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

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A microsecond-resolution pulse-heating technique was used for the measurement of heat of fusion of molybdenum. The method is based on rapid resistive self-heating of the specimen by a high-current pulse from a capacitor discharge system and measuring current through the specimen, voltage across the specimen, and radiance temperature of the specimen as functions of time. Melting of the specimen is manifested by a plateau in the 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 36.4 $\mathrm{kJ \cdot mol^{-1}}$ for the heat of fusion of molybdenum with an estimated maximum uncertainty of $\pm 6\%$.

KEY WORDS: heat of fusion; high temperatures; melting; molybdenum; refractory metals; transient techniques.

1. INTRODUCTION

Because of the difficulties involved in performing accurate thermophysical measurements at high temperatures by conventional methods, a microsecond-resolution transient technique was developed in our laboratory [1]. In this paper, application of this technique to the measurement of heat of fusion of molybdenum is described.

The method for measuring heat of fusion is based on rapid resistive self-heating of the specimen by a short-duration current pulse from a capacitor discharge system. While the specimen is heating, simultaneous

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measurements of current through the specimen, voltage across the specimen, and radiance temperature of the specimen are made with microsecond resolution. Details regarding the construction and operation of the high-speed pyrometer used for measuring temperature, the technique for measuring electrical quantities, and the method used to obtain heat of fusion are given elsewhere [1–3].

2. MEASUREMENTS ON MOLYBDENUM

Measurements were made on nine molybdenum specimens in the form of wires with the following nominal dimensions: diameter, 1.6 mm; and length, 50.8 mm. The specimen was clamped into a specimen chamber with approximately 26 mm of the specimen exposed between the clamps. Voltage probes, made of molybdenum strips (6.4 mm wide and 0.13 mm thick) sharpened to a knife edge on one end, were placed on knife marks about 24 mm apart made 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. Each experiment was conduced with the specimen in an argon environment at slightly above atmospheric pressure.

The molybdenum specimens were selected from three different groups of wire. The mass per unit length of each group differed due to small differences in cross-sectional area. Measurements of the mass per unit length of each group yielded values of 0.1972, 0.1993, and 0.2008 $g \cdot cm^{-1}$. As reported by the manufacturer, the molybdenum material was 99.9+% pure. The major impurities reported by the manufacturer are as follows: C, 20 ppm; Fe, Si, and Ni, each 10 ppm or less; O_2, 9 ppm; and N_2 and H_2, each 1 ppm or less.

In a typical experiment, the capacitor bank was charged to an initial voltage of about 8.0 kV and discharged in a crowbar mode of operation.

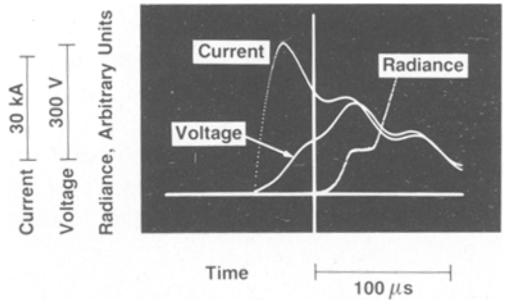

Fig. 1. Oscilloscope trace photograph showing the current, voltage, and radiance waveforms during a typical experiment.

The specimen was heated from room temperature through the melting temperature to a radiance temperature of about 2900 K in approximately 100 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 dissimilar shape between the current and the voltage traces is due to the rapidly increasing resistance of the specimen as it heats. The peak voltage across the specimen was typically between 300 and 350 V and the peak current through the specimen was typically between 50 and 54 kA. The plateau in the radiance trace indicates the melting of the specimen.

The liquid specimen continues to heat for approximately another 400 K above the melting temperature. The heating rate in the solid phase was about $3 \times 10^7 \mathrm{K \cdot s^{-1}}$ at a temperature approximately 200 K below the plateau and the heating rate in the liquid phase was about $2 \times 10^7 \mathrm{K \cdot s^{-1}}$ at a temperature approximately 200 K above the plateau.

