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Experimental Measurements and Calculation of Fracture Toughness Coefficient of a Hydroxyapatite Composite with Small Concentrations of Additives of Multi-Walled Carbon Nanotubes

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Abstract. The fracture toughness coefficient K_c of the composite ceramics for medical applications based on hydroxyapatite (HA) with additives of multi-walled carbon nanotubes (MWCNTs) were investigated. Sintering of the composites was carried out at a temperature of 1100°C in an argon atmosphere. The rate of the heating up to temperature of sintering was 20 K/min. HA is a bioactive matrix, and the additives of MWCNTs were used with the purpose of increasing the fracture toughness coefficient K_c. Nanoindentation tests were carried out using microhardness tester Affri DM8 with Vickers pyramid-shaped diamond indenter under a load of 4.9 N. It was found that the additives of MWCNTs with the concentration up to 0.5 wt % lead to a small increase of the K_c of the composite.

INTRODUCTION

Hydroxyapatite (HA) is a biomaterial that is often used for reconstruction of bone tissues due to the fact that HA has a chemical similarity with the mineral component of human bone tissue [1]. HA has high biological activity, osteoconductivity and biocompatibility with human bone tissue.

However, the weak mechanical properties of HA, in particular, the low values of the fracture toughness coefficient K_c, decrease the possibilities of medical applications of this material. For improving the mechanical properties of HA it is possible to use the additives of multi-walled carbon nanotubes [2].

MWCNTs have small size, a high aspect ratio (length to diameter), large specific surface, high mechanical properties such as Young's modulus, modulus of rigidity [3, 4]. Carbon nanotubes (CNTs) have a structure similar to type I collagen fibrils in bone, the diameter of which is several nanometers [5].

CNTs have already demonstrated their potential as an effective reinforcement for HA and other ceramic materials to improve their mechanical properties, in particular, to increase fracture toughness [6]. This is due to their mechanical [3], and thermal properties [7, 8]. It is known that the thermal processes during sintering can significantly influence on the resulting density and strength of the obtained composite material.

In [9] for ceramic composite of HA with the additives (up to 0.5 wt %) of MWCNTs, the compression strength was increased in 13 times and the Vickers microhardness of the composite was increased by 30%. The presence of additives of MWCNTs also leads to a significant increase of density for composite ceramics at the same sintering conditions. It indicates the activation of sintering as a result of the addition of MWCNTs [9].

Leonov, Dvilis in [10] demonstrated that with an increase of the amount of single-walled carbon nanotubes (SWCNTs) up to 1 wt % observed the increase of the fracture toughness coefficient of zirconium oxide composite

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with yttrium (3YSZ/SWCNTs). It was found that for composite with 1 wt % SWCNTs the value of K_c is 38% higher than the K_c for unreinforced 3YSZ ceramics.

In [11] the fracture toughness of HA bioceramics was increased by 56% due to the addition of 4 wt % MWCNTs. In [12] it was found that the addition of up to 4 wt % MWCNTs to the HA matrix leads to increase of the fracture toughness K_c by 92% and elastic modulus by 25% in comparison with pure HA ceramics without additives of MWCNTs. Sarkar et al. reported that the fracture toughness of the HA composite with the addition of 2.5 wt % MWCNTs is 30% more than the fracture toughness of HA ceramics without additives [12, 13].

The difference in values of fracture toughness of composite materials at the same concentration of MWCNTs indicates about the significant influence of the distribution of MWCNTs in the ceramic material on the resulting values of the mechanical properties of the composites. The fracture toughness of composite materials can be significantly improved using lower concentrations of additives of MWCNT in the case of better distribution of the nanotubes in the HA matrix. In purpose to ensure a homogeneous distribution of MWCNT the dispersing processes such as mechanical methods of treatment [14] ultrasound combined with the addition of surfactants [15, 16] are used.

The study of the influence of low concentrations of additives of multi-walled carbon nanotubes on the fracture toughness of HA-MWCNT composite ceramics during low-tech mechanical mixing is the aim of this research. This is the first steps of our group in improving the synthesis technology of HA composite by searching optimal concentration of MWCNTs and the way to achieve a homogeneous distribution of MWCNTs. The experimental measurements of the fracture toughness coefficient K_c of the ceramic composite hydroxyapatite material with the additives of multi-walled carbon nanotubes with concentrations up to 0.5 wt % were done.

EXPERIMENT

Hydroxyapatite (HA) powder was obtained in the reaction between calcium carbonate and orthophosphoric acid. Calcination of the obtained calcium phosphate precipitate was carried out at 900°C for one hour. The calcined HA powder was mechanically mixed with multi-walled carbon nanotubes (MWCNTs). Conditions of mixing (frequency and mixing time) were the same for all series of samples. Mixing of HA powder and MWCNTs powder was carried out in a ceramic mortar for two hours. Cylindrical compacts 3–5 mm in height and 8 mm in diameter were made from the obtained mixture of powders by uniaxial double-sided pressing under a pressure of 120 MPa. Sintering of the compacts was carried out at a temperature of 1100°C in an argon atmosphere. The heating rate up to sintering temperature was 20 K/min. The first series of samples did not contain MWCNTs. The second series contained 0.1 wt % MWCNTs. The third—0.5 wt % MWCNTs.

