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# Microwave sintering of biogenic hydroxyapatite ceramics for reconstructive surgery

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## Abstract

*Ceramics based on biogenic hydroxyapatite have been produced via a microwave sintering at 1000 °C for 5, 10, 15, 20 and 30 min. It was shown that all of the ceramics studied exhibit volumetric shrinkage (2.3–4.6 %), which increases with increasing sintering time at maximum temperature. It was established that the total porosity did not depend on sintering time at 1000 °C and was equal to 38–40 %. Moreover, in all of the materials an open porosity dominated. The ultimate compression strength was in the range 35–40 MPa.*

***Keywords:*** *bioceramics, hydroxyapatite, porous materials, microwave sintering*

## I. Introduction

Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$ has structural and chemical similarity to minerals in bone and teeth. Thus, HA has been widely used in medical and dental applications in forms of granules, rods, discs and coatings on metallic implants. In literature, many methods for synthesizing HA have been reported, including sol-gel reverse microemulsion, hydrothermal, microwave-hydrothermal, precipitation and solid-state reaction methods [1,2]. HA derived from natural materials such as bovine bone, fish bone, coral, seashell, eggshell has an advantage: it inherits some properties of the raw materials such as the pore structure and composition [3–7]. Porous HA ceramics have attracted a great deal of attention in the field of bone regeneration as they allow bone cells to penetrate into the interconnected pores and to grow on their biocompatible surfaces [8–10]. However, even though the biocompatibility of HA is excellent, their poor mechanical property limits its applications.

In order to overcome these problems, microwave sintering was found to show great potential in ceramics processing. During the last years, microwave processing of ceramic materials, which ranged from structural ceramics to functional ceramics, has been widely investigated by many researchers. As a processing method, microwave sintering not only offers shorter time of processing but is also able to impart better physical and mechanical properties to the final sintered ceramic [11,12]. The application of this technique to HA sintering is still relatively new. At present, most of the studies in this area are focused on HA synthesis rather than ceramics preparation [13–15].

The aim of the present work was to prepare porous biogenic hydroxyapatite (BHA) ceramics by microwave sintering and to investigate their structure and properties.

## II. Experimental

Starting powder was biogenic hydroxyapatite (BHA) with a particle size of <160 μm derived from bovine bone by calcination at 800 °C for 3 h. The powder was pressed by two-axial cold pressing in a stainless steel mold at 200 MPa to form disk-shaped samples with a diameter of 6 mm and height of 11 mm, according to the British Standard for compression tests (No. 7253). All samples were sintered in a high temperature microwave furnace (1.5 kW, 2.45 GHz) in air at 1000 °C (heating rate 10 °C/min) for different sintering time: 5, 10, 15, 20 and 30 min.

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The crystalline phases of the prepared materials were identified by X-ray diffraction (XRD) analysis with CuK$\alpha$ radiation using a diffractometer Ultima IV (Rigaku, Japan). The porous structure was analyzed by scanning electron microscopy (SEM) (REM-106I, Selmi, Ukraine). A quantitative microstructure analysis (SIAMS PhotoLab) was employed to measure the pore and particle size. The densification of the sintered samples was estimated from volume measurements. Mechanical tests on the uniaxial compression were conducted using the universal machine Ceram test system.

