



Effect of sintering temperature on structure and properties of highly porous glass-ceramics

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Abstract

Highly porous biomaterials with a structure close to that of cancellous bone have been prepared using biogenic hydroxyapatite and glass of the $\text{SiO}_2\text{-Na}_2\text{O-CaO}$ system by a replication of the polymer template structure. It has been established that during sintering of the samples the hydroxyapatite decomposes, which involves the formation of glass-ceramics containing phases of renanit NaCaPO_4 , calcium phosphate silicate $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$, calcium pyrophosphate $\text{Ca}_2\text{P}_2\text{O}_7$ and impurities of hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. Structural characteristics and mechanical properties of the obtained materials are promising for the replacement of defective cancellous bone.

Keywords: glass-ceramics, hydroxyapatite, highly porous materials, template, biomedical application

I. Introduction

Today, the method for replacement of defective bone tissue via filling of restorable cavities with bioactive materials followed by resorption of them by an organism and filling voids with newly-formed bone tissue is considered to be the simplest and most acceptable for orthopedy, traumatology and stomatology applications. In order to provide a reliable implant-bone fixation, easy penetration of body fluids and good material-in-bone growth, an implant material should possess an interconnected structure of pores sizing within 100–600 μm and a porosity of over 70% [1,2]. Furthermore, a material should not either provoke inflammatory reactions or contain toxic degradation products. Besides, for gradual mechanical loading of new-formed bone tissue, the rate of material bioresorption should be consistent with the rate of new tissue formation. Mechanical properties of highly porous materials should be good enough to enable required manipulation during their implementation in human body. The material itself should undergo sterilization without degradation of its functional properties.

Highly porous implant materials for filling cancellous bone defects have been produced through techniques of freezing, leaching, frothing and sintering, which have been developed in technology for production of glass and ceramics [3–6]. However, they do not provide either control of homogeneous pore distribution in material and pore sizes or a possibility to reach the required strength. The method using replication of a polymer matrix structure makes it possible to obtain a high-porosity structure with desired pore sizes and a homogeneous pore distribution. It includes putting a slip on a porous organic permeated template, thermal template destruction and sintering of the ceramic carcass, which preserves the shape of the template [5].

In spite of the perfect bioactive properties of both synthetic and biogenic hydroxyapatite (HA), high strength porous materials based on HA are hard to produce under laboratory conditions [6,7]. Therefore, HA based ceramics have been strengthened by adding bioactive glass [8,9]. In order to avoid possible inflammatory processes or implant rejection, the final composition should be as close to the composition of human bone tissue as possible. However, the problem of production of strong highly porous materials has not been solved yet. Bioactive glasses belong to the $\text{SiO}_2\text{-}$

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Na₂O-CaO system (with addition of 6 mol% P₂O₅) and their bioresorption degree depends on the glass composition to a great extent [10]. 45S5Bioglass® (containing 45.0 mol% SiO₂, 24.5 mol% CaO, 24.5 mol% Na₂O and 6.0 mol% P₂O₅) produced by Hench in 1969 is the most known [11]. Its shortcomings are rather high melting temperature (1370 °C) to be provided under laboratory conditions and high inclination to liquation and crystallization.

Additionally, bioactive properties of HA based ceramics can be regulated through partial HA replacement with more dissolvable phases such as tricalcium phosphate Ca₃(PO₄)₂, calcium pyrophosphate Ca₂P₂O₇, renanit NaCaPO₄ etc. Binary calcium/alkaline metal phosphates exhibit higher solubility compared to tricalcium phosphate thanks to replacement of Ca²⁺ with a cation having bigger radius and smaller charge [12–14]. Calcium pyrophosphate takes an important part in regulation of many biological processes and stimulates the formation of bone tissue to greater extent as compared to HA [15]. Calcium silicate phosphate Ca₅(PO₄)₂SiO₄ is considered to be a promising material for replacement of bone tissue as well [16,17].

