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Mendeleev Commun., 2016, **26**, 543–545

Mendeleev Communications

Vacuum-made nanocomposite of low-temperature hydroxyapatite and hard nonstoichiometric titanium monoxide with enhanced mechanical properties

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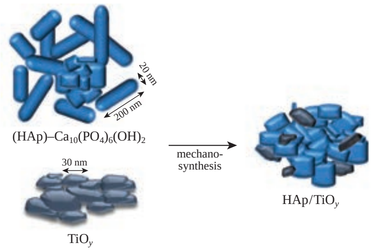
DOI: 10.1016/j.mencom.2016.11.029

The doping of hydroxyapatite (HAp) with 10 or 20 wt% titanium monoxide (TiO_y), substoichiometric $TiO_{0.92}$ or superstoichiometric $TiO_{1.23}$, leads to a considerable reduction in the initial temperature of composite compaction and to an increase in the microhardness and density of the composite material, as compared to plain HAp.



The development of biotechnologies and bone tissue engineering is based on osteoconstructional matrix materials.[1] Hydroxyapatite (HAp) is among the most suitable materials for this purpose. However, the mechanical properties of HAp ceramics do not always meet the specified requirements. The use of nanocrystalline HAp makes it possible to obtain a less porous material and to improve its mechanical properties.[2–4] Titanium microparticles or ions are used for the modification of HAp since titanium is biocompatible. Moreover, it was found[5,6] that HAp with implanted Ti ions (Ti-modified HAp) exerts a bactericidal effect.

In this work, we were the first to prepare a low-temperature HAp-based nanocomposite using vacuum annealing in order to avoid the oxidization of a titanium monoxide modifier in air. The vacuum-made composite was prepared with the use of titanium monoxide TiO_y of different stoichiometry. The initial materials and composites were studied in detail at different stages of heat treatment with the use of X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) method, pycnometry and microhardness measurements.

The low-temperature crystalline HAp $Ca_{10}(PO_4)_6(OH)_2$ [Figure 1(*a*)] was produced by deposition from calcium hydroxide and phosphoric acid solutions (pH 9).[7] The HAp prepared is preferable in terms of biocompatibility and bioactivity, but it does not possess the thermal stability permitting high-temperature annealing. According to the XRD results, the synthesized HAp features a high degree of crystallinity, a hexagonal structure with space group $P\bar{6}3/m$ and a near-natural morphology [Figure 1(*a*)]. Microcrystalline powders of hard titanium monoxide TiO_y ($y = 0.92$; 1.23) have been synthesized by high temperature vacuum solid-phase sintering.[8] Nanocrystalline TiO_y was produced by the fragmentation of coarse crystalline titanium monoxide powder in a Retsch PM 200 planetary ball mill for 8 h.[9] The nanoparticles of titanium monoxide (10 or 20 wt% of substoichiometric $TiO_{0.92}$ or superstoichiometric $TiO_{1.23}$) were added to HAp. Pressed pellets were annealed in a vacuum (10^{-3} Pa) in quartz ampoules at temperatures of 400 and 600 °C for 4 h without low-temperature sintering additives.[10] On the one hand, the annealing temperatures are low to avoid the decomposition of HAp, *i.e.*, to retain its biological activity; on the other hand, they are high enough in order to create conditions for diffusion processes and ceramic hardening.

The powders of a HAp/TiO_y mixture with different compositions showed a morphology similar to that of TiO_y nanopowder as the agglomerates of nanoparticles with a minimal size of about 20–30 nm [Figure 1(*b*)]. The pure HAp particles milled in the same way did not show such a morphology. Figure 1(*c*),(*d*) shows a typical surface morphology of powders with different TiO_y contents. The characteristics of the initial nanopowders and composites are given in Table 1. The density of the composite

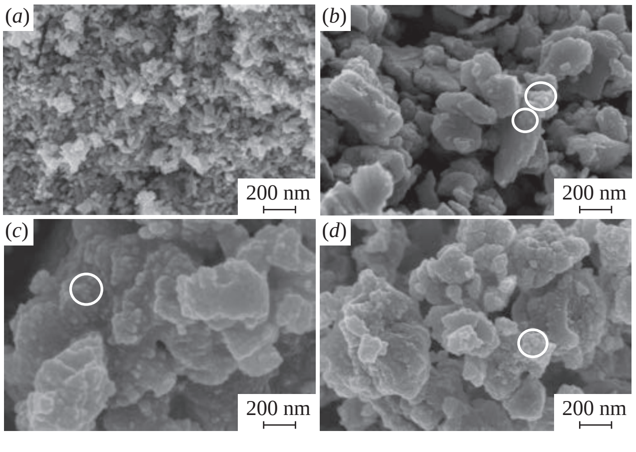


Figure 1 SEM microphotographs of the powders of (*a*) initial crystalline HAp with the formula $Ca_{10}(PO_4)_6(OH)_2$; (*b*) substoichiometric titanium monoxide $TiO_{0.92}$ after milling; (*c*),(*d*) HAp/10 and 20 wt% $TiO_{0.92}$ powders, respectively, after milling for 8 h. Circles show some agglomerates of nanoparticles.

