Experimental investigation of linear thermal expansion of pyrolytic graphite at high temperatures

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Abstract. Using the previously described [1] experimental setup for investigation of the thermophysical properties of refractory materials under high pressure and temperature a few experiments with pyrolytic graphite were carried out. The density of the material was equal to 2.18 g/cm³. Experimental data on the linear thermal expansion in the perpendicular and parallel to the basal plane direction were obtained. Thermal expansion in the perpendicular to the basal plane direction during the heating from room temperature up to the melting point was 16.4 ± 1.6%. The results obtained allow calculating the density of pyrolytic graphite in the wide range of high temperatures up to the melting point.

1. Introduction
There is no experimental data on isobaric thermal expansion of pyrolytic graphite in the temperature region above 3300 K in the literature at present. Meanwhile, such data are necessary for constructing wide-range equations of state for carbon, as well as working with pyrolytic graphite in this temperature range.

In this paper we propose a method for investigating the thermal expansion of dense graphites in the high-temperature region up to the melting point at pressures of about 1 kbar. Using this method, an isobaric linear expansion of pyrolytic graphite in the temperature range 3300-4800 K at a static pressure of 1 kbar was experimentally determined.

2. Peculiarities of graphite expansion in the high temperature region
Literature data on the coefficient of linear expansion of pyrolytic graphite in the high temperature range up to 3300 K are presented, for instance, in [2].

According to these data for a graphite crystal there is a large (about one order of magnitude) difference between the coefficient of linear expansion along and across the basal plane. This circumstance can cause mechanical destruction of the samples due to the appearance of thermomechanical stresses in them during their fast heating. To reduce this effect a movable collet allowing the sample to expand freely along its axial direction was used.

The existing experimental data on the volumetric expansion of graphite in the temperature range up to the melting temperature are either calculated [3, 4] or obtained in experiments in non-isobaric conditions, as in [5]. The difficulty of isobaric experiments with graphite is explained by the above-mentioned features, as well as by the active sublimation of carbon, which intensifies at the temperatures above 3000 K. Thereby it was required to develop an experimental technique that makes
it possible to obtain data on the thermal expansion of graphite materials in the temperature range 3300-5000 K.

3. Experimental technique
The developed method consists in fast heating of the sample to $T_m$ and above in a time of about 1-2 milliseconds due to homogeneous volumetric heat release when an electric current pulse of a large amplitude passes through it. Heating is carried out under isobaric conditions in a high-pressure chamber at a static pressure of a buffer inert gas (Ar) up to 2 kbar.

To measure the temperature of the sample, an original high-speed two-channel pyrometer based on spectral ratio method was developed. Spectral separation of thermal radiation from the sample is provided by a spectrometer realized on a spherical diffraction grating with optical filters. The temperature is measured in a narrow spectral range of about 25 nm in the wavelength region $\lambda_1 = 0.650 \mu m$ and $\lambda_2 = 0.862 \mu m$.

The size and therefore expansion of the sample is measured with the help of shadowgraphy and photographic registration of the incandescence of the heated sample. The general principles of this method are schematically depicted in figure 1.

![Figure 1. Simplified diagram of the photoregistration system.](image)

The system of photographic registration is based on a high-speed digital CCD camera "VideoSprint", implemented on a CMOS CCD sensor having a resolution of 1280x1024 pixels. The maximum capture frequency of the full frame is 500 Hz, the pixel size of the CCD array is 12x12 μm, and the dynamic range is 59 dB. The resulting 10-bit gray images allow using the methods for recognizing of the boundaries of a specimen with high accuracy and measuring the linear dimensions of samples with an accuracy of about 2-3 pixels. The camera has an external synchronization input that enables the measurement to start at a specified time or on a signal from the pyrometer when the sample reaches a certain temperature.

To eliminate the effect of optical distortions in the carbon vapors, a plate of K8 optical glass was placed above the surface of the graphite facing the camera. The thickness of the glass was 0.3 mm, and the dimensions were about 2 * 8 mm. The glass was located close to the sample surface, almost completely eliminating the image distortions caused by the carbon vapor. Nevertheless, in the area where the dimensions were measured, i.e. in the field of view of a high-speed video camera, there was no contact between the glass and the sample because of local optical distortions. This follows from the
fact that in several experiments the interaction between the heated sample and the glass is clearly visible on the frames, and it does not permit to measure the expansion of the sample. Using the camera, the distance between the glass surface and the sample was also evaluated to be equal to about 20 microns.