Callcut and Knowles [18] described a route to produce a highly porous composite material on the basis of synthetic HA and glass of the Na₂O-CaO-P₂O₅ system using a polyurethane-foam template at 1250 °C for 8 h. The reached strength was 0.02 MPa, which is not high enough for the doctor's manipulations to be performed without destruction of material. To increase the strength to 0.08 MPa, sintered samples were coated with a slip layer and subjected to additional sintering at 1250 °C for 8 h. The mean pore size in the obtained material was 500 μm.

Scalera *et al.* [7] produced highly porous HA from powder pretreated in the temperature range 600–900 °C. In the next step, a slip was obtained by using 2% PVA solution. Highly porous samples were prepared at a maximal temperature of 1300 °C for 3 h after preheating at 500 °C for 1 h. The structural-mechanical properties of the samples were established to significantly depend on HA powder preheating temperature. The powders, prior annealed at 900 °C, exhibited the best strength (0.48 MPa).

To achieve a homogeneous slip on the polymer template, not only the procedure of immersion was used, but also its combination with electric spraying [19]. Then, a highly porous HA has been produced through combination of procedures of replication and filling voids with gel followed by heat treatment at 1200 °C [20].

To produce a suitable implant material, it is important not only to reach required performance properties, but also to lower the material cost as much as possible via the use of available non-expensive starting materials and heat treatment temperatures that are accessible for most of laboratory furnaces, that is, in the range 900–1000 °C. As described above the necessary properties of highly porous materials can be obtained only at temper-

atures >1200 °C. Hence lowering of sintering temperature is very attractive from the power-saving viewpoint as it results in reducing the cost of material and makes the production procedure easier.

The aim of this work was to prepare highly porous glass-ceramics using biogenic HA and SiO₂-CaO-Na₂O glass. The highly porous glass-ceramics were prepared by replication of the structure of a polymer template combined with reduced sintering temperature. The effect of the sintering temperature on the structure and properties of the obtained material was also investigated.

II. Experimental

Highly porous samples were prepared using biogenic hydroxyapatite (BHA) and SiO₂-Na₂O-CaO glass and replication of the structure of a polymer template. This procedure includes putting a glass-ceramic slip on the polyurethane-foam template followed by drying and annealing in a muffle furnace. The SiO₂-Na₂O-CaO glass was chosen because of its non-crystallinity and similarity to the Hench's glass, which is highly biocompatible. However, we did not add CaO, which makes it possible to reduce the sintering temperature of glass, as Ca ions could be incorporated into the structure from the hydroxyapatite.

The following starting materials were used: i) BHA obtained via annealing of large livestock bones at 900 °C, ii) glass prepared at 1100 °C by melting of glass-forming component and iii) commercial polyurethane foam template (Mark ST 3542 "Interform", Ukraine) with permeable porous structure (porosity of 95% and predominated pore sizes within 500–700 μm).

The water based slip was prepared by milling of BHA together with glass (component ratio BHA/glass = 1:1) by wet method (the solid phase content was 60 mas.%). To improve the template surface wetting with the slip, 0.2 mas.% PVA solution was added. The slip-impregnated template was subjected to drying at 105 °C for 1 h followed by heat treatment in the muffle furnace at 350 °C for 1 h and annealing at maximal temperatures of 800, 900, 1000 and 1100 °C for 1 h. The heating rate within the temperature range 20–350 °C was slow, namely 3 °C/min, which is due to the necessity to avoid the material destruction and decomposition of the polyurethane-foam template. The heating rate of 5 °C/min was used in the temperature range from 350 °C to the maximal sintering temperature.

The obtained materials were examined by scanning electron microscopy (SEM) applying a REM-106I microscope (Selmi, Ukraine). Phase composition was determined by XRD using an Ultima IV Rigaku (Japan) diffractometer with CuKα radiation. IR spectra were taken with an FCM Fourier spectrometer in the wavenumber range 4000–400 cm⁻¹ using KBr as a reference.

