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Measurement of the Radiance Temperature (at 655 nm) of Melting Graphite Near Its Triple Point by a Pulse-Heating Technique[1]

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Measurements of the radiance temperature of graphite at 655 nm have been performed in the vicinity of its triple point by means of a rapid pulse-heating technique. The method is based on resistively heating the specimen in a pressurized gas environment from room temperature to its melting point in less than 20 ms by passing an electrical current pulse through it and simultaneously measuring the radiance temperature of the specimen surface every 120 μs by means of a high-speed pyrometer. Results of experiments performed on two different grades of POCO graphite (AXM-5Q1 and DFP-1) at gas pressures of 14 and 20 MPa are in good agreement and yield a value of 4330 ± 50 K for the radiance (or brightness) temperature (at 655 nm) of melting graphite near its triple point (triple-point pressure, ~ 10 MPa). An estimate of the true (blackbody) temperature at the triple point is made on the basis of this result and literature data on the normal spectral emittance of graphite.

KEY WORDS: dynamic techniques; graphite; high temperature; melting; refractory material; triple point.

1. INTRODUCTION

The solid–liquid–vapor triple point of graphite has been the subject of numerous studies, particularly during the past two decades; reviews of the investigations may be found in the literature [1, 2]. Although most measurements of the triple-point pressure have yielded values in the range of 10–11 MPa, considerable disagreement exists among measurements of the triple-point temperature, with reported values spanning the range of

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approximately 4000 to 5000 K. The major problem in such measurements arises from the high vapor pressure of graphite at elevated temperatures. As the triple point is approached, a plume of carbon or soot forms near the specimen surface, thereby severely limiting the accuracy of optical pyrometry.

In the present study, the radiance temperature (at 655 nm) of melting graphite near its triple point was determined from measurements based on a rapid pulse-heating technique. The basic method involved resistively heating the specimen, in a pressurized gas environment, from room temperature to its melting temperature in less than 20 ms by passing an electrical current pulse through it and simultaneously measuring the radiance temperature of the specimen surface every 120 μs by means of a high-speed pyrometer. The effects of specimen evaporation on temperature measurements was minimized by the addition of a small amount of oxygen to the pressurizing inert gas; the opaque carbon vapor combined with the oxygen to form optically transparent (in the vicinity of 655 nm) gases, CO and CO_2. The high specimen heating rate (of the order of $10^5\,K \cdot s^{-1}$) tended to minimize the effect of convective turbulence in the pyrometer sighting path on the temperature measurements. Measurements were performed on two grades of POCO graphite (AXM-5Q1 and DFP-1) at gas pressures of, nominally, 14 and 20 MPa.

2. MEASUREMENT SYSTEM

The high-speed measurement system includes an electric power-pulsing circuit and its associated measuring and control circuits, a high-pressure experiment chamber, a high-speed photoelectric pyrometer, and a data acquisition system. A functional diagram of the measurement system is presented in Fig. 1.

The power-pulsing circuit consists of the specimen in series with a battery bank, an adjustable resistor (water-cooled Inconel tube), and a fast-acting switch. Adjustments to the battery bank voltage (up to 54 V) and to the length (hence, resistance) of Inconel tube in the circuit, prior to pulse heating, enable control of the specimen heating rate. The timing of various events, such as closing/opening the switch and triggering the electronic instruments, is achieved by means of time-delay pulse generators.

The experiment chamber is an ultra-high-pressure vessel capable of providing a gas environment at pressures up to 200 MPa. Two optical ports (viewing cone of about 20°) through the cylindrical wall on opposite sides of the vessel facilitate the alignment of the specimen and provide a sighting path for the pyrometer through sapphire windows (diameter, 25 mm; thickness, 32 mm). The specimen/mount assembly is supported