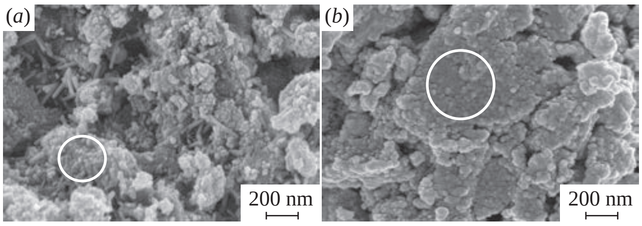


Figure 2 Microphotographs of HAp/TiO_y composite powders after heat treatment: HAp/10 wt% $TiO_{0.92}$ after annealing at (*a*) 400 °C and (*b*) 600 °C. (*a*) Nanorods after secondary crystallization of ball milled HAp.

Table 1 Physical and morphological properties of the initial materials and composites determined at ambient temperature.

Compound or composite	Density/ g cm^{-3}	Microhardness of sample/MPa	Specific surface/ m^2 g^{-1}	Δm after degassing (%)
HAp initial	2.93	138.43±12.65	98.80±0.65	7.12
HAp milled	2.81	138.43±12.65	8.85±0.06	2.70
$TiO_{0.92}$ initial	4.97	991.96±20.32	9.98±0.18	0
$TiO_{0.92}$ milled	4.48	–	18.69±0.14	0
$TiO_{1.23}$ initial	4.87	1323.47±11.87	2.29±0.06	0
$TiO_{1.23}$ milled	4.36	–	12.62±0.06	0
HAp + 10% $TiO_{0.92}$	2.94	136.71±9.09	13.03±0.11	1.49
HAp + 20% $TiO_{0.92}$	3.09	102.57±7.36	10.11±0.07	1.02
HAp + 10% $TiO_{1.23}$	2.90	127.57±4.98	12.12±0.06	2.51
HAp + 20% $TiO_{1.23}$	3.07	100.14±10.96	10.00±0.08	1.34

material is higher than that of pure HAp both in the initial state and after heat treatment. The mechanochemical synthesis in a planetary ball mill allowed us to produce a denser material with a layered structure, which is suitable for cold pressing and sintering.

One of the most important processes affecting the properties of ceramics is the compaction of materials with variations in the quantity, dimensions and shapes of pores. At the initial stage of ceramic production (500–800 °C), volumetric expansion was observed; then, compaction came into play above 800 °C. The maximal density and, consequently, the maximal strength of HAp-based ceramics was achieved after annealing at 1250–1300 °C.[11] The analysis of the surface morphology of composites revealed the presence of sintered or partially sintered particles of sizes from 50 nm to 1 μm already after annealing at 400 °C. The secondary crystallization of HAp as rod-like formations in pores and spaces between agglomerates was observed [Figure 2(*a*)]. According to published data,[12] crystallization leads to the strengthening of ceramics. Upon annealing at 600 °C, the number of micropores decreased, and the microstructure became more compact (Figure 2). The agglomerates consisted of sintered particles 20–40 nm in size, and sintering caused no particle growth; *i.e.*, the nanostate of the composites after thermal treatment was retained.

Figure 3 demonstrates the microhardness of pure HAp and composites as a function of annealing temperature. An analysis of the experimental data revealed that the composites produced with the use of TiO_y had almost 15% higher density and to 10% higher microhardness than HAp ceramics without additives.

The properties of the composites depend considerably on the amount and stoichiometry of the additives. A maximal density was achieved in HAp/20 wt% $TiO_{0.92}$, and a maximal microhardness, in HAp/20 wt% $TiO_{1.23}$ after annealing at 600 °C.

