



Structure evolution and properties of biogenic hydroxyapatite-based biocomposite

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Abstract

Two-step sintering has been used to investigate the structure evolution and properties of the biogenic HA/glass composite containing 50 wt.% Na₂O-B₂O₃-SiO₂-based glass. The borosilicate glass facilitated the sintering process due to the viscous glass flow and stabilized the HA phase against thermal decomposition. It has been established that the structure significantly changes, becoming more homogeneous and fine-porous, in going from the charge to two-step sintered biogenic HA/glass composite in comparison with the normal sintering. The composite samples underwent significant deformation and macropore formation (0.05–2 mm) after normal sintering at 1000°C. After two-step sintering pore minimization down to 50–100 μm occurred. The volume changes achieved 10 %. It was found that general porosity reached 15.5 %, open porosity – 74 %, compression strength – 219 MPa and composite solubility – 0.175 % mass loss after two-day soaking in physiological solution.

Keywords: *hydroxyapatite/glass composite, sintering, charge, structure*

I. Introduction

Biocomposites have generated wide-spread interest during last years. Many investigations have been conducted to find ideal materials for bone substitutes. Among them, hydroxyapatite (HA) and bioglass are the most promising materials. HA is the major mineral component of bone and teeth, with a chemical formula of Ca₁₀(PO₄)₆(OH)₂. It can promote faster bone regeneration and direct bonding to regenerated bone (without intermediate connective tissue) [1–3]. HA manufactured from bovine bone retains the chemical composition and pore structure of the bone mineral [4–6]. Since the report on its bone-bonding properties in 1971 by Hench, the silicate-based bioactive glass has been of primary interest for biological applications. Later studies revealed that several silicate-based glasses also have the ability to enhance bone formation and bond to surrounding tissue [2, 7–10]. Development of HA/glass composites allows one to unite the advantages of the individual components

[11–15]. The classical formula of Bioglass melts at around 1450°C. Addition of B₂O₃ causes lowering of glass melting temperature down to 950–1050°C [16–21]. Lower temperatures are much more economical to produce various bioglass compositions.

In our previous works, preparation of samples via two-step sintering process has been reported [22,23]. Two-step sintering is a novel technique used to suppress the accelerated grain growth that usually occurs during the final firing stage [24]. It consists of two stages: i) the first sintering of a glass composite charge at selected temperature T_1 and ii) the second sintering of a pellet obtained by uniaxial pressing of the milled and sieved primary sintered material at temperature T_2 ($T_2 < T_1$). In view of the importance of prognostication of biocomposite properties, and production of materials with required characteristics, it is interesting to study the evolution of the structure and sintering parameters of the composite. Therefore, the aim of this study was to investigate the structure evolution and properties of the biogenic HA/glass composite, containing 50 wt.% Na₂O-B₂O₃-SiO₂-based glass as a sintering aid.

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II. Experimental

The investigation was two-staged:

- i. Study of normal sintering and structure of biogenic HA/glass composite charge.
- ii. Study of two-step sintering and structure of biogenic HA/glass composite compacts.

At the stage (i) the crucible with biogenic HA/glass composite charge (HA/glass composite containing 50 wt.% Na_2O - B_2O_3 - SiO_2 -based glass) was put in a blast oven and heated in air up to 1000°C with a heating rate of $4\text{--}5^\circ/\text{min}$. The furnace construction included the asbestos cover plate with a “window” made of quartz glass, which was used for visual observation over thermal processing of the charge (Fig. 1). All visual changes were registered with a digital camera. The stage (ii) meant sample preparation via two steps. In this case the sintered material obtained in the first stage was milled, sieved and uniaxially compacted (at 150 MPa) in a stainless steel mold and sintered again at 800°C .

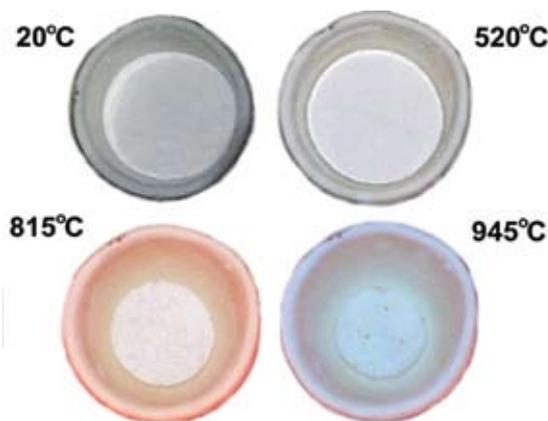


Figure 1. Sintering observation of charge of biogenic HA/glass composite

X-ray diffraction (XRD) analysis with $\text{CuK}\alpha$ radiation was used to determine the phase composition of materials. The material microstructure was analyzed using a scanning electron microscopy (SEM). Macrostructural observation was studied by digital camera Kodak EasyShare Z812 IS with magnifying glass. In addition, volume shrinkage, density and porosity changes in the composite samples upon the secondary sintering were measured. The pycnometric density was determined by the toluene displacement (Archimedes) method. The compression strength and microhardness were measured by testing machine PSU-50 and by diamond pyramid hardness machine PMT-3. Physiological solution was used to evaluate the solubility *in vitro* of composite samples at 37°C for 2 days. According to the previous studies [22,25], the ratio samples mass/solution volume was 0.033 g/ml.