3. RESULTS

The heat of fusion of each molybdenum 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 as illustrated for a typical experiment in Fig. 2. For comparison purposes, the radiance temperature of the specimen is also displayed in Fig. 2. The energy absorbed by the specimen above an

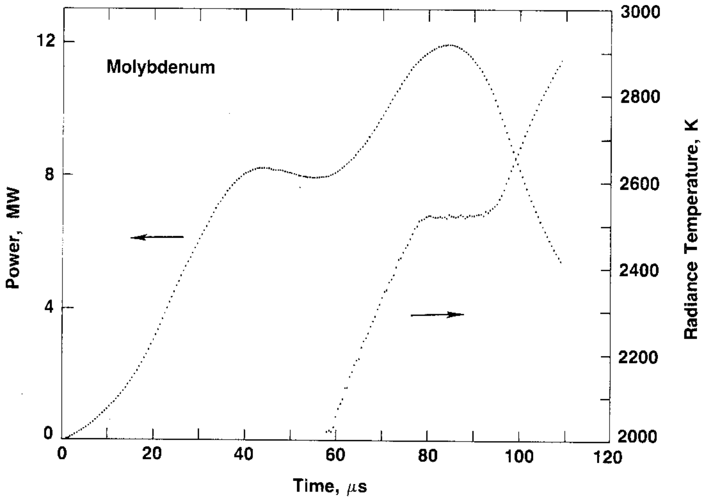

Fig. 2. Absorbed power (obtained from each individual measurement of current and voltage) and radiance temperature of the specimen during premelting, melting (plateau), and postmelting periods for a typical experiment.

arbitrary radiance temperature (2200 K) was determined by integrating power point-by-point over time to a radiance temperature of about 2900 K. The measured mass per unit length of the molybdenum sample, the room temperature length of the effective specimen, and the atomic weight of molybdenum (95.94) were used to express measured 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 was not required. The result for a typical experiment is illustrated in Fig. 3, which shows the relationship of radiance temperature as a function of absorbed energy.

The radiance temperature data as illustrated in Fig. 3 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 of the lack of sharp discontinuities at the beginning and at the end of the melting plateau, those data points which lie in the transition between premelting and the plateau and postmelting and the plateau were excluded from the data fits. The dashed lines in Fig. 3 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, 3.1–5.1 K; plateau region, 1.5–2.8 K; and postmelting region, 1.0–2.1 K. The beginning and end of the melting plateau were defined by the intersections of the temperature versus absorbed energy curves for each region. The heat of fusion for each experiment was obtained from the difference between the value of absorbed energy at the

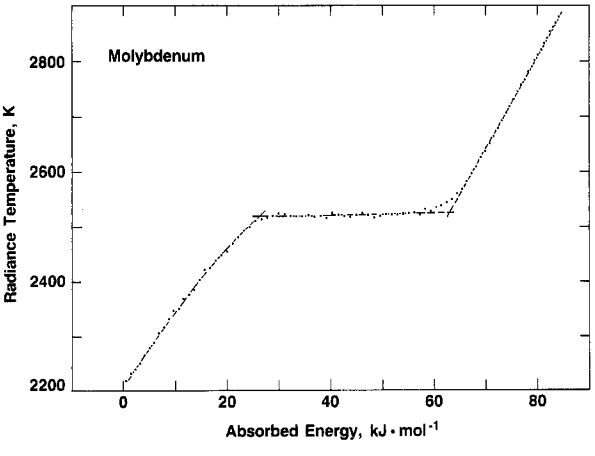

Fig. 3. Variation of radiance temperature as a function of absorbed energy by the specimen above 2200 K obtained by integrating power point-by-point over time during premelting, melting (plateau), and postmelting periods for a typical experiment.

