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Effect of sintering conditions on physical properties of carbonated hydroxyapatite ceramics

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The carbonated hydroxyapatite powder was obtained by reaction of calcium carbonate with ortho-phosphoric acid. The compacted powder samples were sintered in the 800–1000°C range in dry carbon dioxide atmosphere under atmospheric pressure. It is revealed that ceramics synthesized in such conditions is the AB type carbonated hydroxyapatite. The carbonization kind varies from mainly B type (at relatively low sintering temperatures) to mainly A type (at high ones). The carbonic gas atmosphere did not allow to suppress disintegration of a carbonated apatite at a sintering temperatures above 1100°C, a partial decomposition of the B type apatite occurs with calcium oxide release. As a result, porosity of the ceramics increases and its mechanical properties drop sharply. However, at temperatures below 1100°C, the carbon dioxide favors the activated shrinkage of compacts due to accelerated diffusion migration of the powder particles. In particular, the maximum density of ceramics (~94 % from the theoretical value) is reached at 1000°C.

Порошок карбонизированного гидроксилапатита получен путем проведения реакции между карбонатом кальция и ортофосфорной кислотой. Изготовленные из него прессовки спекались в интервале температур 800–1000°C в атмосфере сухого углекислого газа (при нормальном давлении). Керамика, полученная таким способом, является карбонизированным гидроксилапатитом АВ-типа. Вид карбонизации изменяется от преимущественно В-типа при относительно низких температурах до преимущественно А-типа — при высоких температурах спекания. Выше 1100°C происходит частичный распад апатита В-типа и выделение окиси кальция. При этом пористость керамики увеличивается и резко падают ее механические свойства. При температурах ниже 1100°C, атмосфера углекислого газа способствует активированной усадке прессовок благодаря ускорению диффузионной миграции частиц порошка. В частности, это приводит к достижению высокой плотности керамики (~94 % от теоретического значения ГА) при температуре 1000°C.

The mineral component of bone tissues is finely dispersed hydroxyapatite (HA) which contains numerous impurities. Therefore, the chemical composition of bone implants should be consistent as much as possible to that of biological apatite in order to improve the biological response of organism to the HA implants. Since the impurities are very different in chemical nature, it is feasible to introduce only impurities present in bone at highest concentrations when studying systematically the bone implants in vivo. First of all, these are carbonate ions having concentration in the bone 5–8 wt. % [1, 2]. The carbonate ions may have occupied two kinds of positions in the HA structure [3–5]. The first are the sites occupied by PO_4^{3-} ions forming the frame of crystal lattice (so called B type substitution), the other are sites of OH^- groups (A type substitution). The substitution of the both positions is not isomorphous in the balance of ion charge and size. Thus, various kinds of structural defects appear during formation

of a carbonated HA, which may affect considerably the mechanism of linkage at the implant/tissue interface and, consequently, the bioactivity of the implant.

The biological implants are usually ceramic and not powder products. This is due to the fact that powders are easily washed out of the bone defect by body liquids while the ceramics are resistant against those. However, some difficulties arise in the ceramics preparation from carbonated HA (CHA) powder, caused by the fact that the active sintering temperature exceeds the CHA decomposition temperature. The final product in this case is usually oxyhydroxyapatite which is bioactive but has a rather low resorption rate in biological environment. Therefore, to prepare an appropriate functional ceramics, the processing conditions should hinder the decomposition process or at least decelerate it. One of the simplest decisions was found to be the sintering in CO_2 atmosphere [7–9].

Wet and dry carbon dioxide atmospheres were tested. A complex relation of the impurity composition of the initial powder and the kind of gaseous atmosphere on the one hand and the sintering characteristics and the properties of the ceramics on the other one. So, it was shown [9] that the temperature dependence of the compact shrinkage is independent of the sintering atmosphere (whether being air or wet or dry carbon dioxide). When the compact contains CO_3^{2-} groups, the carbonization extent of HA powder in a compact effects decisively the process acceleration while the atmosphere plays a stabilizing part. However, the mechanism of the densification has not been clarified up to now.

The aim of this work was to study the effect of temperature conditions on the sintering of compacted CHA in CO_2 atmosphere and to find and explanation of the sintering mechanism.

