

# Effect of Sintering Atmosphere on the Selected Properties of the Natural Origin Hydroxyapatite Materials

JADWIGA BRZEZIŃSKA-MIECZNIK, BEATA MACHERZYŃSKA, KRZYSZTOF HABERKO, AGATA STROJNY,  
WŁODZIMIERZ MOZGAWA, MIROSLAW M. BUĆKO, ANNA PYDA

AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Kraków, Poland  
e-mail: jbrzez@agh.edu.pl

## Abstract

Natural origin hydroxyapatite was extracted from the long cortical part of pig bones by treatment with the hot NaOH solution. After that, the material was carefully washed with distilled water, dried, and calcined in air at 450°C. The samples compacted under 200 MPa were subjected to heat treatment at 1000°C in air, CO<sub>2</sub>, O<sub>2</sub>, Ar and N<sub>2</sub> atmospheres. It was found that sintering atmosphere influences greatly densification of the system, sample morphology, chemical stability and elastic properties. The materials sintered in air showed high density characterized by low open porosity and relatively large faceted grains. Heat treatment in the remaining atmospheres led to essentially lower densification. Grain sizes in these cases were much smaller. It was found that CO<sub>2</sub> atmosphere arrested decomposition of the material; no free CaO appeared, and additional CO<sub>3</sub><sup>2-</sup> groups were built into the hydroxyapatite structure.

**Keywords:** Hydroxyapatite, Sintering, Microstructure – final, Sintering atmosphere, Mechanical properties

## WPLYW ATMOSFERY SPIEKANIA NA WYBRANE WŁAŚCIWOŚCI MATERIAŁÓW OTRZYMYWANYCH Z HYDROKSYAPATYTU NATURALNEGO

Hydroksyapatyt pochodzenia naturalnego został uzyskany z długiej części korowej kości wieprzowych drogą obróbki w gorącym roztworze NaOH. Następnie, materiał starannie przemyto wodą destylowaną, wysuszone i kalcynowano w powietrzu w 450°C. Próbkę wyprasowaną pod ciśnieniem 200 MPa poddano obróbce cieplnej w 1000°C w atmosferach powietrza, CO<sub>2</sub>, O<sub>2</sub>, Ar lub N<sub>2</sub>. Stwierdzono, że atmosfera spiekania wpływa znacząco na zagęszczenie materiału, jego morfologię, skład chemiczny i właściwości sprężyste. Materiały spieczone w powietrzu pokazały wysokie zagęszczenie charakteryzujące się niską porowatością otwartą i względnie dużymi ziarnami o płaskich ścianach. Obróbka cieplna w pozostałych atmosferach prowadziła do znacząco mniejszego zagęszczenia. Rozmiary ziaren w tych przypadkach były znacznie mniejsze. Stwierdzono, że atmosfera CO<sub>2</sub> zatrzymywała rozkład materiału; nie występował wolny CaO i dodatkowe grupy CO<sub>3</sub><sup>2-</sup> wbudowywały się w strukturę hydroksyapatytu.

**Słowa kluczowe:** hydroksyapatyt, spiekanie, mikrostruktura finalna, atmosfera spiekania, właściwości mechaniczne

## 1. Introduction

Hydroxyapatite ceramics, due to its chemical and structural similarity with the mineral part of bones and teeth, can be applied as the filling agent in dentistry and bone surgery. It shows no cito-toxic and cancerogenic properties after implantation to the living organism. Its characteristic feature is bioaffinity and bioactivity both in the soft and hard tissues [1, 2].

Two general types of hydroxyapatite are known: the natural origin one received from animal bones and synthetic one prepared by chemical reactions. Both materials find medical applications. The basic difference between these materials is the fact that the natural origin one contains in its structure carbonate groups, magnesium, sodium, potassium and trace elements. It makes it closer to the human bones [3].

