International Journal of Thermophysics, Vol. 15, No. 3, 1994

Measurement of the Heat of Fusion of Tantalum by a Microsecond-Resolution Transient Technique

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Received December 28, 1993

The heat of fusion of tantalum was measured using a microsecond-resolution pulse-heating technique. The technique is based on rapid (about 100-μs) resistive self-heating of a specimen by a high-current pulse from a capacitor discharge system and measuring the current through the specimen, voltage across the specimen, and radiance temperature of the specimen as functions of time. Melting of a specimen is manifested by a plateau in the radiance temperature versus time function. The time integral of the power absorbed by the specimen during melting yields the heat of fusion. Measurements gave a value of 34.8 kJ · mol $^{-1}$ for the heat of fusion of tantalum, with a total uncertainty of $\pm 6\%$. Electrical resistivity of solid and liquid tantalum at its melting temperature was also measured.

KEY WORDS: electrical resistivity; heat of fusion; high temperatures; melting; pulse heating; refractory metals; transient techniques; tantalum.

1. INTRODUCTION

The microsecond-resolution pulse heating technique developed earlier in our laboratory [1] has been used to measure the heats of fusion of the refractory metals niobium [1], molybdenum [2], and tungsten [3]. The technique is based on rapid (about 100-μs) resistive self-heating of wire specimens by short-duration current pulses from a capacitor discharge system. During heating of a specimen, simultaneous measurements of the current through the specimen, voltage across the specimen, and radiance from the specimen are made with microsecond resolution. A minor improvement to the data acquisition system has been made with the recent

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0195-928X/94/0500-0505$07.00/0

introduction of a 10-MHz (0.1 μs between data points) 12-bit oscilloscope which increases the possible data acquisition rate by a factor of five. In this paper, application of the technique to the measurement of the heat of fusion of tantalum is described. Other details regarding the construction and operation of the measurement system are given elsewhere [1, 4, 5].

2. MEASUREMENTS ON TANTALUM

Measurements were made on five tantalum specimens in the form of wires with the following nominal dimensions: 1.6-mm diameter and 57-mm length. Each specimen was prepared by sanding its surface with a fine sandpaper and then heat treating by subjecting it to three current pulses (each of 290-ms duration) from a battery bank that heated the specimen to a peak radiance temperature of about 2400 K. Each specimen was clamped into a specimen chamber with approximately 32 mm of the specimen exposed between the clamps. Knife marks, made about 25 mm apart on the middle portion of each specimen, were used to position voltage probes made from tantalum strips (6.4 mm long and 0.25 mm thick). The knife marks defined an "effective" specimen free of axial temperature gradients for the experiment. The mass of each "effective" specimen was determined from the distance between knife marks and the measured mass per unit length (0.3259 g · cm^{-1}) of the tantalum wire. As reported by the manufac-

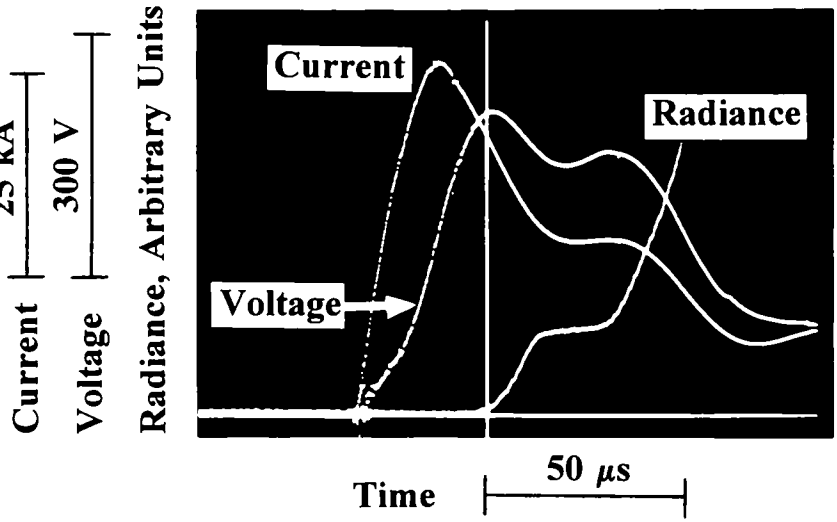

Fig. 1. Oscilloscope trace photograph showing current, voltage, and radiance waveforms during a typical experiment on tantalum (specimen 1 in Table I).

turer, the tantalum material was 99.9 + % pure, with the following major impurities (ppm): O, 61; W, 50; Ni, 32; Fe, 30; N, 20; C, 18; Al, Ca, Cr, Co, Cu, Mg, Mn, Mo, Nb, Si, Sn, Ti, V, and Zr, each 10 or less; and H, 5 or less. Each experiment was conducted with the specimen in an argon environment at slightly above atmospheric pressure.