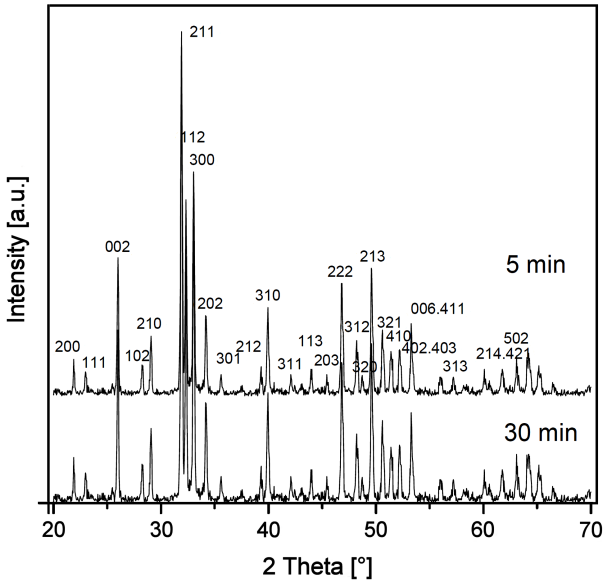


**Figure 1. Typical XRD pattern of BHA after microwave sintering at 1000 °C for 5 and 30 min**

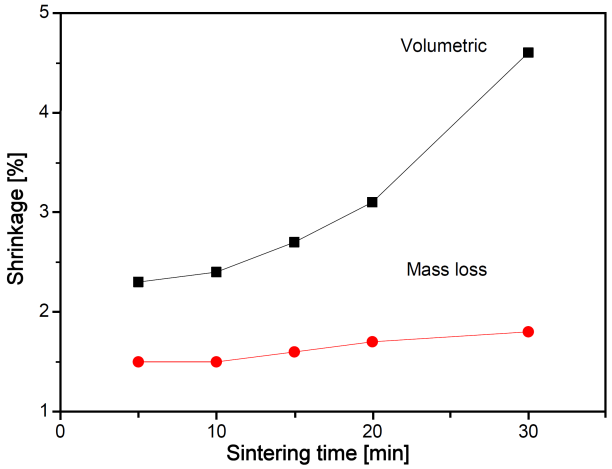


**Figure 2. The effect of sintering time on the volumetric shrinkage and weight loss of BHA samples under microwave sintering at 1000 °C**

## III. Results and discussion

Figure 1 shows a typical XRD pattern of BHA after microwave sintering at 1000 °C for 5 and 30 min, because XRD patterns for all samples sintered for the different sintering time are the same. It was established that the phase composition of BHA ceramics did not depend on sintering time. Moreover, BHA keeps the phase composition (hydroxyapatite $Ca_5(PO_4)_3(OH)$, JCPDS No. 09-0432) under sintering which confirms the thermal stability of BHA up to 1350 °C [16,17].

Figure 2 demonstrates the effect of sintering time on the volumetric shrinkage and weight loss under sintering. The volumetric shrinkage was established to increase from 2.3 up to 4.6 % with increasing of sintering time from 5 to 30 min., whereas the weight loss slowly increased from 1.5 to 1.8 %.

It was shown that the total porosity did not depend on sintering time at 1000 °C and was equal to 38–40 %. The open porosity for all prepared ceramics was 90–95 % of the total porosity.

The microstructure of BHA sample after microwave sintering is demonstrated in Fig. 3. As it can be seen, the structure is homogeneous with a uniform pore distribution. According to the SEM analysis photos (Fig. 4), the minimum pore size slowly increases from 0.15 to 0.22 μm with increasing sintering time from 5 to 30 min. It can be attributed to the pore coalesce, i.e. consolidation of small pores in large pores, due to the bulk and surface diffusion processes that is more thermodynamic favourable. The average pore size is 0.35–0.5 μm, and most of pores are within 0.2–0.8 μm. Even there are some differences in the microstructure of BHA samples, the influence of sintering time on the grain size is not so pronounced (Fig. 5). Thus, the average grain size in the sintered samples is in the range from 0.35 to 0.55 μm, and an increase in sintering time at the maximum temperature does not lead to significant increase in the grain size. The uniform structure may be related to the fact that during microwave sintering temperature field equally distributed in the whole sample volume. In cases when the particle size is commensurate with wavelength, like an ultrasound processing, microwave may destroy agglomerates and inhibit grain growth. Thus, the grain size does not increase.

The compression strength of the BHA ceramics did not depend on sintering time and porosity and was equal to 35–40 MPa, that was close to that of native bone [18].

## IV. Conclusions

Bioceramics based on biogenic hydroxyapatite (derived from bovine bone by calcination at 800 °C for 3 h) have been prepared via a microwave sintering at 1000 °C for 5, 10, 15, 20 and 30 min. It was established that the total porosity did not depend on sintering time and materials with a porosity of 40% and compression strength close to that of native bone (35–40 MPa) can be prepared by microwave sintering at 1000 °C for 5 min, which significantly reduced the cost of material.

