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Structure and properties of superelastic hard carbon phase created in fullerene-metal composites by high temperature-high pressure treatment

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Treatment of a fullerene soot extract and metal (Co) powder mixture under pressure of 5 and 8 GPa at 1000 °C leads to the transformation of fullerites into superelastic hard phase (SHP) and to simultaneous sintering of the powder mixture to nonporous composite material reinforced by the SHP particles. The structure of the SHP particles reveals a topological relation to the initial fullerite crystal morphology. Upon indentation, the SHP particles demonstrate an elastic recovery of up to 96%. The universal microhardness of the SHP particles $HU = 26$ GPa, and their microhardness $HV = 35$ GPa. A high ratio between the microhardness and elastic modulus ($HV/E = 0.19$-0.21) of the SHP particles makes them perspective candidates for design of materials with superior wear resistance and tribological properties. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4726155]

I. INTRODUCTION

Since the discovery of fullerenes, the structure and properties of the products of their transformation under pressure have been comprehensively studied as a function of processing parameters (temperature, pressure, treatment time, etc).[1–3] It is shown that fullerene molecules upon high-pressure high-temperature (HPHT) treatment either undergo polymerization or collapse with the formation of hard phases. The density and hardness of the new phases increase with treatment pressure. These studies were performed generally on pure C_{60} and C_{70} fullerites, while the intermediate product of their preparation, toluene-soluble soot extract (SE) (a black polycrystalline powder mixture of C_{60} + up to ~45 wt. % C_{70} + higher fullerenes[4]) in some cases provides the best properties of high-pressure phase for reinforcement of wear-resistant metal matrix in composites.[5,6] At present, it is recognized that the optimal combination of high wear resistance and low friction coefficient can be provided by hard and elastic materials, which are characterized by a high ratio of hardness to elastic modulus, H/E, since they can accommodate the surface deformation and absorb shock loads without failure.[7] Hard carbon phases formed under HPHT as a result of fullerene collapse exhibit superelastic properties[8] that can be used for design and synthesis of metal-based composite materials (CM) reinforced by superelastic hard carbon particles using metal-fullerene powder mixture as the source material for sintering at HPHT. The reinforcing particles have hardness of about 16 GPa and elastic modulus near 92 GPa, and their elastic recovery upon indentation exceeds 85%.[5] The purpose of the present work was to study the effect of synthesis pressure on the structure and properties of the carbon particles formed from fullerene soot extract for the reinforcement of cobalt-based composite materials.

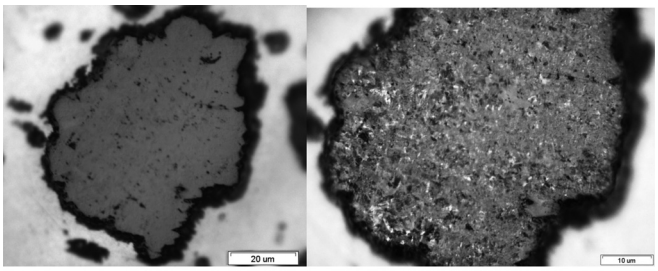
II. EXPERIMENTAL TECHNIQUES

The samples (5 mm in diameter and 3–4 mm in height) of cobalt-based CM were prepared from the mixtures of metal powder (99.8% pure cobalt, 5–12 μm in powder particle size) and 10 wt. % toluene-soluble extract from fullerene soot (SE) containing 55 wt. % C_{60}, 38 wt. % C_{70}, and higher fullerenes. The fullerene soot extract particles are the mechanical aggregates of fullerite crystals of 0.5–10 μm in size. The average particle size is 47 μm. The cobalt and SE powders were mechanically mixed by hand for 5 min. The precompacts obtained at a pressure of 500 MPa were further densified to CM at quasi-hydrostatic pressure of 5 and 8 GPa at ~1000 °C (heating under pressure at a rate of 30–50 °C/s and holding for 0.5 min) in a toroid-type hydraulic press.