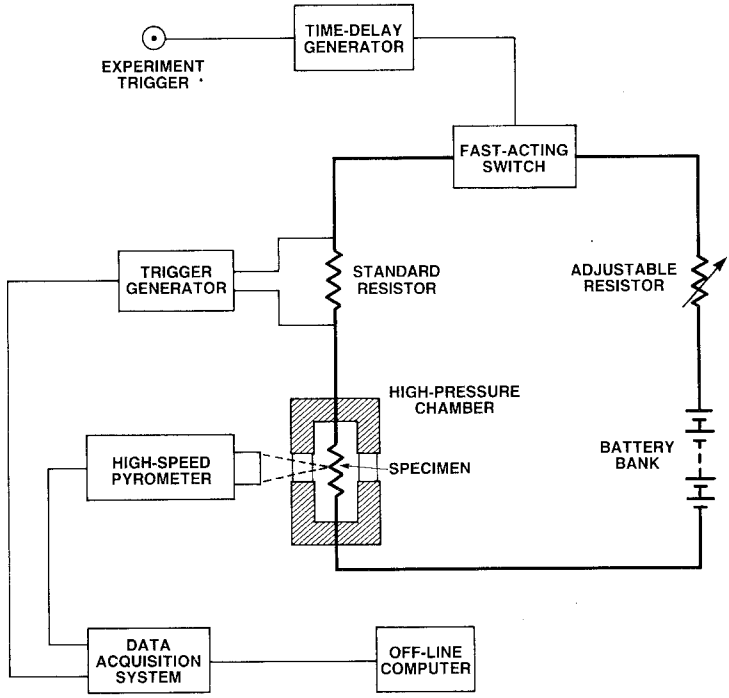

Fig. 1. Functional diagram of the measurement system.

from the closure head which contains electrical feedthroughs for the pulse-heating current. The specimen is clamped between two electrodes in the mounting assembly: a stationary lower electrode and an upper electrode which is connected to a flexible (phosphor-bronze) bellows to allow for thermal expansion of the specimen along its axial direction during rapid pulse heating.

The high-speed pyrometer is capable of measuring the temperature of a rapidly heating specimen with a time response of 50 μs [3]. Thermal radiation from a circular target area (0.5-mm diameter) on the specimen is focused by the lens system in the pyrometer through an interference filter (bandwidth of 30 nm centered at 655 nm) onto a silicon photodiode. The photocurrent from the diode is converted by a high-stability amplifier to a proportionate voltage, which is then digitized (13-bit resolution) by the data acquisition system at selectable rates of up to 100 kHz.

The details concerning the construction and operation of the basic measurement system are given in earlier publications [4, 5].

3. MEASUREMENTS

Specimens were fabricated in the form of rectangular strips from a fine-grain polycrystalline graphite which was supplied by the manufacturer in the form of thin (0.5-mm) sheets and designated either POCO AXM-5Q1 or POCO DFP-1. The nominal dimensions of each strip was 25 mm long by 3 mm wide. The center portion of each strip was "necked-down" in order to define a small "effective" specimen with nominal dimensions of 2 mm long by 1 mm wide. This procedure delineated the melt zone and, at the same time, reduced the effective surface area of the specimen, hence the amount of carbon vapor released during melting.

Prior to each pulse experiment, the specimen was mounted vertically inside the experiment chamber, which was then filled with the desired amount of oxygen (partial pressures in the range 1 to 4 MPa) and, finally, pressurized with argon to either 14 or 20 MPa, depending on the experiment. Pressure was measured by means of a Heise bourdon tube gauge, with a precision of 0.03 MPa. Upon equilibration of the gas mixture, the pyrometer was focused on the surface of the "effective" specimen. The specimen was then rapidly heated from room temperature to its melting

