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The Melting Point of Palladium by a Pulse Heating Method

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The melting point of 99.95^{+}% pure palladium was measured by means of a subsecond duration pulse heating technique. The average temperature at the melting point for three specimens was 1827 K with an average absolute deviation from the mean of 0.1 K. The total error in temperature is estimated to be not more than ± 4 K.

KEY WORDS: high temperatures; melting point; palladium; pulse heating.

1. INTRODUCTION

In recent years, the rapid development of high-temperature technologies has required improvements in the methods of determining temperature. Because of the importance of secondary reference points in the calibration of high-temperature sensors, the list of eight secondary reference points above the freezing point of gold given in the text of the International Practical Temperature Scale of 1968 (IPTS-68) [1] was extended in 1977 [2] to seventeen. Of these seventeen, nine secondary reference points (five out of six above 2400 K) are based, at least in part, on measurements by Cezairliyan and coworkers with a pulse heating technique [3, 4], in which the entire experiment is performed in less than 1 s. Conventional steady-state and quasi-steady-state techniques are generally limited to temperatures lower than 2500 K because of severe problems (heat loss, chemical reactions, evaporation, loss of mechanical strength) that are created by the exposure of the specimen to high temperatures for extended periods of time (minutes to hours).

The melting point of palladium is listed as a secondary reference point on

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the IPTS-68 with a value of 1827 K. The listed value is based on a conversion to the IPTS-68 of three experimental determinations [5–7] obtained about 50 years ago by visual optical pyrometry. In the present work, an independent redetermination of the melting point of palladium has been carried out by a rapid pulse heating technique in which temperature is measured with a high-speed photoelectric pyrometer. The short measurement time (less than 1 s) of our technique tends to minimize the problems (mentioned above) associated with quasi-steady-state experiments; in particular, specimen evaporation which, in the case of palladium, is enhanced by the relatively high vapor pressure near its melting point.

The method is based on rapid resistive self-heating of the specimen from room temperature to its melting point in less than 1 s by the passage of an electrical current pulse through it. The specimen temperature is measured at the rate of 1200 times per second with a high-speed photoelectric pyrometer [8]. The data are recorded with a digital data acquisition system, which has a time resolution of 0.4 ms and a full-scale signal resolution of about 1 part in 8000. Details regarding the construction and operation of the measurement system and other pertinent information, such as error analysis, etc., are given in earlier publications [3, 4].

2. MEASUREMENTS

Emission spectrographic analyses of the specimen material by the manufacturer indicate that it was $99.95^{+}\%$ pure, containing the following impurities (in ppm by mass): Si, 150; Mg, 55; Fe, 45; Al, 20; Zr, 15; Pt, Au, 10 each; Cu, less than 10. The material was supplied in the form of cylindrical rods from which three tubular specimens were fabricated by an electroerosion technique. The nominal dimensions of the tubes were: length, 75 mm; outside diameter, 6.4 mm; wall thickness, 0.5 mm. A rectangular sighting hole (0.5 × 1 mm) was fabricated through the wall at the middle of each tube, as shown in Fig. 1, thereby approximating blackbody conditions. In order to compensate for the cross-sectional nonuniformity created by the hole, a portion of the specimen was removed by grinding a flat along the length of the tube, excluding the 1 mm length of the hole. The sighting hole was fabricated 0.8 mm off center from the tube axis to improve the blackbody quality.

Each specimen was clamped vertically onto electrodes in an experiment chamber [3] designed for experiments with the specimen either in vacuum or in a controlled atmosphere. The lower electrode was attached to a flexible connection which allowed for thermal expansion of the specimen in a downward direction.

Prior to the experiment, adjustments were made to a resistance in series with the specimen and to the voltage from a battery bank in order to achieve the desired heating rate. Each specimen was then resistively heated in an

