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Mechanochemical Synthesis of Polymer-Containing Composites Based on Boron Nitride

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Abstract

The effect of high-energy mechanical treatment on the formation of the structural-phase state of highly filled composite powders UHMWPE/BN, UPTFE/BN, UHMWPE/Fe/BN, UPTFE/Fe/BN is investigated. Mechanochemical synthesis of composites was carried out in a water-cooled planetary ball mill in the atmosphere of argon. The phase composition and structural characteristics were studied by means of X-ray phase analysis and IR spectroscopy. It was established that Fe/BN composites are formed as a result of mechanical treatment for 2 min in the mixture of iron with hexagonal boron nitride *h*BN; in addition, the phases of cubic boron nitride *c*BN, iron nitride $FeN_{0.056}$, and iron boride Fe_2B appear. During the mechanochemical synthesis of the composites of Fe/BN with polymers UHMWPE and UPTFE, the size of the crystallites of cubic boron nitride increases slightly. Mechanical treatment of the mixtures of polymers with *h*BN is not accompanied by the transition of hexagonal boron nitride to the cubic modification, and the size of *h*BN crystallites decreases slower in comparison with the mixtures with the Fe/BN composite. IR spectroscopic studies showed that the size of the original particles of *h*BN affects the change in the supramolecular structure of the polymer, while the polymer molecules are not destroyed.

Keywords: mechanochemical synthesis, mechanocomposites, iron, boron nitride, ultra-high molecular weight polyethylene, ultra-dispersed polytetrafluoroethylene

INTRODUCTION

New elastic polymeric composite materials for radiation protection from neutron and γ-radiation are under development at present. In this connection, composites of ultra-high molecular weight polyethylene (UHMWPE) and ultrafine polytetrafluoroethylene (UPTFE) with the compounds of boron and heavy metals (tungsten, iron) are of interest.

A promising method of obtaining composite powders of filled polymers is the technology of solid-phase deformation mixing which is implemented in high-energy planetary ball mills . Mechanical treatment of the polymer leads to its modification due to the changes in its supramolecular arrangement and molecular structure because of the processes involving the rupture of intramolecular bonds and linking. However, the phase state and the degree of dispersion of the filler play a fundamental role in the formation of the composite under high-energy mechanical action, which largely determines the nature of its interaction with the polymer and the distribution in the matrix [1].

Composite materials based on UHMWPE and UPTFE filled with the disperse particles of boron carbide or nitride, as well as metals (iron, tungsten) find various applications as the materials for protection from γ-, neutron and electromagnetic radiation [2] and as tribotechnical materials for making the frictional units for technical devices operating under the conditions of cold climate [3].

The goal of the work was to study the effect of high-energy mechanical action on the formation of the structural phase state of highly filled composite powders UHMWPE/BN, UPTFE/BN, UHMWPE/Fe/BN, UPTFE/Fe/BN.

EXPERIMENTAL

The powders used in the work were: UHMWPE of GUR 4120 grade, manufactured by Ticona GmbH, with the molecular mass of $4 \cdot 10^6$ g/mol and particle size 100–160 μm; UPTFE with particle size 0.1–1.0 μm; hexagonal boron nitride (*h*BN) of GM grade, carbonyl iron with particle size 2–5 μm.

Mechanocomposites of the composition Fe–50 mass % BN (Fe–50 BN), UHMWPE–90 mass % BN (UHMWPE–90 BN), UPTFE–90 mass % BN (UPTFE–90 BN), UHMWPE–90 mass % Fe/BN (UHMWPE–90 Fe/BN), UPTFE–90 mass % Fe/BN (UPTFE–90 Fe/BN) were synthesized by means of mechanochemical synthesis (MCS) in the AGO-2 planetary ball mill with water cooling in the argon atmosphere. The vial volume was 250 cm^3, ball diameter 5 mm, ball load 200 g, the weighted portion of the mixture under treatment 10 g, the frequency of vial rotation around the common axis ~1000 r.p.m. The duration of MCS was 2 min.

X-ray structural analysis was carried out with a D8 Advance diffractometer (Bruker, Germany) using the characteristic Cu$K_{\alpha 1}$ radiation (λ = 1.5406 Å). Phase analysis was carried out using the database of X-ray standards ICDD PDF-2. Calculation and refinement of the structural parameters were carried out by means of the least squares with the full-profile analysis of diffraction patterns in the TOPAS software using Pawlay's iterative procedure. Investigation of the microstructural characteristics (crystallite size and microstrain) was carried out with the help of the double Voight methodology. According to this methodology, the dependence of diffraction profiles on the size of crystallites and microstrain is described in the generalized form by Voight functions.

