



Structural transformations in hydroxyapatite ceramics as a result of severe plastic deformation

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Abstract

Severe plastic deformations lead to structural transformations in dense microcrystalline hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) ceramics and particularly to formation of nanocrystalline structure with α -tricalcium phosphate (α -TCP) and amorphous calcium phosphate (ACP) inclusions. In the present work we studied the substructure and hardness of ceramics using nanoindentation and Transmission Electron Microscopy (TEM). Our results are in agreement with the cluster mechanism of the HA structure ($\text{Ca}_9(\text{PO}_4)_6$, $\text{Ca}_3(\text{PO}_4)_2$ and PO_4^{3-}) model representing deformation of HA by cluster fragmentation and cluster-boundary “sliding”.

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1. Introduction

Calcium phosphate (CP) ceramics are widely used for bone replacement and regeneration. Hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) ceramics prepared using a high-temperature treatment are characterized by large-grain structure, slow resorption rate and growth kinetics of bone tissue contact, as well as by low osteoconductive ability. Therefore, fabrication of nanocrystalline CP ceramics is of current interest. As in the case of metallic materials, severe plastic deformation (SPD) is an advantageous way of ultrafine grain structure formation. To our knowledge, the substructural changes in crystalline HA, as a result of SPD, have not been studied yet.

It was shown that during indentation of crystalline HA its grain size decreases as a result of plastic deformation [1,2]. It is known that deformations of microcrystals [3], HA ceramics [4], human

dental enamel [5] and HA-based coatings of different structures [6–8] are elastic–plastic. In Ref. [2] it was noted that the hardness of nanocrystalline samples corresponds to the average values of hardness of HA microcrystals, and that the highest plasticity was observed in amorphous calcium phosphate (ACP). However, there is no classified data describing HA the plastic deformation mechanism.

Generally, a plastic component in deformation is associated with dislocation mobility. During investigation of submicrocrystalline ceramics intra-grain structure of nanocrystalline and microcrystalline HA coatings with equilibrium grain structure [2–9] and of the coatings regions upon nanoindentation [2] growth-induced and strain-induced dislocations in the grains bulk have not been found. Frank dislocations, related to stacking faults in indentation deformed regions of fluorine-substituted HA single crystal have been revealed [1].

Due to HA atomic structure features, the probability of strain-induced dislocations in the majority of the grains is low. This may be explained by large length vectors of complete

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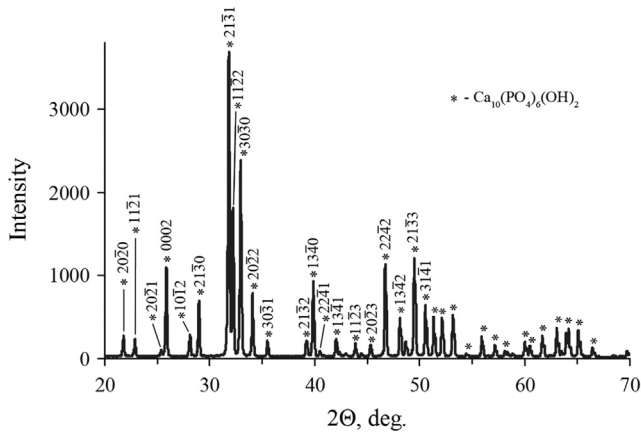


Fig. 1. X-ray diffraction pattern of the initial HA ceramic sample.

translation equal to lattice parameters ($a=0.94$ nm, $c=0.68$ nm). The dislocation energy should be very high. The core size of the edge and screw dislocations in HA should be equal to 19 and 90 sizes of the unit cell respectively according to theoretical calculations [10].

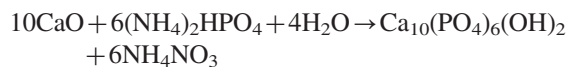
The present work was aimed on revealing structural transformations in dense microcrystalline hydroxyapatite ceramics upon severe plastic deformation.

2. Experimental procedures

2.1. Samples preparation

The samples of dense ceramics were fabricated in the form of pellets 9 mm in diameter and about 1 mm in thickness by uniaxial pressing of HA powder at 150 MPa, followed by heating for sintering at 1200 °C for 2 h.

