Thermophysical properties of graphite HOPG and HAPG in the solid state and under melting (from 2000 K up to 5000 K)

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Abstract. Experiments with HOPG graphite grade showed that the melting temperature of graphite equals 4800-4900 K and that the melting of graphite is possible only at elevated pressures. The data were obtained for resistivity, specific heat and input (Joule) energy up to 5000 K. HAPG (Highly Annealing Pyrolytic Graphite) is a form of highly oriented pyrolytic graphite. HAPG specimens in the form of strips (thickness 30 microns) were placed in a cell (between two plates of glass-sapphire). The specimen temperature was measured by a high speed pyrometer. The heat of fusion for both graphite grades (heated in a confined volume) was less (and specific heat – higher) than for the case with nearly free expansion. A possible reason for the observed effects is discussed in the report.

1. Introduction
Carbon and its compounds are increasingly used as structural materials in modern high-temperature machines and installations. The use of such materials in the nuclear and aviation industry involves studies in extreme conditions at high temperatures and pressures. Thus, there is a practical need to study the thermophysical properties of carbon. In addition, studies have not only applied, but also have a great scientific value. The development of science requires knowledge of the properties of substances, in particular, the elaboration of phase diagrams will help to understand the behavior of substances in a broader range of temperatures, which in turn will help in the development of the new materials.

The beginning of experimental studies to obtain the properties of carbon are referred to 1911 [1], when it was made the assumption that impossible to obtain liquid carbon at atmospheric pressure. Stationary methods have a number of basic problems, such as the need to maintain simultaneously high temperatures and pressures. For graphite, this problem is most important, since for the crucible there is no more refractory material than graphite.

The transient methods are more effective: rapid heating of specimens by a laser or electric current gives data for higher temperature. The main problem is measuring the true temperature of the specimen. It can be considered proved that for pure metals, rapid heating (up to fractions of a microsecond), allows to obtain the equilibrium thermodynamic properties (specific heat, enthalpy at the beginning of melting, heat of fusion) as well as temperature [2].
The additional difficulties have appeared under fast heating of the graphite: the anisotropic structure, sublimation from the solid phase, the density dependence on the method of manufacture, etc. These features must be taken into account when measuring the temperature of graphite, especially near the melting point [3,4].

In this article the method of pulsed electric heating is used, which gives a fairly uniform heating under the condition of good uniformity of the initial substance. Currently, graphite is the most refractory material. Due to this main property the structural materials based on graphite are widely used in aviation, aerospace and in nuclear industry.

Up to now the resulting phase diagram of carbon is still not acquired a final form. Moreover there is still discussion about the magnitude of the melting temperature of carbon. And experiments to investigate the properties of liquid carbon are limited. Graphite under heating begins to sublimate (similar to "dry" ice) at normal pressure, while at high temperature (≈ 3000 K) graphite actively sublimates and cannot pass into the liquid phase. The reason is of its triple point (the region of simultaneous existence of solid, gaseous and liquid phases). The carbon triple point has not only high temperature but also (the most important) high pressure, above 120 atmospheres [5]. Therefore, to obtain a liquid phase, it is necessary to have a high pressure during heating. In pulsed experiments, a high pressure is achieved by placement a specimen in a confined volume between isolated plates.

To study the properties of graphite at high temperatures, typically use a short (of the order of tens of nanoseconds or units of microseconds) heating by electrical current or laser radiation. The heat losses of all types (thermal radiation and contact heat losses at the ends) are negligible due to the rapid heating. While maintaining the initial shape of the sample, which also takes place at fast heating, digital oscilloscopes and fast pyrometers provide sufficiently accurate data on the resistivity, input energy (Joule energy) and high temperature.

