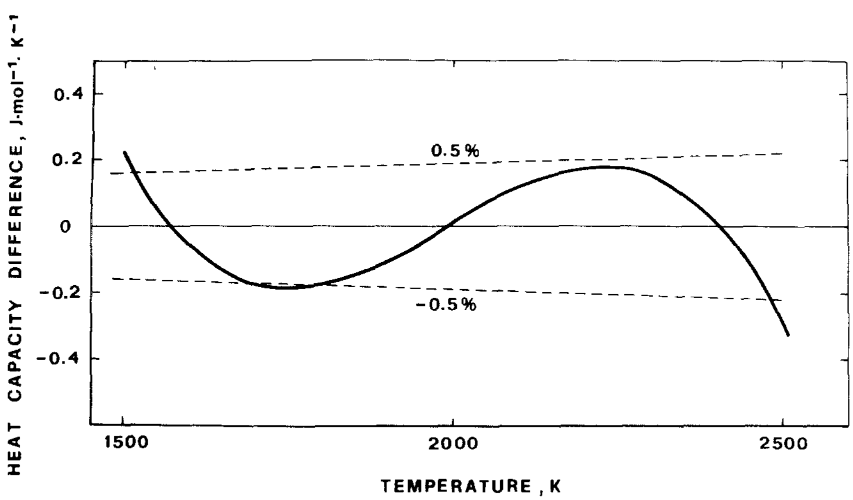

Fig. 1. Comparison of heat capacity measurements of SRM molybdenum performed at NBS and at IMGC on the same specimen. The curve is the difference between the IMGC results and the NBS results (represented by the zero line).

third degree polynomial with the method of least squares. The difference between this fit and Eq. (1) is presented in Fig. 1 for the overlapping temperature range. The heat capacity difference is within ±0.5% for most of the temperature range. Part of the difference at the high temperature end may be due to the fact that experimental measurements at IMGC were limited to 2500 K for specimen safety reasons and data at the highest temperature partially depend on results on the whole temperature range (a smoothing temperature versus time polynomial is used over the whole range to compute the heating rate).

3.2. Electrical Resistivity

The following function (standard deviation 0.06%) represents a least squares fit of the electrical resistivity data of Table II:

$$\rho = 5.6661 + 1.0263\ 10^{-2}T + 9.6454\ 10^{-6}T^2 - 1.4513\ 10^{-9}T^3 \qquad (2)$$

in the temperature range 1300–2500 K, with ρ in $10^{-8}\ \Omega \cdot \mathrm{m}$, and T in K. Tabulated values of this equation are reported in Table III.

Reference 2 contains the data obtained at NBS on two specimens of the same SRM molybdenum. Specimen 1 of that paper is the same

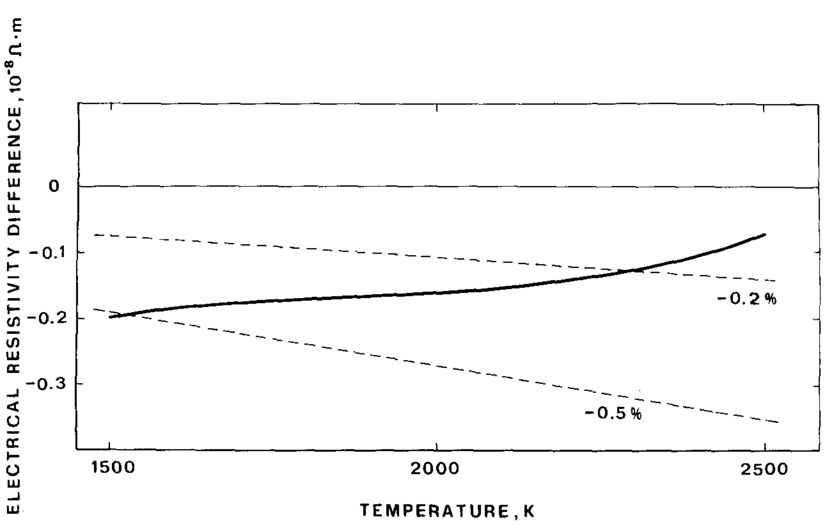

Fig. 2. Comparison of electrical resistivity measurements of SRM molybdenum performed at NBS and at IMGC on the same specimen. The curve is the difference between the IMGC results and the NBS results (represented by the zero line).