The CM microstructure was examined by optical microscopy (Olympus GX51). The carbon phases obtained from fullerites under pressure were characterized with a WiTec CRM 200 confocal Raman imaging system. For the XRD examination, the isolated carbon particles were extracted from CM by boiling the samples in aqua regia for 2 h. The x-ray spectra were collected on DRON-3 M diffractometer using Cu Kα radiation. The microhardness of the superelastic hard phase (SHP) carbon particles was measured with a PMT-3 tester and a Universal Tester UMT-3MO (CETR) at a load of 0.5 N. The tribological and abrasive wear tests were performed on a UMT-3MO (CETR) Universal Tester.

III. EFFECT OF SYNTHESIS PRESSURE ON THE STRUCTURE AND MECHANICAL PROPERTIES OF THE CARBON PARTICLES FORMED FROM FULLERENE SOOT EXTRACT

A specific feature of the CM synthesis from a metal-fullerene powder mixture upon high pressure/high-temperature (>800 °C) treatment is the transformation of fullerites



a b

FIG. 1. Optical micrographs of the SHP carbon particle in cobalt-based CM synthesized at 5 GPa, 1000 °C in conventional (a) and polarized (b) light.

into SHP particles and simultaneous sintering of the mixture to dense composite material reinforced by these particles. The microstructure of a carbon particle obtained from SE in cobalt-based CM under pressure of 5 GPa is shown in Fig. 1. The carbon particle on the polished surface of the CM sample is seen as light gray homogeneous inclusion (Fig. 1(a)). Polarized light reveals fine optically anisotropic domains corresponding to the initial fullerite crystals within this particle (Fig. 1(b)).

The x-ray diffraction profiles of the SHP particles obtained at a pressure of 5 and 8 GPa (Fig. 2) are similar to the diffraction patterns of graphite-like carbon obtained from C_{60} and C_{70} at pressures of 3–8 GPa at temperatures above the limit of fullerene cage stability.[9,10] Our spectra contain four peaks, whose diffuse nature indicates a disordered character of the structure. The peak center of the strongest reflection for the particles obtained at 5 GPa corresponds to the interplanar spacing of 0.343 nm. For the particles obtained at 8 GPa, analogous peak corresponds to a spacing of 0.328 nm, which is

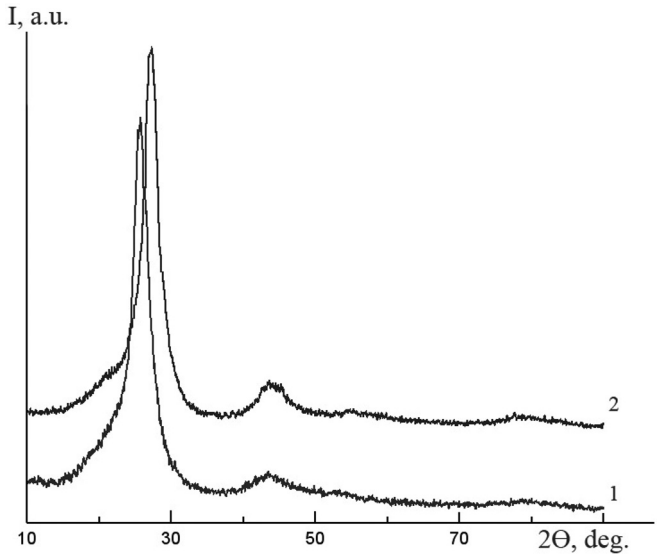


FIG. 2. XRD spectra collected at ambient conditions from the SHP carbon particles extracted from the CM (Co + 10 wt. % SE) after quenching to ambient pressure from 5 (1) and 8 GPa (2).