The precipitate was prepared by reaction of calcium carbonate (special purity grade, Merck) and ortho-phosphoric acid (analytical purity grade). The ortho-phosphoric acid solution was poured rapidly into a aqueous calcium carbonate suspension under continuous stirring. The synthetic reaction proceeded at 45°C for 24 h until neutral pH value was attained. The precipitate was then isolated by centrifugation, dried in an oven at 90°C, grounded in a porcelain mortar, and sieved through a 100 μm sieve. The compacts for sintering were prepared by single-axial pressing in a steel mould, the compacting pressure being 120 MPa. The samples were sintered in dry carbon dioxide for 2 h at 800–1200°C at a 100°C steps. Five series of the samples (10 pieces in each) were prepared.

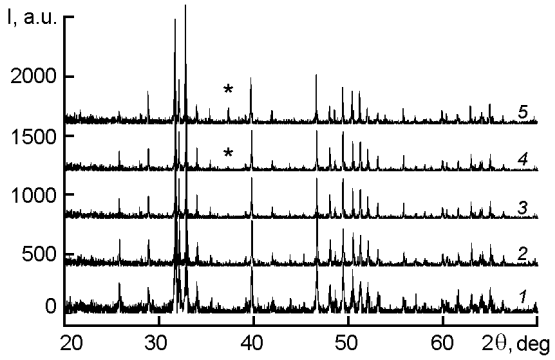

Fig. 1. Diffraction patterns of ceramic samples sintered at temperatures (°C): 800 (*1*), 900 (*2*), 1000 (*3*), 1100 (*4*), 1200 (*5*) in carbon dioxide atmosphere. CaO phase is marked by (*).

X-ray measurements were carried out using a Philips APDW40C diffractometer in CuKα radiation in the 2θ angle range 20–70° with scanning pitch of 0.01° and scanning time 0.6 s. IR spectra were measured using a BIO-RAD FFS 175 spectrometer (Germany) with 2 cm^{-1} resolution and accumulation of 200 scans. The samples were compacts of CHA ceramics and chips of KBr single crystal powdered in an agathic mortar. Electron microscopic measurements were performed using a ESEM Quanta 400 scanning microscope (Germany). Dilatometric measurements were carried out by a laboratory dilatometer at the measurement absolute error of 1 %. The temperature was controlled by a chromel-alumel thermocouple at 1°C accuracy. Specific weight of the ceramic samples was measured by Archimed method and averaged for 10 samples in each series. Microhardness was determined by Vickers method under 2 N maximum load and compressive strength, using a laboratory testing machine.

The diffractometric data have shown that the samples sintered at 800–1000°C have the crystal structure of HA (Fig. 1). The diffraction patterns of the samples sintered at 1100–1200°C revealed, beside the main apatite reflection, an additional one which is usually associated with the principal maximum of calcium oxide. The lattice constants *a* and *c* of the compact material increase steadily with increasing sintering

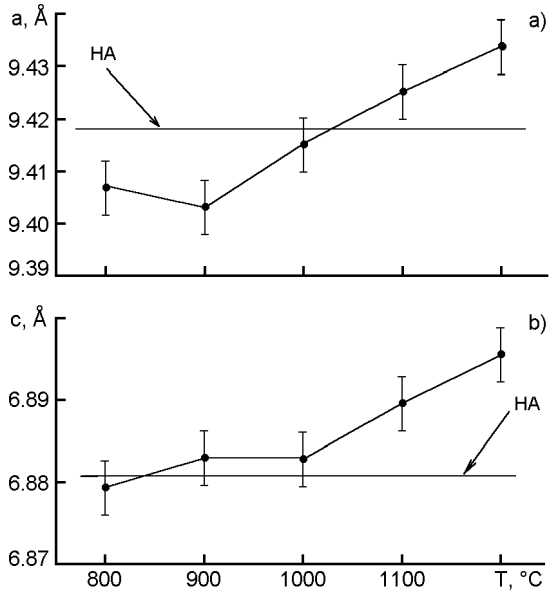

Fig. 2. Dependence of the lattice constants *a* (a) and *c* (b) of ceramics on sintering temperature.