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

Specimen No.	Heating time to start of melting (μs)	Radiance temperature at start of melting (K)	Duration of melting plateau (μs)	Slope of melting plateau ($K \cdot \mu s^{-1}$)	Heat of fusion ($kJ \cdot mol^{-1}$)
1	78.4	2520	16.4	0.12	36.8
2	87.8	2516	23.9	0.21	35.3
3	82.5	2524	20.4	0.26	36.6
4	84.4	2522	21.8	0.22	36.4
5	74.5	2516	14.2	0.13	37.2
6	83.3	2524	16.8	0.23	36.0
7	84.2	2518	20.2	0.26	36.6
8	89.8	2514	28.4	0.09	36.2
9	80.6	2520	19.3	0.13	36.8

end of the melting plateau and the absorbed energy at the beginning of the melting plateau. The experimental results for heat of fusion of molybdenum are given in Table I. The average of these values is 36.4 $kJ \cdot mol^{-1}$, with an average absolute deviation of 0.4 $kJ \cdot mol^{-1}$ and a maximum absolute deviation of 1.1 $kJ \cdot mol^{-1}$.

4. ESTIMATE OF ERRORS

The uncertainty in the determination of the melting duration is the single 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 ± 1 μs, which corresponds to a maximum uncertainty in the heat of fusion of about ± 5%. Uncertainties in other quantities, current, voltage, temperature, mass, etc., are 1% or less each. The maximum uncertainty from all sources in the reported value of the heat of fusion of molybdenum is estimated to be ± 6%. Details regarding the sources and estimates of errors using the present measurement system are given in a previous publication [1].

5. DISCUSSION

Measurements of the heat of fusion of molybdenum reported in the literature were performed by means of either levitation calorimetry [4–6] or microsecond-resolution capacitor discharge techniques [7–11]. A comparison of the result of the present work is presented in Table II. The values reported in the literature fall into two groups: those in the range

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

Investigator	Ref. No.	Year	Heat of fusion ($kJ \cdot mol^{-1}$)	Technique
Treverton and Margrave	4	1970	34.8	Levitation calorimetry
Berezin et al.	5	1971	36.6	Levitation calorimetry
Lebedev et al.	7	1971	41.3	Pulse heating
Martynyuk et al.	8	1975	38.0	Pulse heating
Lebedev et al.	9	1976	39.8	Pulse heating
Shaner et al.	10	1977	35.8	Pulse heating
Seydel and Fischer	11	1978	48.5	Pulse heating
Betz and Frohberg	6	1980	39.1	Levitation calorimetry
Present Work		1988	36.4	Pulse heating

34.8–36.6 $kJ \cdot mol^{-1}$ and those above 38 $kJ \cdot mol^{-1}$. The disagreement between these two groups of values, about 4 to over 15%, is approximately correlated with experimental technique. Two of the three values in the lower group were obtained from levitation calorimetry and all but one value in the upper group were obtained from pulse heating techniques. The values in the range 34.8–36.6 $kJ \cdot mol^{-1}$ are within 5% of the value reported here. The values in the upper group are from about 5 to 14% higher than the present value except that of Seydel and Fischer [11], which is about 33% higher than the present value.

Using the value of 36.4 $kJ \cdot mol^{-1}$ for the heat of fusion of molybdenum and 2894 K for the melting temperature of molybdenum [12], a value of 12.6 $J \cdot mol^{-1} \cdot K^{-1}$ for entropy of fusion of molybdenum is obtained. This experimental value is considerably higher than the value 7.4 $J \cdot mol^{-1} \cdot K^{-1}$ suggested by Gschneidner [13] for body-centered-cubic metals.

The radiance temperature of the specimen during the melting period of each experiment shows a small positive slope (Fig. 2 and Table I), a behavior typically observed in capacitor discharge experiments. In the present experiments, the maximum rise in radiance temperature due to the slope of the melting plateau is 5 K. The values of the slope observed in these experiments on molybdenum are typically less than one-half those observed in experiments on niobium using the same experimental system [1]. It has been suggested that this slope occurs as a result of a change in apparent emissivity of the metal or as a result of nonequilibrium melting in the specimen. Either reason may also explain the lack of sharp discontinuities in the heating curve at the beginning and at the end of the melting period.

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