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FUNCTIONAL AND STRUCTURAL NANOMATERIALS

Effect of Hydrogenation of C_{60} Fullerenes on the Properties of Their Transformation Products at High Pressures and Temperatures

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Abstract—New superelastic superhard carbon materials are obtained from C_{60} fullerites hydrogenated in the solid state in a hydrogen atmosphere to a content of 0.4 wt % H (formula ~$C_{60}H_{3.5}$). Raman spectroscopy, light and electron microscopy, dynamic indentation, and tribological tests are used to study composite materials (CM) synthesized from mixtures of powders of Co and 10-wt % fullerites C_{60} or $C_{60}H_{3.5}$ under a pressure of 8 GPa at a temperature of 800°C. Hydrogenation of the initial fullerites increases the degree of amorphization of the structure of the high-pressure graphite-like phase, while its hardness increases by more than 2.5 times, up to ~52 GPa, and the elastic modulus during indentation increases by about 3 times, up to 333 GPa. The hydrogenation of C_{60} fullerites is a promising method for improving the tribotechnical characteristics of the superelastic hard phase formed during the thermobaric treatment of fullerites, as well as CMs reinforced with particles of such a phase: the CM friction coefficient decreases from 0.25 to 0.01 with a significant increase in wear resistance.

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INTRODUCTION

The hydrogenation of fullerites has been widely studied with the aim of using them in hydrogen storage [1, 2]. Hydrogen molecules fill the tetrahedral and octahedral pores of the face-centered cubic (fcc) lattice of fullerite [3], and when the hydrogen concentration reaches more than 4.5 wt %, the destruction of the lattice and the amorphization of fullerite begin [4]. The dehydrogenation reaction is irreversible because it leads to the collapse of fullerene molecules [5].

The introduction of hydrogen into the composition of diamond-like coatings in many cases favorably affects their tribological properties [6, 7]. The nanocluster graphene structure, which is close to diamond-like carbon in terms of the combination of high hardness and superelasticity [8–10], is formed from fullerenes upon heating under pressure due to the collapse of fullerene molecules. In this work, the hydrogenation of initial fullerenes is used as a factor influencing the structure of high-pressure carbon phases. The fact that C–H bonds of weakly hydrogenated fullerene break more easily than carbon bonds in fullerene [11] can trigger the mechanisms of chemically activated crosslinking of neighboring fullerene molecules by single C–C bonds and change the scenario of phase transformations upon heating under pressure.

In terms of applications, it is of interest to use the hydrogenation of fullerene to improve the physical and mechanical properties of compact materials synthesized under pressure based on it. In industry, the pressures used are limited to 8–9 GPa, high pressures are used only in laboratories. For this reason, the synthesis of superhard samples from fullerene at pressures of ~8 GPa is most interesting for practical applications, which has influenced the choice of conditions for

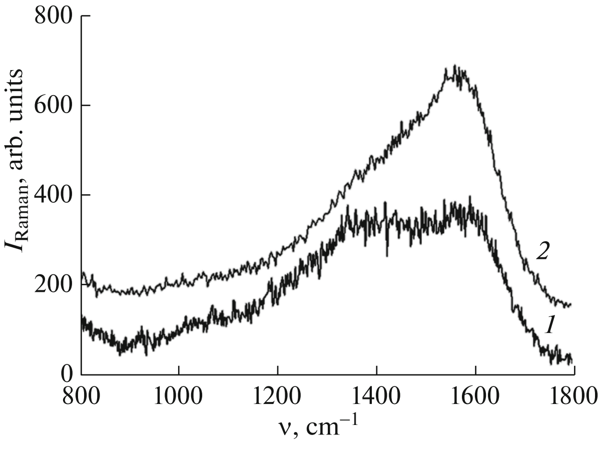

Fig. 1. Raman spectra of carbon particles obtained from nonhydrogenated (*1*) and hydrogenated (*2*) C_{60} fullerites.

obtaining samples in this study. Metal-matrix composite materials (CM) with a filler of carbon phases were obtained to study the possibility of their application as antifriction highly wear-resistant materials [12]. The use of CM is intended to overcome the problem of the brittleness of superhard bulk samples obtained from fullerenes under pressure.