Spectroscopic studies were carried out using the IR FT spectrometer Nicolet iS10 (Thermo Scientific, the USA) by means of frustrated total internal reflection at the diamond crystal within the range 4000–400 cm^{-1}.

RESULTS AND DISCUSSION

Intense mechanical treatment of the system of hexagonal boron nitride with iron Fe–50 *h*BN causes the changes in the phase composition already after the treatment for 2 min. Along with the Fe/BN composite, the cubic modification *c*BN is formed, as well as the phases of iron nitride $FeN_{0.056}$ and iron boride Fe_2B (Fig. 1, *a*, curve *1*). The appearance of iron nitride and boride phases may point also to the structural changes in BN under the shock-and-shear loading [4]. A strong decrease in the intensity of (002) peak *h*BN may be due to a substantial decrease in the size of its crystallites. When using soft and plastic polymers UHMWPE, UPTFE and *h*BN powders, cubic boron nitride is not formed (see Fig. 1, *b*, curves *2*, *3*). The appearance of milled iron is recorded in the UPTFE–90 BN system (see Fig. 1, *b*, curve *3*).

X-ray structural analysis demonstrated an increase in the value of lattice parameter *c* of *hBN* in the systems with iron (Table 1). The use of plastic polymers slows down grinding boron nitride crystallites. For instance, the size of crystallites $L_{h\mathrm{BN}}$ in the composite with UHMWPE is 60–65 nm, and in the composite with UPTFE it is ~10–12 nm.

A specific feature of the structure of *c*BN in the composites of the systems UHMWPE–Fe/BN and UPTFE–Fe/BN is an increased parameter of the cubic lattice $a_{c\mathrm{BN}}$ = 0.3618–0.3619 nm; crystallite size increases, too, from ~25 nm to 4–45 nm. The formation of the *c*BN phase is characteristic of the composites containing Fe. It may be assumed that it is iron, including that formed as a result of the milling, that acts as the catalyst of the transition of the hexagonal BN phase into the cubic one [5].

Figure 2 shows the IR Fourier spectra of composites of the systems UPTFE–90 BN, UHMWPE–90 BN and UHMWPE–90 Fe/BN, synthesized mechanochemically for 2 min in the atmosphere of Ar.

For *h*BN within the wavenumber range 4000–400 cm^{-1}, the bands of in-plane asymmetric B–N vibrations at 1380 cm^{-1} and out-of-plane vibrations of B–N–B atoms at 817 cm^{-1} are characteristic. Asymmetric absorption bands related to hexagonal boron nitride with the maxima at 1308 and 757 cm^{-1}, as well as a broad band at 1000–1100 cm^{-1}, characteristic for B_nN_m fragments in sp^3 hybridization are observed in the resulting