In a typical experiment, the capacitor bank was charged to an initial voltage of approximately 6.7 kV and discharged in the crowbar mode of operation [1]. The temperature of a specimen increased from room temperature through the melting temperature to a radiance temperature of about 3200 K in approximately 100 μs. As the specimen heated, data for each measured quantity were recorded at a rate of 5 MHz (0.2 μs between data points) using the newly installed data acquisition system mentioned in Section 1. An oscilloscope trace photograph showing the time variation of current, voltage, and specimen radiance for a typical experiment is shown in Fig. 1. The voltage trace does not follow the shape of the current trace because the resistance of the specimen increases rapidly with temperature. The peak voltage across the specimen was typically between 350 and 380 V and the peak current through the specimen was typically between 42 and 44 kA. The plateau in the radiance trace indicates the melting of the specimen. The heating rate of the specimen before and after the melting region was estimated to be approximately 1×10^7 K $\cdot$ s^{-1}.

3. RESULTS

The heat of fusion of each tantalum specimen was determined from the energy absorbed by the specimen during the melting period. The experimental data for current and voltage were used to compute absorbed power for each individual point. The energy absorbed by the specimen above an arbitrary radiance temperature (2300 K) was determined by integrating power point-by-point over time to a radiance temperature of about 3400 K. The measured mass per unit length of the tantalum wire, the room temperature length of the effective specimen, and the atomic mass of tantalum (180.948 [6]) were used to express absorbed energy in units of J $\cdot$ mol^{-1}. Because of the speed of the experiments, correction for heat losses due to thermal radiation or conduction were not required. The result for a typical experiment is illustrated in Fig. 2, which shows the relationship of radiance temperature as a function of absorbed energy.

The radiance temperature data as illustrated in Fig. 2 were fitted by the least-squares method, to a quadratic function for the premelting region and linear functions for the melting (plateau) region and the postmelting region. Because the beginning and end of the melting plateau do not have sharp discontinuities, those data points which lie in the transition between

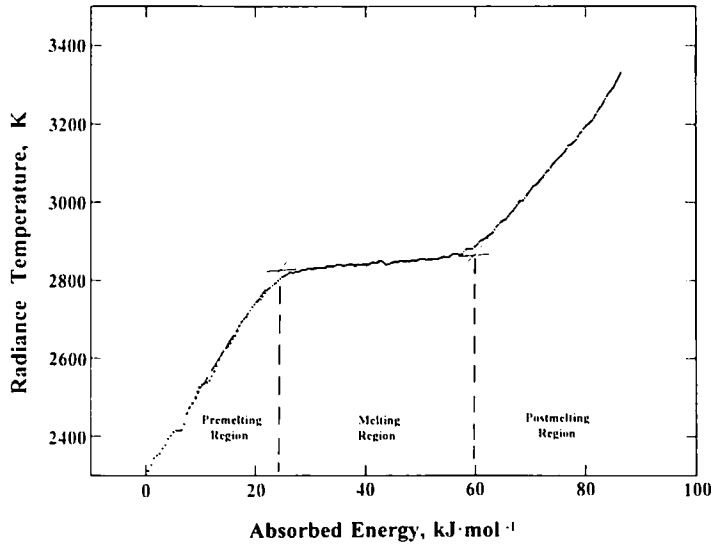

Fig. 2. Variation of radiance temperature as a function of absorbed energy by a specimen above 2300 K obtained by integrating power point-by-point over time during premelting, melting (plateau), and postmelting periods for a typical experiment on tantalum (specimen 1 in Table I).

premelting and the plateau and postmelting and the plateau were excluded from the data fits. The dashed lines in Fig. 2 represent the least-squares fits to the data in each region. The standard deviation of the fits in each region ranged between the following minimum and maximum values: premelting region, 6.8–8.4 K; plateau region, 2.4–3.4 K; and postmelting region, 2.4–3.2 K.

As shown in Fig. 2, the melting plateau typically showed a positive slope. However, the determination of the heat of fusion was independent of this slope. The melting plateau for each specimen was defined by the intersections of the temperature versus absorbed energy function for the plateau region with the functions for the premelting region and the postmelting region. The heat of fusion was obtained from the difference between the value of absorbed energy at the end of the melting plateau and that of the absorbed energy at the beginning of the melting plateau. The experimental results for the heat of fusion of tantalum are given in Table I. The average of these values is 34.8 $kJ \cdot mol^{-1}$, with a maximum absolute deviation of 0.1 $kJ \cdot mol^{-1}$.