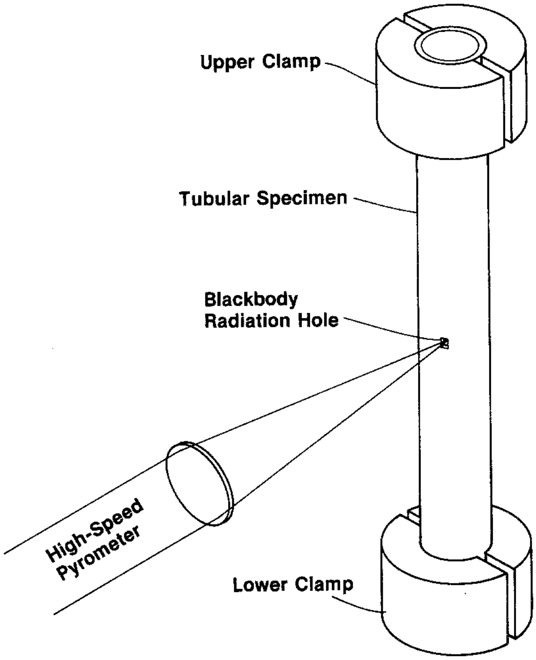

Fig. 1. Schematic diagram showing the arrangement of the tubular specimen (75 mm long, 6.4 mm outside diameter), the clamps and the temperature measurement system.

argon environment at about 0.2 MPa (~2 atm) from room temperature to the melting point by the passage of an electrical current pulse through it. The duration of the current pulse varied from 550 to 600 ms. The corresponding heating rates ranged between 3740 and 3570 $K \cdot s^{-1}$.

Figure 2 presents an oscilloscope trace photograph showing the variation in radiation from a specimen, as seen by the pyrometer, during a typical experiment in which the specimen was pulse heated to its melting point. The plateau in the specimen radiance indicates the region of the solid to liquid transformation. In all cases, the transformation to the liquid phase was interrupted by the hydrodynamic collapse of the specimen, thus opening the electrical circuit. After each experiment, the window of the experiment chamber was checked for possible coatings arising from specimen evaporation. No evidence of any coating was observed.

Upon completion of the experiments, the high-speed photoelectric pyrometer was calibrated against a tungsten filament reference lamp which, in turn, had been calibrated against the NBS Photoelectric Pyrometer by the Radiometric Physics Division at NBS. All temperatures reported in this work, except where explicitly noted otherwise, are based on the IPTS-68.

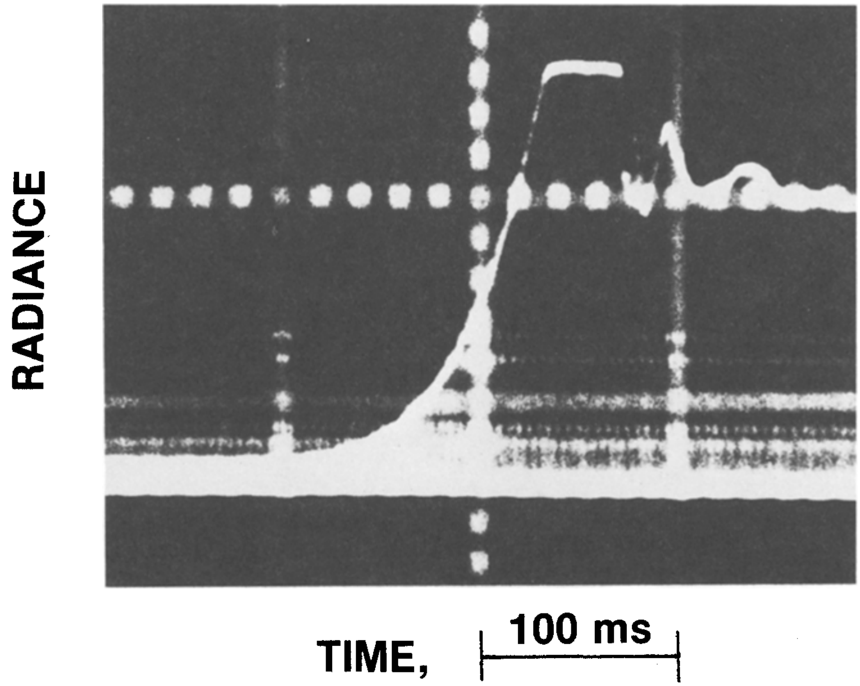

Fig. 2. An oscilloscope trace photograph of the radiance of specimen 3 (as observed by the pyrometer) during an experiment in which the specimen was pulse heated to its melting point. Dots forming the horizontal lines in the pyrometer output correspond to the radiance from a reference source.

3. RESULTS

In determining the specimen temperature from the measured spectral radiance, corrections were made to account for the departure of the specimen from true blackbody conditions and for the light scattering effect of the optics in the pyrometer. Based on geometrical considerations only, the blackbody quality of the specimen was estimated to be 0.98 by De Vos's [9] method. The 2% correction in radiance corresponds to an upward correction in temperature of 3.1 K at 1800 K. For the pyrometer/specimen configuration of the present work, 1.2% of the measured radiance comes from the specimen surface surrounding the blackbody radiation hole. Normal spectral emittance of the specimen near its melting point is about 0.4 at 0.65 μm, the effective wavelength of the pyrometer [10]. A correction to measured radiance for scattered light, taking into account the emittance of the specimen surface, yields an upward correction in temperature of 1.1 K at 1800 K.

