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Thermophysical properties of POCO AXF-5Q graphite up to melting

G. Pottlacher,[a] R.S. Hixson,[b] S. Melnitzky,[a] E. Kaschnitz,[a] M.A. Winkler,[b] and H. Jäger[a]

[a] *Institut für Experimentalphysik, Technische Universität Graz, Petersgasse 16, Graz, A-8010, Austria*

[b] *Los Alamos National Laboratory, Los Alamos, NM, USA 87545*

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ABSTRACT

Measurements of the thermophysical properties of a particular POCO graphite (AXF-5Q) have been made up to melting. Results were obtained in two different laboratories using two heating rates. Data for temperature, volume, enthalpy, and electrical resistivity are shown. The measured melting point was found to be 4900 K ± 200 K.

INTRODUCTION

The melting temperature of carbon has been the subject of much recent work, but is still poorly known. The melting point of most metallic elements are typically known to a few Kelvin, but there is still an uncertainty of about 1000 K for carbon. Current experimental results for the melting point fall roughly into two groups, those at ~4000 K and those at ~5000 K. Values of 4000 K– 4400 K are typically found by flash-heating and laser-heating techniques, while resistive pulse-heating experiments yield results in the 4500-K to 5000-K range. Shown in Table 1 are a summary of measured melting points for graphite as found in the literature for flash and laser heating techniques. Results from resistive pulse-heating experiments are given in Table 2. A detailed discussion of previous results has been given by Ronchi et al. (1992).

Because of the uncertainties in the thermophysical properties of carbon, experiments have been performed on POCO graphite. These measurements were done as a collaborative effort between two different laboratories, but using samples from the same source, and, therefore, with identical properties. POCO graphite AXF-5Q was chosen for its fine grained composition, and its high mechanical strength.

TABLE 1

Summary of values for the melting temperature of various kinds of carbon reported by different authors, for flash and laser heating techniques.

Author	T(K)	p(bar)
Basset (1939)	4000	100
Bundy (1963)	4100	9,000
	4100	125,000
Diaconis (1971)	4100–4300	102
Gokcen (1976)	4130	120
Heremans (1988)	4450	1
Malvezzi (1986)	3900	1
Ronchi (1992)	4100 ± 50	110
Schoessow (1968)	4180 ± 4300	100
Steinbeck (1990)	4450	–
Venkatesan (1984)	4300	–
Vereshchagin (1977)	4035	100

TABLE 2

Melting temperatures found by resistive pulse heating methods.

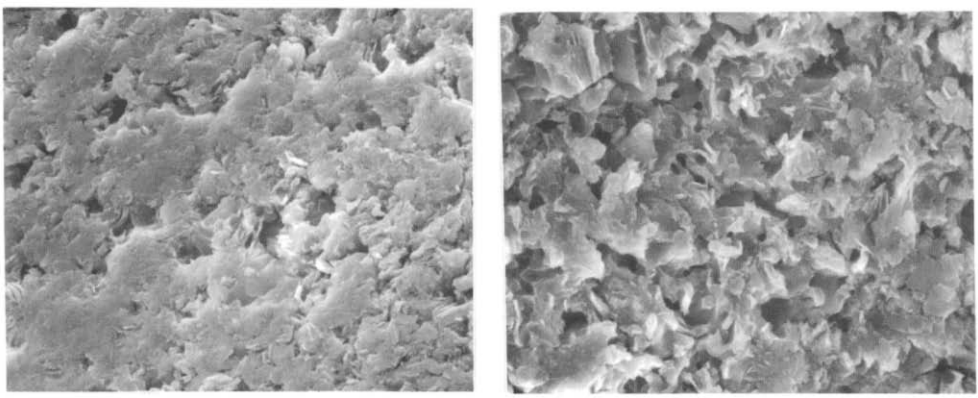
Author	T(K)	p(bar)
Bundy (1963)	4600	70,000
Baitin (1989)	5080	100
Cezairliyan (1990)	4530 ± 150	100
Kirillin (1985)	5050	110
Scheindlin (1988)	>4700	100
Shaner (1984)	4800	4,000
Vereshchagin (1977)	5010	50,000
This work	4900 ± 200	3,000