## 2. Experimental

The starting material was obtained from the long pig bones with removed their heads. The cortical part of bones was used. After removing soft tissues bones were treated with the 4M NaOH aqueous solution at 90°C for 24 h. This operation was repeated for another 24 h with the new NaOH solution. Then the material was washed with distilled water until pH = 7.5 in the filtrate was reached. The dried and ground in a mortar material was heat treated at 450°C in O<sub>2</sub> atmosphere for 1 h in order to oxidize remaining traces of the organic matter. Then the powder was attrition ground using 2 mm zirconia (TOSOH) balls in isopropanol for 1 h. The weight ratio of the powder to balls corresponded to 1:10. Dry uniaxial compaction of the samples under 11 MPa was followed by isostatic repressing under 200 MPa. The tube furnace allowed us to sinter the samples at 1000°C for 1h with 5°C/min. rate of temperature increase in air, O<sub>2</sub>, Ar, N<sub>2</sub> and

CO<sub>2</sub> atmospheres. The gas flow rate in each case corresponded to 1 dm<sup>3</sup>/min.

Phase composition was determined by the X-ray diffraction (CuKα<sub>1</sub> radiation, X'Pert Pro, Philips PANalytical equipment) and lattice parameters by the Rietveld method. Lattice parameters allowed us to calculate the volume of the unit cell. Transmission IR spectra in the range of 4000 – 400 cm<sup>-1</sup> of the starting powders and sintered materials were prepared using Bio-Rad FTS 60 MV equipment. Resolution of 4 cm<sup>-1</sup> was received using 256 scans. Absorption bands were based on the data in [4].

Hydrostatic weighing and water absorption allowed us to determine apparent density and open porosity of the sintered materials. Specific surface area of the starting powders and samples subjected to heat treatment was determined by the nitrogen adsorption using the BET isotherm and equipment Quantachrome, model Nova 1200e. Pore size distribution in the powders compacts and sintered samples was determined using Hg porosimetry and Quantachrome Pore Master equipment.

SEM micrographs of the sintered material fracture surfaces were observed using the microscope Nova NanoSEM-200. Ultrasonic measurements allowed us to determine elastic properties of the sintered samples.

### 3. Results and discussion

Fig. 1 shows diffraction patterns of the samples sintered in indicated atmospheres. Hydroxyapatite was the only constituent of the material sintered in CO<sub>2</sub> atmosphere. In remaining atmospheres CaO appears in the concentration lower than 1 %.

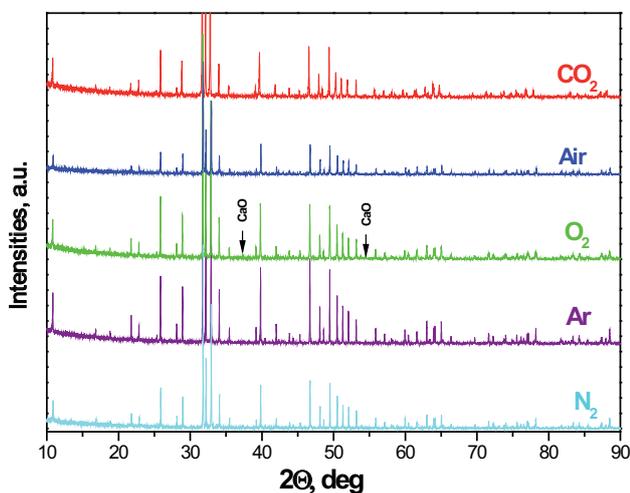


Fig. 1. X-ray diffraction patterns of the samples sintered in indicated atmospheres.

Table 1. Characteristics of samples sintered in air, CO<sub>2</sub> i Ar.

Atmosphere	Apparent density [g/cm <sup>3</sup> ]	Open porosity [%]	Water absorption [%]	Specific surface area [m <sup>2</sup> /g]	Unit cell volume [Å <sup>3</sup> ]
Air	3.00 ± 0.02	0.63 ± 0.28	0.21 ± 0.18	-	528.7
CO <sub>2</sub>	2.55 ± 0.01	17.65 ± 0.39	6.89 ± 0.25	1.2 ± 0.1	534.2
O <sub>2</sub>	2.72 ± 0.01	12.79 ± 0.33	4.69 ± 0.22	1.3 ± 0.1	528.5
Ar	2.69 ± 0.02	13.27 ± 0.36	4.92 ± 0.20	1.1 ± 0.1	529.1
N <sub>2</sub>	2.60 ± 0.03	14.23 ± 0.37	5.29 ± 0.23	1.1 ± 0.1	529.3

The IR absorption spectra reveal that bands corresponding to CO<sub>3</sub><sup>2-</sup> groups (1400-1550 cm<sup>-1</sup> and about 880 cm<sup>-1</sup>) and OH<sup>-</sup> groups (about 633 cm<sup>-1</sup> and about 3572 cm<sup>-1</sup>) in the sintered samples are different compared to the starting material.

