

TITLE THERMOPHYSICAL PROPERTIES OF POCO AXF-5Q GRAPHITE UP TO MELTING

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

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ABSTRACT

Measurements of the thermophysical properties of a particular POCO graphite (AXF-5Q) have been made up to melting. We obtained results in two different laboratories using two heating rates. We present data for temperature, volume, enthalpy, and electrical resistivity. Our measured melting point was found to be $4900 \text{ K} \pm 200 \text{ K}$.

I. INTRODUCTION

The melting temperature of carbon has been the subject of much recent work, but is still considered to be poorly known. This is true in spite of improved experimental techniques available today. The melting point of most metallic elements are typically known to a few kelvins, but there is still an uncertainty of about 1000 K for carbon. Current experimental results for the melting point fall almost into two groups, those at $\sim 4000 \text{ K}$ and those at $\sim 5000 \text{ K}$. Values of 4000 K–4400 K are typically found by flash-heating and laser-heating techniques, while wire pulse-heating experiments yield results in the 4500-K to 5000-K range. In Table 1 we show a summary of measured melting points for graphite as found in the literature. A detailed discussion of previous results has been given by Ronchi et al. (1992).

Values for electrical resistivity and heat capacity of carbon above 3000 K are very scarce, and the results seem to depend upon the material used.

Because of the uncertainties in the thermophysical properties of carbon, we have performed measurements 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 relatively homogeneous composition, and its high mechanical strength.

Table 1

Summary of values for the melting temperature of carbon reported by different authors, static pressure indicated.

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
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

II. EXPERIMENTAL DETAILS

Sample from the same batch of POCO AXF-5Q graphite ($\rho_o = 1.83 \text{ g.cm}^{-3}$) 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 come from capacitor banks, with charging voltages varied between 10 kV to 20 kV. Current through the sample and voltage along the sample are measured, along 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 as well as possible, we have made photographs of the surface and the interior of a sample with a scanning electron microscope. In Fig. 1a we show a photograph of the sample surface, magnified by 2020 \times . We show a similar photograph of the interior of a cut sample in Fig. 1b. Irregularities in the structure are observed. Measurements of sample impurities were made with an energy dispersive x-ray spectrometry system, and show less than a 1% concentration of Cl, K, and Fe.

Measurements were made on a microsecond timescale at Los Alamos (Hixson, 1990), and on both a microsecond and nanosecond timescale at Graz (Kaschnitz, 1991; 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.