III. Results and discussion

According to the visual observation at stage (i) the biogenic HA/glass composite charge started shrinking at $\sim 520^\circ\text{C}$, which is attributable to the silicate formation processes. As shown earlier [26], the visible shrinkage of glass charge and silicate formation processes began at $450\text{--}500^\circ\text{C}$. The maximum shrinkage for the biogenic HA/glass composite charge was observed at $\sim 815^\circ\text{C}$, which may be related to the formation of glass phase at the same temperature in the case of only glass charge [26]. The appearance of “molten drops of glass” at composite surface at 945°C may be attributed to the action of capillary forces. At higher temperatures, “vitrificated” composite surface did not change.

The morphology of the sintered composite at stage (i) is shown in Fig. 2. The “vitrificated” material and numerous pores can be observed. As seen, the materials are characterized with inhomogeneous pore structure with pores having sizes from $\sim 50\ \mu\text{m}$ to 2 mm.

Despite its high porosity, the application of biomaterial preparation via one-step is limited because of significant deformation of composite samples under sintering [24].

According to the XRD data (Fig. 3), the biogenic HA/glass composite after stage (ii) consists of considerable amount of amorphous phase and HA with a Ca : P ratio close to 5 : 3. It seems that no secondary phase is present in the sample. The detected phase is in good agreement with the JCPDS card number 74-0566 for HA. The XRD results obtained in this study for the composite are consistent with the results reported by Van Landuyt et al. [25] and Muralithran and Ramesh [26] for the effect of sintering temperature on the phase stability of synthetic HA.

Fig. 4 shows the macrostructure of biogenic HA/glass composite after secondary sintering. In comparison to the composite sintered via one-step sintering, structure of the material processed by the two-step sintering became more uniform with the average pore size of about $50\text{--}100\ \mu\text{m}$.

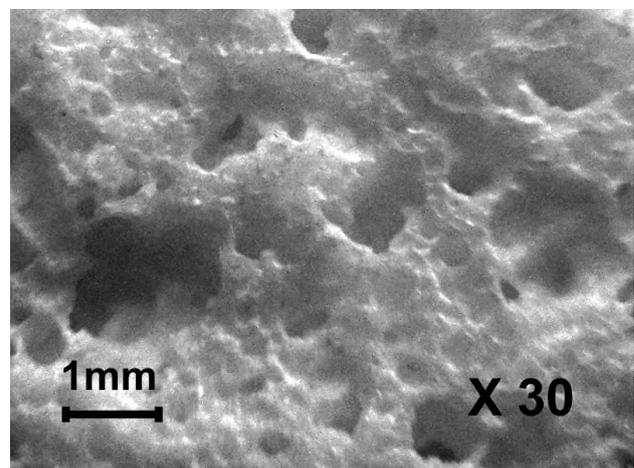


Figure 2. Macrostructure of biogenic HA/glass composite after first sintering (visual observation)

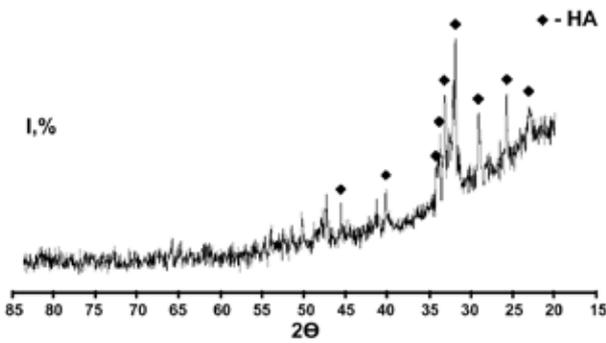


Figure 3. XRD biogenic HA/glass composite.