The increase of relative intensity of the bands corresponding to CO<sub>3</sub><sup>2-</sup> in the material sintered in CO<sub>2</sub> atmosphere is higher than in the starting material. Simultaneously intensity of the bands corresponding to OH<sup>-</sup> decreases essentially. Argon, nitrogen and oxygen atmospheres lead to the disappearance of the CO<sub>3</sub><sup>2-</sup> bands. The remaining bands showing maximum at 1091 cm<sup>-1</sup> and 1033 cm<sup>-1</sup> correspond to the triply degenerated asymmetric stretching n<sub>3</sub> P-O vibrations and the one at 960 cm<sup>-1</sup> could be related to the symmetric n<sub>1</sub> stretching P-O vibrations. Absorption maxima at 600 cm<sup>-1</sup> and 570 cm<sup>-1</sup> come from the triply degenerated n<sub>4</sub> O-P-O bending vibrations.

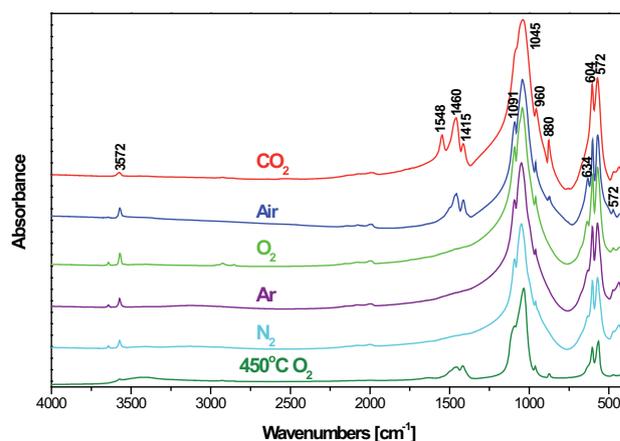


Fig. 2. IR spectra of the samples sintered in indicated atmospheres.

In the case of the samples sintered in CO<sub>2</sub> atmosphere a decrease of the 1091 cm<sup>-1</sup> band occurs. As it was shown in [5, 6] this phenomenon occurs when additional CO<sub>3</sub><sup>2-</sup> become incorporated into the hydroxyapatite structure. It can be substituted for OH<sup>-</sup> and PO<sub>4</sub><sup>3-</sup> groups. This is substantiated by the nearly total disappearance of the bands corresponding to hydroxyl groups and decrease of the 1091 cm<sup>-1</sup> intensity band, which corresponds to PO<sub>4</sub><sup>3-</sup> group. This conclusion seems also to be corroborated by the essentially different volumes of the unit cells in the case of the materials sintered in different atmospheres. This volume is 534.2 Å<sup>3</sup> in the material heat treated in CO<sub>2</sub> atmosphere and 528.5 Å<sup>3</sup>, 529.1 Å<sup>3</sup> and 529.3 Å<sup>3</sup> in O<sub>2</sub>, Ar and N<sub>2</sub>, respectively (see Table 1).

Apparent density, open porosity, water absorption and specific surface area of the materials sintered in different atmospheres are shown in Table 1.

Fig. 3 demonstrates pore size distribution of these samples. Sintering in air atmosphere at 1000°C results in den-

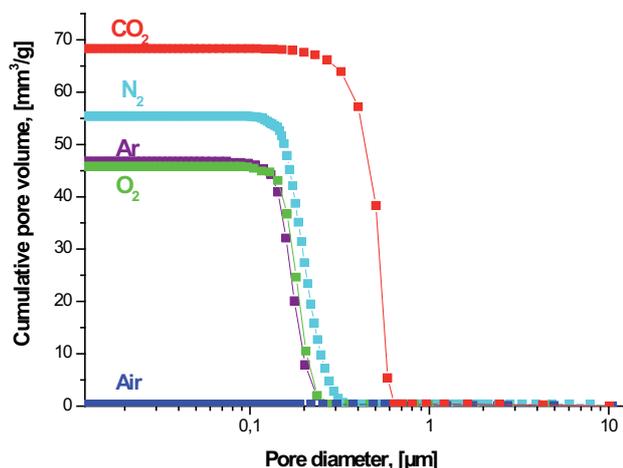


Fig. 3. Pore size distribution curves in green and samples sintered in indicated atmospheres.

se samples with small open porosity. These samples are characterized by relatively large grains, well faceted grains (Fig. 4a). Sintering in the remaining atmospheres gives samples of much lower densification and higher porosity, what is reflected by the pore size distribution measurements (Fig. 3).