2. The study of graphite HOPG
In the experiment [6] it was obtained the properties of graphite UPV-1T (analogue of the widely used graphite HOPG). In figure 1 the main result of this experiment is shown. The important note to figure 1. The melting region measured by radiation plateau (two vertical lines) is shifted in the E axis to the right-hand side. The reason is in the absorbed a part of input energy by a glass plate during a short time of heating. Thus the both parts of the melting region (the start and the finish of melting) are shifted to higher input energy approximately one and the same value (~ 10 % as an average for six studied specimens). Melting region measured for the six specimens (likes figure1) gives the average result: 11 ± 1 kJ/g - the start of melting and 20 ± 1 kJ/g – the finish of melting.

A high-speed pyrometer (made by V.N. Korobenko [6]) was used to record the temperature of the specimen. The main components of the pyrometer were: silicon PIN- photodiode, an interference filter with half bandwidth of 16 nm at a wavelength of 900 nm, two lenses, trans-impedance amplifier and glass or quartz fiber. Settling time of the pyrometer was 12 nanoseconds with an accuracy of 1%. Linearity of the pyrometer (output voltage to 1.8V) was checked by recording of a radiation spectral density of a LED (AL - 124A) , having a linear dependence of the radiation power from the current flowing through the emitting diode.

Temperature measurements were carried out on the surface radiation of the graphite strips ("a"-plane) at a wavelength of 900 ± 8 nm using Planck equation. Calibration of the pyrometer signal was made under specific energy E = 9.1 kJ/g - corresponding to the graphite temperature 4500 K, according to [7]. It was assumed that above 4500 K the emissivity of graphite is constant and does not depend on temperature.
Figure 1. [6] The dependencies of the specimen voltage (U), the temperature (T), and the resistivity (ρ) against the energy input (E) for the pulsed electrical heating of a graphite strip.

The two vertical lines mark the melting region, measured by surface radiation. The time of heating equals ≈ 2μs.

The start of melting takes place at ~ 5,500 K (under elevated but not measured pressure), the end - at ~ 6000 K (also at higher pressure). Estimation of pressure [6] gives 5-10 kbar for melting region (the last value for inner graphite layer; the whole specimen thick – 300μm). Electrical resistivity ρ - refers to the initial size of the specimen.

1 - Cusp at this point shows the start of melting which is determined by volume properties (voltage and resistivity);

2 - Cusp at this point shows the finish of melting which is determined by the volume properties (voltage and resistivity).

To make pressure value to be higher (instead of only two glass plates used with a specimen between) we prepared a special cell [8] with doubled pressed of the specimen in two directions (figure 2).

Figure 2. Cell for the experiment with a specimen in a confined volume.

Figure 3. Temperature dependence of the specific heat (with dynamic pressure growth) for HOPG graphite. The starting moment of melting (4900 K) is fixed only according to heat capacity (shown by the arrow).
After gluing the sample (shown in the center of figure 2) clamped by the screws (through the insulating plate 1), and then tightened with large screws on the side end (2). In the upper insulating plate 1 in the center one can see the hole for the output of radiation during experiment. Top cover with transparent window (removed) protects the input lens of the pyrometer from destruction by broken glass fragments.

New cell gives new effect in specific heat for the specimen heated in a limited volume (figure 3).

The beginning of melting (4900 K) is fixed in figure 3 by heat capacity curve (arrow). The value of the input energy is around 15 kJ/g (up to start of melting), which is different from the values (10.5 kJ/g) obtained for samples sandwiched between glass-quartz plates. This feature may be explained by the increased magnitude of pulse pressure, and the cell may support longer duration of this pressure. The value of the melting temperature (4900 K) has not changed. Thus, by limiting the expansion of graphite, the additional energy enters into the atomic lattice.

According to figure 3 the heat capacity of the solid phase increased significantly (at least doubled) in comparison to lower pressures. There is actually a steep drop heat capacity from the solid phase and ending in the two-phase region. Effect of high specific heat in solid state is achieved by the significant influence of the increasing pulse pressure and increased its duration.