MATERIALS AND METHODS

The initial C_{60} (99.9% purity) was hydrogenated in the solid state in a hydrogen atmosphere at a pressure of 50 MPa and a temperature of 320 °C for 6 h without the use of catalysts [13]. The hydrogen content in the hydrogenated samples was determined by gas chromatography (Elementar Analysensysteme GmbH vario EL cube) and sample degassing upon heating (RHEN 602 LECO analyzer) at a level of 0.40–0.45 wt %, which approximately corresponds to the composition $C_{60}H_{(3-3.5)}$. It is most likely that hydrogen saturates two valences at once when one bond is broken, then the resulting composition can be represented as a mixture of the most probable compounds $C_{60}H_2$ (25–50%) and $C_{60}H_4$ (50–75%). The X-ray phase analysis of fullerites was performed in the reflection mode (Cu radiation, Rigaku Ultima 4 diffractometer). CM samples with a height of 2.5 and 5 mm in diameter were synthesized from a mixture of cobalt powders with 10 wt % of hydrogenated and nonhydrogenated fullerites at a pressure of 8 GPa at 800°C in a toroid-type high-pressure chamber [14]. Temperature control was carried out using a chromel-alumel thermocouple. The structure of the high-pressure phases was studied by Raman spectroscopy (Horiba Jobin-Yvon Lab.RAM HR; $\lambda = 473$ nm), optical microscopy (Olympus GX51), scanning electron microscopy (SEM) (Quanta 3D DualBeam), and high-resolution transmission electron microscopy (HRTEM) (Tecnai Osiris FEI).

The mechanical characteristics of carbon particles (indentation hardness H_{IT}, indentation elastic modulus E_{IT}, and elastic recovery $\eta_{IT} = W_{elast}/W_{total}$, where W_{elast} and W_{total} are the elastic and total indentation work, respectively) were determined using a dynamic ultramicrohardness tester DUH-211S (Shimadzu) according to the ISO14577 standard (GOST 8748-2011) using a Vickers indenter at a load of 500 mN in the loading-unloading mode at a loading rate of 70 mN/s. Tribological testing of the CM samples was carried out on a CETR UMT-3MO setup according to the pin-on-disc scheme at a load of 1 kg at a linear velocity of 0.3 m/s. The friction coefficient μ was determined during circular motion along a counterbody made of steel with a hardness of 62 HRC. Tests for abrasive wear were performed in a similar way when sliding the samples on sandpaper (electrocorundum, grain size 18 μm) along a fresh track. The wear rate *I* was determined from the CM mass loss during the passage of a path 9 m long.

RESULTS

The hydrogenation of fullerite C_{60} to ~0.40 wt % leads to an insignificant shift in the positions of X-ray peaks, which indicates a slight increase in the lattice parameter (from 14.169 to 14.194 Å) while maintaining the fcc crystal structure. This agrees with the data presented in [4] for high hydrogen contents in C_{60}.

The hydrogen content in the synthesized high-pressure carbon phase corresponds to its content in the initial fullerite. The Raman spectra of carbon particles (Fig. 1) obtained from hydrogenated fullerites at 8 GPa (800°C) are a wide asymmetric band characteristic of graphite-like particles obtained from C_{60} at a pressure of more than 9 GPa [8], while the symmetric "double-humped" spectrum of the particle obtained from nonhydrogenated C_{60} fullerites is typical of the carbon phase obtained from C_{60} crystals at 8 GPa.

