Mechanical Properties of the Superhard Polymeric and Disordered Phases Prepared From C_{60} , C_{70} , and C_{2N} under High Pressure

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Using high-pressure-high-temperature treatment of fullerites it is possible to prepare new carbon materials, including polymerized fullerites, amorphous carbon, and nanocrystalline diamond-plus-graphite composites. We have studied the mechanical properties (hardness, Young modulus, fracture toughness coefficient) for some of new phases. The interrelationship between hardness and density, established for the fullerite-based carbon phases, is in good accordance with the corresponding data for amorphous carbon.

[fullerite C_{60} , C_{70} , hardness, fracture toughness, Young modulus]

I. Introduction

Preparation of non-traditional hard carbon phases is the motivation to study different fullerites under pressure. The majority of carbon materials have both high mechanical characteristics and low density. Diamond is a leader with the highest elastic and mechanical characteristics among other substances. Carbon fibres have the extremely large strength/density ratio [1].

Recently three new classes of metastable carbon materials were prepared using high pressure - high temperature treatment of fullerites: i) polymerized phases composed of C_{60} molecules connected by covalent bonds [2-6]; ii) amorphous carbon with different share of sp^2 and sp^3 atomic sites [4,5,7-9]; and iii) nanocrystalline diamond-plus-graphite composites [4,9]. Until recently the mechanical properties of these three groups were not studied in details. The interest in mechanical properties of the new carbon phases increased essentially due to the theoretical predictions [10] that dense C_{60} phases may possess elastic moduli and hardness higher than those of diamond because of the "touching" of rigid C_{60} molecules. The supposed "touching" of C_{60} molecules is rather doubtful, but there still is a hope to obtain new hard and dense carbon phases from C_{60} under pressure. The samples of amorphous carbon obtained from C_{60} by different technique [5,8] displayed a high level of hardness in the scratching experiments.

Recently, amorphous carbon modifications containing a high share of sp^3 bonds have also attracted much attention because of their potential applications including wear-resistant coating and thin-film semiconductor devices [11]. The maximum content of sp^3 sites for such films now amounts to ~80 % [12]. High-pressure treatment of C_{60} gives the possibility of preparation of amorphous sp^3 -reached carbon in the bulk form [4] suitable for the accurate study of mechanical characteristics. Comparison of the ordered 3D-polymerized and disordered carbon phases obtained from fullerites with the amorphous carbon films is of great importance for the theory of carbon materials.

The technological importance of nanocrystalline diamond ceramics [13] has stimulated this study as well because high-pressure treatment of C_{60} allows to prepare diamond-plus-graphite composites with ultrafine grains [9].

The purpose of the present work is to study the mechanical characteristics of the new carbon phases prepared from

different fullerites, including C_{60} , C_{70} , and the disordered higher fullerene extract C_{2N} ($50 < 2N < 170$).

II. Experimental

A new version of the "toroid" chamber was used for high-pressure-high-temperature generation (up to 12.5 GPa in the temperature range 300-1800 K) in a large volume (up to 30 mm³). The samples were placed into the Pd or Pt cells and heated by passing electric current through the outer graphite container. We used fullerite powders produced at Russian Scientific Center "Kurchatov Institute", with the C_{60} content not less than 99.9 % and C_{70} content not less than 95 %.

The new phases were synthesized as bulk samples with size of 1-2 mm. The density of samples was measured by the pycnometric method. The structure of samples was examined by x-ray diffraction (Cu $K\alpha$). The Young modulus was studied by the ultrasonic method using measurements of the longitudinal velocity of ultrasound at 5 MHz by the Papadakis method. The mechanical characteristics were investigated by means of indenting the diamond Vickers pyramids under the loads 1.96 and 5.5 N. The loads were varied depending on the pattern of crack formation around the indentations. The Vickers hardness H_V , the fracture toughness coefficient K_{Ic} and the yield stress were calculated, according to the procedure proposed in Ref. 14.

III. Results and Discussion

The detailed x-ray diffraction and Raman spectroscopy study of carbon phases prepared from C_{60} is considered in Refs. 6 and 9. At a relatively low temperature of heating under high pressure ($T < 500$ °C at $P = 12.5$ GPa and $T < 900$ °C at $P = 8.5$ GPa) we observed the gradual 3D polymerization of C_{60} [6]. The high-temperature heating resulted in the complete disordering of C_{60} with destruction of molecules. Formation of the sp^2 - sp^3 carbon networks and further diamond-plus-graphite nanocrystalline composites [9] occurred at higher temperatures.