3. Graphite HAPG investigation

3.1. HAPG-graphite under fast heating in thin glass plates

We investigated the properties of graphite grade HAPG (a form of highly oriented pyrolytic graphite with very small angles of crystal orientation) in the temperature range 2000-5000 K. Numerous (various initial density) types graphite have already been investigated; however, new types have entered the market, e.g., Highly Annealing Pyrolytic Graphite (HAPG) [4], which is a kind of highly oriented pyrotic graphite. However, the high temperature properties of this comparatively new material have not, in fact, been investigated.

The HAPG specimens manufactured by AtomGraph AG (Russia, Moscow) has a density 2.25 g/cm³ and the following composition: C, 99.999%; S, 3 ppm; and other admixtures, below 1 ppm. During manufacturing of the specimen, the annealing temperature was equal to ≈ 3300 K. We placed the HAPG specimens, 0.03 × 5 × 17 mm strips (5 × 17 mm dimensions with respect to the a plane), in a high pressure cell, that is, between the two 3.5 × 8 × 15 mm glass-sapphire plates. Figure 4 shows the layered surface of the specimen, (about 30 µm thick).

![Image](Figure 4. The part of the HAPG graphite surface. Bar equals 300 µm.)
We pressed the specimen between the plates and then glued the plates, 1.5–2 mm thick, made of glass or laminate on the side cell facets. We pressed the cell (from the ends) between the two electrodes. As a result, the specimen was confined in a closed volume. Heating and expansion of the specimen give a result in a pressure increase in the cell much above 100 atm, which is necessary to obtain the liquid phase of carbon [3,4].

Highly Annealed Pyrolytic Graphite (HAPG) is a mosaic crystal and a further improvement of the well-known Highly Oriented Pyrolytic Graphite (HOPG). Mosaic crystals, in contrast to ideal crystals, consist of many small ideal crystals, called crystallites. Compared with commonly used specimens HOPG, HAPG specimens contain significantly fewer defects (stages of cleavage, edge dislocations, grain boundaries). The important HAPG application is an obtaining graphene by micromechanical cleavage. Using the HAPG allows you to get thinner graphene specimens with lower content of inner defects.

Russian authors I.G. Grigorieva and A.A. Antonov [9] who are may be the first who drew attention to the special properties of graphite HAPG. The specimens of graphite HAPG, investigated in these experiments, were elaborated in the Laboratory of Grigorieva and Antonov. Our aim – to investigate bulk properties of HAPG (the most perfect anisotropic graphite with a small number of inner defects); in particular, to measure the melting temperature, which still has not established the value.

Graphite HAPG (thickness 30 μm, width 5 mm, length 15 mm) is sandwiched between two quartz plates (thickness of 3.5 mm each). This assembly is glued laterally between two plates of glass. The side view of the specimen surface (after the cleaning the side) is shown in figure 5.

![Figure 5](image)

**Figure 5 [10].** The side view of the specimen HAPG (after the cleaning). Bar equals 10 μm.

### 3.2. Method and temperature measurement

A cell made from sapphire has some problem under melting itself. In this case, the decrease in transmittance of radiation through melted sapphire has appeared (when it is melted in contact with the high temperature graphite). For quartz this is not a problem - it stays transparent when it melts. Therefore, the use of sapphire, it is desirable to carry out the experiment so quickly (about 1-2 microseconds) that in the contact layer sapphire did not have time to melt. We measured the specimen temperature by means of the high-rate pyrometer. The wavelength engaged was $\lambda = 856$ nm. We calibrated the pyrometer against the SI-10-300 temperature lamp at 2515 K. We calculated the temperature of the HAPG specimen surface according to the formula:
\[ T = \frac{C_2}{\lambda \ln \left( \frac{u U_0 \varepsilon_{n \lambda}}{u U_0 \varepsilon_{n \lambda}} \left( \exp \left( \frac{C_2 \mu}{RT_0} \right) - 1 \right) \right) + 1} \] (1)

\( C_2 \) is the constant in the Plank formula; \( U_0 \) and \( U \) are the pyrometer signal upon calibration and the signal from the specimen; \( \varepsilon_{n \lambda} \) and \( \varepsilon_{n \lambda} \) are the normal spectral emissivities of the tungsten ribbon (the SI-10-300 tungsten lamp) and the HAPG specimen surface; \( \tau_\lambda = \prod \tau_\lambda \) - is the total transmittance of the NC-7 neutral filter (\( \tau_1 \)) of the elements that are absent in the pyrometer calibration; \( T_0 = 2515 \text{ K} \) is the SI-10-300 lamp temperature.

