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Measurement of the Heat of Fusion of Tungsten by a Microsecond-Resolution Transient Technique[1]

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A microsecond-resolution pulse-heating technique was used for the measurement of the heat of fusion of tungsten. The method is based on rapid (100 to 125 μs) resistive self-heating of a specimen by a high-current pulse from a capacitor discharge system and measuring current through the specimen and voltage across the specimen as functions of time. Melting of a specimen is manifested by changes in the slope of the electrical resistance versus time function. The time integral of the power absorbed by a specimen during melting yields the heat of fusion. Measurements gave a value of 48.7 kJ · mol^{-1} for the heat of fusion of tungsten with an estimated maximum uncertainty of ±6%. The electrical resistivity of solid and liquid tungsten at its melting temperature was also measured.

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

1. INTRODUCTION

This paper describes measurements of the heat of fusion of tungsten using a microsecond-resolution transient technique developed previously in our laboratory [1]. The method is based on rapid (100 to 125 μs) resistive self-heating of the specimen by a short-duration current pulse from a capacitor discharge system. During heating of the specimen, simultaneous measurements of current through the specimen and voltage across the specimen are made with microsecond resolution. Specimen radiance is also measured in order to monitor heating rates and relative changes in tem-

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perature of the specimen. Details regarding the construction and operation of the measurement system are given elsewhere [1–3]. In the present work, specimen resistance rather than specimen radiance was used to determine the beginning and end of the melting period.

2. MEASUREMENTS ON TUNGSTEN

Measurements were made on seven tungsten specimens in the form of high-purity wires with the following nominal dimensions: 1.6 mm in diameter and 57 mm in length. Prior to the experiments, two of the specimens (specimens 1 and 2 in Table I) were subjected to four heating pulses (about 600 ms long to a radiance temperature of approximately 2500 K) from a battery bank. The surfaces of the other specimens were cleaned using a very fine sandpaper. A specimen was clamped into an experiment chamber with approximately 28 mm between the clamps. Voltage probes, made of tantalum strips (6.4 mm wide and 0.25 mm thick) sharpened to a knife edge on one end, were placed on knife marks made about 24 mm apart on the middle portion of the specimen. The knife marks defined an "effective" specimen free of axial temperature gradients for the duration of the experiment. The mass of each "effective" specimen was determined from the distance between knife marks and the measured mass per unit length ($0.3698\ g \cdot cm^{-1}$) of the tungsten wire. As reported by the manufacturer, the tungsten material was 99.9 + % pure, with the following major impurities (ppm): O, 80; Fe, 54; Cr, 13; Si, Ni, Zr, and Mo, each 10 or less; N, Na, K, Cu, Sn, and Pb, each 5 or less; and Li and Al, each 1 or less. Each experiment was conducted with the specimen in an argon environment slightly above atmospheric pressure.

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

Specimen No.	Heating time to start of melting (μs)	Duration of melting period (μs)	Heat of fusion ($kJ \cdot mol^{-1}$)
1	77.4	20.8	48.2
2	75.3	17.7	48.5
3	72.6	16.8	49.2
4	76.8	18.1	48.8
5	75.4	16.2	48.6
6	76.4	19.2	48.9
7	74.2	18.2	48.8
Average			48.7

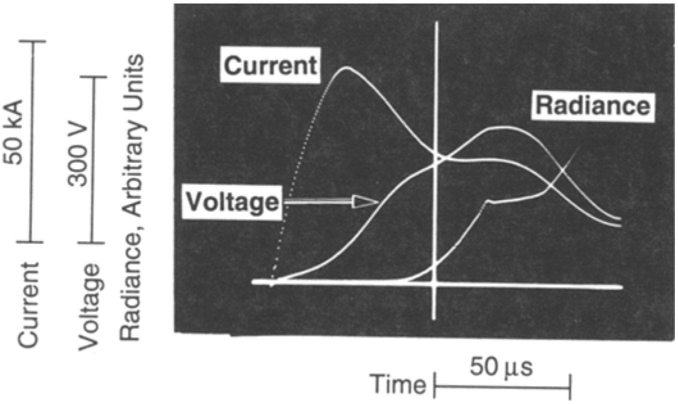

Fig. 1. Oscilloscope trace photograph showing current, voltage, and radiance waveforms during a typical experiment on tungsten (specimen 2 in Table I).

In a typical experiment, the capacitor bank was charged to an initial voltage of approximately 8.3 kV and discharged in the crowbar mode of operation [1]. The specimen was heated from room temperature through the melting temperature to about 400 K above the melting temperature in approximately 110 μs. 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 400 and 460 V and the peak current through the specimen was typically between 53 and 56 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 about 1×10^7 K $\cdot$ s^{-1}.