temperature (Fig. 2), where the *a* value is smaller than that of stoichiometric HA at sintering temperatures lower than 1000°C and higher above this temperature value. The *c* value in the wide temperature range was higher than in HA. It is difficult to judge the nature of these alterations basing only on X-ray data. Therefore, the IR spectra of the same samples (Fig. 3) must be taken into consideration. The absorption bands of carbonate ions (875 cm^{-1}, 1400–1550 cm^{-1}) are present in all the spectra. Consequently, the samples are carbonated hydroxyapatites. As for the kind of substitution, the samples sintered at temperatures lower than 1000°C manifest mainly the bands of B type substitution which correlates well with the lattice constant values (the *a* value of a CHA is smaller than that of HA) [10]. The samples sintered at temperatures above 1000°C show an additional absorption at 1545 cm^{-1}, which is associated with A type substitution. Simultaneously, the both lattice constants increase considerably; this also is consistent with the known data [4, 11]. The A substitution becomes predominant as compared to the B sites at those temperatures. It is to note that a slight splitting of phosphate bands in the 570–602 cm^{-1} range is seen, i.e. the short-range environment of PO_4^{3-} ions is distorted strongly by the carbonate substitutions. The samples are in the strained

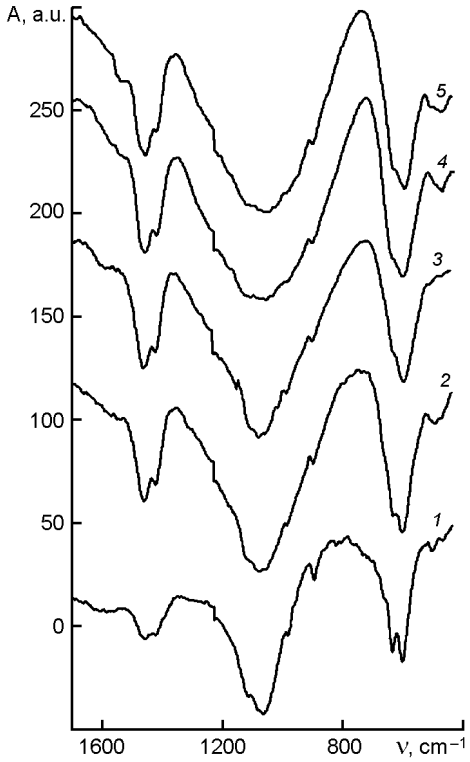

Fig. 3. IR spectra of ceramic samples sintered in carbon dioxide atmosphere. Designations as in Fig. 1.

states, which may result in improved biological properties of the implants prepared from such ceramics (due to the expected increased the resorbtion rate). Hence, sintering the compacts of CHA in the dry carbon dioxide atmosphere in the whole studied temperature range results in AB formation of AB type ceramics, where the A type substitution extent increases as the sintering temperature rises. As a consequence, compacts of predominant B-type CHA during sintering decompose with formation of calcium oxide (Fig. 1).

These variations in the phase composition affect the mechanical characteristics of the ceramics (Table). All the characteristics increase as the sintering temperature rises up to 1000°C, and drop sharply above the temperature. The ceramics density is 94 % of the theoretical value for HA and then decreases down to 70–72 %. The compressive strength and the micro-hardness also decrease with reducing density. Such peculiarities were not observed before when sintering CHA compacts in air [12] when the density, compressive strength, and microhardness steadily increased with rising sintering temperature. This is due to the fact

Table. Density (ρ), Vickers microhardness (H_V) and compression strength (τ_c) of carbonated hydroxyapatite ceramics sintered at various temperatures

T_s, °C	ρ, g/cm^3	H_V (±10 %), MPa	τ_c (±10 %), MPa
800	2.65±0.01	127	219
900	2.88±0.01	156	224
1000	2.97±0.01	171	200
1100	2.23±0.01	118	14
1200	2.26±0.01	126	25

that the final product in the study [12] was an HA and in our case, a CHA. Thus, the sintering atmosphere of CHA compacts has a stabilizing effect on the phase composition and properties of the ceramics.

