MECHANICAL PROPERTIES OF HYDROXYAPATITE REINFORCED BY METALLIC TITANIUM

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Abstract

This study is aimed at the development of calcium phosphate (hydroxyapatite-based) cement reinforced by titanium particulate. The introduction of particulate titanium with an average particle size of 5 µm in a quantity of up to 30-40 wt.% resulted in increasing the bend and compressive strengths to 28 and 140 MPa, respectively, and increased the fracture toughness more than fourfold (to 0.81 MPa·m$^{1/2}$).

Keywords: calcium-phosphate cements, hydroxyapatite, titanium, mechanical properties

INTRODUCTION

Materials based on hydroxyapatite (HA), an analog of the mineral component of bone tissue, are regarded as the most perspective materials for replacing bone tissue defects [1,2]. Calcium phosphate cements (CPC) are considered to be the most perspective materials for plastic reconstruction of bone tissue defects. Unlike sintered ceramics, CPCs can be surgically shaped to conform to the defect in bone tissue, providing tight contact with the tissue, and set at the defect site to form solid calcium phosphate body *in vivo*. The main disadvantage of CPCs is low level of mechanical properties (compressive strength is usually lower than 100 MPa), which is insufficient to provide reliability of cement-made implants at physiological loads and severely limits the use of CPCs to only non load-bearing applications. CPCs represent a paste of two or more components that interact and harden at the physiological temperature to give calcium phosphates (HA, or dicalcium phosphate). The state of the art dealing with CPCs has been considered in detail [3, 4]. An attempt to enhance the mechanical characteristics of CPCs by introducing dispersed particles, in particular, ceramics, resulted in about a 1.7-times increase in strength (for example, from 40 to 70 MPa [5]). The most considerable effect may be achieved in CPC reinforcement by particles of a flexible metal, especially titanium, which is biologically compatible and widely used in orthopedics [6]. This investigation is devoted to reinforcement of calcium phosphate cements that are hardened to give a compact material at a physiological temperature with titanium particles.

EXPEREMENTAL

The powder component of cements was based on HA, 60 wt.%. The rest 40 wt.% were represented by tricalcium phosphate (TCP) and tetracalcium phosphate (TTCP). The average particle sizes of powders used were 3-10 µm.

The powders were mixed in a planetary mill with titanium powder with an average particle size of about 5 µm taken in a quantity of up to 40 wt.%. Aqueous solution of magnesium hydrophosphate (50 wt.%) was used as the hardening liquid (HL). The amounts of the HL depend on powder compound, exactly on titanium content. HL was added in

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amounts of 60-35 wt.% with titanium content increasing. The cement setting time was determined with a Vicat apparatus based on the instant of disappearance of the Vicat needle trace on the sample surface. During the experiments no effect of titanium content in the powder on the setting time was found. After setting, the moulded samples were placed into a physiological solution (0.9% NaCl in distilled water) and maintained at 37°C at 100% relative humidity. The three-point bending strength and fracture toughness K_{Ic} (SENB method, a 200 µm-thick edge notch [7]) of the samples were measured using 40x4x4 mm test beams and the compressive strength was measured on 6-8 mm high cylindrical samples (diameter 8 mm).

RESULT AND DISCUSSION

According to X-ray diffraction data the sample containing no titanium (cement matrix) after hardening was composed of dicalcium phosphate dihydrate (DCPD, $CaHPO_4.2H2O$) (about 55 wt.%) and HA (about 45 wt.%). In order to attain a homogeneous distribution of titanium particles in the cement, the titanium and calcium phosphate powders were mixed prior to the addition of the HL. After HL addition and setting and hardening of the cement paste, samples with low pore content and an uniform distribution of titanium particles were obtained. Figure 1 shows the variation of the material bend and compressive strengths, and Fig.2 presents the variation of the material fracture toughness versus the content of particulate titanium.