Table I. Experimental Results on the Heat of Fusion of Tantalum

Specimen No.	Heating time to start of melting (μs)	Duration of melting period (μs)	Heat of fusion (kJ · mol^{-1})
1	55.7	22.7	34.9
2	62.4	26.5	34.7
3	58.9	26.9	34.8
4	57.2	25.2	34.9
5	64.3	27.3	34.8
Average			34.8

4. ESTIMATE OF UNCERTAINTIES

The single largest contributor to the uncertainty in the measured value of the heat of fusion is the uncertainty in the determination of the times for the beginning and the end of the melting period. This is true even with the improvement in the rate of data acquisition because the measured radiance data do not have sharp transitions at the ends of the melting plateau. In the present experiments this uncertainty was estimated to be not more than ± 1 μs, which corresponds to an estimated maximum uncertainty in the heat of fusion of $\pm 5\%$. Estimated maximum uncertainties in other quantities, current, voltage, mass, etc., are 1% or less each. The total uncertainty (square root of the sum of the squares of the various individual uncertainties) in the reported value of the heat of fusion of tantalum is $\pm 6\%$. Details regarding the sources and estimates of uncertainties using the present measurement system are given in a previous publication [1].

5. DISCUSSION

The measurements of the heat of fusion of tantalum reported in the literature (Table II) show a large range of values, with the highest reported value [11] being almost 54% larger than the lowest reported value [13]. This large range suggests the existence of unreported problems when working with tantalum. In the present work, consistent results for the shape, length, and temperature of the melting plateau for Ta specimens were not achieved until specimens were subjected to the preexperiment heating pulses described in Section 2. If the highest and lowest reported values for heat of fusion of tantalum are excluded, then four [7, 9, 10, 11]

Table II. Heat of Fusion of Tantalum Reported in the Literature

Investigator(s)	Ref. No.	Year	Heat of fusion ($kJ \cdot mol^{-1}$)	Technique
Lebedev et al.	7	1971	36.6	Pulse heating
Lebedev and Mozharov	8	1976	37.4	Pulse heating
Shaner et al.	9	1977	36.2	Pulse heating
Arpaci & Frohberg	10	1982	33.8	Levitation calorimetry
Gallob et al.	11	1985	41.6	Pulse heating
Berthault et al.	12	1986	32.0	Pulse heating
Jäger et al.	13	1992	27.1	Pulse heating
Present work			34.8	Pulse heating

of the remaining five values are well within the reported total uncertainty ($\pm 6\%$) of the present value. The 1976 value reported by Lebedev and Mozharov [8] is 7.5% above the present value.

Using the value of $34.8\ kJ \cdot mol^{-1}$ for the heat of fusion of tantalum and 3256 K (on ITS-90) for the melting temperature of tantalum [14], a value of $10.7 \pm 0.6\ J \cdot mol^{-1} \cdot K^{-1}$ for the entropy of fusion of tantalum is obtained. This value is about 5% lower than the value reported by this laboratory for niobium [1].

The experimental data for current and voltage were also used to determine the electrical resistivity of each specimen at its melting point. The electrical resistance of each specimen and the mass density of tantalum ($16.6\ g \cdot cm^{-3}$) were used to compute average values for the electrical resistivity of solid tantalum (ρ_s) and of liquid tantalum (ρ_l) at its melting temperature. The results for electrical resistivity, based on room-temperature dimensions, are $1.10\ \mu\Omega \cdot m$ for solid tantalum and $1.20\ \mu\Omega \cdot m$ for liquid tantalum at its melting temperature. These values yield 1.09 for the resistivity ratio (ρ_l/ρ_s). The electrical resistivity result for solid tantalum (ρ_s) is about 5% lower than the estimated value ($1.15\ \mu\Omega \cdot m$) obtained by extrapolating to the melting temperature the results reported previously by this laboratory [15]. The only results for electrical resistivity based on room-temperature dimensions reported in the literature [7] are about 8% higher than the present value for ρ_s and about 9% higher for ρ_l. However, the values for the resistivity ratio (ρ_l/ρ_s) are within 1% of each other. Comparisons with other results reported in the literature were not made because the reported electrical resistivity results were corrected for thermal expansion of the material.

ACKNOWLEDGMENT

This work was supported in part by the Microgravity Science and Applications Division of NASA.

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