MEASUREMENT OF THE GRÜNEISEN COEFFICIENT
OF SOME ANISOTROPIC CARBON MATERIALS

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Results of measurement of the Grüneisen coefficient of two anisotropic materials (4KMS carbon–carbon composite and UPV-1 pyrolytic carbon) are presented. The values of the Grüneisen coefficient are calculated on the basis of the measured amplitude of mechanical stresses arising in the material with absorption of electron-beam energy. The results for the 4KMS composite include not only a negative value of the Grüneisen coefficient in the range of electron energy density of several tens of joules per square centimeter but also its anomalously low value as compared to other materials. Significant decay of the stress wave propagating over this material is noted. The Grüneisen coefficient of the UPV-1 sample varies depending on the sample orientation.

Key words: *electron beams, carbon–carbon composite, anisotropy, Grüneisen coefficient.*

Composites are rather promising and interesting materials. A particular group of composites consists of carbon–carbon composites, i.e., materials obtained from carbon fibers with the matrix being filled by carbon.

Calculation of thermoelastic stresses upon pulsed heating by radiation in such materials is rather complicated for a number of reasons: possible nonuniform heating over the depth of the material, complicated pattern of stress waves arising in such an inhomogeneous material, transformation of these stresses propagating in the depth of the composite, etc. Composite materials under pulsed radiation by an electron beam with duration of tens of nanoseconds or by laser radiation with duration of several nanoseconds were considered in several papers (see, e.g., [1, 2]). Materials with a two-dimensional structure were studied, which made it possible to construct a phenomenological models that could involve Grüneisen coefficients directly measured in experiments [1–3].

In the present work, we made an attempt to consider the behavior of a material with three-dimensional anisotropy (4KMS carbon–carbon composite) under pulsed heating and to compare the results obtained with data for a material based on the same substance but with a typical two-dimensional structure (pyrolytic carbon and UPV-1 pyrocarbon). Pyrocarbon is obtained by means of methane deposition onto a hot graphite surface; hence, its structure is actually two-dimensional. Figure 1 shows a typical form of the surface of a sample cut out from a composite billet. The untreated surface of a pyrocarbon plate on the side of methane deposition is shown in Fig. 2.

We chose the Grüneisen coefficient as a parameter characterizing the material behavior. The energy input was performed by a pulsed electron beam with duration of several tens of nanoseconds. The energy of electrons absorbed by the material is finally converted to the thermal energy of the substance lattice and generates thermoelastic stresses in the material. The process of energy transfer to lattice atoms is normally rather fast; if the electron pulse is short as compared to the relaxation time of the material, the profile of the arising waves of thermoelastic stresses is close to the profile of energy release in the material [4]. An exception is materials with low electrical conductivity, such as dielectrics, and some semiconductors where the relation between the energy-release profile and stresses is more complicated.
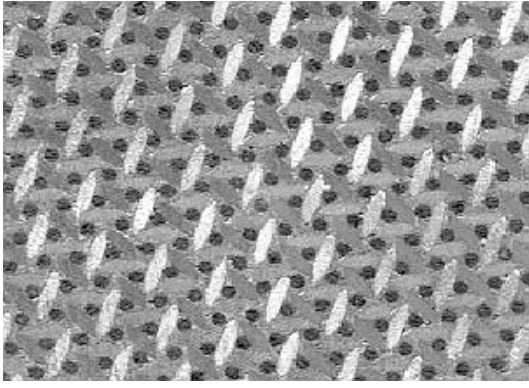
Fig. 1   Fig. 2

Fig. 1. Surface of a 4KMS carbon–carbon composite sample (the matrix composed of carbon fibers is visible; the scale is 1.7 : 1).
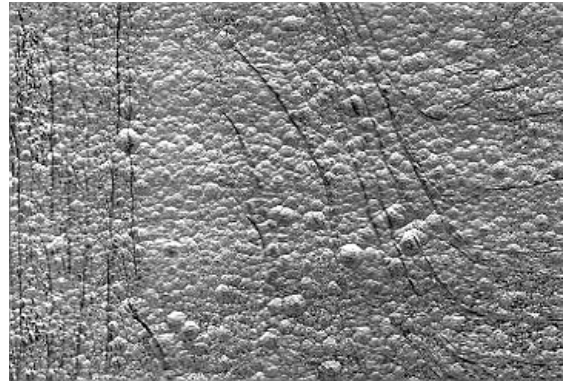
Fig. 2. View of the UPV-1 pyrocarbon surface from the side of deposition (the scale is 2.3 : 1).