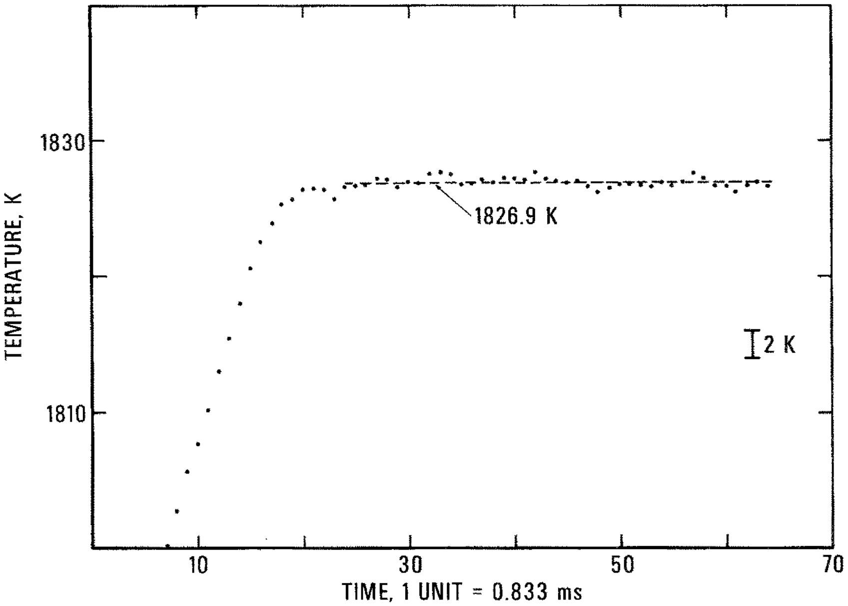

Fig. 3. Variation of the temperature of specimen 3 near and at the melting point of palladium.

The temperature of a specimen just before and during the solid to liquid phase transformation is illustrated in Fig. 3; the points represent temperatures obtained from individual pyrometer readings taken every 0.833 ms. The melting temperature (1826.9 K) of the specimen was obtained by averaging the individual points along the segment of the plateau indicated by the dashed line.

The results on melting temperature are summarized for each specimen in Table I. The average melting temperature for the three specimens is 1826.9 K, with an average absolute deviation from the mean of 0.1 K. It may be concluded that the melting point of palladium is 1827 K.

Table I. Experimental Results for the Melting Point of Palladium

Specimen number	Heating rate[a] ($K \cdot s^{-1}$)	Number of temp. at plateau	Melting pt. (K)	Standard dev. (K)
1	3,740	31	1,827.1	0.3
2	3,600	15	1,826.8	0.3
3	3,570	41	1,826.9	0.4

[a] Derivative of the temperature versus time function (at approximately 20 K below the melting plateau) obtained by fitting the temperature data before melting to a quadratic function in time with the least squares method.

4. ESTIMATE OF ERRORS

A detailed analysis of the sources and magnitudes of errors involved in the measurement of specimen temperature with the NBS pulse heating system has been given in an earlier publication [4]. Specific items in the analysis were recomputed whenever the present conditions differed from those in the earlier publication. The error contributions to the measurement of temperature in the present work arising from the reference lamp, the pyrometer, and the specimen are summarized in Table II.

The maximum error in calibration of the tungsten filament reference lamp by the Radiometric Physics Division at NBS for temperatures at about 1800 K is about 2 K. A comparison of lamp calibrations repeated during the course of several years indicates that the drift of the reference lamp between calibrations is about 1 K at about 1800 K.

The uncertainties in visual alignment of the pyrometer with the reference lamp during calibration and with the blackbody radiation hole in each of the specimens during the pulse experiments may introduce a further error in temperature measurement. Based on the analysis of experimental results from a series of tests with steady-state radiation sources, the error arising from this uncertainty is estimated to be about 1 K at about 1800 K. The temperature error that results from uncertainties in the reproducibility of the pyrometer calibrations (based on two successive calibrations within 1 day) is not more than 1 K.