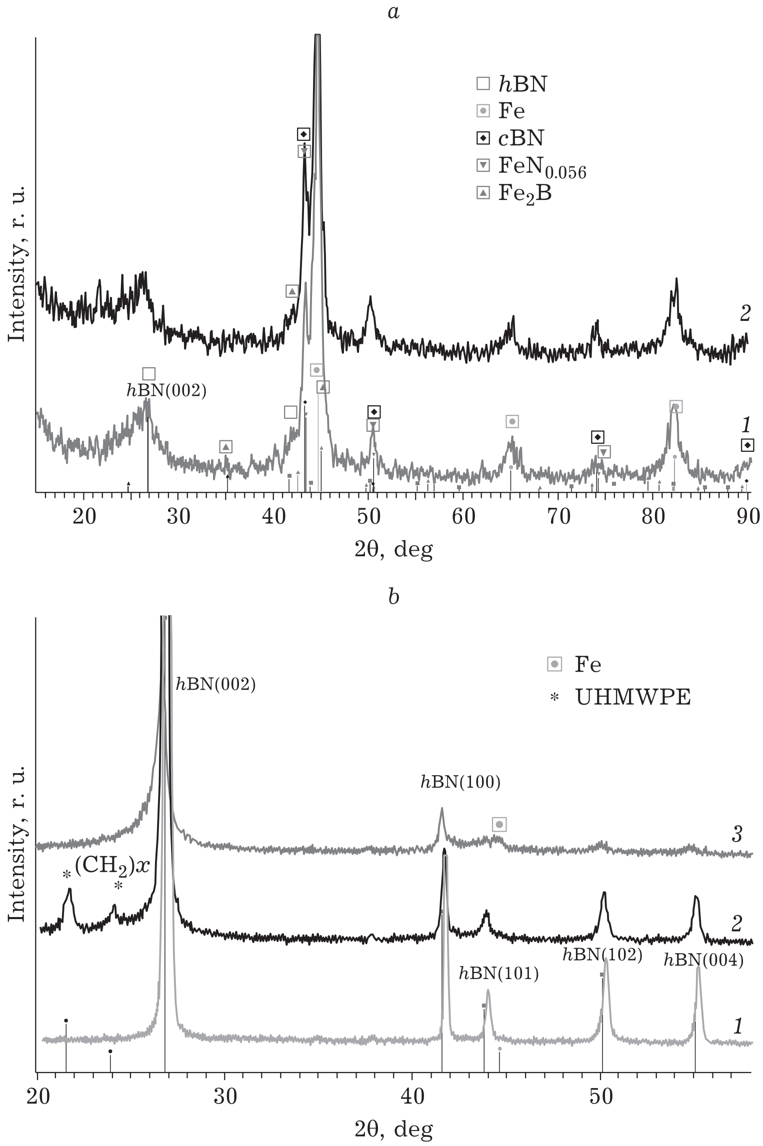

Fig. 1. X-ray patterns: *a* – composites in the systems Fe–50 *h*BN (*1*) and UHMWPE–90 Fe/BN (*2*); *b* – initial *h*BN (*1*) and composites in the systems UHMWPE–90 *h*BN (*2*) and UPTFE–90 *h*BN (*3*). MCS conditions: 2 min, Ar atmosphere.

TABLE 1

Data of X-ray structural analysis of the composites based on *h*BN (MCS: 2 min, Ar)

Parameter, nm	Data from the PDF ICDD database	Fe/BN	UHMWPE/Fe/BN	UPTFE/Fe/BN	UHMWPE/BN	UPTFE/BN
			hBN, $P6_3/mmc$			
a	0.2504	0.2489	0.2484	0.2486	0.2506	0.2493
c	0.6656	0.6721	0.6774	0.6780	0.6666	0.6669
L		6	7	5	63	12
			cBN, $F\text{-}4_3m$			
a	0.3616	0.3615	0.3618	0.3619	–	–
L		25	40	45		
			Fe, $Im\text{-}3m$			
a	0.2866	0.2866	0.2872	0.2875	–	0.2918
L		23	14	14		9

Note. Dash means that the phase is not observed.

