MECHANICAL PROPERTIES OF NANOSTRUCTURED B_{4}C/C_{60} AND c-BN/C_{60} COMPOSITES PREPARED BY HPHT METHOD

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Abstract: Nanostructured boron carbide/C_{60} (B_{4}C/C_{60}) and cubic boron nitride/C_{60} (c-BN/C_{60}) carbon-ceramic composites were prepared by a high-energy ball milled pre-treatment of the parent materials with the addition of a CS_{2} solvent followed by a high-pressure/high-temperature (HPHT) treatment. The elastic moduli were calculated based on the experimentally measured density and velocity values of the longitudinal and transverse bulk acoustic waves (BAW) in the specimens. 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 had been calculated and compared with the data defined by the pulse-echo method. The microhardness and flexural strength of the samples were measured also.

Keywords: NANOSTRUCTURED COMPOSITES, HPHT TREATMENT, MECHANICAL PROPERTIES

1. Introduction

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 (σ/ρ = 200 MPa⋅cm^{3}/g^{3}) [1,2], and so do the carbon fiber–reinforced polymers (σ/ρ up to 400 MPa⋅cm^{3}/g^{3}) [3]. In this case, both materials are neither high-hardness (hardness H ≤ 1 GPa), nor heat-resistant (operating temperature less than 200 °C). The known carbon–carbon composite materials are durable and 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) [4].

Our goal was to develop a technique for commercial production of the carbon-based composite materials that are at the same time highly durable, lighter, highly rigid and heat-resistant. With 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 exceeds the diamond parameters. Another well-known material, boron carbide B_{4}C, is light (ρ = 2.52 g/cm^{3}), high-hardness (H ≈ 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 [5].

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 [6-8].

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/σ ≈ 3. For nanostructured materials, the relation between tensile stress and grain size is described mathematically by the Hall–Petch equation [9-10]:

\[ \sigma(d) = \sigma_0 + k d^{-1/2} \]

where \( \sigma \) is the tensile (yield) stress, \( \sigma_0 \) 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.

Ultrasonic methods are among the basic and important methods for the diagnostics and nondestructive testing of materials, including the nanostructured ones. In this paper, we used the ultrasonic methods (laser ultrasound and acoustic microscopy) to investigate the elastic properties (Young's modulus, in particular) and microstructure of nanostructured carbon-composite ceramics, depending on the composition and preparation conditions.

Mechanical properties of B_{4}C ceramics, prepared by a high-energy ball milled pre-treatment of the parent materials followed by a hot-pressing sintering were studied in [11].

2. Experimental procedure

2.1. Materials and processing

The B\textsubscript{4}C boron carbide powder (average grain size of 100 nm) is mixed with powdered molecular C\textsubscript{60} (average grain size of 1 μm) in a weight ratios in the range from 80/10 to 50/50 wt.% in a vibratory mill. Then, the nanostructured boron carbide/C\textsubscript{60} (B\textsubscript{4}C/C\textsubscript{60}) and boron nitride/C\textsubscript{60} (c-BN/C\textsubscript{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 20g.

Sulfur compound, in this case carbon disulfide CS\textsubscript{2}, dissolving the C\textsubscript{60} fullerene, was added to the resulting B\textsubscript{4}C/C\textsubscript{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\textsubscript{60} solid binder (matrix) in the nanocomposite at HPHT-treatment [12]. Then, the mixture of B\textsubscript{4}C/C\textsubscript{60}/CS\textsubscript{2} was triturated in an agate mortar to obtain a uniform consistency and was used for preparing the specimens. 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 specimen 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.
2.2. Experimental

2.2.1. Ultrasonic measurements

The BAW velocities were measured with a pulse-echo method in two ways: by laser optoacoustic excitation of ultrasonic pulses [13-14], and by acoustic microscopy [15-16]. For ultrasonic measurements, we used the specimens 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 specimens containing the C_{60} component of 50wt.% (denoted S50) and 10wt.% (denoted S10) were taken for studies.

![Samples for ultrasonic measurements.](image)

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\(_4\)C/C\(_{60}\) ceramics ranged from 2.125 to 2.301 (± 0.002) g/cm\(^3\) for the specimens with 50wt.% C\(_{60}\), and from 2.333 to 2.548 g/cm\(^3\) for the specimens with 10wt.% C\(_{60}\). The data on the elastic moduli of the HPHT-treated specimens were compared to the applicable data for the specimens prepared without the addition of carbon disulfide.

Figure 2 shows the waveforms of ultrasonic pulses of the specimen S50-2 obtained by the laser optoacoustic method (a) and the acoustic microscopy method (b).

![The waveforms of ultrasonic pulses of the specimen S50-2 obtained by the laser optoacoustic method (a) and the acoustic microscopy method (b).](image)

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 specimens, the data on BAW velocities, densities and elastic moduli of B\(_4\)C/C\(_{60}\) carbon-ceramic composites are presented in Table 1. We found that the specimens with the addition of carbon disulfide have higher velocities and modules at almost the same density.