EXPERIMENTAL DETAILS

Samples from the same batch of POCO AXF-5Q graphite (ρ_o = 1.83 g.cm^{-3}) have been studied in two different laboratories using experimental techniques that allow heating at nanosecond and microsecond rates. Wire-shaped samples (1-mm diameter, 20-mm length) were resistively self-heated by passing large electrical currents through them in a high-pressure medium. The heating currents are produced by capacitor banks, with charging voltages varied between 10 kV to 20 kV. Current through the sample and voltage along the sample are measured, together with optical measurements of temperature and of volume expansion. Experiments are performed in high-pressure vessels, with windows allowing optical diagnostics. For this

work, pressures to 3000 bar have been used with both argon and water as the pressure medium.

In order to characterize the samples microscopically, photographs of the surface and the interior of a sample were made with a scanning electron microscope. In Fig. 1a is shown a photograph of the sample surface, magnified by a factor of 2020. A similar photograph of the interior of a cut sample is shown in Fig. 1b. Irregularities in the structure are observed indicating that while the material appears to be homogeneous on a macroscopic scale, microscopic inhomogeneities exist. Measurements of sample impurities were made with an energy dispersive x-ray spectrometry system, and show less than a 0.1% concentration of Cl, K, and Fe.



(a) (b)

Fig. 1. a) Photomicrograph of the surface of a POCO graphite sample magnified by a factor of 2020. b) Photomicrograph of an interior slice of a POCO graphite sample also magnified 2020 times.

Measurements were made on a microsecond timescale at Los Alamos (Hixson, 1990), and on both a microsecond and nanosecond timescale at Graz (Kaschnitz, 1992; Pottlacher, 1987). Details for these systems may be found in the above references. One major difference in the experiments at the two different laboratories is that at Los Alamos argon gas is used as the pressure medium while at Graz, water is used.

Temperature Measurements

Temperatures are measured using radiation pyrometers with fast PIN photodiodes at both laboratories. For the measurements at Graz, temperature is determined usiug the radiation intensity of the melting plateau of a tungsten sample of the same dimensions, and at the same exact location as the graphite sample as a calibration tie poiut. Temperatures may then be found

using the Kirchoff-Planck law by forming ratios of the radiance at unknown temperature T to that at the tungsten melt point $T_{m,\omega}$. At the melting point of tungsten, the pyrometer detects a constant radiance with intensity

$$J_{m,\omega}(T_{m,\omega}) = \frac{g \cdot \varepsilon(\lambda, T_{m\omega}) \cdot C_1}{\lambda^5 \cdot \left[\exp(C_2/\lambda \cdot T_{m,\omega}) - 1\right]} \quad , \tag{1}$$

where $T_{m,\omega}$ is the melting temperature of tungsten, g is a geometric factor, $\varepsilon(\lambda, T_{m,\omega})$ is the normal spectral emissivity of tungsten at its melting temperature, and C_1 and C_2 are radiation constants. The spectral emissivity value of Cezairliyan (1992) is chosen for the melting point of tungsten, with $\varepsilon(\lambda, T_{m,\omega}) \approx 0.38$ for $\lambda = 800$ nm. The radiation intensity of a graphite sample at temperature T is given by

$$J(T) = \frac{g \cdot \varepsilon(\lambda, T) \cdot C_1}{\lambda^5 \cdot \left[\exp(C_2/\lambda \cdot T) - 1\right]} \quad . \tag{2}$$

The value of $\varepsilon(\lambda, T)$ for graphite is taken to be 0.8 (Cezairliyan, 1990). Using Eqs. (1) and (2) and forming ratios of intensities, the temperature is calculated from:

$$T = C_2/\lambda \cdot \ln\left\{1 + \frac{\varepsilon(T)}{\varepsilon(T_{m,\omega})} \cdot \frac{J_{m,\omega}(T_{m,\omega})}{J(T)} \cdot \left[\exp\left(C_2/\lambda \cdot T_{m,\omega}\right) - 1\right]\right\} \quad . \tag{3}$$

The ratio of emissivities is assumed to be constant over our measured temperature range.