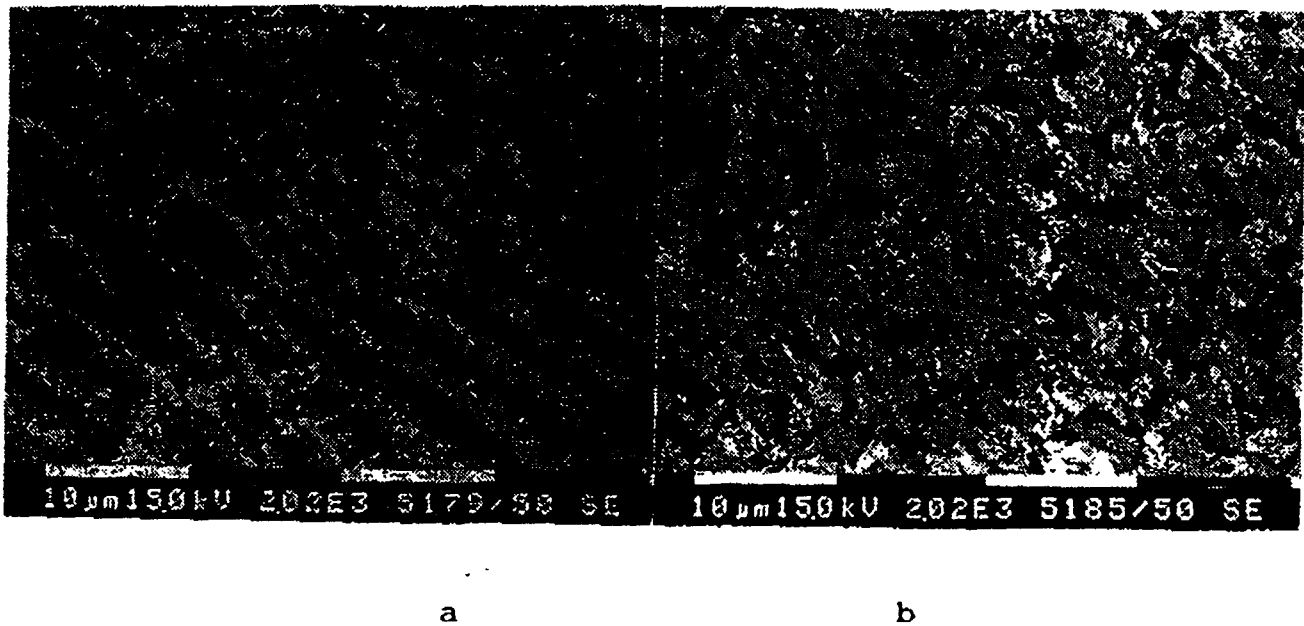


Fig. 1. a) Photomicrograph of the surface of a POCO graphite sample. b) Photomicrograph of an interior slice of a POCO graphite sample.

II.1. Temperature Measurements

Temperatures are measured using radiation pyrometers at both laboratories. For the measurements at Graz, temperature is found using 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. 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

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

where $T_{m,\omega}$ is the melt temperature of tungsten, g is a geometric factor, $\epsilon(\lambda, T_{m,\omega})$ is the spectral emissivity of tungsten at its melt temperature, and C_1 and C_2 are radiation constants. Here we take $\epsilon(\lambda, T_{m,\omega}) = 0.38$ and $\lambda = 800$ nm (Cezairliyan et al., 1992). The intensity of radiation of a graphite sample at temperature T is given by

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

Here we have taken $\epsilon(\lambda, T)$ for graphite to be 0.8 (Cezairliyan, 1990). Using Eqs. (1) and (2) and forming ratios of intensities, we obtain an expression for temperature.

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

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 Kirchoff-Planck law, but using an extrapolated tie point. We assume $T = 3000$ K for an enthalpy value of 5.027 MJ.kg⁻¹ found by using the recommended values of Hultgran et al. (1973). The temperatures are calculated from measured radiation intensities by forming ratios of intensity at temperature T to that at the graphite melt point T_m . Measurements are made at a wavelength of 700 nm. The assumption is made that the emissivity of graphite is constant, independent of temperature.

II.2. Enthalpy

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

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

where $I(t)$ and $V(t)$ are the measured current and voltage arrays, and m is the sample mass. H_o is the enthalpy of the reference state.

II.3. Electrical Resistivity and Volume

The measured currents and voltages also may be used to calculate electrical resistivity:

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

Here A_o is the initial cross-sectional area of the sample, and l the length. The resistivities calculated using (6) 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 we form

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

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, 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.

III. RESULTS

Measured values for the quantities discussed above for both laboratories will be presented here along with selected literature values.

III.1. Temperature

Using the two previously discussed temperature calculation schemes, we obtain very comparable values of temperature versus time, presented in Fig. 2a,b.

From Fig. 2 it may be seen that under similar heating conditions the Graz experiment detects the onset of melt at about 36 μ s, and the Los Alamos experiment finds the beginning of melt at about 40 μ s. Both experiments show a melt temperature at about 4900 ± 200 K. This value compares favorably with those found in Table 1.

Our measured temperatures may be plotted against enthalpy as shown in Fig. 3.

Shown in Fig. 3 are the least square fits to the data of Graz, Los Alamos, and Baitin et al. (1989). Our fits are given by

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

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

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

for the Graz data with $3000 \text{ K} \leq T \leq 4900 \text{ K}$. The fit given by Baitin et al. is

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

for $3400 \text{ K} \leq T \leq 5080 \text{ K}$. The fit given here for the Graz data is for the slow (microsecond) experiment. Results from the fast (nanosecond) experiment have the same slope as the slow experiment, but shifted to somewhat higher enthalpy values. We assume that the fast experiment may not be heating the sample homogeneously.