<table>
<thead>
<tr>
<th>( \rho ) (±0.002) g/cm(^3)</th>
<th>( V_L ) km/c</th>
<th>( V_T ) km/c</th>
<th>( E ) (±3) GPa</th>
<th>( G ) (±1) GPa</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S50-1*</td>
<td>2.125</td>
<td>8.15</td>
<td>4.42</td>
<td>117</td>
<td>41</td>
</tr>
<tr>
<td>S50-1</td>
<td>2.125</td>
<td>8.62</td>
<td>4.44</td>
<td>111</td>
<td>42</td>
</tr>
<tr>
<td>S50-2*</td>
<td>2.293</td>
<td>8.42</td>
<td>5.27</td>
<td>150</td>
<td>63</td>
</tr>
<tr>
<td>S50-2</td>
<td>2.301</td>
<td>8.95</td>
<td>5.06</td>
<td>149</td>
<td>59</td>
</tr>
<tr>
<td>S50-3H1</td>
<td>2.238</td>
<td>8.30</td>
<td>5.03</td>
<td>136</td>
<td>56</td>
</tr>
<tr>
<td>S50-3H2</td>
<td>2.238</td>
<td>8.05</td>
<td>4.66</td>
<td>121</td>
<td>48</td>
</tr>
<tr>
<td>S10-1*</td>
<td>2.333</td>
<td>6.72</td>
<td>4.00</td>
<td>92</td>
<td>37</td>
</tr>
<tr>
<td>S10-1</td>
<td>2.333</td>
<td>7.42</td>
<td>4.05</td>
<td>97</td>
<td>37</td>
</tr>
<tr>
<td>S10-3</td>
<td>2.342</td>
<td>8.16</td>
<td>4.33</td>
<td>114</td>
<td>43</td>
</tr>
<tr>
<td>S10-4</td>
<td>2.391</td>
<td>7.97</td>
<td>4.70</td>
<td>133</td>
<td>54</td>
</tr>
<tr>
<td>S10-5</td>
<td>2.548</td>
<td>11.3</td>
<td>6.32</td>
<td>260</td>
<td>102</td>
</tr>
<tr>
<td>S10-5**</td>
<td>2.548</td>
<td>11.6</td>
<td>7.27</td>
<td>307</td>
<td>130</td>
</tr>
</tbody>
</table>

* - without CS\(_2\) additives
** - acoustic microscopy data

The specimen S10-5 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 specimens S10-3 and S10-4. 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 specimen 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 specimens 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 specimens 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 is not durable. The hardness of the material obtained by us is within 10–70 GPa, and the material is highly rigid.

2.2.2. Acoustic microscopy

The principle of the acoustic microscopy is well known [15-17]. 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). The 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 SIAM Scanning impulse acoustic microscope (50÷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. Ultrasound 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 specimen. The C2-scan represents the echoes from the medial layer of the specimen, and the C3-scan is formed using parts of the A-scans array representing the echoes from all of the specimen volume.

Using parts of the A-scans array lying in a predetermined time slot, we can construct an acoustic image (a C-scan) of a certain layer in the specimen volume. The thickness of this layer (h) and its position to be installed on an array of A-scans.

Figure 3 illustrated the acoustic waveforms (A-scans) and internal microstructure images (C-scans) of the specimen S50-2. 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 specimen. Their size reaches 500 microns.

Figure 4 shows an A-scan and an integral acoustic image (C-scan) of the specimen S10-5.

The concentration of pores in this sample is considerably smaller than in the others, and accordingly, the density is higher.

The local velocity of longitudinal waves is equal to 11.9 km/s, which exceeds the integral values obtained by optoacoustic method.

Figure 5 shows an A-scan and an integral acoustic image (C-scan) of the specimen S10-5. The kind of reflection from the bottom of the sample on the B-scan indicates its great heterogeneity.

4. Conclusion

The possibilities of acoustic microscopy for the study of elastic properties and microstructure in the bulk nanostructured carbon-composite ceramics are demonstrated.

Nanostructured boron carbide/C60 (B4C/C60) and cubic boron nitride/C60 (c-BN/C60) 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 were calculated based on the experimentally measured density and velocity values of longitudinal and transverse BAW in the specimens. The sound velocities were measured with a pulse-echo method by laser optoacoustic excitation of ultrasonic pulses.

Several nanostructured B4C/C60 composite specimens prepared with the addition of carbon bisulfide demonstrated sufficiently high values of the sound velocities and elastic moduli. The elastic moduli of the specimens were as follows: Young’s modulus E = 140–150 GPa, bulk modulus K = 80–105 GPa, shear modulus G = 58–63 GPa.

A certain B4C/C60 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.

The elastic moduli of the c-BN/C60 specimens 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.

5. References


6. Acknowledgments

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