In the Los Alamos experiment, temperatures are also found using the Kirchhoff-Planck law, but using an extrapolated tie point rather than a melting thermal arrest. We take $T = 3000$ K for an enthalpy value of 5.027 MJ.kg^{-1} found by extrapolating the recommended values of Hultgren (1973). Temperatures are calculated from measured radiation intensities by forming ratios of intensity at temperature T to that at the tie point. Measurements are made at a wavelength of 700 nm. The assumption is made that the emissivity of graphite is constant, independent of temperature.

Enthalpy

Electrical current through the sample, together with voltage along the sample are measured on each experiment. From these data we may calculate enthalpy from

$$H(t) - H_o = \frac{1}{m} \int_{to}^{t} I(t) V(t) dt \tag{4}$$

where $I(t)$ and $V(t)$ are the measured current and voltage values, and m is the sample mass between voltage probes. H_o is the enthalpy of the reference state at $P = 3$ kbar and $T = 293$ K.

Electrical Resistivity and Volume

The measured currents and voltages are used to calculate electrical resistivity:

$$\rho_o(t) = \frac{V(t)A_o}{I(t)l} \tag{5}$$

Here A_o is the initial cross-sectional area of the sample, and l the length between voltage probes. The resistivities calculated using (5) are not corrected for the changing volume of the sample. More accurate results for resistivity are found if the changing radius, or cross-sectional area of the sample is measured or known. Then

$$\rho(t) = \rho_o(t)\frac{r(t)^2}{r_o(t)^2} \quad , \tag{6}$$

where $\frac{r}{r_o}$ is obtained from the volume measurement.

Volumes are measured quite differently in the two laboratories. At Graz, snapshots are taken at discrete times using a fast camera system with a Kerr cell shutter. At Los Alamos, however, volumes are found using a shadowgraph technique combined with an image-converter streaking camera. This system yields continuous volume data as a function of time.

RESULTS

Measured values for the quantities discussed above for both laboratories are presented here together with selected literature values.

Temperature

Using the temperature calculation schemes discussed in the previous section comparable values of temperature versus time are obtained, as shown in Fig. 2.

From Fig. 2 it may be seen that under similar heating conditions the Graz experiment detects the onset of melt at about 40 μs, and the Los Alamos experiment finds the beginning of melt at about 36 μs. Both experiments show a melt temperature at about 4900 $\pm$ 200 K. This value compares favorably with those found in Table 2 for other pulse heating experiments.

Measured temperatures are shown plotted against enthalpy in Fig. 3. Also shown in Fig. 3 are the least square fits to the data of Graz, Los Alamos, and Baitin (1990). The best fits to our data are given by

$$H = 2.064 \times 10^{-3}\ \mathrm{T} - 1.853 \tag{7}$$

for the Los Alamos data for 2840 K $\leq$ T $\leq$ 4775 K, and

$$H = 2.641 \times 10^{-3}\ \mathrm{T} - 3.923 \tag{8}$$

for the Graz data with 3000 K $\leq$ T $\leq$ 4900 K. For comparison, the fit given by Baitin (1990) is

$$H = 2.488 \times 10^{-3}\ \mathrm{T} - 2.409 \quad , \tag{9}$$

for 3400 K $\leq$ T $\leq$ 5080 K. In Eqs. 7, 8, and 9, H is in MJ $\cdot$ kg^{-1}. The fit given here for the Graz data is for the slow (microsecond) experiment. Results from the fast (nanosecond) experiment are comparable to those from the slow experiments.