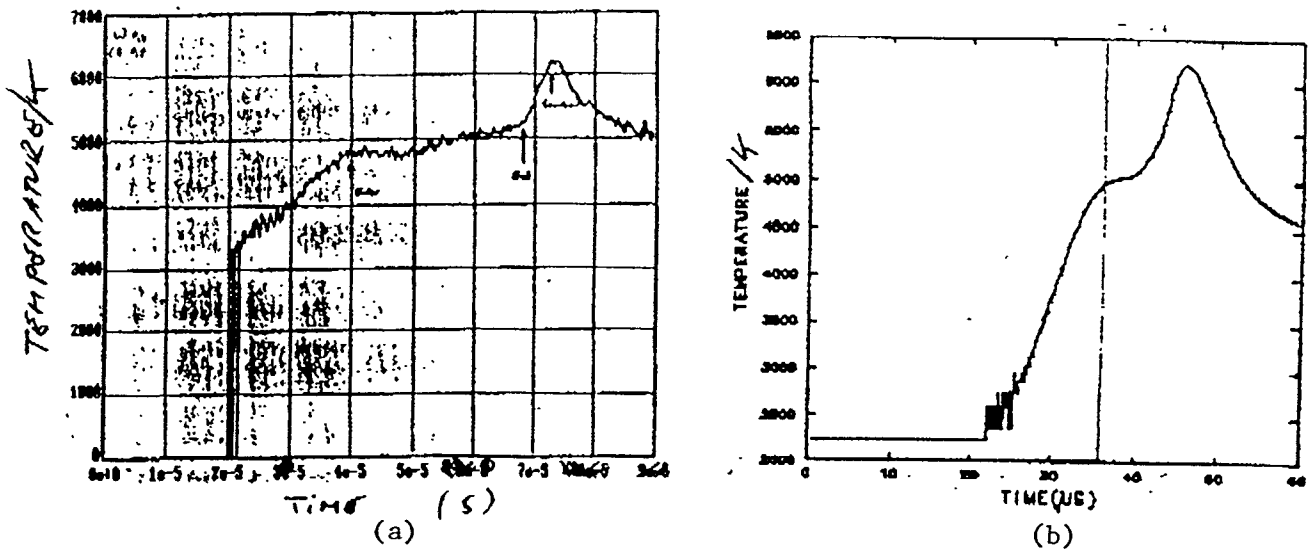


Fig. 2. a) Temperature versus time obtained with the slow Graz experiment (single shot). b) Temperature versus time obtained with the Los Alamos experiment (single shot).

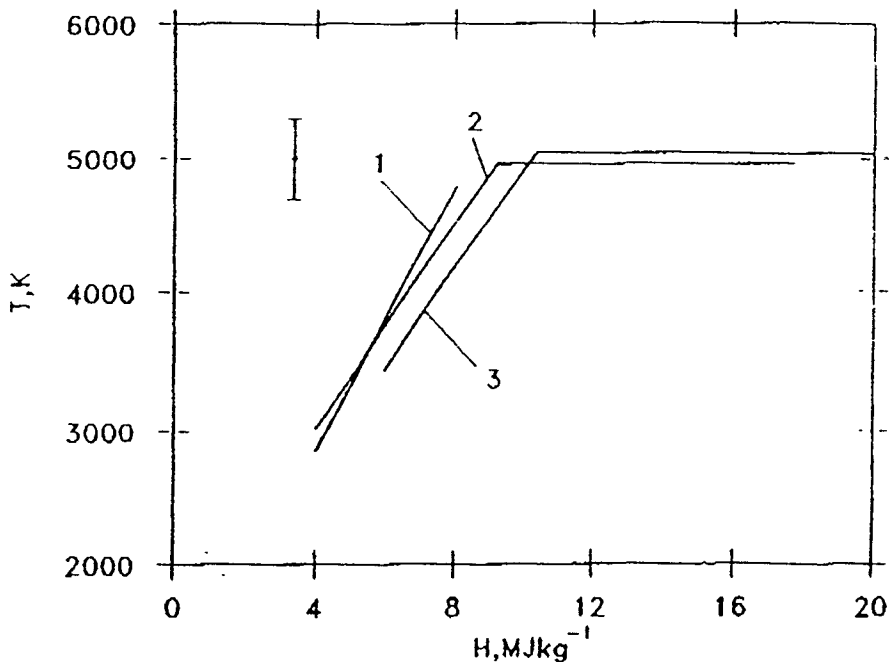


Fig. 3. Temperature versus enthalpy. (1) Los Alamos data, (2) Graz data, and (3) Baitin et al. (1989).

We take an uncertainty of $\pm 200 \text{ K}$ for all of our measurements, error bars that appear to be well justified by looking at Fig. 3. Besides the obvious difference in slopes for the Graz and Los Alamos experiments, our results are in good agreement. The values of Baitin et al. show higher enthalpy values after melt, but they used higher-density graphite samples, with $\rho_0 = 2.25 \text{ g} \cdot \text{cm}^{-3}$.

Our measurements allow a rough estimate of the heat of fusion to be made. This value and other literature values are shown in Table 2.

Table 2

Summary of values for the enthalpy of melting of carbon, reported by different authors (p ambient pressure).