The uncertainty in the scattered light correction is approximately 0.1% in radiance, which corresponds to less than 0.2 K at about 1800 K; this error is small when compared with the magnitude of other errors involved in determining temperature. The specimen chamber window was checked for

Table II. Sources and Magnitudes of Errors in the Measurement of Temperature at About 1800 K

Source	Error (K)
Reference lamp	
Calibration	2
Drift between calibrations	1
Pyrometer	
Alignment	1
Calibration	1
Specimen	
Temperature nonuniformity	3
Blackbody quality	1
Total error in temperature[a]	4

[a] Square root of the sum of squares of the individual errors.

changes in attenuation due to vapor deposition before and after each melting experiment, but no changes were detected.

The single largest source of error in temperature measurements is due to the nonuniformity of temperature within the specimen, which arises from (a) variations in specimen thickness along the length of the specimen, (b) heat transfer from the specimen to the clamps, and (c) radiative heat loss from the specimen surface. Item (a), which can be estimated from potentiometric measurements of resistance across small intervals along the specimen length (at room temperature), may create a temperature nonuniformity of about 2 K. The magnitude of the axial temperature gradient arising from (b) can be estimated by solving the transient heat conduction equation [11], based on the assumption of constant properties; computations indicate that the average temperature in the "effective" specimen (the middle one-third of the tube) is approximately 1 K lower than the midpoint value. The radial temperature difference across the thin specimen wall arising from (c) is estimated to be less than 0.1 K. No corrections were made to the measured temperatures for these small axial and radial temperature gradients. Therefore, the total error arising from temperature nonuniformity in the specimen is estimated to be about 3 K.

The uncertainty in the correction for departure from true blackbody conditions is about 0.5% in radiance; this corresponds to an error in temperature of approximately 1 K at about 1800 K. Assuming that the various error contributions are uncorrelated, we conclude that the total error in the temperature measurements at (or near) 1800 K is not more than ±4 K.

5. DISCUSSION

Results for the melting point of palladium as reported in the literature are presented in Table III, along with the corresponding values based on the IPTS-68 for comparison with the present work. All of the investigations prior to our work involved quasi-steady-state heating techniques and, except for measurements by Day and Sosman [14], visual optical pyrometry to measure temperature. Melting temperatures were determined by measuring the relative brightness of blackbodies at the melting points of gold and palladium and calculating the upper temperatures by means of Planck's law (based on accepted values for the gold point and the second radiation constant). In the experiments by Day and Sosman, the melting temperature of palladium was measured by (nitrogen) gas thermometry, a technique which is rarely used at these high temperatures because of the severe experimental problems.

The results obtained during the period 1929–1936 by Fairchild et al. [5] and by Schofield [6, 7] form the basis for the secondary reference point value of 1827 K assigned to the melting temperature of palladium. Earlier measurements on palladium yield values that range between 1822 K by Day and

Table III. Values for the Melting Point of Palladium Reported in the Literature

Investigators	Ref.	Year	Constants[a]		Melting point (K)	
			T_{Au} (K)	c_2 (cm · K)	As reported[b]	On IPTS-68
Nernst and Wartenberg	12	1906	1,337	1.460	1,814	1,825
Waidner and Burgess	13	1907	1,337	1.450	1,819	1,825
Day and Sosman	14	1910			1,822.2 ± 2	1,822
Hoffman and Meissner	15	1919	1,336	1.430	1,830	1,829
Fairchild et al.	5	1929	1,336	1.432	1,826.6 ± 0.5	1,826.4[c]
Schofield	6	1929	1,336	1.432	1,828 ± 2	1,827.8[c]
Schofield	7	1936	1,336	1.432	1,827.4 ± 1	1,827.2[c]
Present work			1,337.58	1.4388	1,827 ± 4	1,827

[a] Values of T_{Au} (gold point) and c_2 (second radiation constant) used by the investigator.

[b] Except for the melting point reported by Day and Sosman [14], which was obtained by gas thermometry, all others were obtained by pyrometry based on the given values of T_{Au} and c_2.

[c] Basis for the secondary reference point value of 1827 K listed in the text of the IPTS-68 [1].

Sosman [14] and 1829 K by Hoffman and Meissner [15]. A review of the various investigations of the palladium melting point prior to 1920 has been published by Waidner et al. [16].

The value of 1827 ± 4 K obtained in the present work by a pulse heating method (heating rate $\sim 10^4$ K · s^{-1}) is the same as the accepted value for the palladium melting point (1827 K) based on quasi-steady-state experiments. This agreement strengthens the basis for the secondary reference points above 1800 K, which were determined from measurements by dynamic techniques.

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