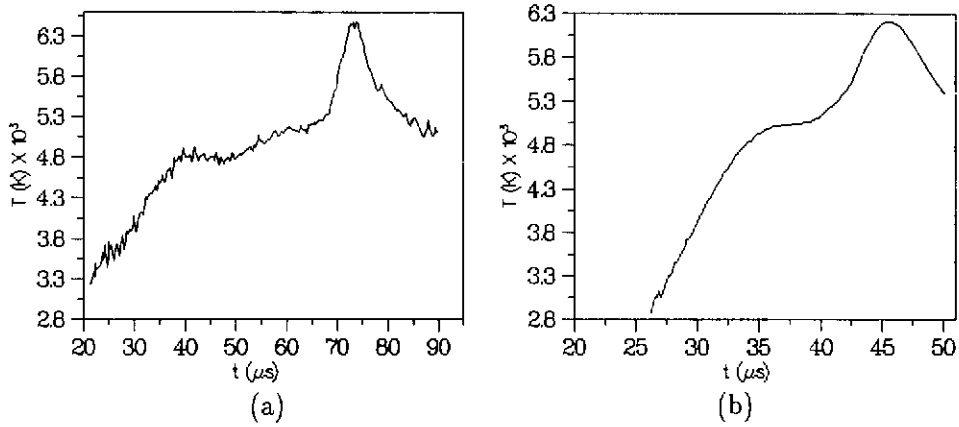


Fig. 2. a) Temperature versus time data from the slow Graz experiment (single shot). b) Similar results obtained with the Los Alamos experiment (single shot).

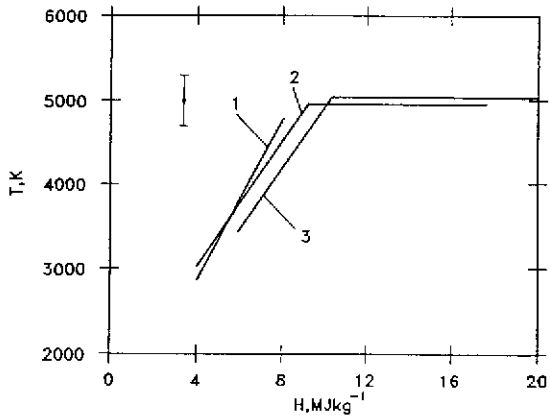


Fig. 3. Temperature versus enthalpy. (1) Los Alamos data, (2) Graz data, and (3) Baitin et al. (1990).

Temperature uncertainties of ±200 K are estimated for our measurements, reflected in the error bar shown on Fig. 3. Besides the obvious difference in slopes for the Graz and Los Alamos experiments, results are in reasonable agreement. The values of Baitin (1990) show higher enthalpy values after melt.

These measurements allow a rough estimate of the heat of fusion to be made, and this value was ~9 MJ · kg^{-1} for the Los Alamos data, and ~8 MJ · kg^{-1} for the Graz slow experiment. These values compare favor-

ably with literature values of 8.69 MJ · kg^{-1} (Bundy, 1963), 10.4 MJ · kg^{-1} (Baitin, 1990), 8.7 MJ · kg^{-1} (Heremans, 1988), and 8.7 MJ · kg^{-1} (Steinbeck, 1990).

Our measurements show a linear dependence of temperature on enthalpy in the solid phase, as do the data of Baitin (1990). Specific heat values obtained from the fits given above differ by more than 20%, but this is within expected uncertainties. Values for C_p calculated from our data are compared to literature values in Table 3.

Table 3

Values of heat capacities of solid graphite for temperatures above 2500 K.

Author	C_p (J · kg^{-1} · K^{-1})	T(K)
Baitin (1990)	2488	3000–5080
Cezairliyan (1985)	2189	3000
Scheindlin (1988)	2664	4000
	3107	4500
Taylor (1980)	2168	2500
Van Thiel (1992)	2435	5000
	2331	4000
This work		
Los Alamos	2064	2840–4775
Graz	2641	3000–4950

Volume

The best fit to our volume results are

$$V/V_o = 0.1522\ \mathrm{H} + 1.175 \tag{10}$$

for 0.125 ≤ H ≤ 8.5 MJ · kg^{-1} for the Los Alamos data, and

$$V/V_o = 0.0812\ \mathrm{H} + 1.0 \tag{11}$$

for 0.0 ≤ H ≤ 9 MJ · kg^{-1} for the Graz data.