Also, parameters such as mass loss and volume

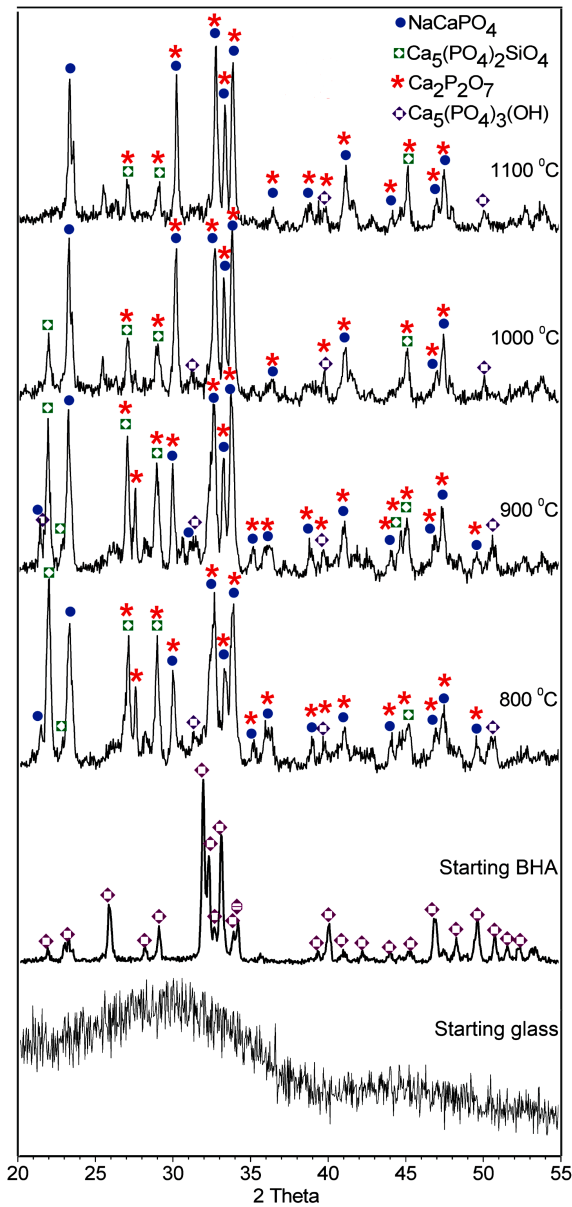


Figure 1. XRD patterns of starting materials and highly porous glass-ceramics prepared at different sintering temperatures

shrinkage upon sintering were determined by means of geometric measurements of samples before and after sintering. Total porosity was calculated by considering the apparent density and density measured at room temperature using Archimedes method with toluene as the immersion liquid. Open porosity was determined by hydrostatic weighing in toluene. The compressive strength of the samples (20 × 20 × 20 mm) was measured using a mechanical testing machine (Ceram Test System, Ukraine) at a cross-head speed of 0.2 mm/min. Special experiments *in vitro* were made to estimate bioresorption of materials, in particular their solubility in the physiological isotonic solution (0.9% NaCl water solution) at 36–37 °C. A ratio of 1 g of scaffold to 50 ml of solution was used in all experiments. The samples were removed from physiological solution after 2 days,

washed with distilled water and dried at 100 °C. The bioresorption of glass-ceramics samples was obtained by means of weight loss measurements. The measurements were carried out in triplicate.

III. Results and discussion

Figure 1 illustrates XRD data for the starting materials and highly porous bioceramics obtained in the temperature range 800–1100 °C. The XRD patterns of the starting BHA powders show a crystalline HA ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ (JCPDS, Card No. 09-432)) and amorphous glass structure. Under sintering BHA decomposes with the formation of glass-ceramics due to the aggressive action of the glass phase. The XRD patterns demonstrate overlapping of the main peaks, which makes difficult a proper identification of the basic phases. Nevertheless it was established that the obtained glass-ceramics contained crystalline phases such as: renanit NaCaPO_4 (JCPDS, Card No. 76-1456), calcium silicate phosphate $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$ (JCPDS, Card No. 21-0157), calcium pyroposphate $\text{Ca}_2\text{P}_2\text{O}_7$ (JCPDS, Card No. 33-0297) and impurities of HA $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ (JCPDS, Card No. 09-432). With increasing sintering temperature from 800 to 1100 °C the peaks of calcium silicate phosphate become less intense that may be related to phase transformations and phases predominance of renanit and calcium pyroposphate.