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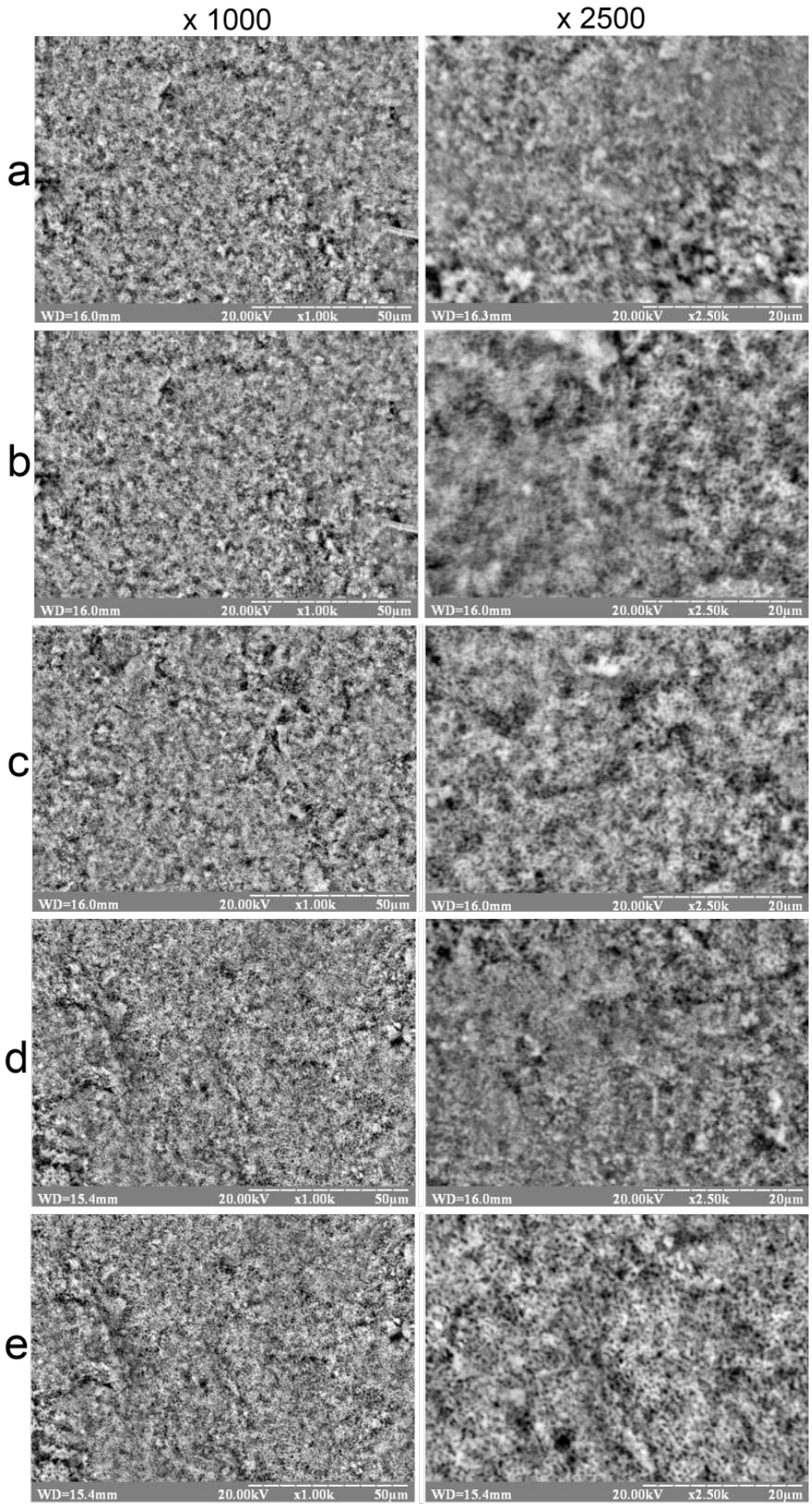


**Figure 3. SEM of BHA samples after microwave sintering at 1000 °C for different sintering time: a) 5, b) 10, c) 15, d) 20 and e) 30 min**