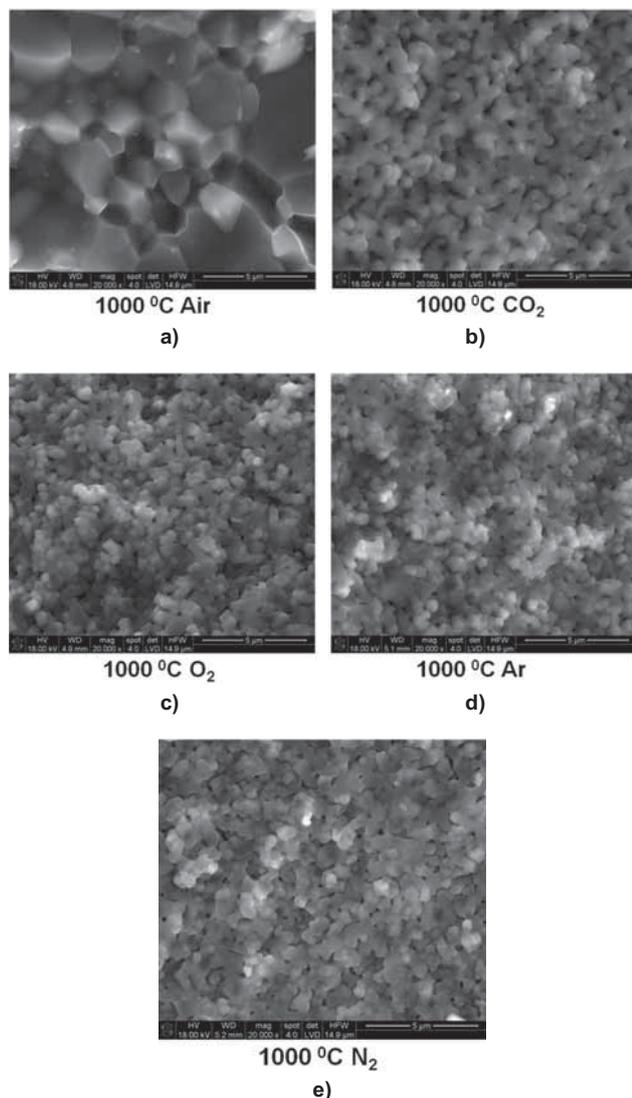


Fig. 4. Fracture surfaces of the samples sintered at 1000°C in different atmospheres: a) air, b) CO<sub>2</sub>, c) O<sub>2</sub>, d) Ar, and e) N<sub>2</sub>.

Table 2. Elastic properties of the samples sintered in different atmospheres.

Atmosphere	Young modulus [GPa]	Shear modulus [GPa]	Poisson ratio
Air	92.99 ± 1.31	36.90 ± 0.38	0.26 ± 0.02
CO <sub>2</sub>	35.05 ± 2.52	13.91 ± 0.77	
O <sub>2</sub>	49.32 ± 3.48	19.57 ± 1.35	
Ar	44.90 ± 1.18	17.82 ± 0.59	
N <sub>2</sub>	41.97 ± 3.48	16.66 ± 0.95	

Contrary to the material heat treated in air atmosphere, those heat treated in the remaining gasses show the fine-grained microstructure. Elastic properties are strictly related to densification of the systems (Table 2).

#### 4. Conclusions

Sintering atmospheres influences chemical hydroxyapatite chemical stability. Samples heat treated at 1000°C in CO<sub>2</sub> shows presence hydroxyapatite as the only phase. An increase of the CO<sub>3</sub><sup>2-</sup> groups concentration occurs in this atmosphere. Other investigated atmospheres lead to the appearance of small CaO fraction. Air atmosphere leads to the highly densified samples of relatively large and well faceted grains. The other atmospheres result in the material of low density, especially well visible in CO<sub>2</sub> atmosphere. Contrary to air atmosphere the remaining ones give fine grained samples. Young and shear modules are the higher the higher is density of the sample.

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