The solid-state disordering of fullerite C_{70} was found to occur at lower temperatures ($T \sim 250$ °C at $P = 12.5$ GPa and $T \sim 400$ °C at $P = 8.0$ GPa). The conclusion that C_{70} is less stable under pressure-temperature treatment is also supported by literature data [15]. The disordered phases obtained from C_{70} have smaller density than the samples prepared from C_{60} at the same conditions, and they contain a larger fraction of atoms in the graphite-like sp^2 states. The pressure-induced

polymerization of C_{70} is a one-dimensional process [15] in contrast to the 2D and 3D polymerization of C_{60} at the same pressures. The reason for different behavior of fullerite C_{70} under pressure seems to be the non-spherical shape of C_{70} molecule.

Table I. Experimentally measured density ρ , hardness H_V , fracture toughness coefficient K_{Ic} , and Young modulus E for some carbon phases obtained from C_{60} , C_{70} , and C_{2N} fullerites under high-pressure and high-temperatures (T_{syn}) treatment (structural types of phases are indicated in parentheses: P is meant for polymerized fullerite phases, Am - for amorphous phases of different nature, D&G - for diamond-plus-graphite nanocrystalline composites, and G - for predominantly graphitic-like disordered phases).

T_{syn} (°C) / (phase)	ρ (g/cm ³)	H_V (GPa)	K_{Ic} (MN/m ^{3/2})	E (GPa)
C_{60} (12.5 GPa)				
200 (P, 3D)	2.3	33.6±2.2	5.5±0.4	
300 (P, 3D)	2.6	36±7	plastic	350
400 (P, 3D)	2.8	26.4±0.7	plastic	400
450 (P, 3D)	3.0	52±6	7.9±1.4	
500 (Am)	3.15	76±1	15±4	700
550 (Am)	2.8	75±5	8.6±1.3	
600 (Am)	3.0	75.5±1	8.0±1.5	
650 (Am)	2.9	73±5	7.6±1.2	
700 (Am)	3.2	69±6	7.1±0.5	
900 (D&G)	3.0	87±10	8.2±1.8	
	±0.15			±100
C_{70} (8 GPa)				
600 (G+P)	2.2	9.4±2.0	3.7±0.2	
12.5 GPa				
300 (G)	2.1	≤ 1		
400 (G)	2.2	9±1		
800 (G)	2.4	18±2		
C_{2N} (12.5 GPa)				
500 (Am)	2.0	21±1.5	plastic	
600 (Am)	2.1	24.6±2.2	4.3±1.5	
Diamond	3.515 ^a	100–150 ^a	7–10 ^a	1140 ^b
cubic BN	3.49 ^a	40–60 ^a	2–5 ^a	970 ^b
Steels	7.8–8.0 ^b	2–4 ^c	up to 28 ^d	≈200 ^b

^a Reference [16]; ^b Reference [17]; ^c Reference [18];

^d Reference [19].

The disordered higher fullerene extract C_{2N} ($50 < 2N < 170$) transform to the denser amorphous state under pressure. This transformation is accompanied by the partial polymerization and appearance of sp^3 sites. The increase of temperature results in the collapse of C_{2N} molecules, that may be detected by the graphitization of sample. We observed the graphitization of C_{2N} samples at 700 °C under pressure 8 GPa and at 550 °C under 12.5 GPa.

The mechanical characteristics for some phases are presented in Table I. We have established that the C_{60} and C_{70} polymerized phases have the Young modulus and hardness by 2–10 times less than those for diamond and comparable with

the mechanical characteristics of sapphire or cubic BN. Some of the polymerized fullerite phases have the high fracture toughness coefficient or are even plastic at room temperature. The disordered and nanocrystalline phases have the mechanical characteristics which are by 1.2–2 times inferior to the corresponding values for diamond, and the fracture toughness coefficient even higher than that of diamond. One should indicate a high level of hardness for the graphitic amorphous phases prepared from C_{70} . We have also established that the C_{70} -based phases are less hard than structurally similar phases prepared from C_{60} at the same pressure.

Fig. 1. Comparison of the experimental hardness for the polymerized C_{60} modifications prepared at $P=8$ GPa ($\square$) and 12.5 GPa ($\square$), amorphous phases obtained from C_{60} ($\circ$), C_{70} (Δ), and C_{2N} ($*$) fullerites, and diamond-plus-graphite composite ($\diamond$) with the known data for amorphous carbon (dashed line as the least square linear interpolation for experimental points from Ref. [12]).

