

Properties of hydroxyapatite doped by fullerenes and carbon nanotubes

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INTRODUCTION

Hydroxyapatite (HAP) - the material is close in composition to human bone tissue, therefore it is used for medical purposes to replace and treat patients or damaged parts of the body. The number of patients who need operations to restore bone integrity is quite large. For example, for the United States, this figure is 1 million people or more annually (of which over 300,000 are prosthetics of the hip and knee joints, dental implants are also of the same order) [1].

Previously conducted studies show that materials containing fullerenes and carbon nanotubes (C₆₀ and CNT) have special mechanical, tribological, optical, sorption properties, combining in one material difficult to reconcile properties (for example, low density with high strength, high adhesion and low coefficient friction, high strength and high plasticity) [2-4]. It was established that fullerenes and CNTs are not only stable nanoparticles, which change the properties of the material due to their presence as components of fillers of the composite material, but also act as tools for influencing the structure of the matrix as a stimulator of synergistic structuring processes [5]. The combination of the known properties of hydroxyapatite (HAP), such as biocompatibility and good water solubility, with the properties of carbon nanoparticles (electron deficiency, the ability to interact with free radicals, the stability of the shape and number of atoms) suggests the production of new bioactive materials with improved characteristics.

A significant increase in the physical and mechanical properties and tribotechnical characteristics of materials can be achieved by creating composites containing carbon nanostructures. In this connection, the study of the properties of composites based on hydroxyapatite and fullerenes, hydroxyapatite and carbon nanotubes, carried out in this paper, is of scientific and practical interest.

1. TECHNOLOGICAL AND DIAGNOSTIC TECHNIQUES

To prepare composite samples, we used separately prepared C₆₀ solution in toluene, suspension of carbon nanotubes (CNTs) in toluene, and aqueous colloids of synthetic HAP - Ca₁₀(PO₄)₆(OH)₂. The preparation of composites with the necessary concentration of C₆₀ and CNTs was provided by mixing the calculated amount of a C₆₀ solution or a CNT colloid in a single tube with an aqueous colloid of synthetic HAP. Then the prepared mixture was mixed in ultrasonic bath UZV-2/150-TH (operating frequency - 27 kHz, generator power - 80 W) for 40 min. Composite films were prepared by watering the prepared suspension onto the polished surface of steel and NaCl single crystals, followed by drying in air and sintering. The samples were dried at 60°C for 20 hours. Sintering was carried out in a muffle furnace at a temperature of 800 ° C for 2 hours. The mass fraction of fullerenes C₆₀ and CNTs introduced into the ceramic matrix varied for different samples in the range of 0.1 ... 3 mass%.

The structure was studied using a scanning electron microscope LEO 1420VP at accelerating voltages of 20-80 keV.

The mechanical strength of samples of HAP and samples of HAP modified with C₆₀ and CNT was determined on a tensile machine in a tensile machine. To carry out tribotechnical tests of the obtained composite material, a modernized tribometer was used, as in [6], operating according to the scheme of circular motion of a sample with respect to a stationary counterbody. The tribometer is equipped with a device for measuring the coefficient of friction by the method of tensometry with obtaining the characteristic of frictional forces on the computer. The test samples were in the form of disks with a diameter of 40 mm, the function of the counterbody was performed by a rod made of 65G steel. The tests were carried out at a sliding speed of 0.1 m /s, and the friction path L = 5200 m. The contact pressure was 15 MPa.

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The IR spectra of the samples of HAP, C₆₀, CNT, HAP-C₆₀, and HAP-CNTs were recorded using the Thermo Nicolet Nexus FT-IR Fourier spectrometer FT-Raman module in the range 400–1600 cm⁻¹, corresponding to the active vibrations of HAP molecules, fullerene C₆₀ and CNT.

2. STRUCTURAL STUDIES

The structures of pure hydroxyapatite and hydroxyapatite modified with C₆₀ or CNT have a significant difference. In Fig. 1 shows images of the surface of HAP and composite samples of HAP-C₆₀ and HAP-CNT.