Author	ΔH (MJ \cdot kg $^{-1}$)	p (bar)
Bundy (1963)	8.69	48,000
Baitin (1989)	10.4 ± 0.4	100
Heremans (1988)	8.7	–
Steinbeck (1990)	8.7	–
This work		
Los Alamos	>9	3,000
Graz	>8	3,000

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

Table 3

Values of heat capacities of solid graphite for temperatures above 2,000 K, reported by different authors.

Author	C_p (J \cdot kg $^{-1}$ \cdot K $^{-1}$)	T(K)
Baitin (1989)	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

III.2. Volume

The best fit to our results for volume are

$$V/V_o = 0.1522 H + 1.175$$

for $0.125 H \leq 8.5$ MJ \cdot Kg $^{-1}$ for the Los Alamos data. Results for the Graz data are

$$V/V_o = 0.0812 H + 1.0$$

for $0.0 \leq H \leq 9$ MJ \cdot kg $^{-1}$.

The 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 at a density of $\sim 0.9 \text{ gm}\cdot\text{cm}^{-3}$. 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 our streaks show that they may occur on the time scale of our microsecond experiment. Because of the initial irregular structure of the samples, as well as the scatter shown in our volume records and the possibility of inhomogeneous heating, we must assume an uncertainty of at least 10% for volumes.

III.3. Electrical Resistivity

Our results for electrical resistivity are shown in Fig. 4a and 4b, plotted against enthalpy and temperature, respectively. Also shown are other values found in the literature, with a large scatter evident.

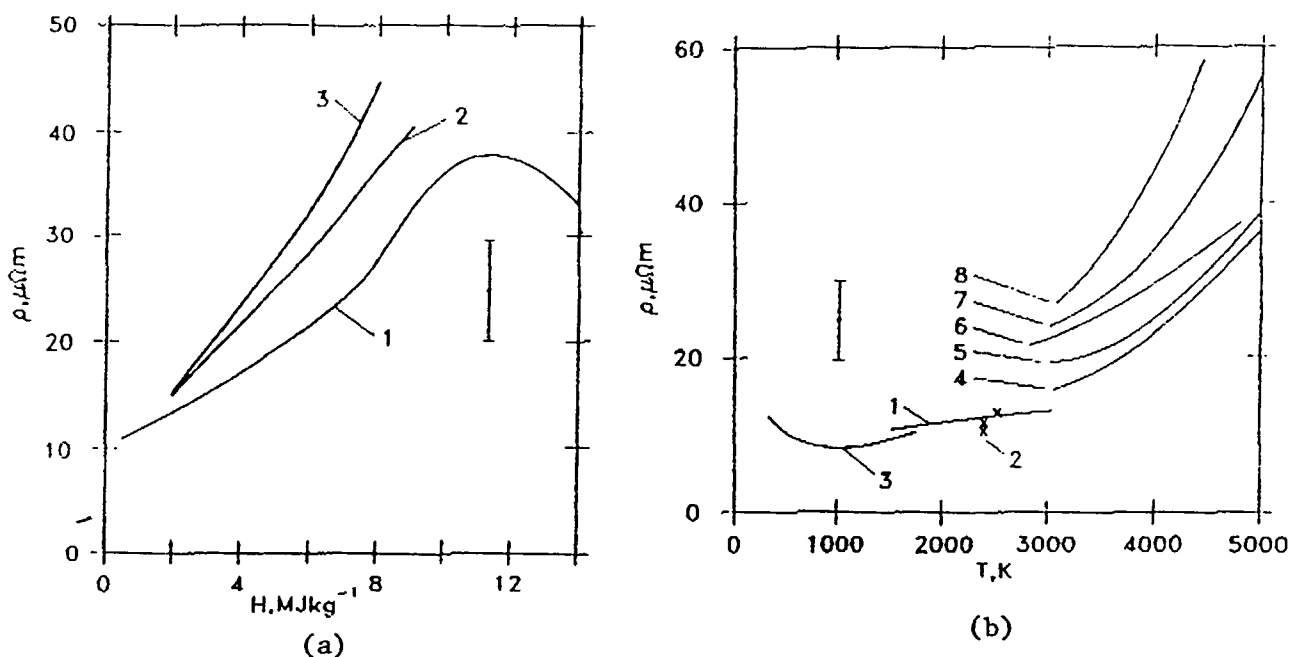


Fig. 4. a) Resistivity plotted versus enthalpy. 1) Graz data (not volume corrected), 2) Los Alamos data (volume corrected), 3) Graz data (volume corrected). b) Resistivity plotted versus temperature. Shown are the data of 1) Cezairliyan and Miller (1985), 2) Taylor et al. (1980), 3) Dobrosavljevic et al. (1987), 4) fast Graz experiment (no volume correction), 5) slow Graz experiment (no volume correction), 6) Los Alamos, 7) slow Graz data, and 8) fast 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 above and mentioned by Lebedev and Savratimskii (1986). Inhomogeneous heating would lead to nonuniform expansion, and thus large error bars on both volumes and resistivities. Errors are estimated at 10–20% for our measured resistivities.

