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Opto-acoustic and Acoustic Microscopy Studies of Microstructure, Elasticity and Defects in B_4C/C_{60} and c-BN/C_{60} Nanocomposites

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Carbon-ceramic nanocomposites based on boron carbide with fullerene C_{60} (B_4C/C_{60}) and cubic boron nitride with C_{60} (c-BN/C_{60}) were prepared by a high-energy ball milled pre-treatment of the initial mixture of components with the addition of a CS_2 solvent followed by a high-pressure/high-temperature consolidation. Elastic properties of the composites were characterized by the elastic moduli calculated on the bases of the experimentally measured density and values of velocities of the longitudinal and transverse bulk acoustic waves (BAW) in the samples. The BAW velocities were measured with a pulse-echo method by laser optoacoustic excitation of ultrasonic pulses. Acoustic microscopy was used to visualize the bulk microstructure and internal defects, and to measure the local values of BAW velocities of specimens on which the elastic moduli were calculated.

Keywords: elastic moduli, acoustic microscopy, laser optoacoustic, carbon-ceramic nanocomposites.
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1. Introduction and preliminaries

One of the characteristics of a durable, lightweight, hard, and high-refractory material is a ratio of the tensile strength or bending strength (in units of MPa) and its density (in units of g/cm^3) σ^*/ρ. Thus, a B95 aluminum alloy has the highest value of σ^*/ρ ($\sigma^*/\rho \approx 200$ MPa$*$cm^{3*}g^{-1}) [1], and so has the carbon fiber–reinforced polymers (σ^*/ρ up to 400 MPa$*$cm^{3*}g^{-1}) [2]. In this case, both materials are neither with high hardness (hardness $\leqslant 1$ GPa), nor heat-resistant (operating temperature less than 200 °C). The known carbon-carbon composite materials are durable and

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heat-resistant, but are not highly hard. (Tensile strength of Carbon glassy is 600–1000 MPa, ρ=1,5 g/cm^3, σ^*/ρ from 400 to 600) [3]. Our goal was to develop a technique for production of carbon-based composite materials that are at the same time highly durable, lighter, highly rigid and heat-resistant. For this purpose we took very hard materials as a basis and, with the help of nanocarbon, made them less brittle and more heat-resistant. The cubic boron nitride c-BN hardness is inferior only to diamond, and its thermal and chemical stability is superior. Another well-known material, boron carbide B_4C, is light (ρ = 2,52 g/cm^3), with high hardness (H $\approx$ 35 GPa), and refractory (operating temperature up to 2000 °C), but both of these materials are extremely fragile, which makes it almost impossible to determine their σ^*/ρ parameter. The strength characteristics include hardness, tensile strength, elastic modulus (Young's modulus), proportional limit, and yield strength. There is a close correlation between the modulus and strength of the ceramic materials, which is confirmed by numerous works [4–6]. It is known that the tensile strength of the materials at temperatures less than 0,5 T_m (melting) is combined with hardness by the empirical relationship $H/\sigma_t \approx 3$. For nanostructured materials, the relation between tensile stress and grain size is described mathematically by the Hall–Petch equation (1) [7, 8]:

$$\sigma(d) = \sigma_0 + kd^{-1/2} \tag{1}$$

where σ is the tensile (yield) stress, σ_0 is a material constant for the starting stress for dislocation movement (or the resistance of the lattice to the dislocation motion), k is the strengthening coefficient (a constant specific for each material), and d is the average grain diameter. Therefore, to improve the strength of the material, it is necessary to carry out its nanostructuring. Among the basic and important methods for the diagnostics and nondestructive testing of materials, including the nanostructured ones, are ultrasonic methods. In this paper, we used the ultrasonic methods (laser ultrasound and acoustic microscopy) to study the elastic properties (Young's modulus, in particular) and microstructure of nanostructured carbon-composite ceramics, depending on the composition and preparation conditions.