We measured the transmittances, by means of the Shimadzu UV-240.

The authors of [11] obtained for of the \( \alpha \)-plane of the annealed pyrolytic graphite, at 1086 K (solid state) and at the wavelength 860 nm, the average value of normal emissivity \( \varepsilon_{n \lambda} = 0.6 \). The authors of [12] obtained for of liquid carbon at the wavelength 650 nm the value 0.6. We supposed a weak dependence of on the temperature and the wavelength (650–860 nm) and took the value = 0.6 for the solid and the liquid carbon phases. Specific heat was calculated by the formula:

\[ C_p(T_{ref}) = \frac{E(t_{i+n}) - E(t_i)}{T(t_{i+n}) - T(t_i)} \] (2)

where \( E \) – specific Joule energy; \( T \) – specimen temperature; \( t_i, t_{i+n} \) – the points of the timeline, spaced apart from each \( n (\tau/104) \) (\( \tau \) – the duration of the sweep). For example, with a scanning duration of 10 \( \mu \text{s} \) (minimum time step 1 ns), for \( n = 150 \) we obtain the time \( t_{i+n} - t_i = 0.15 \mu \text{s} \). The result for specific heat is shown in figure 6.

**Figure 6.** Specific heat for graphite HAPG against temperature. 1 – sapphire cell; 2 – silica-glass cell. Arrow shows melting point (4900 K).

**Figure 7 [14].** The data of our experiment for specific heat versus temperature for HAPG graphite in a silica-glass cell (solid curve). Squares - steady state data [13] (higher 3800 K temperatures - calculations in Ref. [13]).

In both cases (figure 6), specific (Joule) energy at the beginning of the melting amounted to 11.5-11.7 kJ/g. The calculation of heat loss in the sapphire is 10% [3,4], thus the energy of the beginning of melting is equal to 10.4-10.5 kJ/g that is generally consistent with data for other graphite grades [3,4].
As can be seen from the data obtained, the dependencies for the samples in the sapphire cell (1) and in a glass-quartz cell (2) nearly coincide, which indicates the correctness of the account of absorption in the liquid phase sapphire. Also, according to the plot, you can pay attention to the jump in the heat capacity before the start of melting (T_{melting} = 4900 K). We suppose that the reason – appearance of pair Frenkel defects before melting in the matter at fast heating.

The comparison of specific heat for HAPG graphite and for steady state measurements of HOPG graphite [13] is shown in figure 7. Our result (solid line) nearly coincides with the steady state data (squares [13]) up to 4600 K. A high specific heat at the temperatures higher 4600 K (up to the melting point at 4900 K) was obtained under fast heating. The rising specific heat in a narrow range just before melting has been observed under fast heating also for metals [2] and carbides [8]. The reason is unknown; we may suppose that this effect may be connected with the appearance of Frenkel pair defects. This assumption was proposed in [15] as one of the ways to explain the abnormal high electron emission and anomalous specific heat rise just before melting for metals. For the first time this idea was published by S. V. Lebedev in 1954. It should be mentioned that this effect does not influence much the values of enthalpy and resistivity at the melting point; besides, the anomalous properties disappear shortly after melting (during microseconds time scale) [15]. The uncertainties of the measurements in this experiment are estimated to be as follows: the Joule energy – 5 %; the resistivity – 5 %; the temperature (excluding ε\textsubscript{nl} error) – 2 %; the specific heat – 15-20 %.