If the electron pulse is incident onto the frontal surface of a homogeneous isotropic material with rather high electrical conductivity and the pulse duration is much smaller than the time of stress propagation over the heating region, the stress on the back side of the plate σ for one-dimensional geometry can be written as [5]

$$\sigma(l,t) = \Gamma \rho E(l - ct)/2, \qquad 0 < t < l/c, \tag{1}$$

where c is the velocity of sound, l is the plate thickness, t is the time, E is the energy absorbed in the material, ρ is the density of the plate material, and Γ is the Grüneisen coefficient.

If the mean free path of electrons is much smaller than the sample thickness, a bipolar stress pulse with compression and extension phases propagates from the irradiated sample toward its back side. The information about the sign and value of Γ is contained in the phase heading the bipolar pulse, because the second phase is caused by reflection from the free irradiated surface of the sample. In irradiation of homogeneous materials, the compression wave is normally the first one to reach the back side of the sample. It is seen from Eq. (1) that the Grüneisen coefficient can be determined if the energy-release profile in the material is known and the stress wave on the back side of the sample is measured.

Carbon–carbon composites are materials with rather high electrical conductivity [6]. In the case of an instantaneous pulse of electrons, therefore, the profile of arising thermoelastic stresses can be expected to repeat the profile of energy release in such a material. Then, using Eq. (1), one can determine the Grüneisen coefficient. If the electron pulse has a finite duration, then, as the composite structure contains particles and fibers of the size of fractions of a millimeter, their partial unloading occurs during the pulse action, and the amplitude of the resultant stresses can be lower. Moreover, the stress amplitude can be reduced owing to decay of waves propagating over the sample and to complex interaction of stresses arising in composite constituents. Hence, the data obtained characterize the Grüneisen coefficient for a chosen orientation of the sample.

The difficulties mentioned are not of principal importance. By choosing a proper spectrum of electrons, one can reduce the absorption depth and measure the magnitude of stress-wave decay beginning from rather thin samples. By increasing the transducer sensitivity, one can pass to electron setups with lower energy density in the beam but with a shorter pulse (approximately within 10^{-9} sec) or use laser setups. By changing the orientation of the samples and the fractions of the sample constituents, one can obtain a clearer idea about the components of the Grüneisen coefficient for the composite.

The present experiments were performed on direct-action electron accelerators with the electron beam exhausted into the atmosphere. For the 4KMS composite, this was an IGUR-3 accelerator with the mean electron energy $E_0 \approx 2$ MeV and approximate duration of the pulse at the half-height of $5 \cdot 10^{-8}$ sec [7]). For pyrocarbon, this was a less powerful setup with the maximum energy of electrons $E_{max} \approx 1$ MeV, mean energy of 0.3–0.5 MeV, and pulse duration at the half-height of $1.3 \cdot 10^{-7}$ sec. The measurement scheme for both material was identical (Fig. 3).
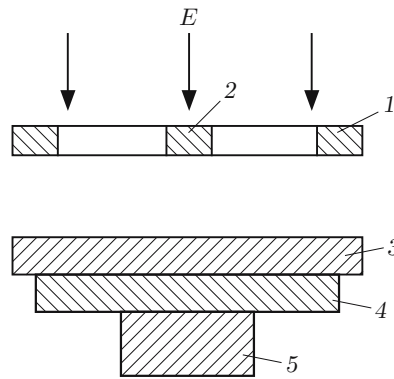
Fig. 3. Measurement scheme: 1) annular calorimeter; 2) central calorimeter; 3) sample; 4) acoustic delay; 5) piezoelectric transducer.