2. Sample preparation

The B_4C boron carbide powder (average grain size of 100 nm) was mixed with powdered molecular C_{60} (average grain size of 1 μm) in a weight ratios in a range from 80/10 to 50/50 wt.% in a vibratory mill. Then the nanostructured boron carbide/C_{60} (B_4C/C_{60}) and boron nitride/C_{60} (c-BN/C_{60}) carbon-ceramic composites were prepared from this mixture by a high-energy ball milled pre-treatment of the parent materials. Refinement and homogenization was carried out in a high-power and high-speed planetary mill AGO-3Y which provides the effective crushing of ingot and mixing of powders at impact of working bodies with acceleration up to 20 g. Sulfur compound, in this case carbon disulfide CS_2, dissolving the C_{60} fullerene, was added to the resulting B_4C/C_{60} powder composite in amounts from 0,1 to 3,0 wt.% in terms of sulfur. This additive serves to facilitate the phase transitions in the subsequent formation of a C_{60} solid binder (matrix) in the nanocomposite at high pressure/high temperature (HPHT) treatment [9,10]. Then the mixture of $B_4C/C_{60}/CS_2$ was triturated in an agate mortar to obtain a uniform consistency and was used for preparing the samples. This mixture was charged into a pressure chamber, fixed to the load pressure between 1,0 and 5,0 GPa and heated to 1000 °C with a holding time of 60–100 sec. The preparation method of boron nitride composite powders and dense samples was similar. After unloading, the sample was examined by X-ray diffraction,

Raman spectroscopy, transmission electron microscopy, and thermogravimetric analysis, and its mechanical properties were studied, including elastic and ultrasonic properties [9, 10].

The structure of the obtained material is described in more detail in [9, 10]. According to these studies, the obtained samples are grains of boron carbide surrounded by amorphous carbon material, which are derivatives of fullerite structures [9]. X-ray phase analysis showed that in the diffractograms of the samples there is an almost unchanged initial spectrum of boron carbide, as well as a wide diffraction peak corresponding to graphite-like amorphous carbon. In the TEM diffraction images of fullerenes derivatives of the samples, obtained at the temperature of 1000 °C, the diffraction plane located at an angle of 70° have been detected. No such planes were found in the samples obtained at a higher temperature of 1200 °C [10]. Instead of 70° planes, various onions structures are observed, as well as strips consisting of graphite-like layers. The electron energy loss spectroscopy (EELS) data show the difference between the material and both graphite and fullerene, but presumably it inherits the structure of the starting fullerene. In the Raman spectra, the observed lines of the original boron carbide, tangential modes of C_{60} and broadened D and G peaks of carbon.

3. Measurements and results

3.1. Ultrasonic measurements

The BAW velocities were measured with a pulse-echo method in two ways: by laser optoacoustic excitation of ultrasonic pulses [11,12], and by acoustic microscopy [13,14]. For ultrasonic measurements, we used the samples in the shape of parts of disks with a 15–17 mm diameter, 2,5–6,0 mm height and nonflatness of the opposite faces ±1 μm/cm (Fig. 1). The samples containing the C_{60} component of 50 wt.% and 10 wt.% were taken for studies.

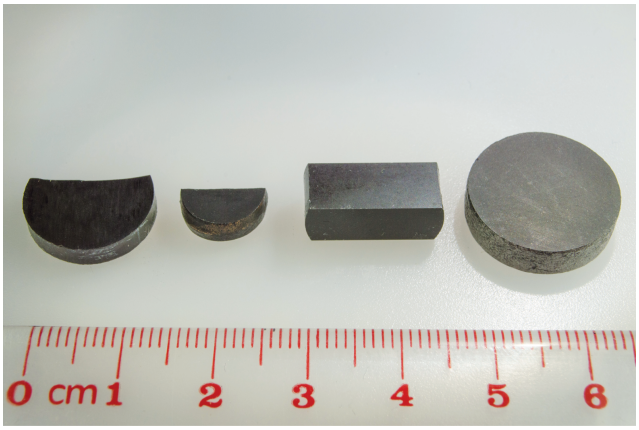

Fig. 1. Samples for ultrasonic measurements

The data on sound velocities of the longitudinal V_L and transverse V_T BAW were obtained with an accuracy of ~1 %; elastic moduli ~2–3 %. The densities of B_4C/C_{60} ceramics ranged from 2,125 to 2,301 (± 0,002) g/cm^3 for the samples with 50 wt.%C_{60}, and from 2,333 to 2,548 g/cm^3 for the samples with 10 wt.%C_{60}. Data on the elastic moduli of the HPHT-treated samples were compared to the applicable data for the sample prepared without the addition of carbon

bisulfide. Fig. 2 shows the waveforms of ultrasonic pulses of the sample No. 2 obtained by the laser optoacoustic method (a) and the acoustic microscopy method (b).