3. RESULTS

The heat of fusion of each tungsten specimen was determined from the absorbed energy during the melting period. The experimental data for current and voltage were used to compute absorbed power and specimen resistance for each individual time. The energy absorbed by the specimen was determined by integrating power point-by-point over time from the beginning to the end of the experiment. The measured mass per unit length of the tungsten wire, the room temperature length of the effective specimen, and the atomic weight of tungsten (183.85) were used to express measured absorbed energy in units of J $\cdot$ mol^{-1}. Because of the speed of the experiments, corrections for heat losses due to thermal radiation or conduction were not required.

In previous work [1, 4], specimen radiance was used to determine the beginning and end of the melting period of the specimen. However, as illustrated in Fig. 1, measured radiance typically did not show a precise transition at the beginning of the melting plateau. For this reason, radiance data were not used in the present work. As illustrated in Fig. 2, specimen resistance plotted as a function of time showed discontinuities in slope at the beginning and end of the melting period. These discontinuities in the slopes of specimen resistance were used, as described below, to determine the times for the beginning and end of the melting period. For comparison purposes, the specimen's radiance is also displayed in Fig. 2.

The resistance data for each specimen were fitted, by the least-squares method, to a quadratic function for the premelting region and linear functions for the melting region and the postmelting region. Those few data points which lie in the transitions between premelting and melting and postmelting and melting were excluded from the data fits. The lines drawn through the points in Fig. 2 represent least-squares fits to the data in each region. The percentage standard deviation of the fits in each region ranged from minimum to maximum values as follows: premelting region, 0.03–0.04%; melting region, 0.03–0.06%; and postmelting region, 0.03–0.08%. The intersection of the premelting curve and the melting curve

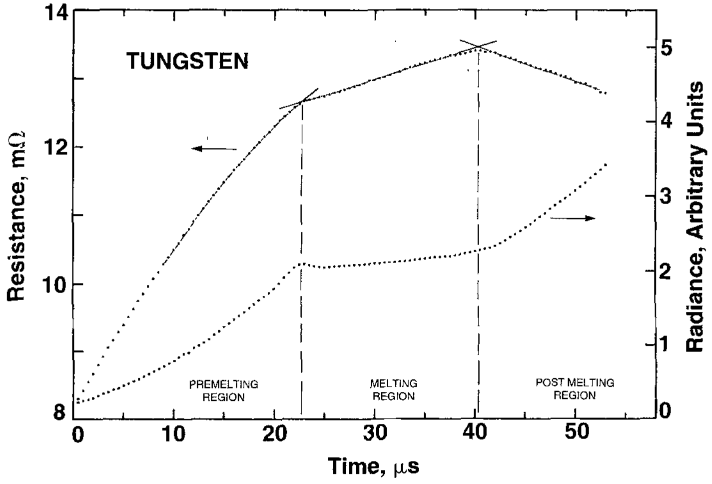

Fig. 2. Variation of electrical resistance (obtained from each individual measurement of current and voltage) and radiance of the specimen during premelting, melting, and postmelting periods for a typical experiment on tungsten (specimen 2 in Table I).

was taken to be the beginning time for melting, and the intersection of the melting curve and the postmelting curve was taken to be the end time for melting. The heat of fusion for each experiment was taken to be the difference between the value for absorbed energy at the end of melting and the absorbed energy at the beginning of melting.

The experimental results for the heat of fusion of tungsten are given in Table I. The average of these values is 48.7 $\mathrm{kJ \cdot mol^{-1}}$, with a standard deviation of 0.3 $\mathrm{kJ \cdot mol^{-1}}$ and a maximum absolute deviation of 0.5 $\mathrm{kJ \cdot mol^{-1}}$.

4. ESTIMATE OF ERRORS

The uncertainties in the determination of the times for the beginning and end of the melting period are the largest contributor to the uncertainty in the value of heat of fusion. In the present experiments this uncertainty was estimated to be not more than $\pm 1\ \mu$s, which corresponds to a maximum uncertainty in the heat of fusion of about $\pm 5\%$. Uncertainties in other quantities, current, voltage, mass, etc., are 1% or less each. The maximum uncertainty from all sources yields an estimate of $\pm 6\%$ in the reported value of the heat of fusion of tungsten. Details regarding the sources and estimates of errors using the present measurement system are given in a previous publication [1].

5. DISCUSSION

The measurement of the heat of fusion of tungsten presented in this work is compared with the values reported in the literature [5–15] in Table II. All but two of these values were measured using pulse heating techniques. The earliest reported values (prior to 1976) are from 12 to 26% higher than the present value and are higher than the values measured later (after 1976). With the exception of a value from levitation calorimetry [10], all the values for the heat of fusion of tungsten reported since 1976 are within the estimated uncertainty ($\pm 6\%$) of the present value. Including the present work, all the values obtained recently (since 1986) from pulse heating techniques are within 4% of one another. Compared to these more recent values from pulse heating techniques, the two values obtained from levitation calorimetry are from 3 to 13% higher.