The electron beam was incident onto the frontal surface of the sample; the back side of the sample was equipped by a piezoelectric transducer glued via an acoustic delay with a low damping ratio. The acoustic delay of the stress wave was used to improve the noise immunity of measurements. All elements were glued by a very thin layer of epoxy glue to minimize its effect on measuring stresses in the composite. As was shown in [8], the thickness of the glue layer exerts a significant effect on the amplitude of the signal being registered, especially in the range of small durations of stress waves (0.1–0.2 μsec and smaller). The signal from the piezoelectric transducer was fed to an S9-4 oscillograph. The load resistance of the transducer was 50 Ω. The magnitude of transmitted energy of electrons incident onto the sample was measured by total-absorption calorimeters [8]. The term "particle energy fluence" means the ratio of the total energy (excluding the rest energy) of all ionization particles penetrating into the volume of an elementary sphere to the cross-sectional area of this sphere. The temperature was measured by copper–Constantan thermocouples.

The transducer was made of TsTS-19 piezoceramics 30 mm in diameter and 12 mm thick. The sensitivity of silica transducers turned out to be insufficient to register the signal from the sample. The transducer was calibrated by comparing signals registered in identical measurement schemes with the action of a pressure pulse on TsTS-19 piezoceramics and on a silica transducer 40 mm in diameter and 10 mm thick. The silica transducer was used as a reference. The pressure pulse was generated by absorption of the electron-beam energy in a plate 10 mm thick, made of the MA-14 magnesium alloy (containing approximately 95% of magnesium). This alloy was chosen as an absorbing material because magnesium and 4KMS composite have similar values of parameters responsible for the electron energy-release profile, namely, the density and atomic number.

Comparisons were performed in different experiments, and the measure for comparisons was the data on the magnitude of energy transfer and duration of the electron pulse. A comparison of pressure-wave profiles registered by both transducers showed that they coincide within the repeatability of energy-release profiles ($\pm10\%$). The piezosensitivity of the transducers used was 1.5 V/MPa (for a load of 50 Ω).

The Grüneisen coefficient of the 4KMS composite was measured as follows. A sample cut out in the form of a disk 60 mm in diameter with an arbitrary orientation of the cut plane with respect to the initial billet of the material was subjected to irradiation. The sample thickness was 10 mm, which was greater than the mean free path of electrons from the IGUR-3 accelerator with the maximum energy in this material. A titanium plate was used as an acoustic delay. Figure 4 shows the oscillogram of the stress pulse obtained in one experiment. It is seen that the tensile wave (negative pulse) reaches the transducer first. For comparison, Fig. 5 shows the oscillogram of the stress pulse in homogeneous isotropic graphite of density of 1.65 g/cm^3.

To check the influence of the sample thickness on parameters of the registered stresses, a sample 15 mm thick cut out in the same orientation was irradiated in the same geometry. The signal amplitude decreased, but the character of the registered stresses remained unchanged.

The influence of the electron-pulse duration on the magnitude of the registered signal (with the pulse duration several times greater and a similar electron spectrum) was checked on an ÉMIR setup [7]. Irradiation reduced the stress amplitude approximately twofold, but the character of the signal remained unchanged.
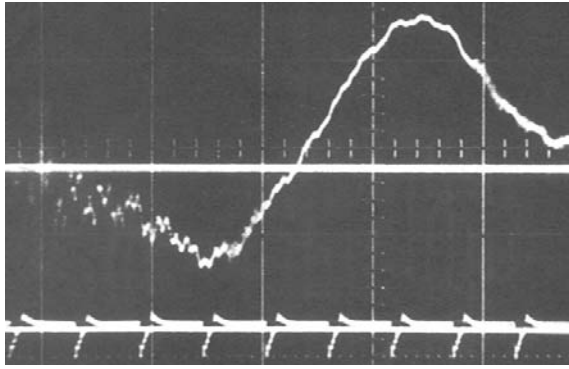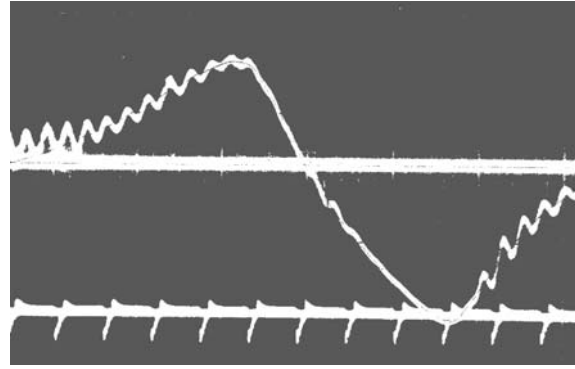
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Fig. 4   Fig. 5

