Effect of synthesis parameters on the structure and properties of carbon particles formed from amorphous fullerites

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Abstract. The effect of high-pressure synthesis temperature on the structure and indentation characteristics of the superelastic hard carbon formed from amorphous fullerites and on the tribological properties of the Co-based composite materials (CM) reinforced by the particles of such carbon has been studied by Raman spectroscopy, high-resolution transmission electron microscopy (HRTEM), indentation measurements, and tribological tests. It is shown that ball milling (for 48 h) of C₆₀ fullerite crystals results in the amorphization of the product of fullerite transformation upon their high-pressure treatment at temperatures above the stability limit of fullerene molecule (~800°C). An increase in synthesis temperature at 8 GPa from 800°C to 1200°C leads to a gradual graphitization of the structure of amorphous fullerite derived carbon. This decreases its hardness and indentation modulus from 32 to 18 GPa and from 256 to 95 GPa, respectively, and increases the elastic recovery (from 80% to 86%). The best tribological characteristics of the CM are attained at the maximum particle hardness, which is realized in the CM synthesized at 800°C. When the synthesis temperature is elevated to 1200°C, the friction coefficient and wear rate of the CM increase, but they remain substantially lower than those of the matrix cobalt.

1. Introduction
The products of high-pressure high-temperature fullerene decomposition are characterized by a unique combination of high hardness and superelasticity. For this reason, they are advantageous, in particular, for reinforcing metal matrix for the development of a new class of composite materials with a low friction coefficient of and high wear resistance [1]. The structure of bulk transformation products of C₆₀ crystals at moderate pressure (3–8 GPa) was studied in [2–5]. It was shown that, at temperatures

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above the upper temperature limit of the stability of fullerene molecule, their collapse under pressure leads to the formation of hard graphite-like phases consisting of curved graphene planes. The structure of a disordered graphite (DG) phase consisting of nanoscale clusters containing 5-10 atomic layers (graphene planes) is characterized by long-range correlations [4], since the layers of the DG structure are parallel to the close-packed (111) planes of the parent fcc C_{60} crystals. Such “hard” carbon exhibits an extremely high elastic recovery upon stress relief [3] due to the ability of curved graphene layers to be compressed without shear and then to expand back to the initial structure. The collapse of amorphous fullerite C_{60} upon heating under pressure at a relatively low synthesis temperature (800°C) results in the formation of highly disordered carbon phase consisting of randomly arranged packets of 2-3 short graphene layers [6]. Such carbon was shown to be substantially harder but less elastic than the carbon formed from crystalline fullerites at the same synthesis conditions. The pressure-temperature diagram of the transformations of amorphous C_{60} fullerite has been constructed in [7]. In the present work, we studied the effect of high-pressure synthesis temperature on the structure and properties of carbon particles obtained from amorphous fullerites as well as on the tribological characteristics of metal-matrix composite materials reinforced by the carbon particles.

2. Experimental
The cobalt-based CM samples of 5 mm in diameter and 3-4 mm high were prepared from mixtures of cobalt powder and 10 wt % C_{60}. The initial fullerites were processed in a Frisch ball mill in an agate mortar with agate balls at low milling rates in a helium atmosphere. The powder mixtures were sintered at a pressure of 8 GPa in a toroid-type high-pressure chamber (toroid-15). The powder pellets pre-compressed at a pressure of less than 1 GPa were placed inside the tubular heater in the central part in order to reduce temperature gradients in the sample upon subsequent sintering. Under pressure, the samples were heated at a fixed rate of up to 100 K/min to a predetermined temperature by passing current through the heater. The sintering duration at fixed pressure-temperature parameters was 45 s. The temperature in the high-pressure cell was controlled by chromel-alumel thermocouples. The thermocouple junctions were placed on the outer wall of the graphite heater at the middle of its height. The structure of carbon phase was identified by the Raman spectra recorded with a WITec high-resolution CRM 200 spectrometer equipped with a confocal attachment. The size of the laser spot at the focus was about 1 μm. The fine structure of the superelastic hard carbon was studied by high-resolution transmission electron microscopy (TEM/STEM TITAN 80-30) at an accelerating voltage of 300 kV. The samples for transmission electron microscopy were prepared by ion beam cutting at Helios NanoLab (FEI, USA). Registration and processing of the obtained images was carried out with Digital Micrograph programs. The indentation properties of the high-pressure carbon phase were measured with Shimadzu dynamic ultra micro hardness tester DUH-211/DUH-211S. The tribological and abrasive wear tests were performed with a UMT-3MO (CETR) Universal Tester.

3. Results and discussion
The powders of the initial crystalline C_{60} fullerite are substantially nonuniform in morphology and particle size. Along with crystallites of 1-2 μm in size, there are nanosize crystallites, the total fraction of which is quite small (Figure 1a). After ball milling, the crystallite size decreases to 100-500 nm, and the grains smaller than 100 nm in size are also present (Figure 1b). The XRD spectra of the ball-milled fullerites exhibit substantial broadening of the C_{60} diffraction peaks and the presence of amorphous structure constituent, as was shown in [8].

The high-pressure treatment of the powder mixtures of cobalt and fullerites at temperatures above the limit of fullerene molecule stability leads to the synthesis of cobalt-base composite materials reinforced by superelastic hard carbon particles. Amorphization of the initial fullerites upon long-time ball milling breaks the packing order of fullerenes and reduces the probability of the formation of regularly oriented graphene plane packets upon heating under pressure [5, 9]. With increasing synthesis temperature from 800°C to 1200°C, the fullerites tend to transform into more stable graphite-like phase, which is exhibited by a series of Raman spectra (Figure 2).
Figure 1. C$_{60}$ fullerites: (a) initial and (b) after ball milling for 48 hours

Figure 2. Raman spectra of the carbon particles formed from amorphous C$_{60}$ at a pressure of 8 GPa at different synthesis temperatures.