The presence of the two types of atomic states causes a great topological variety of disordered structures existing in amorphous carbon. Homogeneity is another characteristic influencing the mechanical properties of carbon disordered phases. In Fig. 1 we consider the hardness vs density dependence for different carbon phases, prepared from the fullerites, in comparison with the linear interpolation for the similar data on amorphous carbon films [12]. Both sets of data are correlated rather well. The increase of hardness for the 3D polymerized C_{60} phases directly indicates the increase of the number of sp^3 sites in accordance with the well known dependence of density from the share of sp^3 sites in amorphous carbon [12]. One should note that the materials discussed include both the homogeneous (for length scale of the medium range order ~ 30 Å) and heterogeneous phases. The data on the Young modulus E (Table I) also agree qualitatively with both theoretical [20] and experimental [12] results for amorphous carbon.

The elastic properties and hardness of fullerite phases obtained in this study are in no way inferior to the characteristics of diamond. The molecular dynamics simulation [21] revealed the carbon network corresponding to the collapsed C_{60} to have the bulk modulus $B=400$ GPa, which is less than that of diamond (but close to it), in accordance with our experimental data. So, the presented experimental data refute the earlier assumption, based on the empirical calculations [10] and indirect experiments [5], that it is possible to prepare C_{60} -based carbon phases more hard or incompressible than diamond. Nevertheless, hardness of the

majority of disordered phases prepared exceeds hardness of all other materials, except diamond. The previous analysis have shown that the elastic and mechanical properties of sp^2 - sp^3 phases are defined by the density of substance, so the only competitors for crystalline diamond are the carbon phases with the density close to or higher than that of diamond.

The hypothetical superhard fullerite phases [10] must have the densities higher than that of diamond since C_{60} molecules should almost "touch" each other in this case. Such intermolecular distances are non-physical because the approach of molecules to each other evokes the appearance of covalent bonds between them, which prevent the approach of fullerene molecules to each other and break the uniformity of compression for molecules. As a consequence, the pressure or temperature increase leads to a distortion of the initial fullerene molecules and evokes a transformation of fullerite into the disordered network with the density, lower than that of diamond.

It is interesting that the diamond-plus-graphite composite ($T_{syn}=900^\circ\text{C}$) has the hardness comparable with the hardness of diamond, although it contains a significant amount of graphite (~50 %). We assume that diamond nanocrystals form a rigid framework in this case. This means a homogeneous distribution of diamond and graphite crystallites in accordance with the situation, when the composite has been formed from a homogeneous carbon network. The 3D polymerized phases of fullerite C_{60} are not so hard, but still very hard comparable with cubic BN. At the same time they may be plastic even at room temperature. Such a combination of mechanical characteristics makes these carbon material as very promising in the high pressure generation technique using the diamond anvil cell, e.g., as the material for gaskets. One should emphasize that diamond and cubic BN become plastic only at very high temperatures (~1000 °C). The plasticity of 3D fullerite polymers may be associated with the mechanism of "switching" of covalent bonds existing between C_{60} molecules. These bonds served as a frame of 3D polymerized phases and form continuous 3D networks from molecular fullerite crystals.

Another important feature of carbon phases prepared from fullerites is the high H_v/E ratio (~0.1), which is comparable or higher than the corresponding value for diamond. The ideal value of microscopic hardness tends toward the values of elastic constants. For other hard materials the H_v/E ratio values are significantly less than that for diamond (see Table I). The presence of defects diminishes the H_v/E ratio for diamond crystals (down to values ~0.07). The fullerite-based carbon phases, being disordered, are less sensible to defects and impurities as far as the H_v/E ratio is concerned. The evident reason for this is connected with the difficulty of formation and movement of dislocations within the polymer structures, amorphous networks, and composite nanocrystalline phases.

IV. Conclusion

We have studied mechanical characteristics for polymerized, amorphous, and nanocrystalline composite carbon phases prepared from different fullerites. A unique combination of high enough hardness and high fracture toughness (or plasticity) have been found for the 3D polymerized C_{60} -based phases. The hardness of disordered and

composite phases attains the values close to those of diamond, while the fracture toughness coefficient may be even higher. We have also established the correlation between the hardness and the density of material, common for the carbon phases of different structural types and similar to that of amorphous carbon films.

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