Fig. 4. Oscillogram of the stress pulse in a 4KMS composite sample 10 mm thick (the distance between the markers is 1 μsec).

Fig. 5. Oscillogram of the stress pulse in isotropic graphite of density of 1.65 g/cm^3 (the distance between the markers is 1 μsec).

TABLE 1

Experimental Values of the Grüneisen Coefficient for the 4KMS Composite

l, mm	Φ, J/cm^2	$\Delta T_{\max}$, K	Γ
10	42	65	−0.012
	49	76	−0.015
15	40	63	−0.006
	53	82	−0.005

Note. $\Delta T_{\max}$ is the maximum heating of the sample.

To calculate the Grüneisen coefficient, we measured the stress amplitude on the basis of the amplitude of the first phase of the registered bipolar signal (negative pulse) and the magnitude of electron-energy transfer leading to sample heating; the boundary conditions between the transducer, acoustic delay, and sample were also taken into account.

In determining the amplitude of electron-energy release in the material $E_{\max}$, we used the ratio of $E_{\max}$ to the magnitude of energy transfer (Φ) — $E_{\max}/\Phi$ [(J/g)/(J/cm^2)] — as a function of the atomic number Z of the absorbing material, which was experimentally determined for the spectrum of electrons of the IGUR-3 accelerator.

To take into account the boundary conditions, we calculated the acoustic impedance of the 4KMS composite on the basis of the measured density and velocity of sound for this composite (tabular values were used for the remaining materials). The mean density of the 4KMS composite was 1.89 g/cm^3. The mean velocity of sound measured for this composite was $2.9 \cdot 10^5$ cm/sec. The measured values of the Grüneisen coefficient of the 4KMS composite for two values of the sample thickness are listed in Table 1.

The test results showed that the 4KMS behavior under rapid heating does not follow the usual pattern. In contrast to metals where a compression–extension wave sequence is formed, 4KMS displays the opposite pattern: the tensile wave is the first one to propagate inward the material. This means that the heated material shrinks rather than expands in the measurement direction, and the Grüneisen coefficient for 4KMS in the temperature range $T \approx 60-80°$C has a negative sign. Moreover, the Grüneisen coefficient of this material is anomalously low as compared to other materials. Thus, for instance, $\Gamma = 1$–2 for metals. Among available data, only fused silica possesses a value of Γ close to the measured one (0.03–0.06 [2, 8]). For comparison, we measured the Grüneisen coefficient of isotropic graphite with approximately the same values of electron-energy transfer, which amounted to 0.045. It should be noted that $\Gamma = 0.6$ for isotropic graphite of density of 1.78 g/cm^3 for energy release above 8000 J/g [9].
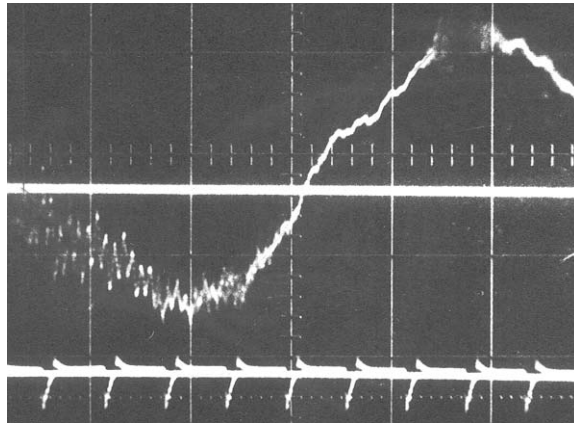
Fig. 6. Oscillogram of the stress pulse in a 4KMS composite sample 15 mm thick (the distance between the markers is 1 μsec).