below $d_{(002)}$ of ideal graphite (0.335 nm)[11] thus indicating the presence of compressed graphene planes. The full width at half maximum (FWHM) of the peaks is 3.3° and 3.2° for the particles obtained at 5 and 8 GPa, respectively. For both types of the particles, the second reflection represented by a diffuse halo (with similar interlayer spacings of 0.207 and 0.206 nm for the particles obtained at 5 and 8 GPa, respectively) at the position corresponding to (100) and (101) graphite reflections indicates a low order in the basal layers.[10] The peaks similar

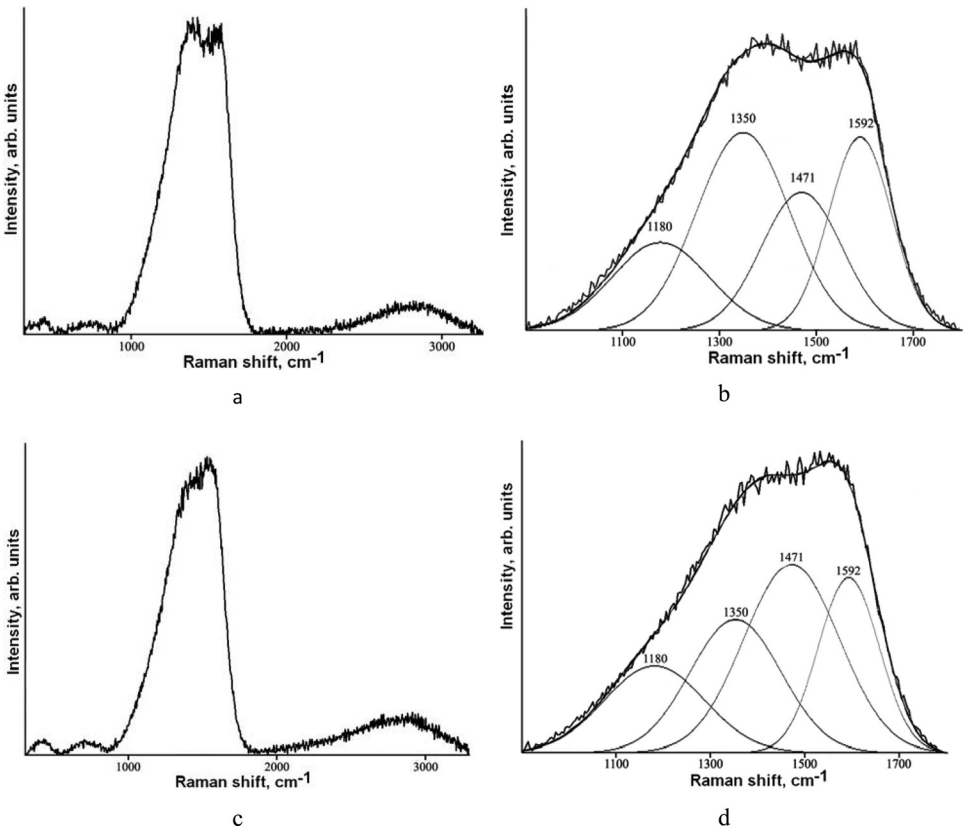


FIG. 3. Raman spectra recorded at ambient conditions from the SHP carbon particles embedded in the CM (Co + 10 wt. % SE) synthesized at 1000 °C and (a) 5 and (c) 8 GPa; (b) and (d) decomposition of the main peaks in the corresponding spectra (left panel).