In the study of the structure of the reinforcing CM carbon phase from C_{60} crystals by light microscopy in polarized light, optical anisotropy is observed, indicating a hereditary relationship with the structure of the initial crystals, shown in [15, 16]. The reason is the presence of long-range order in the orientation of the graphene planes of the synthesized carbon phase within the initial C_{60} molecular crystal. Hydrogenation of the initial fullerites eliminates the optical anisotropy in the structure of the high-pressure phase (Fig. 2), despite the preservation of the crystal structure of the initial fullerites.

Electron microscopic images of the fine structure of the carbon phase obtained from C_{60} and $C_{60}H_{3.5}$ (Fig. 3) show that in both cases it consists of graphene packets characteristic of the nanocluster graphene phase [15]. According to the results of statistical image processing, the packet size of the hydrogenated phase decreases from ~2.0 to ~1.5 nm.

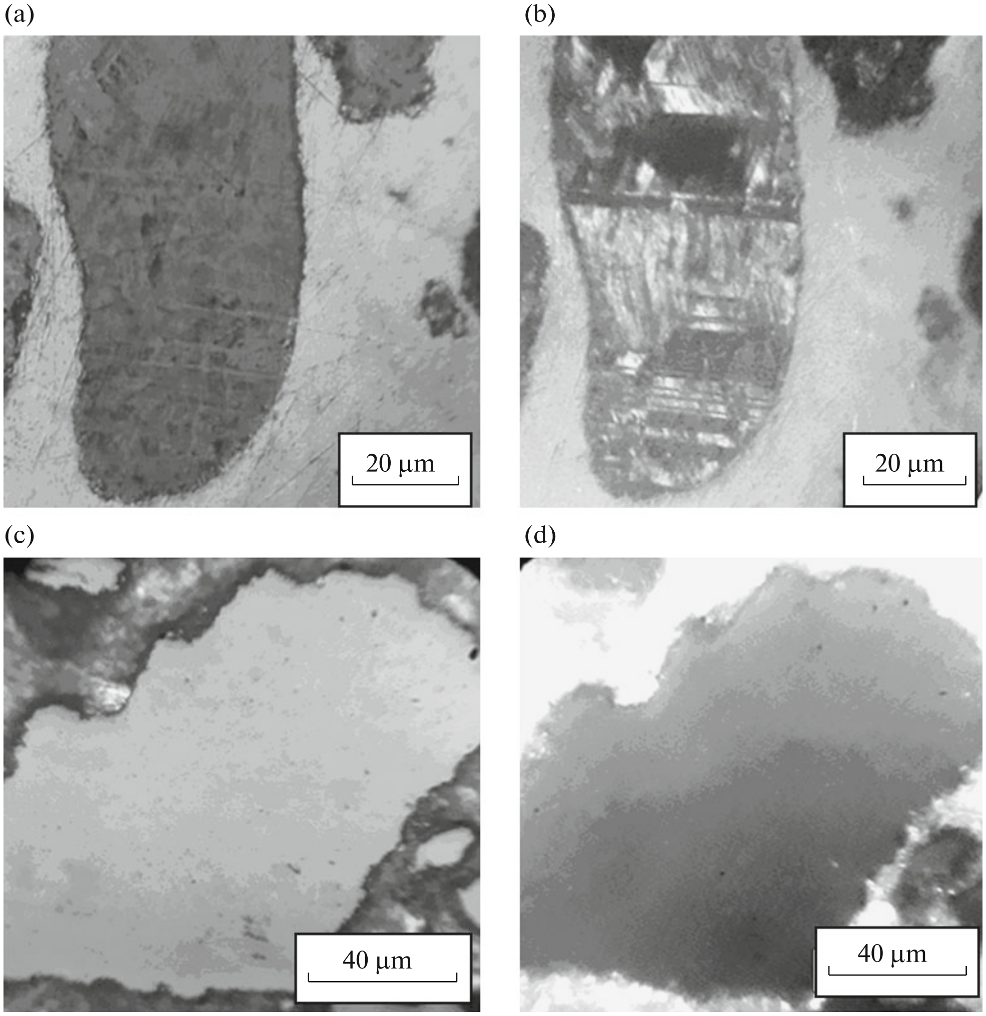

Fig. 2. Particles of high-pressure carbon phases (8 GPa, 800°C) obtained from C_{60} fullerites without treatment (a, c) and after hydrogenation to the composition $C_{60}H_{3.5}$ (b, d). Images (b) and (d) were obtained in polarized light.