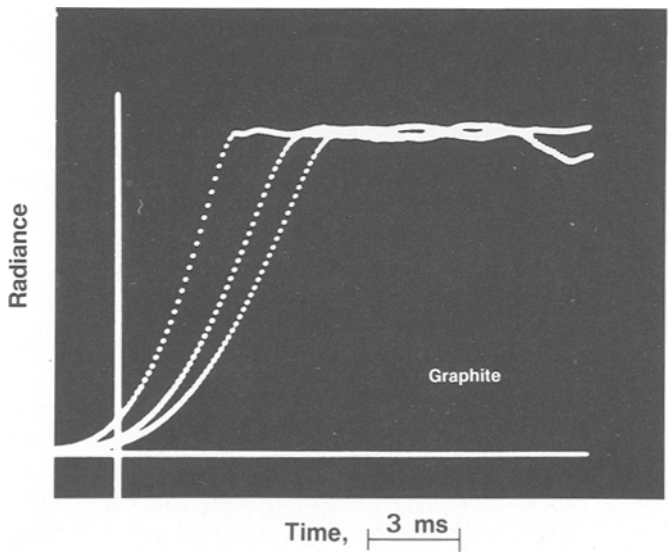

Fig. 2. An oscilloscope trace photograph in which the variations of specimen radiance with time, as measured by the pyrometer during three rapid-heating experiments (with the specimen in a pressurized argon/oxygen gas environment), are superimposed. The plateau in the radiance versus time function indicates that melting has occurred.

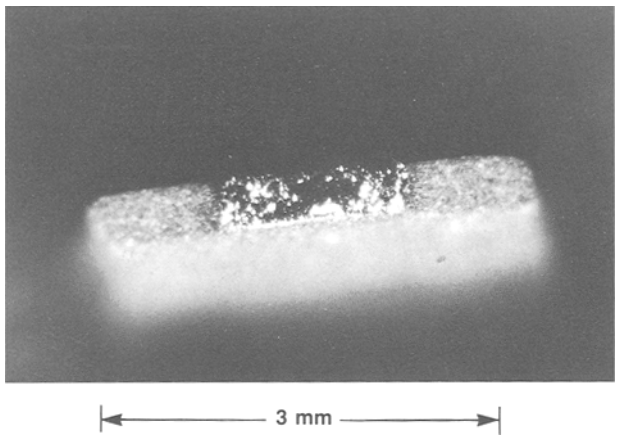

Fig. 3. A photograph of the lower half of the strip specimen taken after the rapid-heating experiment. The glassy appearance provides further evidence that the graphite specimen has undergone melting.

temperature in less than 20 ms by passing an electrical current pulse through it. The magnitude of the current pulse varied with experiment between approximately 150 and 400 A, yielding heating rates nominally in the range 2×10^5 to 4×10^5 K $\cdot$ s^{-1}.

Figure 2 presents an oscilloscope trace photograph in which the time variations of specimen radiance, as measured by the pyrometer in three pulse-heating experiments, are superimposed. For each experiment, the plateau in the radiance versus time function is reasonably well formed and is taken as evidence that the specimen has undergone melting. A glassy appearance of the remaining portion of the melted "effective" specimen, as shown in Fig. 3, provides further evidence that melting has occurred.

Upon completion of the pulse-heating experiments, the pyrometer was calibrated under steady-state conditions with a tungsten-filament lamp which, in turn, had been calibrated by the Radiometric Physics Division at the National Institute of Standards and Technology (formerly the National Bureau of Standards). All temperatures reported in this work are based on the International Practical Temperature Scale of 1968 [6].

4. RESULTS

The variation of radiance (or brightness) temperature at 655 nm of a specimen with elapsed time, during a typical pulse-heating experiment, is presented in Fig. 4. The horizontal line indicates the plateau radiance

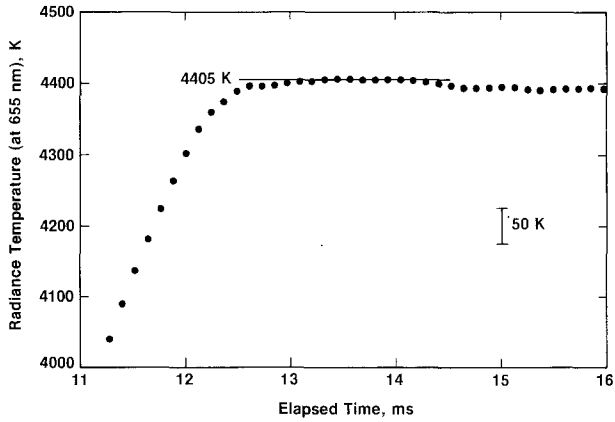

Fig. 4. Variation of radiance temperature (at 655 nm) of graphite just before and during melting as a function of elapsed time in a pulse-heating experiment. The straight line indicates the plateau radiance temperature.

temperature which, in all experiments, was taken as the maximum temperature along the initial flat portion of the plateau.