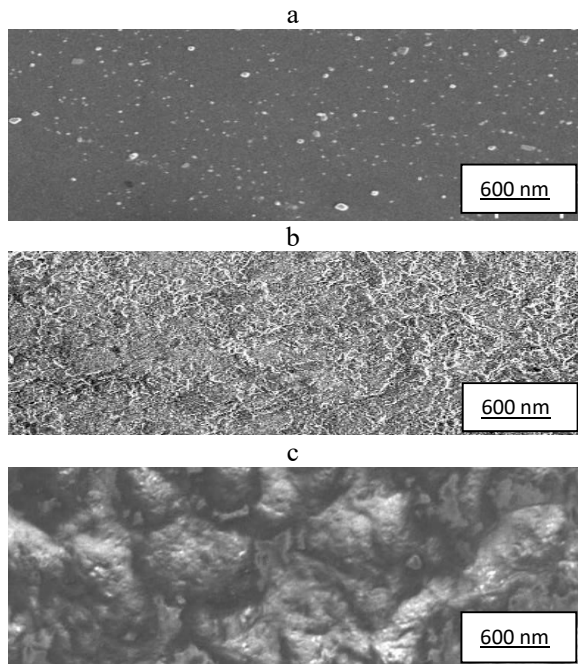


Figure 1 - Structure of the surface of GAP (a), composite samples GAP -0.5% by weight of C₆₀ (b) and GAP-0.5% by weight of CNT (c).

The surface of the GAP with an admixture of C₆₀ is more prominent, is more porous in comparison with pure HAP and HAP with an admixture of CNTs. Differences in the structure are due to the fact that fullerenes C₆₀ and CNT in different ways affect the matrix. This affects both the geometry of the particles, and the interatomic and intermolecular interactions. And as a consequence, with the introduction of fullerenes C₆₀ and CNT, we have different values of mechanical stresses, different temperature coefficients, and different conditions for the formation of phosphide layers in the hydroxyapatite matrix.

3. OPTICAL SPECTROSCOPY

IR transmission spectra of C₆₀, HAP and HAP - C₆₀ are shown in Fig.2.

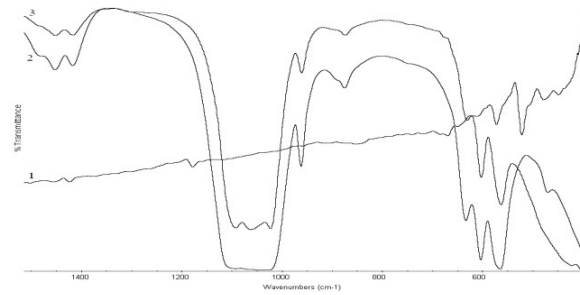


Figure 2. IR transmission spectra: 1-fullerene C₆₀; 2-pure HAP; 3-HAP + 0.5%wt. C₆₀

In the fullerite spectrum that we have registered, four narrow absorption lines are clearly discernible: 526, 578, 1183, and 1426 cm⁻¹. Oscillations corresponding to a frequency of about 526 cm⁻¹ and 578 cm⁻¹ relate to the radial vibrations of the fullerene sphere and are due to interactions of carbon atoms within the C₆₀ molecules. The absorption band of about 578 cm⁻¹ is less susceptible to external action. The characteristic of the intermolecular distance is the line of 1183 cm⁻¹, and the frequency of approximately 1426 cm⁻¹ is sensitive to the influence of charge. These vibrations are related to valence vibrations, and vibrations along the tangent to the sphere of a single CC bond are observed in the region ~ 1183 cm⁻¹, and double C = C bonds in the region of ~ 1426 cm⁻¹ [5]. In the IR spectrum of pure HAP, an intense band of 1000–1130 cm⁻¹ and absorption lines of 635, 605, 567 and 470 cm⁻¹ can be traced. Based on the data on the characteristic frequencies of vibrations of the corresponding groups whose numerical values are given in the atlas [6], the spectra obtained in the present study are identified: a broad band corresponds to the vibrations of amorphous calcium phosphate, the vibrational modes 635, 605 and 567 cm⁻¹ are related to the valence vibrations of the group apatite PO₄, and the absorption line 470 cm⁻¹ is caused by deformation vibrations of the same group.