The electron diffraction patterns (Fig. 4) obtained from an area of 100 nm^2 show annular halos corresponding to the d_{002} reflection of a graphite-like structure. Blurred reflections in Fig. 4a indicate the preferred orientation of graphene nanoclusters inherited from the fcc C_{60} fullerite crystal from which the sample was obtained. The absence of pronounced reflections on the annular halo of the sample from $C_{60}H_{3.5}$ indicates that the graphene nanoclusters in this sample are located more chaotically and with a weaker preferred orientation.

Images of the fracture surface of carbon samples obtained by SEM are shown in Fig. 5. The sample without hydrogen is destroyed with the formation of ridges and rows of parallel steps, which have a close direction within the field of view (Fig. 5a). Upon fracturing of the sample with hydrogen, steps are also observed (Fig. 5b), but they are more smooth, not parallel, and are located more chaotically than in the sample without hydrogen.

At a higher magnification (Figs. 5c, 5d), signs of ductile intergranular fracture are visible, which occurs between granule clusters in the form of grains <40 nm in size [17]. Such grains with a size of several tens of microns were found at high magnification in the structure of hard carbon obtained in [18] during the high-temperature high-pressure treatment of C_{60} fullerites. In the fracture of the nonhydrogenated sample, such grains form ridges with close directionality within the image, while grains of hydrogenated carbon in the fracture form a more uniform surface.

Comparison of the results of the indentation of carbon particles (Tab. 1) shows that hydrogenation of the initial fullerites significantly increases their hardness and elasticity modulus during indentation, while maintaining superelasticity. The ratio of hardness to the indentation modulus, which is recognized as a criterion for the tribological properties of a material [19], decreases from 0.20 to 0.15, but remains high enough

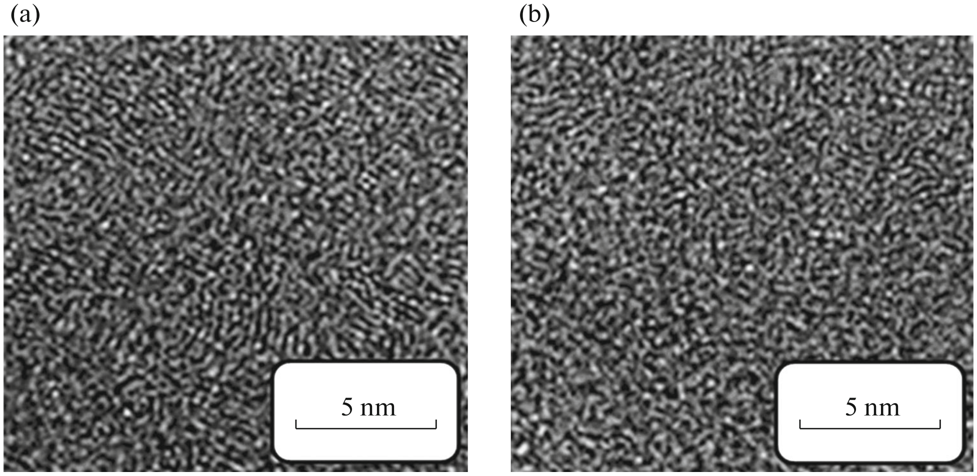

Fig. 3. Electron-microscopy images of the structure of the carbon phase obtained from (a) C_{60} and (b) $C_{60}H_{3.5}$.