On the steady state data [13]: The main contribution to the error in determining the enthalpy above 2900 K - the loss of heat by radiation during the fall of the specimen into the calorimeter. The magnitude of this correction was 2.4 % for the temperature 2890 K and 8.8% for the temperature 3818 K. The corrections were calculated by Stefan-Boltzmann law (emissivity assumed 0.9) [13].

A good coincidence is shown for these two different experiments up to the moment of sharp increase in C\textsubscript{p} under fast heating (higher 4500 K). This is not surprising: no one in stationary experiments did not observe the occurrence of point Frenkel defects.

3.3. HAPG-graphite under fast heating in thick glass plates (higher pressure).

Графит HAPG at high unmeasured pressure in a special cell (with the slight higher pressure in our experiment). The thick glass quartz plates (9 mm instead 3.5 as earlier) were used.

**Figure 8.** The input (Joule) energy E against temperature T for graphite HAPG. The arrow shows the temperature to which it was checked the linearity of the pyrometer. 1 – the start of melting; 2 – the finish of melting.

**Figure 9.** Specific heat against temperature T for the specimen HAPG graphite measured under thick glass plates used. The arrow shows the temperature to which it was checked the linearity of the pyrometer.
The heat of fusion of graphite HAPG (in this experiment with higher pulse pressure) was less than for other experiment with lower pressure. The obtained value of the energy $E \approx 17.8 \text{ kJ/g}$ the end of melting is different from the values obtained for other grades of graphite, where $E$ is higher 21 kJ/g (see figure 1). The heat of fusion can be obtained as the difference of the energies of the beginning and the end of melting. For the experiment with HAPG (figure 8) heat of melting, with the 10% heat loss in the quartz, made up of $\approx 7 \text{ kJ/g}$, in contrast to 10 kJ/g for other experiments at lower pressure.

One can see that under higher pressure (figure 3 for HOPG-graphite and figure 9 for HAPG-graphite) there is a high values for specific heat are appeared in the solid state. Besides, the input Joule energy (in this experiments) at the finish of melting is lower than 20.5 kJ/g (usual value for low pressure). The result coincides with the data obtained by M.Togaya [16]: Joule energy at the start of liquid state diminishes with rising pressure.

4. Measurement error
A pyrometer used at a wavelength $\lambda=860 \text{ nm}$ provides a measurement error of about 10%, or in absolute units of $\pm 50 \text{ K}$ (at the best) to temperatures of the order of 5000 K; for higher temperatures the uncertainty has not been estimated. The accuracy of the measurements was achieved through calibration temperature lamp included in the validation scheme of measuring temperature by optical methods. The measurement error for input specific energy was amounted to $\pm 5\%$; measurement of heat capacity gives $\approx 20\%$.

5. Conclusion
Thermophysical properties for specimens of graphite grades HOPG and HAPG were obtained under fast heating by electrical pulse current.

Under fast heating with elevated pressure a decrease in energy reaching the liquid phase of carbon are obtained for HOPG and HAPG graphite specimens. In millisecond heating of graphite [16] at the stationary high pressure, with the increasing pressure by 15 kbar it was accompanied by a drop in energy input $E$ by 2.5 kJ/g: (20.8 - 18.3) kJ/g. If we proceed from the assumption about saving this relationship, then the data (figures 2,3), a decrease of 2.7 kJ/g should lead to an increase in pressure to 16 kbar. In conditions of thick-walled quartz cell, and with a press of the specimen in two perpendicular directions, - the emergence of such pressure is possible.

The increasing specific heat before melting (higher than for steady state data) give us a supposition that the reason is in appearance pair point Frenkel defects [17] under fast heating.

To obtain the true reasons for the diminishing of the energy of melted graphite, it is necessary to pay attention to the calculations. Methods presented in [18,19] looks suitable for this purpose (due to the flexible choice of the interatomic potential for carbon).

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