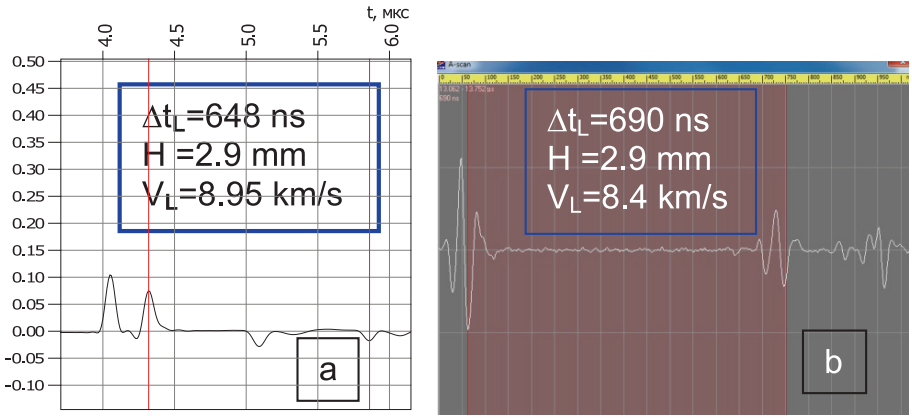

Fig. 2. The waveforms of ultrasonic pulses of the sample No. 2 obtained by the laser optoacoustic method (a) and the acoustic microscopy method (b) (Δt_L — time-of-flight double thickness of the sample; H — thickness of the sample)

The difference in the measured values of the BAW velocity is related to the fact that in the measurements by acoustic microscopy the local velocity values are determined and the elasticity moduli are calculated from these local values. So, the local values can either exceed or be less than the integral values obtained by the laser optoacoustic method. For some samples, the data on BAW velocities, densities and elastic moduli of B_4C/C_{60} carbon-ceramic composites are presented in Tab. 1. We found that the samples with the addition of carbon disulfide have higher velocities and modules at almost the same density. Several composite samples demonstrated quite high values of the sound velocities and elastic moduli. Note that the sample No. 3 (50 wt.% C_{60}) having a parallelepiped shape displays anisotropy of the elastic properties.

Sample No. 7 demonstrated exceptionally high values of the sound velocities and elastic moduli. Its density is also by 6 % higher as compared to the density of the samples No. 5 and No. 6. The velocity of longitudinal waves is equal to 11.3 km/s, which coincides with the measurements of the acoustic microscopy method. The local method of acoustic microscopy in some parts of the sample obtained even higher values of the moduli (Young's modulus exceeding 300 GPa). The hardness of this material is up to 70 GPa; the material is highly rigid.

In the samples of the composite based on the boron nitride (c-BN/C_{60}) we were not able to get any good results when used the above-mentioned values of the HPHT-treatment parameters. The elastic moduli of the samples are as follows: Young's modulus E = 55–80 GPa, the bulk modulus K = 37–58 GPa, shear modulus G = 22–33 GPa. Low elastic moduli indicate the absence of the chemical bond between the c-BN and the resulting HPHT-treatment C_{60} phase. Thus, the resulting composite material sample is not durable.

Sample No. 7 of the composite was synthesized using boron carbide powder with an average grain size of 15–25 nm, as a result of catalytic synthesis with fullerite transformation products. The density of the composite obtained in this work by sintering nanostructured boron carbide is higher than that of composites with a larger grain size. Reducing the content of C_{60} to 10 wt.% simultaneously with the decrease in the grain size of boron carbide led to a significant increase in both elastic characteristics and hardness, the value of the latter reaches a value of 70 GPa.