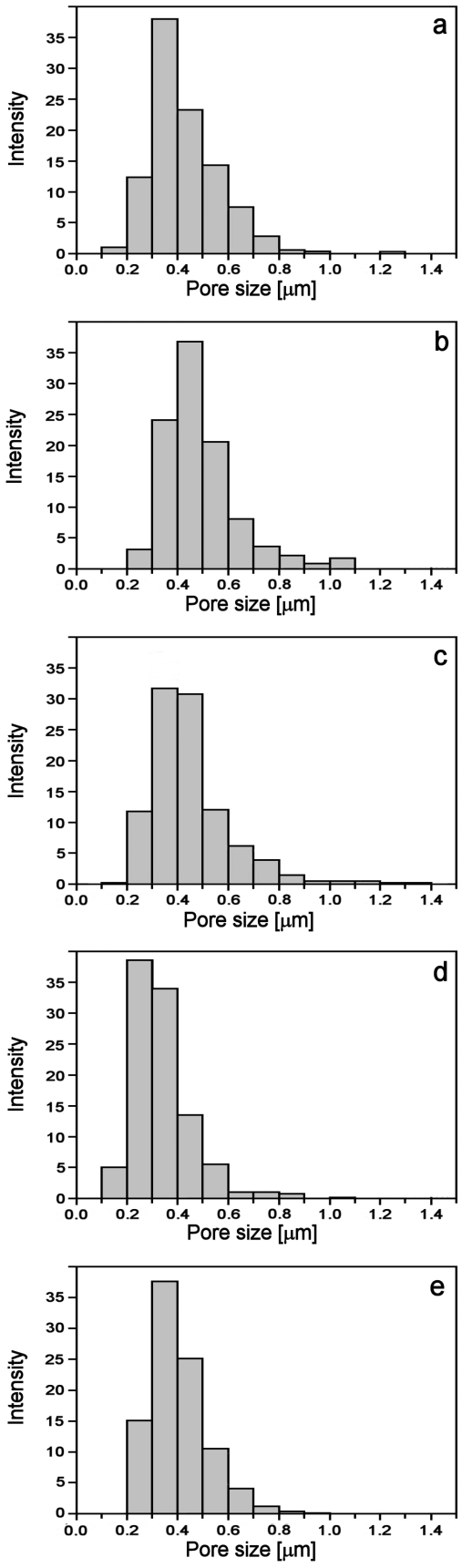


**Figure 4. Pore size distribution for BHA samples sintered at 1000 °C for: a) 5, b) 10, c) 15, d) 20 and e) 30 min**

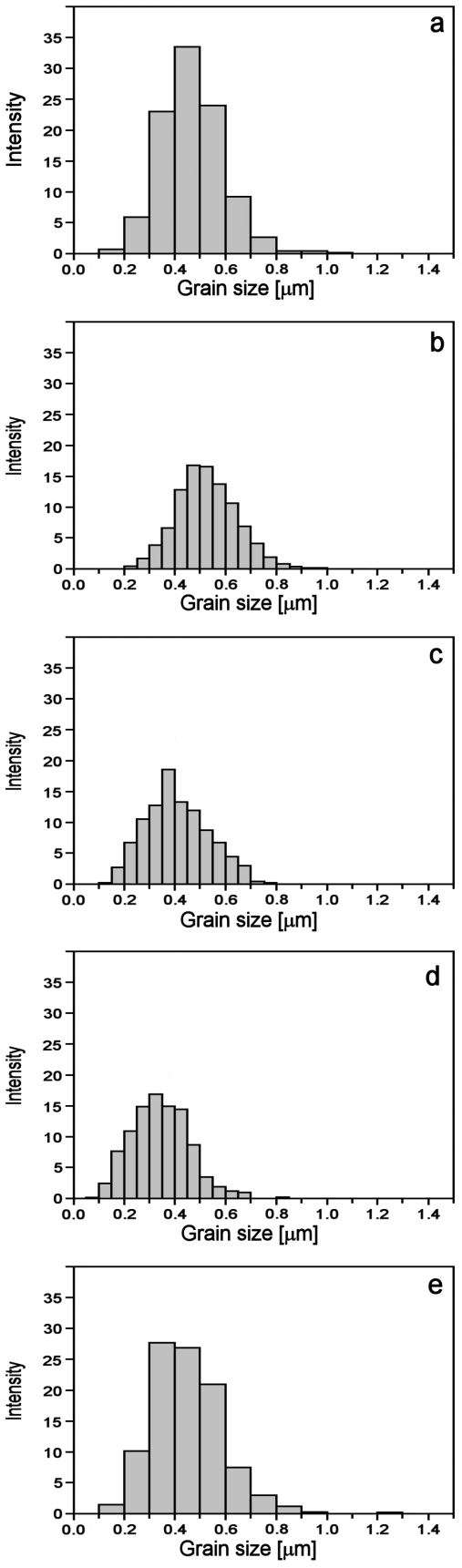


**Figure 5. Grain size distribution for BHA samples sintered at 1000 °C for: a) 5, b) 10, c) 15, d) 20 and e) 30 min**

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