specimen that was subsequently used at IMGC [11]. The data of specimen 1 were fitted to a third degree polynomial, and the difference between this fit and Eq. (2) is presented in Fig. 2 for the overlapping temperature range. The electrical resistivity difference decreases from 0.5% to 1500 K to 0.1% at 2500 K.

4. DISCUSSION

The results of the error analysis are presented in Table IV. The first column takes into account only statistical considerations; the second column also includes estimated contributions of various sources: uncertainties remaining after calibrations, combined effects of measured quantities on computed properties, etc. Details of the method used in preparing the error analysis are given in an earlier publication [7]. Complete and detailed surveys of the literature data of the heat capacity [1, 12] and electrical resistivity [2, 13] of molybdenum have appeared recently. The data obtained in this work are so close to the NBS results that the reader is referred to refs. 1 and 2 for literature comparisons.

Potential causes of differences in these comparison measurements with the pulse heating technique may be found in (1) measurements of mass and of geometrical dimensions, and (2) measured quantities during the experiment (current, voltage drop, temperature, and heating rate). Both the experience and the precision and accuracy of the measured quantities (see Table IV) indicate that mass, geometrical dimensions, current, and voltage are likely to cause minor contributions. Differences in mass and geometrical dimensions will also not be temperature dependent. The largest possible cause of differences is due to the realization of the temperature scale on the high speed pyrometers and the corresponding temperature versus time measurements, from which the heating rate is derived.

Table IV. Precision and Accuracy of Measured and Computed Quantities

Quantity	Precision	Accuracy
Temp., 1500 K	0.2 K	2 K
2000 K	0.1 K	3 K
2500 K	0.2 K	5 K
Voltage	0.02%	0.1%
Current	0.02%	0.1%
Length	0.01%	0.04%
Mass	0.01%	0.1%
Time	0.001%	0.01%
Electrical resistivity	0.06%	1%
Heat capacity	0.3%	3%

The results presented in this work indicate a very good agreement between the data independently obtained at NBS and at IMGC on the same SRM molybdenum specimen. The method of comparison used (measurements on the same specimen) effectively eliminates any difference due to the material or to specimen fabrication. For heat capacity both laboratories quote an accuracy of 3%. The comparison results (Fig. 1) agree to within ±0.5% for the most of the temperature range. The changes in Fig. 1 between positive and negative values also indicate that there are no systematic differences between the results. The values of Fig. 1 are very close to the standard deviation of the fittings (0.4% for NBS values and 0.3% for IMGC values) that represent the typical spread of individual data points from the fitted curves.

For electrical resistivity the claimed accuracy is 1%. The comparison results (Fig. 2) agree to better than 0.5% over the whole temperature range. The shape of Fig. 2 indicates a small systematic difference between the NBS and IMGC data that slowly decreases with increasing temperature. The most likely cause is a small difference (of the order of 0.2%) between the realization of the temperature scale in the temperature range 1500–2000 K.

The results presented in this work confirm the accuracy of the pulse heating technique for measurements of heat capacity and electrical resistivity at high temperatures. For both properties differences of less than 0.5% were found in the temperature range 1500–2500 K, confirming that measurements performed at NBS and at IMGC are compatible. The results are also an indirect proof of the validity of two completely different methods of high speed temperature measurements.

ACKNOWLEDGMENTS

The specimen on which all measurements were performed was loaned by the Dynamic Measurements Group of NBS. Special appreciation is extended to A. Cezairliyan for the active support of this comparison and for the supply of specific NBS results.

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