In the present work, the fracture toughness K_c of ceramic samples was measured using the indentation cracking method. Nanoindentation tests were carried out using microhardness tester Affri DM8 with Vickers pyramid-shaped diamond indenter under a load of 4.9 N. The next stage included measuring the diagonals of the obtained indentation spots and the lengths of radial cracks from the tops of the indents on the surface of the samples using a calibrated measuring system of the Axiovert 220 MAT microscope.

Figure 1 shows the characteristic form of a ceramic surface with the addition of 0.5 wt % of multi-walled carbon nanotubes after indentation and cracking. The values of the crack lengths c and the half-diagonals of the pyramid a were used to calculate the fracture toughness coefficient.

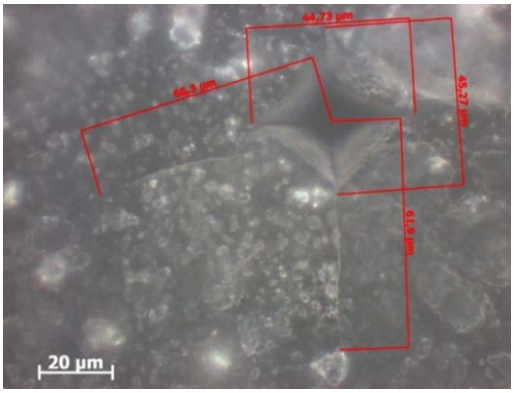

FIGURE 1. Typical bright-field microscope image of ceramic surface of HAp composite with 0.5 wt % MWCNT, immediately after indentation by Vickers pyramid-shaped diamond indenter.

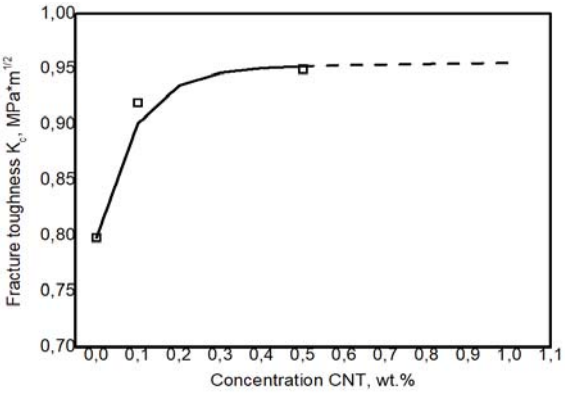

FIGURE 2. Dependence of the average values of the fracture toughness coefficient K_c of the HA–MWCNT composite on the concentration of multi-walled carbon nanotubes (MWCNTs).

The fracture toughness coefficient was calculated using the Niihara [17] equations:

$$K_c = 0.071\,\mathrm{H}a^{1/2}\left(\frac{E}{\mathrm{H}}\right)^{2/5}\left(\frac{c}{a}\right)^{-3/2},\ \frac{c}{a} \geq 2.5, \tag{1}$$

$$K_c = 0.018\,\mathrm{H}a^{1/2}\left(\frac{c}{a}\right)^{-1/2}\left(\frac{\mathrm{H}}{E}\right)^{-2/5},\ \frac{c}{a} \leq 2.5, \tag{2}$$

where E is the Young's modulus, GPa, H is the Vickers hardness of the material, GPa, c is the radial crack length (measured from the angle of the indent (pyramid), a is the half-diagonal of the indent.

RESULTS AND DISCUSSION

Figure 2 shows the dependence of the average values of the fracture toughness coefficient K_c of the HA-MWCNT composite vs. the concentrations of MWCNTs. The extrapolation of the K_c curve in the direction of increasing the concentration of additives of MWCNTs within the framework of the used synthesis technology shows a small increase up to 0.95 MPa m$^{1/2}$ of the fracture toughness coefficient with the increase of MWCNTs additives. For comparison, the fracture toughness of bone in the longitudinal direction, parallel to the long axis of the femur is varied from 1.31 to 2.05 MPa m$^{1/2}$ for specimens that have been taken from people with different ages [18]. For larger effect of improvement K_c in our material, apparently, we need to reduce the inhomogeneous of the nanotubes in the HA matrix: in the sample in some regions the nanotubes located in the form of agglomerates, but in some other regions MWCNTs are absent. The increase of the concentration of nanotubes, apparently, leads to the increase of the agglomerate sizes and the same distribution of agglomerates in HA matrix. Thus, it is necessary to apply other mixing conditions for MWCNTs and HA with the purpose to obtain the improvement of the fracture toughness coefficient.

CONCLUSIONS

Calcium phosphate ceramics based on hydroxyapatite (HA) for medical applications with the additives of multi-walled carbon nanotubes (MWCNTs) was synthesized at temperature 1100°C in an argon atmosphere. The concentration of MWCNTs was varied from 0 to 0.5 wt%. It was found that the presence of additives of MWCNT leads to an increase of the fracture toughness coefficient K_c of composite ceramics. At the same time, in the case of weak mixing of the components of the composite material, the use of concentrations of MWCNTs up to 0.5 wt% do not lead to a sufficient improvement of the fracture toughness coefficient K_c of bioceramics.

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