Volumes obtained with the Los Alamos experiment are greater than those obtained at Graz. The reason for this is not clear, but may be related to the difference in pressure medium used. Volume streaks obtained in the Los Alamos experiment show some evidence for stability problems during expansion, especially at large expansions. This was probably to be expected since by the time graphite melts it is roughly two-fold expanded, and so is at a density of ~0.9 gm·cm^{-3}. This is lower than the density of either pressure medium used at 3 kbar. This means that a material with low density is expanding into a material with higher density, and so instability growth is probable. Exact details of growth rates are unknown, but the Los Alamos volume streaks show that they may occur on a microsecond time scale. Because of the initial mi-

croscopic irregularities in the structure of the samples, as well as the scatter shown in our volume records an uncertainty of at least ±10% is taken for volumes.

Electrical Resistivity

Results for electrical resistivity are shown plotted against enthalpy in Fig. 4a. and temperature in Fig. 4b. Also shown literature values, and large scatter is evident. Literature values do not appear to be volume corrected, and this would explain some of the disagreement. In Fig. 4 all Los Alamos data shown were taken on a microsecond time scale, and Graz data were taken on both microsecond and nanosecond time scales.

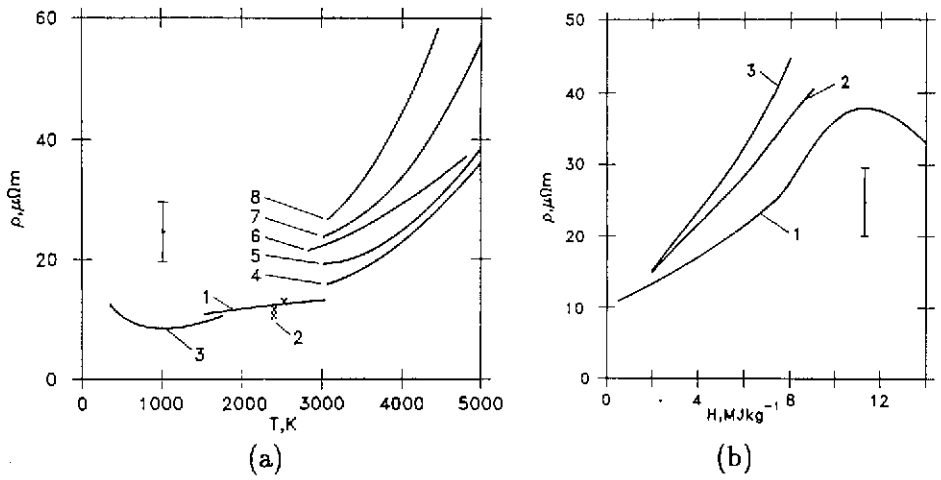


Fig. 4. a) Resistivity plotted versus enthalpy for: 1) Microsecond Graz data (not volume corrected), 2) Los Alamos data (volume corrected), 3) Microsecond Graz data (volume corrected). b) Resistivity plotted versus temperature. Shown are the data of 1) Cezairliyan and Miiller (1985), 2) Taylor et al. (1980), 3) Dobrosavljevic et al. (1987), 4) nanosecond Graz experiment (no volume correction), 5) microsecond Graz experiment (no volume correction), 6) Los Alamos, 7) microsecond Graz data, and 8) nanosecond Graz data.