It was established that the annealing of composites in vacuum quartz ampoules at 400 and 600 °C for 4 h gives rise to different phases depending on the composition of the initial mixture. The annealing of composites containing 10 wt% $TiO_{0.92}$, $TiO_{1.23}$ and 20 wt% $TiO_{0.92}$ at 400 °C did not change the phase structure. In case of 20 wt% $TiO_{1.23}$, a weak halo for titanium dioxide (a rutile phase of TiO_2) was observed, which is indicative of superstoichiometric titanium monoxide oxidation. After annealing a composite with the 20 wt% concentration of substoichiometric $TiO_{0.92}$ at 600 °C, $Ti_{4.5}O_5$, Ti_6O_{11}, and titanium dioxide phases were formed. The $Ti_{4.5}O_5$ phase is ordered and more stable than other TiO_y phases,[9] and the Ti_6O_{11} phase is characterized by the presence of crystallographic shear planes. The presence of such phases can affect the mechanical properties of the material. It can be supposed that oxygen for the oxidation of TiO_y comes from hydroxyl groups. It was observed[13] that, at 1200–1350 °C, the phase composition of HAp changes with the formation of water that moves along the pores. The decomposition of the initial HAp at 1200–1350 °C due to the removal of hydroxyl groups was reported.[14] Although no variation in the phase composition of HAp was detected in our experiments, it is possible that such process has already begun, and a small amount of oxygen may arrive owing to such a mechanism. Upon annealing at 600 °C for 4 h, titanium monoxide in the samples was oxidized to TiO_2. The typical microstructure of composites after annealing is presented in Figure 4.

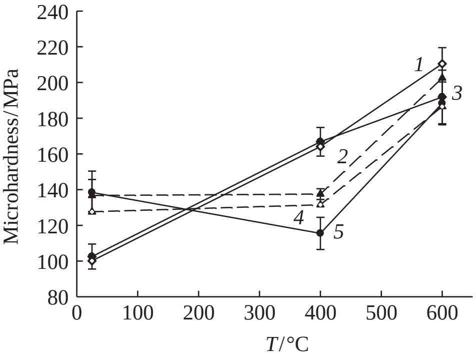


Figure 3 Dependence of the microhardness on the temperature of annealing for different compositions. (*1*) HAp/20 wt% $TiO_{1.23}$; (*2*) HAp/10 wt% $TiO_{0.92}$; (*3*) HAp/20 wt% $TiO_{0.92}$; (*4*) HAp/10 wt% $TiO_{1.23}$; and (*5*) HAp without additions.

Using HAp and TiO_y nanopowders, we produced composite materials, which are superior to HAp ceramics with respect to microhardness and density. The initial compaction temperature decreased by 200–250 °C, as compared with HAp annealed under the same conditions. The temperature reduction is due to the production of a dense layered mixture of HAp and TiO_y nanopowders excluding volumetric expansion at 500–800 °C. It was found that the properties of the composite material depend on the stoichiometry and amount of TiO_y additives. When the concentration of substoichiometric $TiO_{0.92}$ was 20 wt%, $Ti_{4.5}O_5$ and Ti_6O_{11} were detected. The composites were nanodispersed.

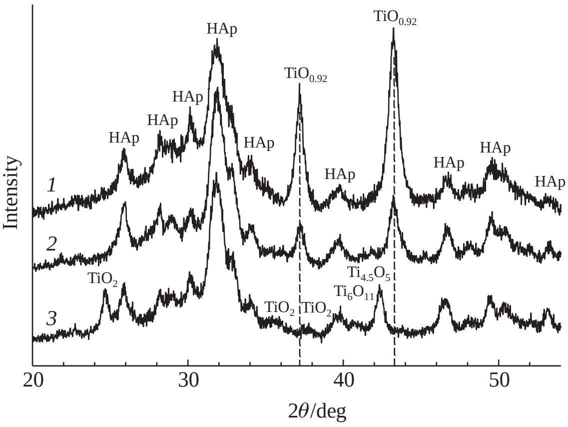


Figure 4 XRD for HAp/20 wt% $TiO_{0.92}$ composite (*1*) before annealing, after annealing at (*2*) 400 °C and (*3*) 600 °C. After annealing at 600 °C, new reflections corresponding to TiO_2 (anatase), $Ti_{4.5}O_5$ and Ti_6O_{11} appeared.

Thus, the results revealed that the use of TiO_y for HAp strengthening allows one to decrease considerably the temperature of complete hardening of the composite in a vacuum and to prepare a dense material without high-temperature treatment. By varying the stoichiometry and concentration of TiO_y, it is possible to purposefully affect the properties of the composite material, in particular, to control the formation of new phases.

We are grateful to V. M. Skachkov and S. Z. Nazarova for their assistance in the experiments. This work was supported by the Russian Science Foundation (grant no. 14-23-00025).

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Received: 20th April 2016; Com. 16/4916