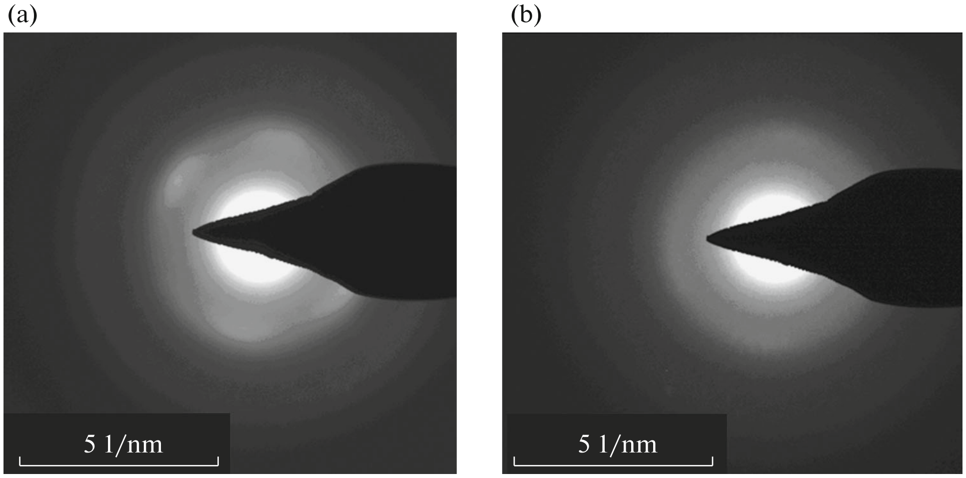

Fig. 4. Electron-diffraction patterns of samples of the carbon phase obtained from (a) C_{60} and (b) $C_{60}H_{3.5}$.

to ensure good tribological properties of CM reinforced with these carbon particles.

When assessing the effect of hydrogenation of the initial fullerites on the friction coefficient and wear rate of the synthesized CMs, a Co-based CM reinforced with diamond particles obtained from fullerenes was used as a reference [20]. According to the results of tribological tests shown in Fig. 6, the friction coefficient for CMs of Co + ($C_{60}H_{3.5}$) is the lowest during the entire test period (Table 1). In terms of wear resistance, this CM is significantly superior to CM made of Co + C_{60}, but inferior to CM reinforced with diamonds (Fig. 7).

DISCUSSIONS

According to the results of structural studies, the hydrogenation of the initial fullerites significantly

Table 1. Characteristics of indentation of carbon particles obtained from nonhydrogenated and hydrogenated C_{60} fullerites and the tribological properties of CM reinforced with such particles

Composition of the initial mixture	Properties of synthesized carbon particles			CM Properties	
	H_{IT}, GPa	E_{IT}, GPa	η_{IT}, [%]	μ	I, mg/m
Co + 10%C_{60}	17.8	89.5	87	0.25	0.19
Co + 10%($C_{60}H_{3.5}$)	51.6	333.0	80	0.01	0.05