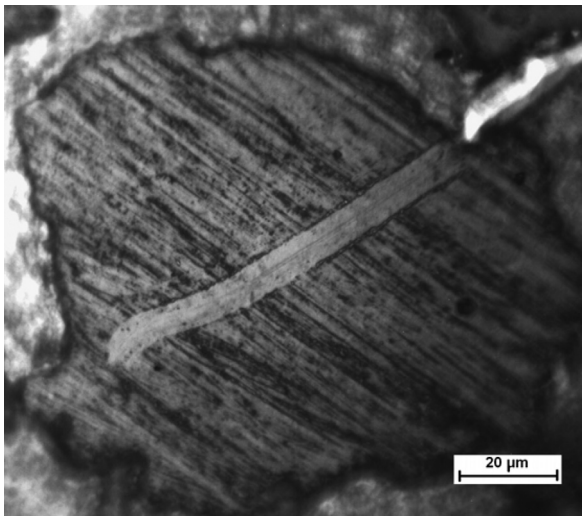


FIG. 4. Trace of scratching by diamond indenter at the SHP particle surface coated by a diamond paste.

to the (004) and (110) graphite reflections in our spectra are very broad and have very low diffuse intensity. Thus, with increasing treatment pressure from 5 to 8 GPa, the $d_{(002)}$ interplanar spacing decreases, but the distortion of the basal layers themselves remains virtually unchanged.

Raman spectra of the SHP carbon particles embedded in the CM synthesized at different pressures are shown in Fig. 3. Spectral decomposition of the band between 900 and 1800 cm^{-1} (right panels in the figure) reveals four broad peaks characteristic of a mixture of disordered sp^3 (1180 cm^{-1} and 1470 cm^{-1}) and sp^2 (D and G peaks at 1350 and 1590 cm^{-1}, respectively) carbons. The relative intensities of the peaks depend on the synthesis pressure: on pressure increase, the total integral intensity of the peaks of disordered sp^3 carbon is increasing with respect to that of the sp^2 carbon-derived D and G peaks that correlate well with the sample microhardness increase (see further in the text). In addition, the samples synthesized at 8 GPa exhibit a decrease in D/G ratio. Such evolution of the spectra is indicative of stage 2 transformation in disordered carbon,[12] i.e., increase of graphene layers in nanocrystalline graphite preceding formation of large graphite crystallites with low defect density.

TABLE I. Deformation characteristics of the carbon particles in the composite materials produced from the Co + 10 wt. % CE powder mixture at 1000 °C, 5 and 8 GPa.

	Pressure (GPa)	
Parameter	5	8
Interplanar spacing *d* (nm)	0.343	0.328
Universal microhardness HU[a] (GPa)	12	26
Microhardness *HV*[b] (GPa)	18	35
Elastic modulus *E* (GPa)	84	188
HV/*E*	0.21	0.19
Elastic recovery *R* (%)	96	90

[a]The universal microhardness *HU* was measured with PMT-3 tester.
[b]The microhardness *HV* was measured with a UMT-3MO Universal Tester according to the Oliver-Pharr method.

The microhardness measurement of the reinforcing particles by conventional methods is a problem, since no indents are seen on their surface in microscope after indentation. To compare the microhardness of the carbon particles obtained at different pressures, we used various methods of the estimation of their response to indentation. First, we measured the universal microhardness[13] accounting for both elastic and plastic deformation responses to indentation by using the projection of the contact area between the sample and indenter under load. For this aim, we designed and used the following technique. The surface of the specimen was coated with a very thin layer of a removable substance (e.g., dry diamond paste). Upon rotation of the PMT-3 tester objective table under a load of 0.5 N, the diamond pyramid indenter removed the paste and left a clean trace (Fig. 4), whose width corresponds to the depth of the pyramid penetration into the particle. After unloading, we measured the trace width and assumed it to be equal to the pyramid imprint diagonal used for the determination of the resistance to the total (elastic and plastic) deformation by the standard technique. The results show that the universal microhardness of the carbon particles increases with synthesis pressure, and the reinforcing particles of the CM synthesized at 8 GPa reach a very high universal microhardness (HV = 26 GPa, Table I). Measurements of microhardness according to the Oliver-Pharr method[14] employing loading-unloading indentation curves (Fig. 5) also show that the microhardness