The structure of the carbon particles formed at a relatively low synthesis temperature (800°C) generally corresponds to the amorphous state (Figure 3a) and contains short packets of 2-3 graphene layers arranged randomly in the amorphous matrix. The Fourier transform of such image is represented by a wide ring typical of amorphous structure (insert in Figure 3a). The structure of the carbon particles formed from amorphous fullerites at a high synthesis temperature (1200°C) consists of more extended curved graphene layers (Figure 3b) than those observed in the structure formed at 800°C. However, unlike graphene nanoclusters obtained from fullerite crystals [5], such packets are randomly oriented, as is clearly shown by the Fourier transform represented by a ring without pronounced preferred directions (insert in Figure 3b). This ring is much narrower than that of the phase synthesized from ball-milled fullerites at 800°C. Thus, the tendency to the formation of graphite-like structure from amorphous fullerite increases with synthesis temperature elevation, which increases the thermodynamic stimulus to achieve the equilibrium state (graphite).
The ball milling of C<sub>60</sub> fullerites for 48 h leads to a significant increase in hardness (18 to 32 GPa) and elastic modulus (from 104 to 256 GPa) of their transformation product at a pressure of 8 GPa at 800°C and decreases its elastic recovery (from 94 to 80%) [6]. This is explained by the fact that the amorphization of the parent fullerites decreases the probability of the formation of graphene plane packets upon heating under pressure and, therefore, the fullerene fragments upon collapse of amorphous (ball-milled) fullerites under optimum synthesis conditions (high pressure and the temperature just above the limit of the stability of fullerene molecule) form more dense spatial network of strong covalent bonds. As the temperature of the synthesis of carbon particles from amorphized fullerites increases from 800°C to 1200°C, the formation of a more equilibrium graphite-like phase is accompanied by a decrease in hardness and indentation modulus of the synthesized carbon particles with a slight increase in elastic recovery (Table 1). Thus, the sintering temperature dependence of the indentation characteristics reflects the structure evolution of the fullerene-derived carbon particles: the hardness decreases and the elasticity increases with increasing degree of graphitization. As is seen from Table 1, the tribological properties of the CM spatially reinforced by 10 wt % of superelastic hard carbon particles substantially depend on the hardness of the carbon phase. The best combination of such properties, i.e., the lowest friction coefficient and wear rate, is exhibited by the CM synthesized at 800°C. With increasing synthesis temperature, the tribological properties of the CM are deteriorated, although, compared with the matrix cobalt (characterized by $\mu = 0.41$ and wear rate $= 6.30$ mg/m), they remain very attractive in the entire range of synthesis regimes used. Note that, in our case, the ratio of hardness to indentation modulus increases from 0.13 to 0.19 with increasing synthesis temperature. Similar results were obtained in [10] for nanocarbon phases derived from C<sub>60</sub> fullerenes at different synthesis conditions. Although the $H/E$ ratio is commonly recognized to better predict the wear resistance of the material than hardness only [11], the data given in Table 1 show that, in the range of properties under consideration, a decrease in hardness is accompanied by an increase in the H/E ratio, but, at the same time, the best tribological characteristics are exhibited by the CM reinforced by the hardest particles.
Table 1. Indentation characteristics (indentation hardness \( H_{IT} \), indentation modulus \( E_{IT} \), and elastic recovery \( \eta_{IT} = W_{elast}/W_{total} \), where \( W_{elast} \) and \( W_{total} \) are the elastic and total indentation works, respectively) of the carbon particles derived from ball-milled \( C_60 \) fullerites and the triboLOGical properties (friction coefficient \( \mu \) and wear rate) of the composite materials reinforced by such particles.

| Synthesis temperature (°C) | Properties of carbon phase | Properties of CM |
|----------------------------|-----------------------------|------------------|
|                            | \( H_{IT} \) (GPa) | \( E_{IT} \) (GPa) | \( \eta_{IT} \) (%) | \( \mu \) | Wear rate (mg/m) |
| 800 | 32 | 256 | 80 | 0.13 | 0.07 |
| 900 | 23 | 140 | 84 | 0.18 | 0.13 |
| 1000 | 22 | 127 | 85 | 0.22 | 0.26 |
| 1200 | 18 | 95 | 86 | 0.23 | 1.50 |

4. Conclusion
Ball milling (for 48 h) of \( C_{60} \) fullerite crystals results in their substantial refinement and in the amorphization of the product of fullerite transformation upon their high-pressure treatment at temperatures above the temperature limit of the stability of fullerene molecule (~800°C). An increase in the high-pressure (8 GPa) synthesis temperature from 800°C to 1200°C leads to a gradual graphitization of the structure of amorphous fullerite derived carbon. This is expressed by the isolation of the D peak in the Raman spectrum and in an increase in the number and extension of graphene layers in HRTEM structure images. The graphitization of the structure of the carbon phase with increasing temperature of high-pressure synthesis decreases its hardness and indentation modulus from 32 to 18 GPa and from 256 to 95 GPa, respectively, and slightly increases elastic recovery (from 80% to 86%). The best tribological characteristics of the Co-based CM reinforced by the carbon particles correspond to the maximum particle hardness, which is realized in the CM synthesized at 800°C. When the synthesis temperature is increased to 1200°C, the friction coefficient and wear rate of the CM increase (from 0.13 to 0.23 and from 0.07 to 1.50 mg/m, respectively), but, at the same time, they remain substantially lower than those of the matrix cobalt.

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