The presence of the carbon dioxide atmosphere contributes to both the maintaining of the initial carbonization to a certain degree and the sintering acceleration. This is confirmed by the dilatometric measurements conducted during sintering the compacts in air and carbon dioxide (Fig. 4). The comparison of the shrinkage curves in these two media (the heating rate in the both cases is 5°/min) shows that the shrinkage rate in the carbon dioxide atmosphere at temperatures close to 1000°C sharply increases and a significant densification in compacts occurrs. However, the densification process in air occurs in a wider temperature range.

The fracture surface microstructure of ceramics sintered at 800–1000°C in carbon dioxide shows (Fig. 5a–c) that an appreciable densification already occurs at 800°C. The fracture surface microstructure of a ceramics sintered at 1000°C in air is presented in Fig. 5d for comparison. Despite the much higher sintering temperature (by 200°C) it is clearly seen that such a ceramics is less dense and its sintering process only starts in those conditions.

The above results enrich the information on the activation effect [7, 9]. The effect of the shrinkage acceleration in the carbon dioxide atmosphere may be associated with the fact that the main mass transport mechanism during the compact densification is based most likely on the sliding the powder particles into the voids therebetween. This process is activated because the boundaries of all particles taking part in the process became rather mobile, providing

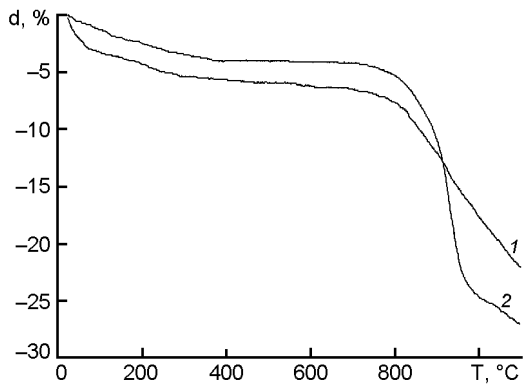

Fig. 4. Dilatometric measurements of shrinkage of compacts in air (*1*) and carbon dioxide (*2*) atmosphere.

thus a low value of the boundary diffusive viscosity and, as a consequence, a higher shrinkage rate. The mobility of the boundaries may be caused by the presence of carbon dioxide atmosphere due to following circumstances: the carbonate ions are weakly kept by the CHA lattice at high temperatures (sintering) and could easily migrate from B positions to A positions and vice versa, because the CO_2 atmosphere prevents their removal from the sample. Chaotic alterations in the lattice constants occur during that motion which could result in slight shortening and/or expansion of the particles (at least near their surfaces), having sizes of a few hundred of nanometer as those at the shrinkage onset, Fig. 5a. Such a "breathing" particle in the diffusive slipping could more easily find an appropriate position in the densification process. Hence, the sintering acceleration in carbon dioxide atmosphere occurs mainly according to the gas-activated shrinkage mechanism, during which the main mass transport occurs by moving a particle as a whole. In the process, the centers of the slipping and vibrating particles move in arbitrary directions, thus providing maximum densification of the entire ensemble.

Thus, the formation and properties of products in the sintering process of carbonate substituted HA powder compacts in the dry carbon dioxide atmosphere in the 800–1000°C temperature range have been studied. As a result, carbonated hydroxyapatite ceramics of AB type substitution has been prepared. The type of substitution is changed from mainly B type to primarily A type as the sintering temperature increases. The B type carbonated apatite is partly de-