The results obtained by XRD are confirmed by IR spectroscopy analysis (Fig. 2), which show that all of the powders are characterized by the presence of vibra-

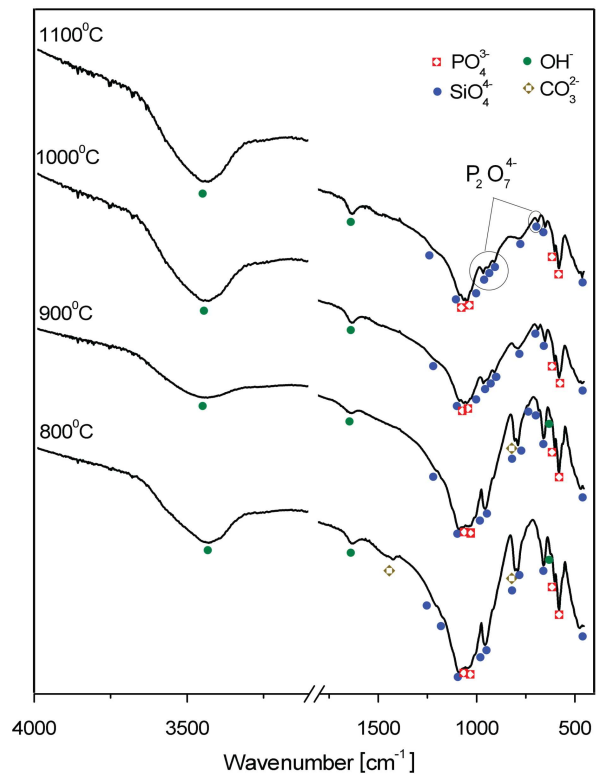


Figure 2. IR spectra of highly porous glass-ceramics prepared at different sintering temperatures

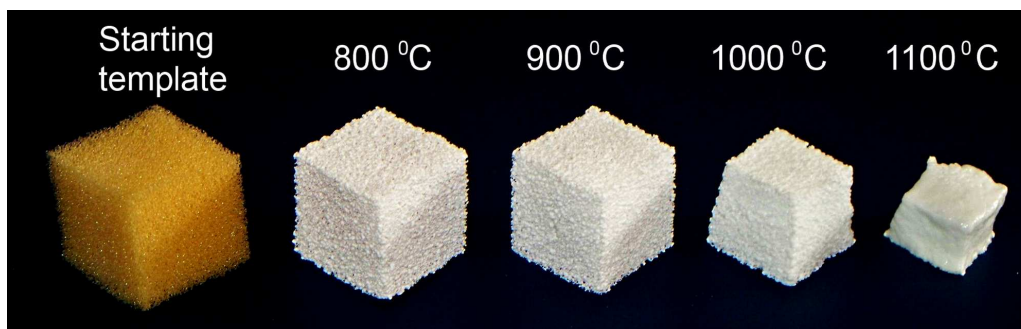


Figure 3. Photo of starting template and highly porous glass-ceramics samples prepared at different sintering temperatures

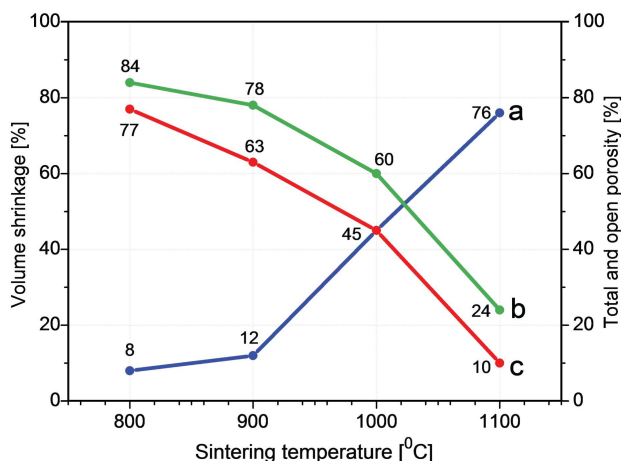


Figure 4. Effect of the sintering temperature on the volume shrinkage (a), total (b) and open (c) porosity of highly porous glass-ceramics