TABLE 2

Experimental Values of the Grüneisen Coefficient and Velocity of Sound in Pyrolytic Graphites [10]

Material	Γ		c, cm/μsec	
	c	a	c	a
UPV-1	0.26 ± 0.04	0.17 ± 0.03	0.36 ± 0.04	0.53 ± 0.05
PG3	0.3	0.2	0.36	0.61
CAPG	0.48 ± 0.03	-0.99 ± 0.15	0.38 ± 0.05	2.2 ± 0.1

Note. The data on orientations of the sample along the carbon-deposition plane and perpendicular to it are given in columns a and c, respectively.

Significant decay of the stress wave in the composite should also be noted: as the sample thickness increases by a factor of 1.5, the value of Γ decreases approximately twofold. The presence of significant dispersion is also seen in the stress-pulse oscillogram in the sample 15 mm thick (Fig. 6): the stress pulse is "smoother" than the profile in Fig. 4.

The Grüneisen coefficient of pyrocarbon was measured as follows [10]. Two samples 60 mm in diameter and 10 mm thick were prepared; the samples had different orientation of planes with respect to the direction of carbon deposition: perpendicular and parallel to the deposition plane. The measurement scheme was the same as that in Fig. 3, but the acoustic delay was a fused silica plate 6 mm thick and 50 mm in diameter.

The Grüneisen coefficient of pyrocarbon was determined in a manner different from that for the carbon composite, namely, by comparisons with the Grüneisen coefficient of aluminum ($\Gamma = 2.09$) with identical values of electron-energy transfer. The reason was the unavailability of measurement results for the dependence $E_{\max}/\Phi$ $[(\mathrm{J/g})/(\mathrm{J/cm^2})]$ for the electron accelerator used. The energy transfer by electrons incident onto the sample was within 6–8 J/cm^2. At such levels of energy, the maximum heating of pyrocarbon reached several degrees, i.e., the sample temperature was close to room temperature.

The measured Grüneisen coefficients and velocities of sound in UPV-1 pyrocarbon and (for comparison) similar data for two foreign pyrolytic graphites PG3 and CAPG, which differ in manufacturing techniques, at a temperature of 300 K are listed in Table 2 [3, 11]. The characteristics of UPV-1 are close to those of PG3 and significantly differ from those of CAPG, which is most probably caused by the difference in manufacturing technologies and crystallite size. CAPG is obtained by compression in the c direction approximately to 30 MPa with simultaneous heating to a temperature above 3000 K; therefore, its structure has the closest resemblance to the graphite single crystal among the materials under study. As it follows from Table 2, a typical feature of CAPG graphite is a change not only in the value but also in the sign of Γ. A substantially weaker dependence of the Grüneisen coefficient on direction in UPV-1 is caused by the small size and weakly expressed preferable orientation of crystallites in this substance.

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It is known that heating of the overwhelming majority of polycrystalline isotropic materials leads to their isotropic expansion. At the same time, heating of single crystals (by virtue of their anisotropy) results in different degrees of expansion in different directions. For different directions, the coefficients of linear expansion can change not only their value but also their sign, depending on temperature.

Thus, a change in sign is observed for crystals with a diamond structure, such as silicon and indium antimonide [12]. A change in sign of the linear expansion coefficient is also observed for crystals with different crystalline structures, such as plaster, calcium, etc., and even for some isotropic solids. The linear expansion coefficient of CAPG measured in two mutually perpendicular directions have different signs [13]. Note that the linear expansion coefficients for two main directions in the graphite crystal are negative [14].