The processing of the obtained digital images was carried out by software, which made it possible to obtain data on the linear dimensions of the sample with an accuracy of one pixel. The sample boundaries were determined as a point of maximum of intensity derivative with respect to the coordinate.

4. Experimental data

Pyrolytic graphite with a density of 2.18 g/cm$^3$ was investigated. The properties of this material made it possible to measure thermal expansion up to the melting point without destroying the samples. Each graphite sample was a small parallelepiped with dimensions of about 1*1*10 mm, 46 experiments were carried out.

The samples were heated by a time of about 1.5 ms to the melting temperature, as evidenced by the melting plateau on thermograms. A typical heating thermogram is shown in Fig. 2. The brightness temperature of the melting point at the wavelength 650 nm was about 4500 ± 80 K for the c-surface. The true temperature was calculated from the brightness temperature under the assumption of a constant emissivity of material in the temperature range 3300-4800 K, the value of the emissivity was taken from the article [6].

![Figure 2](image.png)

**Figure 2.** Typical dependence of the brightness temperature (650 nm) on time for pyrolytic graphite.

The typical image of a glowing pyrographite sample heated to 4000 K is shown in figure 3, an exposure was equal to 6 μs. The image shows slight changes in the incandescence brightness caused by fluxes of graphite vapor, probably due to the insufficiently tight fitting of the protective glass. However, such small distortions were taken into account in the processing of images and practically did not affect the error in determining of the dimensions of the heated sample.
Figure 3. The image of incandescence of the heated pyrographite sample.

The typical curve of the intensity distribution of the incandescence of the heated graphite sample, averaged over 30 lines, is shown in figure 4.

Figure 4. Typical curve for the distribution of the incandescence of a graphite sample at a temperature of 4500 K, depending on the transverse coordinate.

Figure 5 shows a comparison of the sample image at the initial temperature and at a temperature close to the melting point in the experiment of measuring of the expansion perpendicular to the basal plane, an expansion is about 16.4%.
Figure 5. Comparison of the sample image at initial temperature and at a temperature close to the melting point.

5. Analysis of experimental data

The experimental data on the linear expansion of pyrolytic graphite are presented in table 1 and in figure 6.

Table 1. Experimental data on the linear expansion of pyrolytic graphite in a direction perpendicular to the basal plane.

| #  | T, K  | Δl/l₀, % |
|----|-------|----------|
| 1  | 3033  | 8.4      |
| 2  | 3071  | 6.6      |
| 3  | 3209  | 8.4      |
| 4  | 3331  | 8.4      |
| 5  | 3552  | 9.9      |
| 6  | 3603  | 10.35    |
| 7  | 3677  | 9.2      |
| 8  | 3698  | 9.9      |
| 9  | 3955  | 11.5     |
| 10 | 3992  | 11.5     |
| 11 | 4145  | 10.3     |
| 12 | 4283  | 12.8     |
| 13 | 4359  | 12.3     |
| 14 | 4417  | 15       |
| 15 | 4488  | 13.1     |
| 16 | 4641  | 14.2     |
| 17 | 4756  | 16.3     |
| 18 | 4764  | 14.8     |
| 19 | 4769  | 16.4     |
| 20 | 4784  | 16.5     |
For approximation of the coefficient of linear expansion of graphite in a direction perpendicular to the layers, a linear function of the temperature dependence was chosen for the temperature range 3300-4800 K. Thus, the approximation polynomial for the temperature dependence of the coefficient of linear expansion is as follows:

\[ \alpha_\perp = -7.42 \times 10^{-5} + 3.1 \times 10^{-8} \times T \quad [K^{-1}] \]  

(1)

If the dependence of the relative expansion of \( \Delta L / L_0 \) is approximated linearly, we obtain the value of the average coefficient of linear expansion of graphite in a direction perpendicular to the layers at this temperature interval equal to \( \bar{\alpha}_\perp = 4.83 \pm 0.37 \times 10^{-5}K^{-1} \).