Table 1. Densities, bulk acoustic wave velocities, and elastic moduli of B_4C/C_{60} carbon-ceramic composites

Sample No	C_{60} wt.%	Sinte parame-tres GPa/°C	(ρ ($\pm$0,002) g/cm^3)	V_L km/c	V_T km/c	E ($\pm$3) GPa	G ($\pm$1) GPa
1*	50	3/1000	2.125	8.15	4.42	117	41.5
1		3/1000	2.125	8.62	4.44	111	42
2*		5/1000	2.293	8.42	5.27	150	63
2		5/1000	2.301	8.95	5.06	149	59
3-H1		5/1000	2.238	8.30	5.03	136	56
3-H2		5/1000	2.238	8.05	4.66	121	48
4*	10	5/1000	2.333	6.72	4.00	92	37
4		5/1000	2.333	7.42	4.05	97	37
5		5/1000	2.342	8.16	4.33	113.5	43
6		5/1000	2.391	7.97	4.70	133	54
7		4/1000	2.548	11.3	6.32	260	102
7**		4/1000	2.548	11.64	7.27	307	130

$*$ — without CS_2 additives
$**$ — acoustic microscopy data

3.2. Acoustic microscopy

The principle of the acoustic microscopy is well known [12, 13]. Acoustic microscopy is used to measure the local values of ultrasonic velocities (microacoustic technique) and to visualize the bulk microstructure of a sample (scanning acoustic microscopy). Waveform of the reflected signal is an ultrasonic A-scan. 1D- or 2D- scanning of the probe beam over the specimen surface results in the raster-formation acoustic images (B- and C-scans, respectively). A Scanning impulse acoustic microscope (SIAM, operating frequencies 50 $\div$ 200 MHz), designed and fabricated in the AM-laboratory of Emmanuel's Institute of Biochemical Physics, Russian Academy of Science, was used to make the measurements. Ultrashort probing ultrasonic 30–40 ns pulses were used for the measurements. Figures below represent the A- and C-scans. The C1-scan is obtained using parts of the A-scans array representing the reflected acoustic signals (echoes) from the subsurface layer of the sample. The C2-scan represents the echoes from the medial layer of the sample, and the C3-scan is formed using parts of the A-scans array representing the echoes from all of the sample volume. In principle, by using parts of the A-scans array, lying in a predetermined time slot, which is located between the echoes from the surface and from the bottom of the sample, we can construct an acoustic image (a C-scan) of a certain layer in the sample volume. The thickness of this layer (h) and its location in the sample (l) is given by time interval Δt and its position to be installed on an array of A-scans.

Fig. 3 illustrated the acoustic waveforms (A-scans) and internal microstructure images (C-scans) of the sample No. 2. The thickness of the imaging at the C-scan layer is defined

by the time interval marked on the A-scan highlighted by a pink stripe. The spots on the C-scans represent voids or pores in the sample. Their size reaches 500 microns. Fig. 4 shows an A-scan and an integral acoustic image (C-scan) of the sample No. 7.