It follows from these data that, as some materials can have negative linear expansion coefficients, they can also have negative Grüneisen coefficients because $\Gamma \sim \beta$, and the quantity β is a combination of linear expansion coefficients ($\Gamma = \beta C_0^2 / C_V$, where β is the volume thermal expansion coefficient, C_0 is the velocity of sound determined by compressibility, and C_V is the specific heat at constant volume) [15]. Thus, the Grüneisen coefficients of Si and InSb are negative in the same range of temperatures as the linear expansion coefficients [16].

The 4KMS composite structure contains carbon fibers. It is known [17] that carbon plastics have a negative thermal expansion coefficient in the direction of reinforcement fibers, which is caused by a negative coefficient of linear expansion of carbon fibers. Therefore, a negative value of the Grüneisen coefficient of the 4KMS composite is naturally associated with the influence of the coefficient of linear expansion of the fibers.

The experiments performed in the present work revealed that the Grüneisen coefficient of 4KMS has a negative sign in the range of comparatively low positive temperatures, at least up to 60–80°C. A fairly simple expression for the Grüneisen coefficient used in Eq. (1), however, was derived within the Grüneisen approximation, this coefficient being assumed to be independent of temperature. In the general form, the exact thermodynamic definition of the Grüneisen coefficient is [18]

$$\Gamma(V,T) = V\left(\frac{\partial P}{\partial T}\right) \Big/ \left(\frac{\partial E}{\partial T}\right), \tag{2}$$

where P, E, V, and T are the pressure, energy, volume, and temperature, respectively. It is obvious from relation (2) that the Grüneisen coefficient in a wide range of temperatures becomes temperature-dependent because the heat capacity and the thermal expansion coefficient depend on temperature. Thus, the data of the present work and [9] show that the Grüneisen coefficient increases by more than an order of magnitude as the energy release in graphite increases by more than two orders of magnitude. As the Grüneisen coefficient of a composite can be presented as a certain combination of these coefficients for both components (filler and fibers), which can have different signs, the effective value of the coefficient at a particular temperature is determined by relative contributions of these coefficients. Therefore, the dependence of the Grüneisen coefficient of the 4KMS composite on temperature in a wide range of variation of the latter can have a rather complicated form with possible changes in both the value and the sign of the coefficient.

As was noted above, the measured absolute value of the Grüneisen coefficient turned out to be anomalously low. This is most probably caused by the low coefficient of linear expansion of fibers, which was reported in [17] to be more than an order of magnitude lower than that of isotropic graphite. For the same reason, possibly, the Grüneisen coefficient of fused silica is also anomalously low [the coefficient of linear expansion of silica at a temperature close to room temperature is $(4-5) \cdot 10^{-7}$ K^{-1}]. Another possible reason for the low measured value can be the influence of decay of the stress wave passing across the sample, but this cannot be verified at the moment.

The mechanism of the composite behavior under pulsed heating by radiation is difficult to imagine at present. It is necessary to study these materials further and to find the relation of the orientation of the fiber structure, the character of their interlacing in the composite, the degree of filling by isotropic graphite, etc., with the value and sign of the Grüneisen coefficient. Choosing appropriate parameters of the electron beam and test conditions, one can perform investigations in wide ranges of temperatures, manufacturing technologies, etc. It is also necessary to measure the dependence of Γ on the heating time in the range of shorter electron pulses, different spectra, and, possibly, under irradiation by a laser beam. The reason is that the composite contains particles of the order of fractions of a millimeter in size, where partial unloading of stresses can occur.

Thus, the results of the present work show that the parameters of thermoelastic stresses arising in anisotropic materials under pulsed heating by radiation are substantially different from the parameters of stresses in isotropic homogeneous materials. Depending on the chosen direction in the material and irradiation conditions, not only the value of stresses can vary within wide limits but their sign as well. Correspondingly, even high energy release can lead to situations where the resultant stresses can be rather low and even almost vanishing.

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