The obtained experimental dependence of the relative linear expansion of pyrolytic graphite is presented in figure 6. The dashed curves are the approximations for the experimental data obtained, taking into account the constant coefficient of thermal expansion (CTE) in the direction parallel to the layers and the linear temperature dependence of the CTE in the direction perpendicular to the layers. The approximation polynomial for the temperature dependence of the relative linear expansion of pyrographite in the direction perpendicular to the basal plane is as follows:

\[ \frac{\Delta L}{L_0} = 0.16 - 7.42 \times 10^{-5} \times T + 1.55 \times 10^{-8} \times T^2 \]  

(2)

**Figure 6.** Experimental data on the value of linear thermal expansion of pyrolytic graphite in comparison with [2].

Despite the certain scatter of the experimental points it follows from the presented graph that in the interval 3300-4800 K the growth pattern of the relative thermal expansion in the direction parallel to the layers for pyrolytic graphite is similar to the growth pattern at lower temperatures. Thus, it is reasonable to approximate the relative expansion in a given temperature region by a straight line which slope coincides with the slope of the straight line in the high-temperature region (3000-3200K) from the literature [2]. Hence the CTE of pyrolytic graphite in a direction parallel to the layers in the temperature range 3300-4800 K can be taken equal to \( \bar{\alpha}_\parallel = 4.65 \times 10^{-6}K^{-1} \).

From the obtained dependences of the relative expansion of pyrolytic graphite in directions perpendicular and parallel to the basal plane one can calculate the dependence of graphite density on temperature in the temperature range 3000-4800 K. Figures 7 shows the relative density of pyrographite versus temperature in comparison with literature data [2, 3, 5]. Experimental points correspond to a pressure of 1 kbar (i.e. 0.1 GPa). In figure 7 a linear function is used to approximate
the CTE in the direction perpendicular to the layers. To calculate the dependence of the density on the energy introduced in \[5\] the dependence of the specific enthalpy on temperature for graphite published in the GSSSD \([7]\) was used.

![Graph showing dependence of relative density on temperature](image)

**Figure 7.** Dependence of the relative density of pyrolytic graphite on temperature in comparison with the literature data \([2, 3, 5]\).

Thus, the average volume coefficient of thermal expansion at the temperature interval 3300-4800 K can be calculated as

\[
\bar{\beta} = \alpha_\perp + 2\alpha_\parallel = 5.76 \times 10^{-5} K^{-1}
\]  

Assuming that the approximation of the CTE of pyrographite in a direction perpendicular to the layers near the melting point is closer to the experimental data obtained than the approximation by the constant, one can obtain the density and expansion at this temperature. Taking into account the fact that the initial density of the graphite under study was 2.18 g/cm\(^3\), the density of this graphite at the beginning of melting is 1.82 g/cm\(^3\), and the volume change is 16.5%.

6. **Conclusion**

This article presents data on the measurement of the thermal expansion of pyrolytic graphite with an initial density of 2.18 g/cm\(^3\) in directions both perpendicular and parallel to the basal plane in the temperature range 3000-4800 K under isobaric conditions at a static external pressure of 1 kbar. The average coefficient of volumetric expansion of such graphite is calculated in the temperature range 3000-4800 K.

A measurement technique, which presents a certain difficulty due to such properties of material as the pronounced anisotropy of its expansion, the fragility of samples of pyrolytic graphite and its active sublimation at high temperatures, is described.

From the analysis of the obtained experimental data follows that the expansion of pyrolytic graphite in a direction perpendicular to the basal plane agrees within the measurement accuracy with data \([5]\) obtained from non-isobaric heating, as well as calculated data \([3]\). The experiments also show that the temperature dependence of the expansion of pyrolytic graphite corresponds with the experimental data available in the literature for \(T < 3300 \) K \([2]\) up to a temperature of about 4000 K, after which it shows a slightly more intense growth.

**References**

[1] Senchenko V N, Belikov R S and Popov V S 2015 *J. Phys. Conf. Ser.* **653** 012100
[2] Touloukian Y S, Kirby R E, Taylor R K and Lee T Y R 1977 Thermophysical Properties of Matter. Thermal Expansion: Nonmetallic Solids vol 13 (New York: IFI/Plenum)

[3] Kerley G I and Chhabildas L C 2001 Multicomponent-Multiphase Equation of State for Carbon (Sandia report SAND2001-2619) p 50

[4] Khishchenko K V, Fortov V E, and Lomonosov I V 2005 Int. J. Thermophys. 26 479–91

[5] Kondratyev A M, Korobenko V N and Rakhel A D 2016 J. Phys. Condens. Matter 28 265501

[6] Basharin A Yu, Pahomov I S and Scheindlin M A 1991 High Temp.-High Press. 23 543

[7] GSSSD 25-901991 Grafit kvazimonokristallicheskiy UPV-1T. Izobarnaya teploemkost’, ental’piya i entropiya v diapaze temperatur 298,15...4000 K (Moscow: Izdatel’stvo standartov)