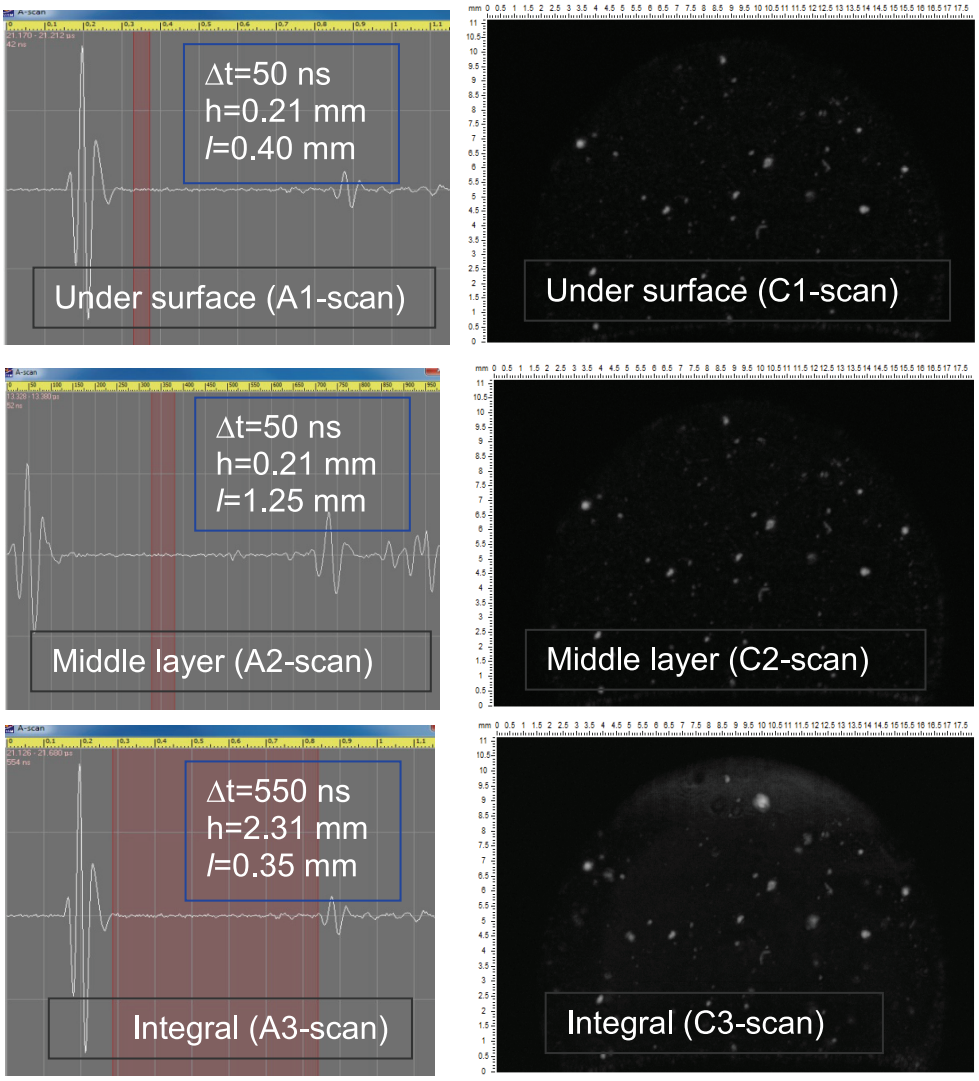

Fig. 3. Acoustic waveforms (A-scans) and images (C-scans) of the sample No. 2

The concentration of pores in this sample is considerably smaller than in the others, and the density is higher, respectively. The local velocity of longitudinal waves is equal to 11.9 km/s, which exceeds the integral values obtained by optoacoustic method. The corresponding value of the Young's modulus is greater than the integral values of the moduli (Young's modulus exceeding 300 GPa, integral value is 260 GPa). Fig. 5 shows the acoustic images of a c-BN/C_{60} composite sample microstructure. The data illustrate the possibilities of the acoustic microscopic inspection. We see quite a large defect/pore and we can determine its position in the sample volume with sufficient accuracy.