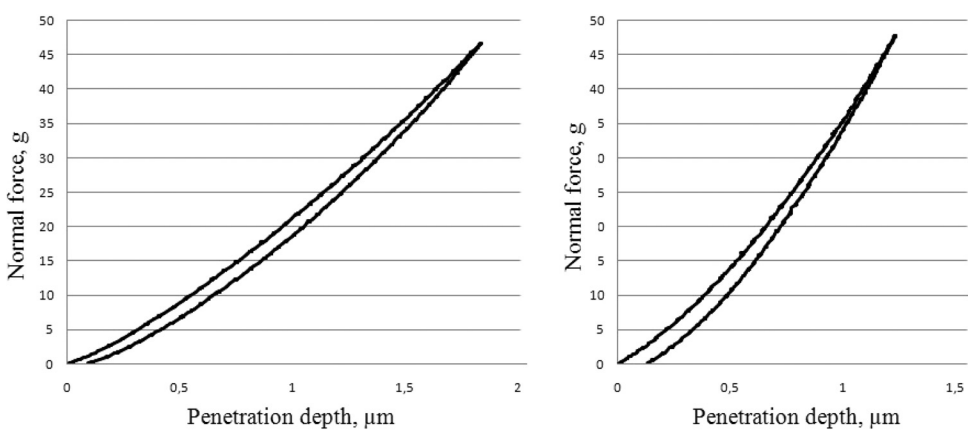


FIG. 5. Indentation curves of the carbon particles in the composite materials obtained from the Co + 10 wt. % CE powder mixture at 1000 °C, 5 GPa (a) and 8 GPa (b).

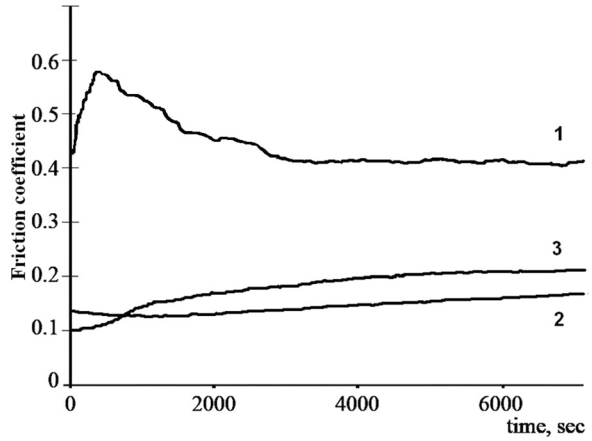


FIG. 6. Friction coefficients of the Co reference sample (1) and the CM prepared from (Co + 10 wt. % SE) at 1000 °C under pressure of 5 GPa (2) and 8 GPa (3).

increases with synthesis pressure by about a factor of two, although these values obtained at a load of 0.5 N are much higher than the universal microhardness data. Recording loading-unloading curves is advantageous as it provides a possibility of estimation and comparison of the elasticity moduli and the rates of elastic recovery during indentation (see Table I). A particular feature of the reinforcing carbon particles is the combination of their high degree of elastic recovery during indentation and high microhardness, which allows us to term them as "superelastic and hard."

IV. EFFECT OF SYNTHESIS PRESSURE ON THE FRICTION COEFFICIENT AND WEAR RESISTANCE OF THE COMPOSITE MATERIALS REINFORCED BY SUPERELASTIC HARD CARBON PARTICLES

The tribological tests of the CM samples were performed with a UMT-3MO (CETR) Universal Tester using a pin-disc scheme at a speed of 0.3 m/s over a disk of high-carbon (100Cr6-type) steel with a hardness of 62 HRC for 2 h under a nominal load of 50 N under conditions of dry friction in air. The friction coefficients of the cast Co reference sample and the CM samples prepared at 5 and 8 GPa are 0.41, 0.16, and 0.21, respectively (Fig. 6). The minimum friction coefficient is observed for the CM samples prepared at 5 GPa. Although they exhibit lower hardness and elastic