Using the value of 48.7 $\mathrm{kJ \cdot mol^{-1}}$ for the heat of fusion of tungsten and 3695 K for the melting temperature of tungsten [16], a value of 13.2 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ for the entropy of fusion of tungsten is obtained.

Electrical resistance data were used to compute average values of electrical resistivity for solid (ρ_S) and liquid (ρ_M) tungsten at its melting temperature. The results for electrical resistivity, based on room-

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

Investigator(s)	Ref. No.	Year	Heat of fusion ($kJ \cdot mol^{-1}$)	Technique
Dikhter & Lebedev	5	1970	61.5	Pulse heating
Lebedev et al.	6	1971	55.0	Pulse heating
Martynyuk et al.	7	1975	54.5	Pulse heating
Shaner et al.	8	1976	46.0	Pulse heating
Seydel et al.	9	1979	50.6	Pulse heating
Bonnell	10	1983	53.0	Levitation calorimetry
Arpaci & Frohberg	11	1984	50.3	Levitation calorimetry
Berthault et al.	12	1986	46.7	Pulse heating
Senchenko & Sheindlin	13	1987	48.0	Pulse heating
Hixson & Winkler	14	1990	48.0	Pulse heating
Kaschnitz et al.	15	1990	47.1	Pulse heating
Present work			48.7	Pulse heating

temperature dimensions, are 1.13 $\mu\Omega \cdot m$ for solid tungsten at its melting temperature and 1.21 $\mu\Omega \cdot m$ for liquid tungsten at its melting temperature. These values yield 1.07 for the resistivity ratio (ρ_M/ρ_S). The electrical resistivity result for solid tungsten is within the combined estimated errors of the value (1.15 $\mu\Omega \cdot m$) obtained by extrapolating to the melting temperature the results reported previously by this laboratory [16]. Those results reported in the literature that are based on room-temperature dimensions [6, 7, 17] are about 2 to 4% higher than the present value for ρ_S and about 2.5 to 5% higher for ρ_M. The resistivity ratios (ρ_M/ρ_S) from these same reports are within 2% of the present value. Valid comparisons with the more recent results reported in the literature are difficult because their electrical resistivity results have been corrected for thermal expansion of the material. However, in the two cases where electrical resistivities based on room-temperature dimensions can be determined from reported volume changes [12, 14], the reported values of ρ_S are about 2% lower than the present value, the reported values of ρ_M are, respectively, 3% lower and about 3% higher than the present value, and the reported resistivity ratios are, respectively, 2% lower and about 6% higher than the present value.

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REFERENCES

1. A. Cezairliyan and J. L. McClure, *Int. J. Thermophys.* **8**:577 (1987).
2. G. M. Foley, M. S. Morse, and A. Cezairliyan, in *Temperature: Its Measurement and Control in Science and Industry, Vol. 5*, J. F. Schooley, ed. (Am. Inst. Phys., New York, 1982), p. 447.
3. J. L. McClure and A. Cezairliyan, *Int. J. Thermophys.* **11**:739 (1990).
4. J. L. McClure and A. Cezairliyan, *Int. J. Thermophys.* **11**:731 (1990).
5. I. Ya. Dikhter and S. V. Lebedev, *High Temp. High Press.* **2**:55 (1970).
6. S. V. Lebedev, A. I. Savvatimskii, and Yu. B. Smirnov, *High Temp. (USSR)* **9**:578 (1971).
7. M. M. Martynyuk, I. Karimkhodzhaev, and V. I. Tsapkov, *Sov. Phys. Tech. Phys.* **19**:1458 (1975).
8. J. W. Shaner, G. R. Gathers, and C. Minichino, *High Temp. High Press.* **8**:425 (1976).
9. U. Seydel, H. Bauhof, W. Fucke, and H. Wadle, *High Temp. High Press.* **11**:635 (1979).
10. D. W. Bonnell, in *Materials Measurements*, J. R. Manning, ed. (NBS Internal Report 83-2772, 1983), p. 123.
11. E. Arpaci and M. G. Frohberg, *Z. Metallkde.* **75**:614 (1984).
12. A. Berthault, L. Arles, and J. Matricon, *Int. J. Thermophys.* **7**:167 (1986).
13. V. N. Senchenko and M. A. Sheindlin, *High Temp. (USSR)* **25**:364 (1987).
14. R. S. Hixson and M. A. Winkler, *Int. J. Thermophys.* **11**:709 (1990).
15. E. Kaschnitz, G. Pottlacher, and L. Windholz, *High Press. Res.* **4**:558 (1990).
16. A. Cezairliyan, *High Temp. Sci.* **4**:248 (1972).
17. I. Ya. Dikhter and S. V. Lebedev, *High Temp. (USSR)* **9**:845 (1972).