The results for plateau radiance temperatures determined from rapid melting experiments on the two different grades of POCO graphite under different conditions of pressure (14 and 20 MPa) are summarized in Fig. 5. As may be seen, the plateau temperatures increase approximately linearly with oxygen content in the pressurizing gas environment. The additional visible radiation being detected by the pyrometer is believed to be the result of exothermic (combustion) reactions of carbon (in vapor form and in the specimen surface) with oxygen [7]. Arguments given in Section 5 suggest that band spectra (e.g., Swan emissions from the C_2 vapor species, etc.) do not contribute significantly to the detected radiation, and therefore, radiance temperatures can be calculated from the measured radiances on the basis of Planck's law without serious error.

The results from experiments at the lower pressure (14 MPa; filled diamonds) appear to be in good agreement with those obtained at the higher pressure (20 MPa; open diamonds and filled circles). This indicates that melting temperature is only a weak function of total pressure in this range.

In order to account for the effect of oxygen on the results, the plateau radiance temperatures were fitted by a linear function of oxygen partial pressure (the solid straight line in Fig. 5) by means of the least-squares method. The function, when extrapolated to zero oxygen content, yields a value of 4328 K for the radiance temperature of melting graphite with a

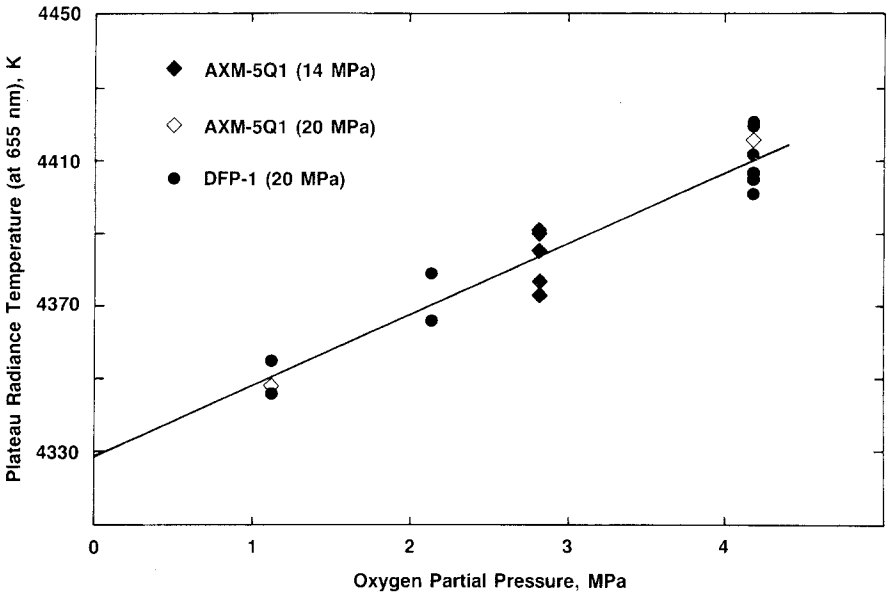

Fig. 5. Plateau radiance temperatures (at 655 nm) as a function of oxygen partial pressure obtained from rapid-melting experiments on two grades (AXM-5Q1 and DFP-1) of POCO graphite in a pressurizing argon/oxygen gas mixture at total pressures of 14 and 20 MPa.

statistical uncertainty of ± 5 K. Taking into account possible systematic and random errors (Section 5), we obtain a value of 4330 ± 50 K for the radiance temperature (at 655 nm) of melting graphite near its triple point.