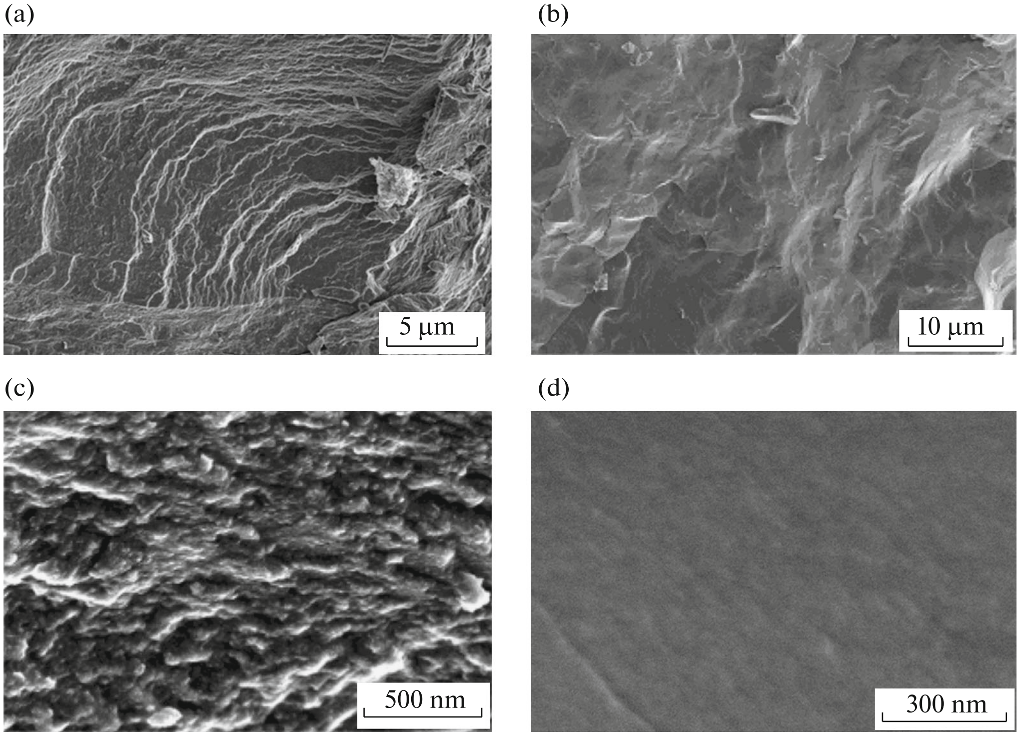

Fig. 5. Fracture surfaces of high-pressure carbon phases obtained from (a, c) C_{60} and (b, d) $C_{60}H_{3.5}$.

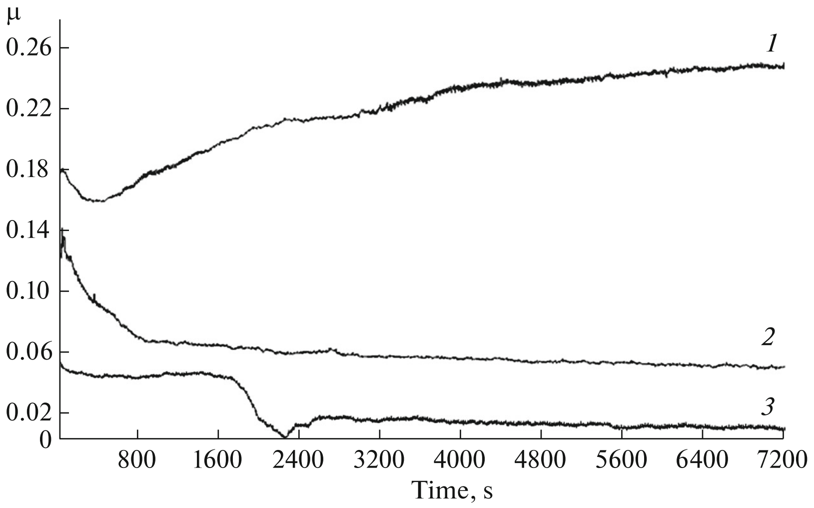

Fig. 6. Friction coefficients of Co-based CM samples reinforced with carbon particles obtained from (*1*) nonhydrogenated and (*3*) hydrogenated C_{60} and (*2*) with diamond particles.

increases the degree of amorphization of high-pressure carbon phases, which is expressed in the disappearance of the optical anisotropy of the particle structure in polarized light, the refinement and random orientation of packets of the nanocluster graphene phase (according to the HRTEM data), as well as in the smoothed and more uniform surface destruction of particles (according to SEM data). Similar structural changes in the high-pressure phase were observed after amorphization of the initial C_{60} fullerites by grinding in a ball mill [21, 22]. Amorphization of the initial fullerites violates the packing order of fullerenes, which reduces the probability of the formation of regularly oriented packets of graphene planes during heating under pressure and increases the proportion of sp^3-hybridized states of carbon atoms,