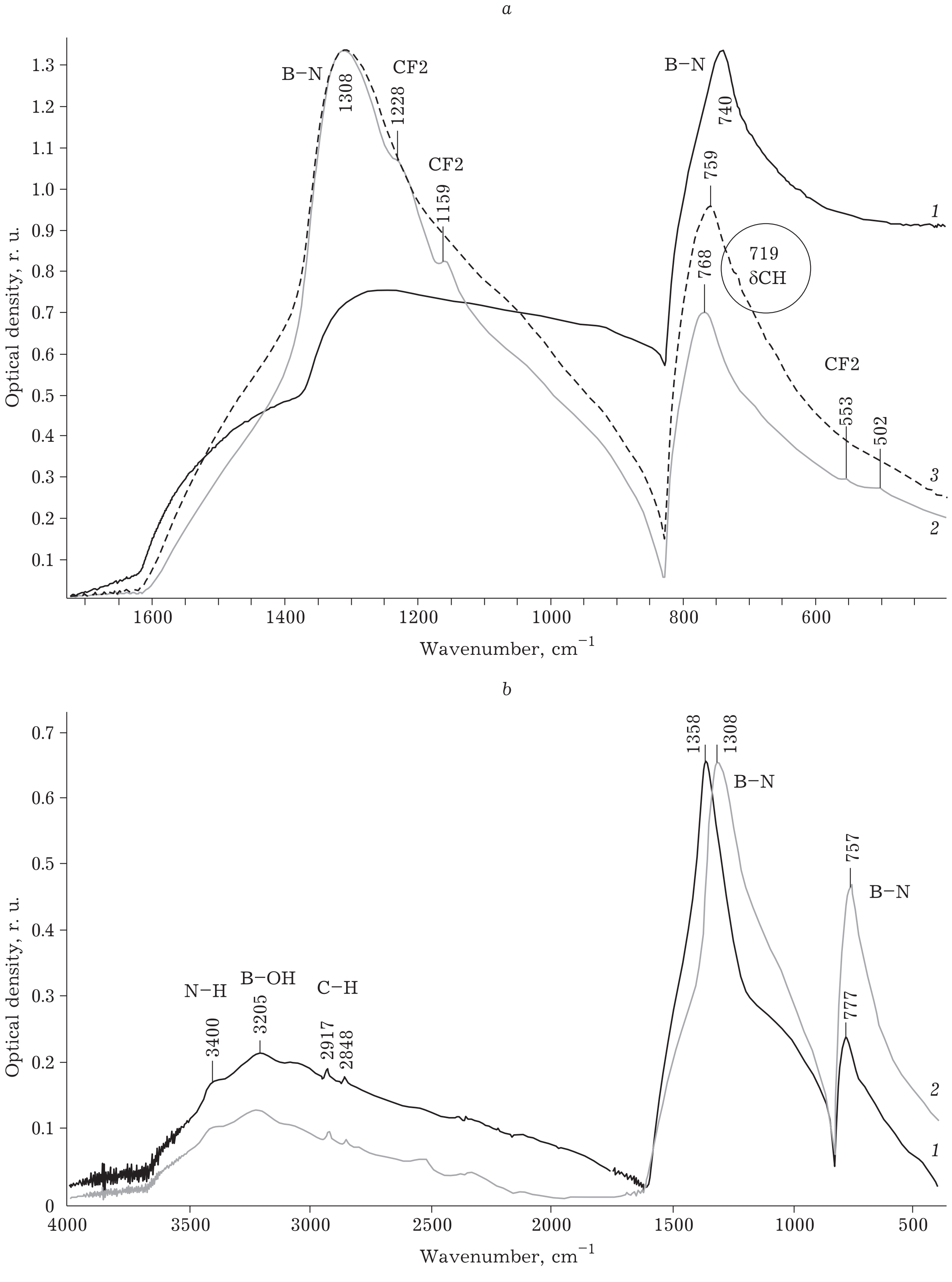

Fig. 2. IR Fourier spectra: *a* – initial *h*BN (*1*) and composites in the systems UPTFE–90 *h*BN (*2*) and UHMWPE–90 *h*BN (*2*), *b* – composites in the systems UHMWPE–90 *h*BN (*1*) and UHMWPE-90 Fe/BN (*2*). Conditions of MCS are shown in Fig. 1.

samples [6]. A large band width points to the fact that the fragments are bound into a three-dimensional network [7].

The appearance of absorption bands within the range 3400–3000 cm^{-1} points to the presence of OH groups in the structure of BN, which is connected with its increased chemical activity with respect to water [8]. The band in the region 3300–3200 cm^{-1} belongs to the stretching vibrations of B–OH, and the band at 3400 cm^{-1} relates to N–H [9].

Grinding of *h*BN during MCS causes an increase in the frequency of in-plane and interplane vibrations of B–N in comparison with the initial state, possibly due to an increase in the strength of the bond with an increase in boron content.

The amount of filler and its dispersion have a significant influence on the formation of composite particles and changes in the supramolecular structure of polymers. So, in the case if coarse powders are used, for example *h*BN with particle size ~40 μm, the structure of the polymers is mainly conserved (including the conformational regularity), in spite of the high filler content (90 mass %). The high degree of polymer filling leads to a small shift of the frequencies, for example, from 1209 to 1228 cm^{-1} for the asymmetric stretching vibrations v_{as} C–F in UPTFE, which points to the intermolecular interaction with the filler. The integral absorption bands of the polymer in the region of bending vibrations are completely overlapped by the intense absorption bands of dispersed filler. The recorded absorption bands of the crystalline regions in the polymers UHMWPE (pendular vibrations $\rho_{CH_2} = 719\ cm^{-1}$) and UPTFE (pendular vibrations $\rho_{CF_2} = 502\ cm^{-1}$) (Fig. 2, *a)* point to the conservation of polymer crystallinity and their plasticity under the conditions of MCS, which leads to an increase in the size of scaly particles within a broad range (50–400 μm) with the uniform distribution of filler particles in them. Oxidative destruction is not observed in the polymers. The use of dispersed Fe/BN powders leads to an increase in the content of OH groups in the sample.

CONCLUSION

High-energy mechanical treatment of the system Fe-*h*BN for 2 min leads to the formation of Fe/BN composite and to the appearance of the cubic modification of boron nitride *c*BN and the phases of iron nitride and boride, $FeN_{0.056}$ and Fe_2B, respectively. The intensity of *h*BN peaks decreases strongly as a result of a substantial decrease in the size of its crystallites. During the mechanical treatment of the mixtures of polymers with *h*BN, hexagonal boron nitride is not transformed into the cubic modification, and the size of *h*BN crystallites decreases with a lower rate in comparison with the Fe/BN composite. Mechanochemical synthesis of polymer-containing composite powders with ultrafine particles of the filler allows obtaining highly filled polymer materials (with not less than 90 mass % of the filler), which are promising materials for protection from γ-, neutron and electromagnetic radiation.

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