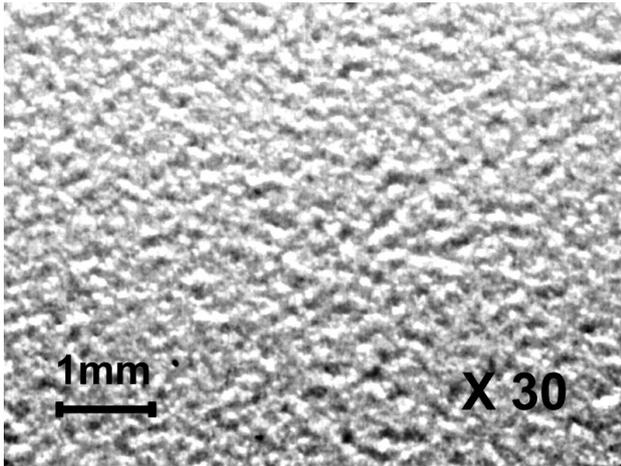


Figure 4. Macrostructure of biogenic HA/glass composite after secondary sintering

Fig. 5 presents SEM micrographs of composite prepared at stage (ii). By analyzing this plane-view observation, the microstructure is characterized by HA agglomerates embedded in glass phase. In addition, the needle-shaped particles up to 25 μm long with random orientation can be observed in the composites. The SEM micrograph confirms also the presence of uniform pore structure with the average pore sizes of $\sim 50 \mu\text{m}$ to $100 \mu\text{m}$.

It was found that the apparent density of porous composite material and porosity upon secondary sin-

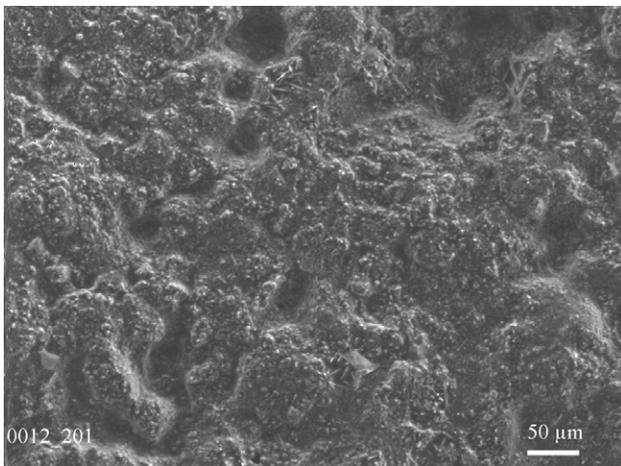


Figure 5. SEM of biogenic HA/glass composite

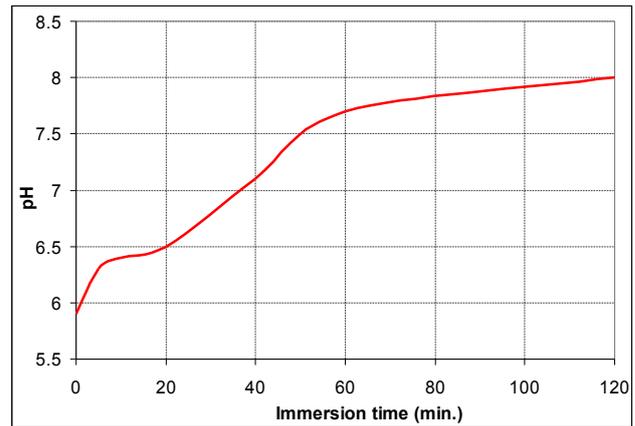


Figure 6. Changes in pH of physiological solution during soaking of composite samples prepared by two-step sintering

tering increased from 2.0 up to 2.15 g/cm^3 and from 19.7 up to 20.9 %, respectively. The pycnometric density of sintered material was 2.73 g/cm^3 . During the secondary sintering the green compacts underwent mass loss (0.3 %), linear (3.4 and 4.0 % in diameter and height, respectively) and volume (10.2 %) shrinkages. The open porosity was found to be 15.5 %, i.e. 74 % of the general porosity. Compression strength and microhardness achieved 219 MPa and 400 HV, respectively. According to the experiments *in vitro*, pH of physiological solution with soaked composite samples increased from 5.9 to 6.3 during first 2 h (Fig. 6). Generally, the composite solubility reached 0.175 % mass loss after two-day soaking in physiological solution.

Thus two-step sintering allows one to design composite samples of required shape for implantation due to the low mass and linear shrinkages after secondary sintering.

IV. Conclusions

Structure observations have revealed considerable homogenization and pore minimization (down to 50–100 μm) in going from the charge to two-step sintered biogenic HA/glass composite. Thanks to the use of borosilicate glass and lower temperature of secondary sintering, the phase analysis showed no HA phase decomposition. Two-step sintering process makes it possible to produce biocomposite samples with needed shape, high enough compression strength and solubility *in vitro* required for their practical use in reconstructive surgery.

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