Experimental investigation of density of pyrolytic graphite up to melting point

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Abstract. This article contains data on the measurement of the density of pyrolytic graphite with an initial density of 2.18 g/cm$^3$ in the temperature range 3000–4800 K under isobaric conditions at a static external pressure of 1 kbar. The features of the experimental technique, representing a certain complexity due to intense sublimation of graphite at high temperatures, are also described.

1. Introduction
At the moment experimental data on the density of pyrolytic graphite in the temperature region above 3300 K are extremely few. Meanwhile, such data are necessary for constructing wide-range equations of state for carbon [1], as well as for studying the thermophysical properties of a graphite crystal.

A distinctive feature of the graphite crystal is a significant anisotropy of physical properties in the directions parallel and perpendicular to the layers of atoms forming the crystal. This is due to the presence of different types of bonds: a strong covalent bond between the atoms in the layer and a weak van der Waals bond between the layers.

The study of the features of the physical processes in layered crystals is of great interest, for instance in connection with the prospects of detecting the effects inherent in low-dimensional (two-dimensional) systems [2]. It should be noted that the strong anisotropy of the binding forces in a crystal of graphite is an exceptional feature of layered crystals and leads to revision of the conditions for the applicability of certain approximations used in describing of the elastic properties of such crystals [3].

In the present paper, we propose a method for measuring the density of graphite samples in the high-temperature region up to the melting point at high pressures. Using this method, an isobaric dependence of the density of pyrolytic graphite was experimentally determined in the temperature range 3000–4800 K at a pressure of 1 kbar.

2. Peculiarities of graphite expansion in the high temperature region
Samples of pyrolytic graphite produced by the State Research Institute of Graphite-Based Structural Materials “NIIGrafit” with a density of 2.18 g/cm$^3$ were used in the experiments. The developed experimental technique allows measuring thermal expansion up to the melting point without destruction of the graphite samples.
Figure 1. The layout of graphite sample mounting with protective glass plate designed to eliminate the effect of optical distortion in carbon vapor.

A large (about one order of magnitude) difference between the coefficient of linear expansion in directions parallel and perpendicular to the graphite layers can cause mechanical destruction of the samples due to the appearance of thermomechanical stresses in them during their rapid heating. In the experimental setup this effect was practically eliminated by the use of a movable collet allowing the sample to expand freely along the axis of its length.

Another specific feature of the graphites is their tendency to form a significant amount of optically dense vapor at temperatures above 3000 K [4, 5]. To reduce the effect of optical distortions in the vapor, it was suggested in [6] to use a thin quartz plate. In this work a thin flat plate of optical glass or melted silica was placed above the graphite surface on which the camera lens was directed. The layout of the glass plate is shown in figure 1.

The thickness of the glass was 0.3 mm and the dimensions were about $2 \times 8 \text{ mm}^2$. The glass was placed close to the sample surface at a distance of about 20 microns. It almost completely eliminates image distortions caused by graphite vapor at high temperatures. The camera allows controlling the absence of contact between the glass and the sample in the area where the measurement of dimensions took place. This absence of contact is confirmed by the fact that in three failed experiments the interaction of the heated sample and the protective glass is clearly visible on figure 2. At these experiments the gradient of brightness in the image strongly distorts the boundaries and does not allow to measure the sample size. Using the camera, the distance between the glass surface and the sample was measured. Photographs of several mounted samples with protective glass gave a distance of about 20 microns.
Figure 2. Photos of the heated sample during successful experiment (a) and failed experiment (b). There is no interaction between the glass and the sample on the photo on the subfigure (a) and there is visible interaction between them on the photo on the subfigure (b).

The experimental setup and measurement technique are similar to those described in detail in [7]. The graphite samples were heated for a time of about 1.5 ms to the melting temperature, which can be additionally confirmed by the presence of a melting plateau on thermograms. The brightness melting temperature was about 4500 K for the c-surface (the surface, perpendicular to the deposition surface, i.e. perpendicular to the basal plane of the pyrographite crystal). In this case the true temperature of pyrolytic graphite was calculated from the brightness temperature under the assumption of a constant emissivity in the temperature range 3300–4800 K, the value of the emissivity was taken from [8]. During the experiments the geometrical dimensions of the sample were measured and then the density of the material was calculated.