When comparing the transmission spectra of the composite material HAP-C₆₀ and pure HAP (Figure 2), the spectral differences due to the presence of C₆₀ fullerene molecules are clearly observed. First of all, the splitting of a wide band in the range 1000–1130 cm⁻¹ into three: 1094, 1060 and 1024 cm⁻¹ and the absence of a 435 cm⁻¹ band. A similar splitting of the wide band was noted earlier in [7], in which various methods of synthesizing HAP were used to obtain a more ordered crystal structure.

Analysis of various methods of synthesis of crystalline HAP was carried out in [8,9], where the authors noted the method of mechanical activation in the synthesis of biocompatible GAP as the most promising. A good resolution of the bands in the

region of 600 and 1000-1100 cm^{-1} in the IR spectra of HAPs indicated a high degree of its crystallinity.

The absence of the 435 cm^{-1} band, in our opinion, is due to deformation and subsequent weakening of the bond under the influence of fullerenes on the surrounding molecules, whose vibrations are shifted to a lower-energy band. In addition to the spectral differences between the initial and modified matrices, a change in the vibrational modes of the C₆₀ molecule was observed, which was manifested by the absence of 1183 and 522 cm^{-1} absorption bands. Such disappearance of the vibration band was already observed earlier in the IR spectra of metal (Li, Na, K) -C₆₀ compounds obtained by doping fullerene films in [9]. Thus, based on these data, the absence of vibrational modes in our case can be caused by the formation of the Ca-C₆₀ complex.

The IR spectra of samples containing CNTs do not have any singularities and are curves reflecting a monotonic increase in transmission with increasing wavelength. A typical spectrum of CNTs is shown in Fig. 3 (curve 1). In the structure of the spectrum of the composite GAP-CNT, the following changes were observed: the presence of the triplet 1110, 1080 and 1008 cm^{-1} in the range 1000-1130 cm^{-1} and the appearance of a new absorption line at a frequency of 408 cm^{-1} . A new line of absorption is caused by the formation of a new bond.

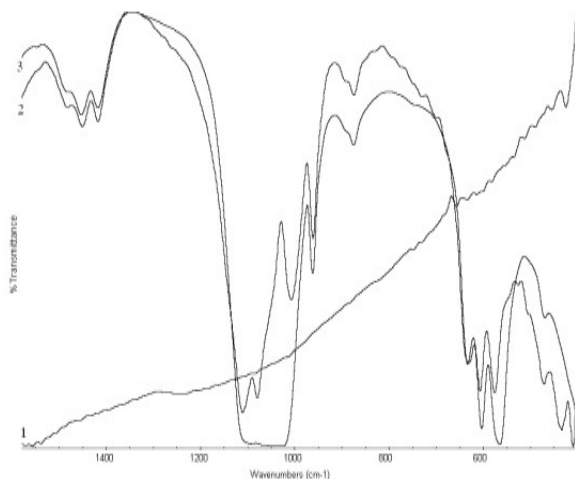


Figure 3. IR transmission spectra: 1 - CNT, 2 - pure HAP, 3 - HAP + 0.5% by weight of CNT.

Initial HAP and the interacting carbonaceous nanoparticles. The changes can be caused by the rearrangement of the electronic structure and the formation of bonds between the atoms of HAP and the fullerenes of C₆₀, HAP, and CNT.

In the samples of GAP-CNT, HAP-C₆₀, the formation of molecular complexes between the

components occurs, as evidenced by the disappearance of C₆₀ absorption bands on the GAP-C₆₀ spectra. And in the spectra of GAP-CNTs, the appearance of a new oscillation frequency, as evidenced by the 408 cm^{-1} line. Such a chemical interaction leads to the ordering of the structure of the ceramic matrix itself (splitting of the broad band 1000-1130 cm^{-1} into three well-resolved oscillations). In addition, for samples containing CNTs, a shift of the lines to the short-wavelength region is observed.