The HA powder was prepared by heterophase synthesis method with mechanochemical activation. Initial reagents were CaO and $(\text{NH}_4)_2\text{HPO}_4$. The synthesis reaction is as follows:



The CaO and $(\text{NH}_4)_2\text{HPO}_4$ (1.0 and 0.6 mol, respectively) reagents were mixed in a planetary mill for 30 min twice: without and with water (300 ml). The mixture was dried at 120 °C.

SPD of sintered ceramic specimens was made in the following way: it was placed in a copper mandrel and twisted (5 revolutions, 1 rpm) on flat anvils at 6 GPa. As a result of deformation, the pellet's fringe region destruction occurred with retention of a compact fragment of the internal region with about 30% of the initial sample volume.

2.2. Characterization

Phase composition of the samples was studied using X-Ray diffraction (XRD, ARL X'TRA). The structure was studied using Transmission Electron Microscopy (TEM, Philips EM-430 ST). Nanoindentation was performed with Nano-Hardness

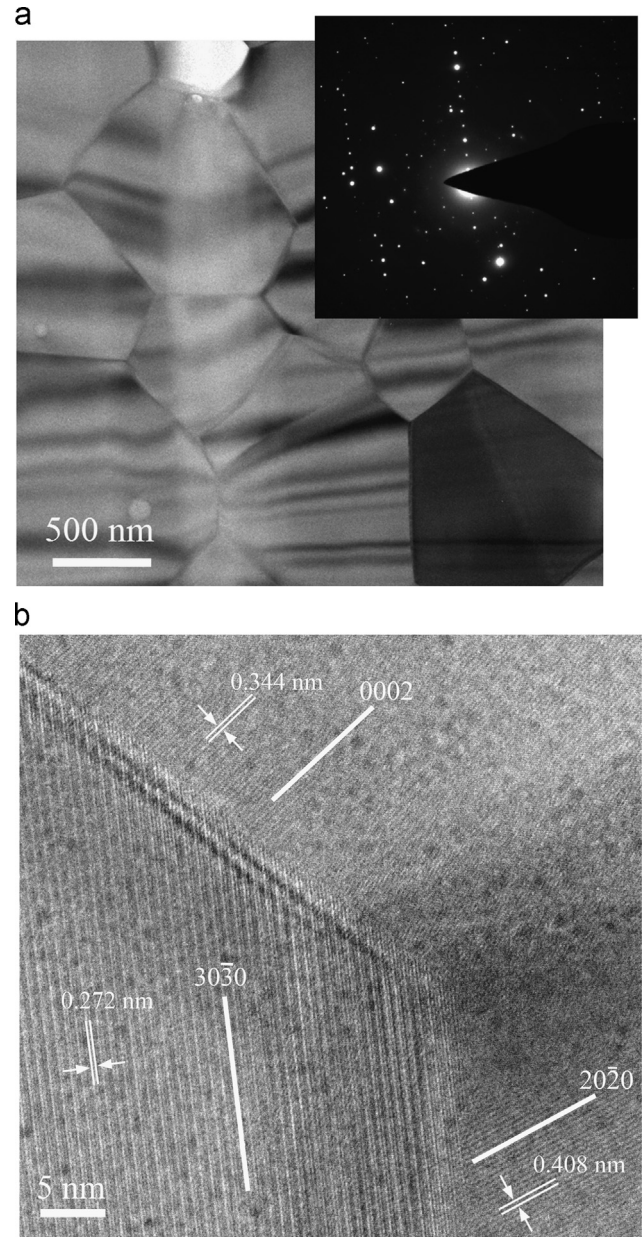


Fig. 2. TEM images of a thin section of the initial ceramic sample: (a) in the amplitude contrast conditions; (b) in the phase contrast conditions. Light lines indicate on resolved planes of the corresponding indices in HA crystal lattice.

Tester (CSM Instruments), equipped with a diamond Berkovich indenter. Cross-section samples were prepared for TEM investigation of initial ceramics and of the compact fragment upon SPD (Quanta 3D).

3. Results and discussion

In Fig. 1, the X-ray diffraction pattern of the initial ceramics is shown. We acquired a complete set of reflections corresponding to HA lattice.

Fig. 2 shows the light-field TEM image under the amplitude contrast conditions (a), the microdiffraction pattern (inset), and the TEM image under the resolution conditions of the crystal lattice

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