3. Experimental data
For experimental investigation of graphite density the samples with the dimensions of about $1 \times 1 \times 10 \text{ mm}^3$ were used. More than fifty experiments with pyrolytic graphite samples were carried out. Experimental data allow to obtain the relative linear expansion and the coefficient of thermal expansion (CTE) of pyrolytic graphite in a direction perpendicular to the layers in the temperature range 3000–4800 K directly from the measurements of the sample size [9]. Beside that, the data allow to obtain the CTE of pyrolytic graphite in a direction parallel to the layers. Despite the certain scatter of the experimental points the experimental data obtained demonstrates, that the growth pattern of the relative linear thermal expansion in the direction parallel to the layers in the temperature interval 3300–4800 K for pyrolytic graphite is similar to the growth pattern at lower temperatures. Thus, it is reasonable to approximate temperature dependence of the relative linear expansion in a given temperature region by a straight line with slope coinciding with the slope of the straight line in the high-temperature range (3000–3200 K) from the literature [10] and so the CTE of pyrolytic graphite in a direction parallel to the layers in the temperature range 3300–4800 K can be taken equal to $\alpha_{\|} = 4.65 \times 10^{-6} \text{ K}^{-1}$. From the acquired dependences of the relative linear expansion of pyrolytic graphite in directions perpendicular and parallel to the basal plane, one can obtain the thermal dependence of density in the concerned temperature range 3000–4800 K. Figures 3 and 4 show the relative density of pyrographite versus temperature in comparison with the literature data [1, 10–12]. Initial densities $\rho_0$ are equal to 2.265 [1, 10], 2.293 [11], 2.25 [12] and 2.18 g/cm$^3$ for this work.

In figures 3 and 4 the curves representing the experimental data obtained correspond to a pressure of 1 kbar, i.e. 0.1 GPa. In figure 3 a linear function was used to approximate the CTE in the direction perpendicular to the layers. In figure 4 approximation the constant CTE in the direction perpendicular to the layers $\alpha_{\perp} = \text{const}$ was added to compare the obtained
Figure 3. Temperature dependence of the relative density of pyrolytic graphite in comparison with data from Touloukian [10], Kerley [11] and Kondratyev [12], $\alpha_{\perp}(T) = A + BT$, $A = 2.27333 \times 10^{-5} \text{ K}^{-1}$, $B = 1.73864 \times 10^{-9} \text{ K}^{-2}$.

Figure 4. Temperature dependence of the relative density of pyrographite in comparison with data from Khishchenko [1], Touloukian [10], Kerley [11] and Kondratyev [12], $\bar{\alpha}(T) = \text{const} = 41 \times 10^{-6} \text{ K}^{-1}$.

Experimental data with some of the theoretical data, which does not demonstrate the growth of CTE near the melting point.
To calculate the temperature dependence of the density, the dependence of the density on the energy introduced in [12] and the dependence of the specific enthalpy on temperature for quasi-single-crystal graphite, published in the GSSSD [13] were used.

Assuming the approximation of the CTE of pyrographite in a direction perpendicular to the layers lying near the melting point is closer to the experimental data obtained than the approximation by a constant, one can obtain the density of the material 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 at the beginning of the melting point is 1.82 g/cm$^3$, and the volume change in solid phase during the heating from room temperature up to melting temperature $(V - V_0)/V_0$ is equal to 16.5%.

4. Conclusion
This article presents data on the measurement of the density of pyrolytic graphite with an initial density of 2.18 g/cm$^3$ in the temperature range 3000–4800 K under isobaric conditions at a static gas pressure of 1 kbar. The original experimental technique representing a certain complexity due to intense sublimation of graphite at high temperatures is described.

An analysis of the experimental data shows that the dependence of the relative density of pyrolytic graphite agrees (within the measurement error) with the data obtained in nonisobaric heating [12], as well as with the calculated data [1, 11]. The experiments also demonstrate that the temperature dependence of the relative density of graphite corresponds to the experimental data available in the literature for the temperature less than 3300 K [10] up to the temperature of about 4000 K, after which a slightly more pronounced fall probably appears.

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