There are many possible explanations for the observed scatter in resistivity data for carbon. One possibility is that the samples are being inhomogeneously heated, as discussed by Lebedev and Savvatimskii (1986). Inhomogeneous heating would lead to nonuniform expansion, and thus large error bars on both volumes and resistivities. Since the samples showed evidence for microscopic inhomogeneities, and the volume data showed scatter, it is very likely that this is the case. Errors are estimated at ±10–20% for our measured resistivities.

Our measured values, and other values found in the literature from similar pulse-heating techniques have scatter, but these disagreements are minor compared to some other measured values. The work of Heremans (1988) and

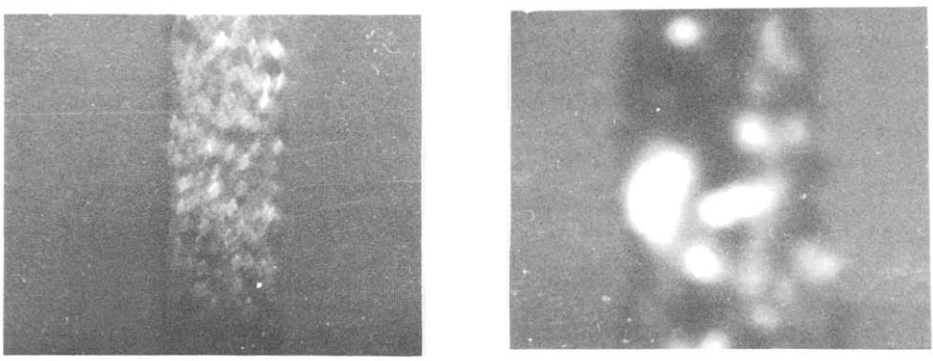
Steinbeck (1990) show values of 30 ± 8 $\mu\Omega$·cm at T~4450 K. At this temperature our results are at least 100 times greater. The cause for this rather large discrepancy has not been found. The best fits to our data are

$$\rho_{el} = 0.1322\ H^2 + 2.2082\ H + 10.3066 \quad (12)$$

for the Los Alamos data with $0.881 \leq H \leq 8.05$ MJ·kg^{-1}, and

$$\rho_{el} = 0.5267\ H^2 - 0.3933\ H + 14.76 \quad (13)$$

for the Graz data with $2.0 < H \leq 9.15$ MJ·kg^{-1}. The volume corrected resistivities of Los Alamos and Graz show reasonable agreement.



(a) (b)

Fig. 5. a) Photograph of a pulse-heated graphite sample above melt, enlarged 10 times. b) Photograph similar to (a), but enlarged 20 times.

DISCUSSION

Results are presented here on thermophysical properties of solid POCO AXF-5Q for temperatures from 3000 K up to melting. Results from both laboratories are in generally good agreement. The measured results are in general agreement with some literature values. Results found by various experimental groups were obtained using a variety of experimental techniques, and obtained using a variety of sample materials, and show a large amount of scatter. More work is required to determined if choice of sample material, heating technique, or heating rate influences results.

Above the melting point the data exhibited a large amount of scatter. From one experiment to another the measured values of C_p could vary by over 50%. This behavior was observed at both laboratories. Experiments at Graz showed evidence for hot spots, or heating inhomogeneities above the melt point. A hot spot is formed when a small volume of the sample is heated to a temperature above the bulk of the material. The resistivity of carbon increases with increasing temperature for T > 1000 K, (Taylor, 1980), and so,

as a hot spot forms, it will heat more rapidly than the surrounding material, and an unstable situation exists. Photographs shown in Fig. 5 show clear evidence for this behavior. Such heating inhomogeneities, combined with the instability formation discussed above, will cause results to be irreproducible.

From Fig. 5 it may be seen that the distribution of hot spots appears to be similar to the initial structure observed on the sample surface.

One primary conclusion of this work is that POCO graphite does not seem to be well suited to our pulse-heating techniques above melting, since it was not possible to obtain reliable data in the liquid phase.

Our measured melt point for the graphite in this investigation was 4900 K ± 200 K. This compares well with values between 4500 K and 5000 K as found in the literature for pulse-heating experiments.

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