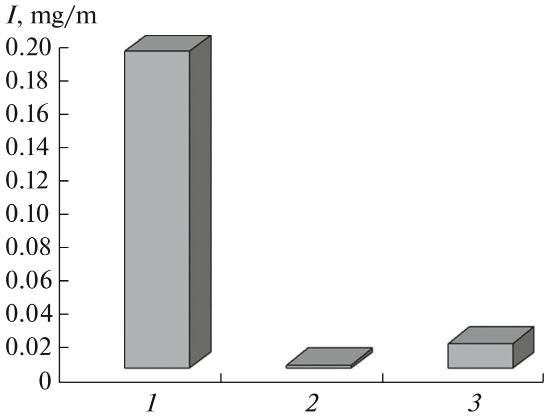

Fig. 7. Wear rate of Co-based CM samples reinforced with carbon particles obtained from (*1*) nonhydrogenated and (*3*) hydrogenated C_{60}, and (*2*) with diamond particles.

which leads to an increase in the hardness of the high-pressure carbon phase while maintaining superelasticity (according to the criterion in [10]). Accordingly, the wear resistance of CMs reinforced with particles of such a phase increases. However, the effect of hydrogenation of C_{60} fullerite in increasing the hardness of the high-pressure phase and in improving the tribotechnical characteristics of CM is much greater than the effect of preliminary amorphization of C_{60} in a ball mill, although after hydrogenation the crystal structure of C_{60} remains practically unchanged. The effect of amorphization of the structure and an increase in the hardness of the high-pressure phase in the case of hydrogenation of the initial C_{60} fullerite can be explained in the light of the concept of chemical activation of carbon to obtain sp^3 structures, according to which hydrogenation changes the scenario of phase transformations during heating under pressure, stimulating the 3D polymerization of fullerene with the formation of superhard phases and preventing the formation of disordered sp^2 carbon [23]. A significant increase in the hardness of the reinforcing phase explains the increase in the wear resistance of CMs, while the record decrease in the friction coefficient is probably due to the presence of hydrogen in the composition of the reinforcing carbon phase, which, as shown on diamond-like films, plays an important role in providing their antifriction properties [7].

Thus, hydrogenation of C_{60} fullerites is a promising method for significantly improving the tribotechnical characteristics of the superelastic solid carbon phase formed from C_{60} during thermal pressure treatment, opening up prospects for using a new CM reinforced with particles of such a phase as an antifriction superwear-resistant material.

CONCLUSIONS

Samples of composite materials were synthesized from a mixture of cobalt powders with 10 wt % of hydrogenated fullerites at a pressure of 8 GPa at 800°C in a high-pressure chamber. Due to hydrogenation of the initial fullerites, the hardness of the high-pressure phase increases by more than 2.5 times, up to ~52 GPa, and the elastic modulus during indentation increases by about 3 times, up to 333 GPa, while the friction coefficient μ decreases from 0.25 to 0.01. In terms of wear resistance, CM made of Co + $C_{60}H_{3.5}$ significantly exceeds CM made of Co + C_{60}, but is inferior to CM reinforced with diamonds. Presumably, hydrogenation changes the scenario of phase transformations upon heating under pressure, stimulating the 3D polymerization of fullerene with the formation of superhard phases and preventing the formation of disordered sp^2 carbon.

The hydrogenation of C_{60} fullerites is a promising method for significantly improving the tribotechnical characteristics of the superelastic hard carbon phase formed from C_{60} during thermobaric treatment, opening up prospects for using a new CM reinforced with particles of such a phase as an antifriction superwear-resistant material.

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CONFLICT OF INTEREST

We declare that we have no conflicts of interest.

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