5. ESTIMATE OF ERRORS

The major sources of error in the temperature data arise from (1) calibration and operation of the pyrometer and (2) physical and chemical conditions of each specimen and its environment.

A detailed analysis of sources and magnitudes of the errors in temperature measurements with high-speed pyrometry is given in an earlier publication [4]. Allowing for differences between present operational conditions and those in the earlier study, we estimate the maximum (random plus systematic) error attributable to pyrometry to be about ± 25 K.

The errors arising from conditions of the specimen and its environment are considerably more difficult to assess. The combustion reaction of carbon vapor with oxygen is known to produce emission spectra [8] which lie within the passband of our pyrometer (30 nm centered at 655 nm),

namely, the triplet bands of CO at 640.1, 643.3, and 646.5 nm and a Swan system of bands at 644.2, 648.1, 653.4, 659.9, and 667.7 nm from the C_2 vapor species [9]; there apears to be little difference in band spectra whether the carbon vapor is produced by resistance heating or by arc heating of the graphite [8].

In the present work, the very strong (blackbody) radiance from the resistively heated specimen is expected to mask completely the carbon vapor emission spectra within the passband of our pyrometer. The masking effect can be seen in the results of detailed measurements [10] of the spectral radiance from the anode of a graphite arc (operated in air). The results show that, in the spectral region from 570 to 850 nm, the arc radiance is equal to that of a blackbody radiator (at 3792 K) to well within experimental error. Although band spectra were observed at shorter wavelengths, no evidence of the CO triplet bands can be seen in the graphite arc data. A Swan system at 554.1, 558.6, and 563.6 nm (intensity ~ 8 times that of the above-mentioned system) can be identified but the peaks are only about 2% above the blackbody continuum, which explains why the weaker system in the region 644.2 to 667.7 nm was not observed. This suggests that the relative contribution of band spectra to the measured radiance in the present work may be even smaller, i.e., negligible, due to (1) the suppression of carbon vapor (hence the C_2 species) by the high speed of our experiments and (2) the stronger radiance from our specimens (at 4330 K rather than at 3792 K).

A measure of variability in the conditions of each specimen and its environment is given by the maximum range of plateau radiance temperature observed for a given oxygen content (see Fig. 5), which yields a random uncertainty of about ± 15 K. If possible systematic uncertainties arising from conditions of the specimen and its environment are included, then the total random plus systematic error (due to all sources including pyrometry) in the reported radiance melting temperature is estimated to be not larger than ± 50 K.

6. CONCLUDING REMARKS

Measurements of the radiance (or brightness) temperature of graphite in the vicinity of its triple point have been described. The results of experiments on two different grades of POCO graphite (AXM-5Q1 and DFP-1) at different gas pressures (14 and 20 MPa) are in good agreement and yield a value of 4330 ± 50 K for the radiance temperature at 655 nm of melting graphite near its triple point. The present work indicates that the melting temperature of graphite is only weak function of pressure, in agreement with other measurements [11] which yield a pressure coefficient for

melting temperature of about 2×10^{-7} K · Pa^{-1}, and therefore the present value of 4330 K can be assigned to the triple-point pressure (~ 10 MPa) without serious error (about -2 K or less).

The corresponding true (blackbody) temperature at the triple point can only be estimated, however, since there appears to be no literature data on normal spectral emittance of graphite at temperatures near the triple point. A data compilation on thermal radiative properties [12] indicates that reported values for normal spectral emittance (between 650 and 665 nm) of nonpyrolytic graphite lie in the range 0.8 to 0.9 at 1500 K and decrease very slowly with increasing temperature. By extrapolating the trend in values beyond the highest reported temperature (~ 3300 K) to temperatures approaching the triple point, we estimate the normal spectral emittance (at 655 nm) of graphite at its triple point to be about 0.8 ± 0.1. On this basis and the present value for radiance temperature (4330 ± 50 K), the true triple-point temperature of graphite is estimated to be 4530 ± 150 K.

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