Our measured values, and other values found in the literature from pulse-heating techniques have much scatter, but these disagreements are minor compared to some other measured values. The work of Heremans et al. (1988) and Steinbeck et al. (1990) show values of $30 \pm 8 \mu\Omega\cdot\text{cm}$ at $T \sim 4450$ K. At this temperature our results are at least 100 times greater. The cause for this rather large discrepancy is explained by Heremans et al. (1988) by the existence of two liquid phases, one conducting and one insulating. We observe no evidence

supporting this possibility.

The best fits to our data are

$$\rho = 0.1322 H^2 + 2.2082 H + 10.3066$$

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

$$\rho = 0.5267 H^2 - 0.3933 H + 14.76$$

for the Graz data with $2.0 < H \leq 9.15 \text{ MJ}\cdot\text{kg}^{-1}$. The volume corrected resistivities of Los Alamos and Graz show reasonable agreement. Better agreement between laboratories is typically found when working with metallic samples.

IV. DISCUSSION

We have reported here results on thermophysical properties of solid POCO AXF-5Q for temperatures from 3000 K up to melt. Results from both laboratories are in generally good agreement. Our measured results are in reasonable agreement with literature values.

Above the melting point we obtained data that 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. 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.

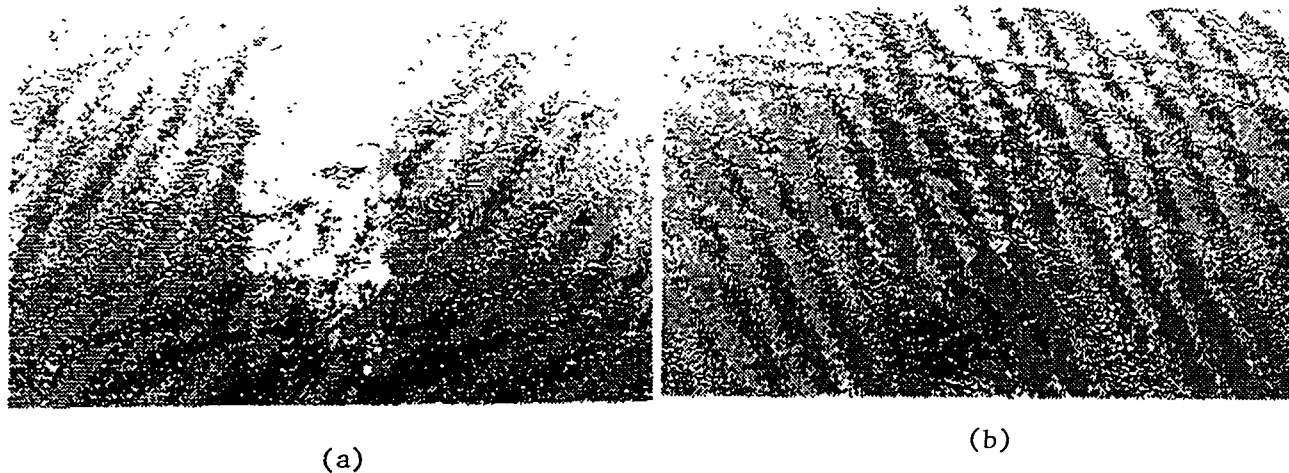


Fig. 5. a) Photograph of a pulse-heated graphite sample above melt, enlarged 10 times. b) Photograph similar to (a), but enlarged 20 times.

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

One primary conclusion of this work is that POCO graphite does not seem to be well suited to pulse-heating techniques above melting. We were unable to obtain reliable data in the liquid phase.

Our measured melt point for the graphite in this investigation was $4900 \text{ K} \pm 200 \text{ K}$. This compares well with results from other pulse-heating experiments. Values between 4500 K and 5000 K are found in the literature for other pulse-heating experiments. The uncertainty in melt point for carbon is found to be much greater than for metals.

In conclusion, we believe that the results for thermophysical properties of carbon seems to depend on the exact material used, as well as on the experimental technique used.

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