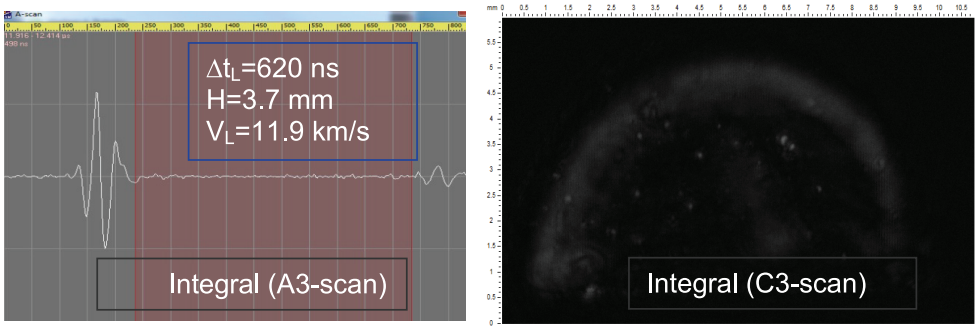

Fig. 4. Acoustic waveforms (A-scans) and images (C-scans) of the sample No. 7

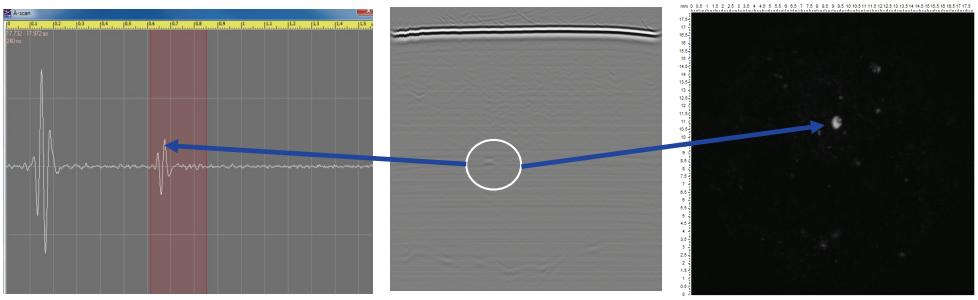

Fig. 5. Acoustic waveforms (A-scans) and images (B- and C-scans) of a sample of c-BN/C_{60}. The kind of reflection from the bottom of the sample on the B-scan indicates its great heterogeneity

Conclusion

The possibilities of acoustic microscopy for the study of elastic properties and microstructure in the bulk nanostructured carbon-composite ceramics demonstrated. Nanostructured boron carbide/C_{60} (B_4C/C_{60}) and cubic boron nitride/C_{60} (c-BN/C_{60}) carbon-ceramic composites were studied to obtain high values of the parameter σ^*/ρ and reduce porosity by adjusting the parameters of the composite synthesis and sintering. Elastic moduli have been calculated based on the experimentally measured density and velocity values of longitudinal and transverse BAW in the samples. The sound velocities were measured with a pulse-echo method by laser optoacoustic excitation of ultrasonic pulses. Several nanostructured B_4C/C_{60} composite samples prepared with the addition of carbon bisulfide demonstrated sufficiently high values of the sound velocities and elastic moduli. The elastic moduli of the samples are as follows: Young's modulus E = 140–150 GPa, the bulk modulus K = 80–105 GPa, shear modulus G = 58–63 GPa. A certain B_4C/C_{60} ceramic composite demonstrated exceptionally high values of the BAW velocities and elastic moduli (Young's modulus exceeding 300 GPa). The hardness of this material is up to 70 GPa, i.e. the material is highly rigid. Elastic moduli of the c-BN/C_{60} samples are not high. Thus the resulting composite material is not durable. Its hardness is within 10–30 GPa, and the material is sufficiently highly rigid. To estimate parameter σ^*/ρ we use is given in the Introduction, the ratio $H/\sigma_t \approx 3$. Then the smallest hardness of 10 GPa get $\sigma^*/\rho \approx$ 1300 MPa$*$cm^{3*}g^{-1}, and for the highest hardness of 70 GPa get $\sigma^*/\rho \approx$ 9000 MPa$*$cm^{3*}g^{-1}. Obviously this is a very high parameter estimation and for more accurate evaluation of its value is required direct measurement of the strength of these materials.

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Исследования микроструктуры, упругих характеристик и дефектов в нанокомпозитах B_4C/C_{60} и c-BN/C_{60} методами оптоакустики и акустической микроскопии

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Нанокомпозиты на основе карбида бора с фуллереном (B_4C/C_{60}) и кубического нитрида бора с фуллереном (c-BN/C_{60}) были приготовлены методом предварительной высокоэнергетической обработки путем размола в шаровой мельнице исходной смеси компонент с добавлением CS_2 и консолидацией полученной смеси в условиях высоких давлений и высоких температур. Упругие свойства композитов характеризовались модулями упругости, рассчитанными на основе экспериментально измеренных значений плотности и скоростей объемных упругих волн в образцах. Скорости упругих волн измерялись методом оптоакустического возбуждения ультразвуковых импульсов лазерно-ультразвуковым дефектоскопом УДЛ-2М. Визуализация микроструктуры и дефектов в объеме образца, определение значений локальных скоростей упругих волн, из которых рассчитывались локальные значения модулей упругости, проводились на сканирующем импульсном акустическом микроскопе SIAM.

Ключевые слова: упругие модули, акустическая микроскопия, лазерная оптоакустика, углеродные керамические нанокомпозиты.