4. MECHANICAL AND TRIBOLOGICAL PROPERTIES

The mechanical strength of samples of HAP modified by carbon nanoparticles exceeds the strength of pure HAP and depends nonlinearly on the concentration of C₆₀ or CNTs. At the same time there is an increase in strength with an increase in the concentration of ULF only to a mass fraction of 1.5-2.0%. Further increase in the concentration of ULF leads to a decrease in strength. Table 1 shows the results of mechanical tests on the rupture of composite samples of HAP-C₆₀ and HAP-CNTs.

Table 1.

Composition of samples	Strength limit, GPa	Composition of samples	Strength limit, GPa
HAP (pure)	78,1	HAP (pure)	78,1
HAP + 0,1% C ₆₀	79,0	HAP + 0,1% CNTs	81,2
HAP + 0,5% C ₆₀	91,0	HAP + 0,5% CNTs	97,6
HAP + 1,5% C ₆₀	122,1	HAP + 1,5% CNTs	128,1
HAP + 2,0% C ₆₀	119,2	HAP + 2,0% CNTs	108,4
HAP + 3,0% C ₆₀	77,3	HAP + 3,0% CNTs	70,3

The effect of C₆₀ fullerenes and carbon nanotubes on the coefficient of dry friction is studied. Even small additives (0.1 mass %) significantly reduce the coefficient of dry friction. With an increase in the concentration of both fullerenes and CNTs, a further decrease in the coefficient of friction is not so significant. Table 2 shows the friction coefficients of samples of HAP modified with fullerenes and carbon tubes at different doses.

Table 2. Friction coefficients of HAP samples modified with fullerenes and carbon tubes.

Composition of samples	Coefficients of Friction	Composition of samples	Coefficients of Friction
HAP (pure)	0,42	HAP (pure)	0,42
HAP + 0,1% C ₆₀	0,32	HAP + 0,1% CNTs	0,30

HAP + 0,5% C ₆₀	0,30	HAP + 0,5% CNTs	0,30
HAP + 1,5% C ₆₀	0,26	HAP + 1,5% CNTs	0,28
HAP + 2,0% C ₆₀	0,24	HAP + 2,0% CNTs	0,23
HAP + 3,0% C ₆₀	0,23	HAP + 3,0% CNTs	0,23

A characteristic feature of the microstructure of the ceramic friction surface is the uniform filling of pores with the material formed during the interaction of ceramics and steel in the presence of fullerenes and carbon nanotubes. The improvement of the tribotechnical properties of GAP including C₆₀ or CNTs is explained by the formation of a finely dispersed structure in which the fullerenes and CNT parts act as a lubricant in friction. In addition, in the process of friction, the counterbody's atoms (in our case Fe), interacting with C₆₀ or CNT, strengthen the very thin surface layer of the test material. Similar processes were observed in [5, 6]. Fullerene-containing HAP layers with a dry friction coefficient of 0.23 were obtained.

CONCLUSIONS

1. It has been established that the adding of fullerenes C₆₀ and CNT in small concentrations (up to 1.5 wt.%) in hydroxyapatite leads to an increase in its strength. With an increase in the concentration of ULF above 2.0 wt. % the tensile strength is reduced.
2. It has been shown that the introduction of carbon nanoparticles into hydroxyapatite leads to the formation of molecular complexes and the ordering of the structure, as evidenced by the disappearance of C₆₀ absorption bands (HAP-C₆₀ samples). At the same mass fraction, carbon nanotubes are more significant than C₆₀, changing the spectra of HAP, which is due to the difference in the volumes of the matrix regions adjacent to the carbon nanoparticles.
3. The decrease in the coefficient of friction of CNT hydroxyapatite is observed at very small fractions of C₆₀ and CNT fullerenes (approximately 0.1-0.2 wt%) introduced into it, which may be caused by the enrichment of the surface layer with carbon nanoparticles when they are formed due to low density of these particles.

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