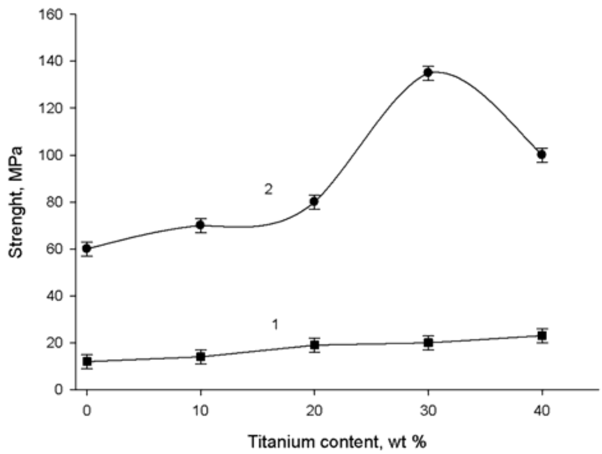

Fig.1. Bending (1) and compressive (2) strength of the composite materials vs. particulate titanium content.

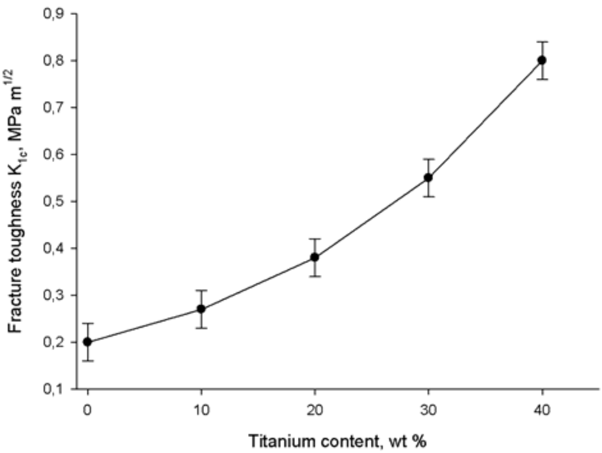

Fig.2. Fracture toughness of the material vs. particulate titanium content.

As the titanium content increases, the strength increases. The bend and compressive strengths for titanium-free cements were 9 and 57 MPa, respectively. The introduction of particulate titanium resulted in maximum values of 28 and 140 MPa; i.e., the strength increased approximately threefold. Upon bending, fracture is due to the tensile stress, while upon compression, it is due to the shear strain. The cement fracture toughness was increased upon reinforcement from 0.17 up to 0.81 $MPa \cdot m^{1/2}$. The possible mechanisms of ductile metal particles influence on the mechanical properties of a brittle (ceramic) matrix have been considered previously [8]. The key reasons are the increase in the fracture surface due to the avoidance of particles by the propagating crack front, the effect of compression stress fields in the matrix, which prevent crack opening and plastic deformation of the particles. The crack propagates across the brittle matrix and avoids the titanium particles. The tensile stress at the crack tip, which depends on distance according to a hyperbolic law, may be rather high and may results in dissipation of the deformation work of the material due to deformation of metal particles. The possibility of this process depends on the binding strength between the matrix and the particles [8]. Titanium and TiO_2 on the surface of the metallic particles do not react with either orthophosphoric acid or HA; the reaction is possible only at high temperatures, but not at physiological temperatures, according to X-Ray diffraction study. Extremum for the dependence of compressive strength versus titanium content may be due to the existence of some critical fraction of particulate metal in a brittle matrix that provides the highest resistance of the brittle matrix to shear fracture. Further increase in the material strength may be expected if strong binding between the matrix and the particles is attained through a chemical reaction, in order to involve the ductile metal in the shear deformation.

CONCLUSIONS

Magnesium-containing CPCs with bend and compressive strengths of 9 and 57 MPa, respectively, were developed. The setting time of the CPCs was about 10 min in a medium with 100% relative humidity. The introduction of particulate titanium with an average particle size of 5 μm in a quantities of up to 30-40 wt.% resulted in an increase in the bend and compressive strengths to 28 and 140 MPa, respectively, and increased the fracture toughness more than fourfold (to 0.81 $MPa \cdot m^{1/2}$). The developed cements surpass known analog in the mechanical properties and can be used for plastic reconstruction of damaged bone tissues.

Acknowledgements

This work is supported by the Russian Foundation for Basic Research, Grants No. 06-03-32192 and No. 08-08-0224.

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