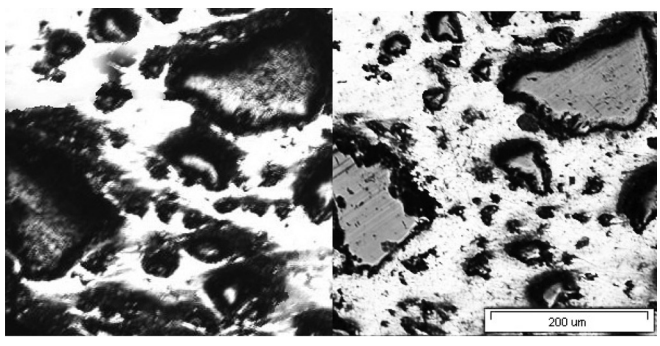


FIG. 7. Microstructure of the CM prepared from Co + 10 wt. % SE (5 GPa, 1000 °C) before (a) and after (b) tribological tests.

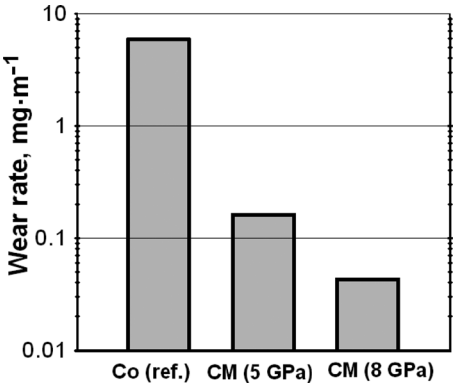


FIG. 8. Abrasive wear rate (mass loss related to sliding distance) of the reference Co sample and the CM samples prepared from Co + 10 wt. % SE at 5 and 8 GPa.

modulus than the samples produced at 8 GPa, their elastic recovery is higher. After the friction test, the particles surface, which acts as load-bearing elements, becomes flat and smooth (Fig. 7). The particles in the tested sample exhibit weak grooves of plastic deformation.

The abrasive wear tests of the CM and reference Co samples were performed in accordance to the pin-disc scheme (sliding over a P 1200 grade abrasive paper at a load of 10 N at a rate of 1.8 m/min). The abrasive wear rate of the samples was estimated after tests for 5 min as the mass loss related to the sliding distance. The wear rates after abrasive wear tests of the reference Co sample and the CM samples prepared at 5 and 8 GPa are 6.30, 0.16, and 0.04 $mg \cdot m^{-1}$, respectively (Fig. 8). The result demonstrates that the abrasive resistance of the CM reinforced by superelastic hard carbon particles increases with increasing particle hardness.

V. SUMMARY

The high-pressure high-temperature treatment (5 and 8 GPa, 1000 °C) of the metal (Co) and fullerene soot extract (10 wt. %) powder mixture results in the transformation of fullerenes to SHP and the consolidation of the powder mixture to the metal-based composite material reinforced by the SHP carbon particles. With increasing synthesis pressure, interplanar graphene spacing of the reinforcing carbon particles decreases from 0.343 to 0.328 nm, whereas the Raman spectrum exhibits increase in sp^3 fraction of carbon atoms. This process is accompanied by an increase in carbon particles' microhardness HV and elastic modulus E from 18 to 35 GPa and from 84 to 188 GPa, respectively. While the elastic recovery R somewhat decreases (from 96% to 90%), it still remains very high and exhibits the superelastic behavior of the carbon phase. The reinforcement of cobalt matrix in the CM by the SHP carbon particles increases the abrasive wear resistance by a factor of ~40 and ~140 for the samples treated at 5 and 8 GPa, respectively, and simultaneously decreases the friction coefficient almost by a factor of two. The CM reinforced by SHP particles with higher elasticity (synthesized at 5 GPa) exhibits the lower friction coefficient (~0.16), while the CM reinforced by the harder carbon particles (produced at 8 GPa) has the higher wear resistance.

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