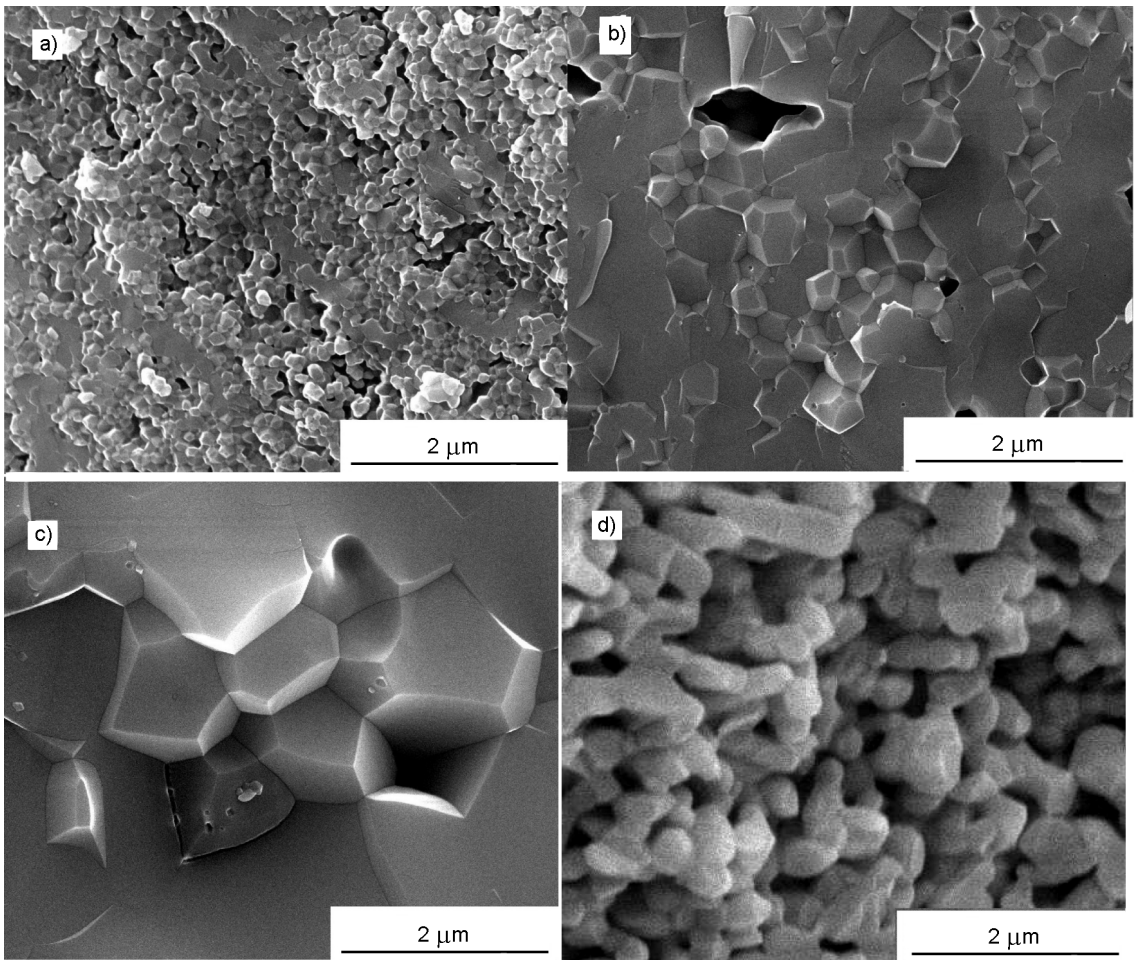

Fig. 5. Microstructure of surfaces of fractured ceramics sintered at (a) 800°C, (b) 900°C, (c) 1000°C in carbon dioxide atmosphere and (d) 1000°C in air.

composed into a biphasic mixture of apatite-calcium oxide at sintering temperatures above 1100°C. In the process, the carbon dioxide sintering atmosphere stimulates an activated shrinkage of the compacted powder due to accelerated diffusive slipping of particles, which results in a very high extent of densification of about 94 % attainable already at 1000°C.

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Вплив умов спікання на фізичні властивості карбонізованої гідроксилапатитної кераміки

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Порошок карбонізованого гідроксилапатиту отримано реакцією між карбонатом кальцію та ортофосфорною кислотою. Виготовлені з нього пресовані зразки спікалися в інтервалі температур 800–1000°С у атмосфері сухого діоксиду вуглецю (при нормальному тиску). Кераміка, отримана у такий спосіб, є карбонізованим гідроксилапатитом АВ-типу. Вид карбонізації змінюється від переважно В-типу при відносно низьких температурах до переважно А-типу — при високих температурах спікання. Вище 1100°С відбувається частковий розпад апатиту В-типу та виділення окису кальцію. При цьому пористість кераміки зростає та різко падають її механічні властивості. При температурах нижче 1100°С атмосфера діоксиду вуглецю сприяє активованій усадці пресовок завдяки прискоренню дифузійної міграції частинок порошку. Зокрема, це приводить до досягнення високої щільності кераміки (~ 94 % від теоретичного значення ГА) при температурі 1000°С.