tions of the PO_4^{3-} and SiO_4^{4-} groups in the wavenumber range $1200\text{--}450\text{ cm}^{-1}$ [9,21–22]. After heat treatment of the samples at 800 °C , the IR spectra are characterized by absorption bands around 1080 and 950 cm^{-1} related to asymmetric ν_3 and symmetric ν_1 valence vibrations of PO_4^{3-} bonds of the phosphate tetrahedron. The $600\text{--}470\text{ cm}^{-1}$ bands are associated with deformation vibrations ν_2 of P–O bonds. The manifestation of the $800\text{--}784\text{ cm}^{-1}$ doublet is evidence for the presence of asymmetric vibrations of Si–O bonds in the SiO_4^{4-} tetrahedron. The shoulder within $1200\text{--}1150\text{ cm}^{-1}$ indicates the presence of valence bridge-like Si–O–Si vibrations. Moreover, the IR spectra contain bands of OH⁻ vibrations, namely valence vibrations in the wavenumber range $3600\text{--}3400\text{ cm}^{-1}$ and deformation vibrations around 1630 and 615 cm^{-1} attributed to adsorbed water. With increasing heat treatment temperature to 1000 °C the intensity of the absorption bands changes (decreases) within the range of $\sim 1200\text{--}800\text{ cm}^{-1}$ and the bands themselves broaden. These changes may be prescribed to the structure rebuilding caused by the changes in the phase composition. The appearance of the ~ 936 and $\sim 905\text{ cm}^{-1}$ bands as well as the shift of the absorption $\sim 950\text{ cm}^{-1}$ band towards smaller wavenumbers by $\Delta = 20\text{ cm}^{-1}$ indicate the replacement of phosphate tetrahedron with SiO_4^{4-} ions, which is confirmed by weakening of the absorption bands in the range of $\sim 650\text{--}$

550 cm^{-1} . The appearance of the $\sim 509\text{ cm}^{-1}$ band at a sintering temperature of 1100 °C is also evidence for the presence of silicate ions in the material structure. The low-intensity $900\text{--}670\text{ cm}^{-1}$ bands reveal the presence of vibrations that are characteristic for P_2O_7 groups and confirm the formation of calcium pyrophosphate $\text{Ca}_2\text{P}_2\text{O}_7$. It is however difficult to definitely specify samples because of overlapping IR spectra bands. In addition, in the spectra of the glass-ceramics sintered at 800 °C absorption bands in the frequency range $\sim 1550\text{--}1350\text{ cm}^{-1}$ are observed, which is typical for carbonate ions CO_3^{2-} . In the sample sintered at 900 °C the absorption band at around 1550 cm^{-1} disappears and at temperature higher than 1000 °C no band related to CO_3^{2-} can be seen, which may be associated with the decomposition of the carbonate component with increasing sintering temperature.

Figure 3 illustrates the appearance of the starting polyurethane-foam template and the samples of highly porous ceramics prepared at different sintering temperatures. The samples prepared at $\geq 1000\text{ °C}$ are characterized by marked volume shrinkage, shape distortion and formation of a vitrified surface. The dependences of the volume shrinkage, total and open porosity on the sintering temperature are presented in Fig. 4. The total porosity of the polyurethane-foam template infiltrated with a slip and dried under the ambient conditions is equal to 86% . The presented results reveal that sharp increase in the volume shrinkage of the glass-ceramic samples from 8 to 76% with increasing sintering temperature causes a decrease in the total and open porosity. At sintering temperature above 1000 °C a closed porosity dominates. The significant volume shrinkage, formation of closed porosity and vitrified surface are related to the properties of the glass phase contained in the prepared samples, in particular to its viscosity at maximal heating temperature. Thus, highly porous materials with predominant open porosity can be prepared at sintering temperature $< 1000\text{ °C}$.

The microstructures of the starting polyurethane-foam template and the prepared highly porous ceramic samples are shown in Fig. 5. The presented micrographs show up that the use of the template structure replication results in obtaining a glass-ceramic material with a cellular structure. With increasing temperature from 800 to 1100 °C the structure becomes less porous. The

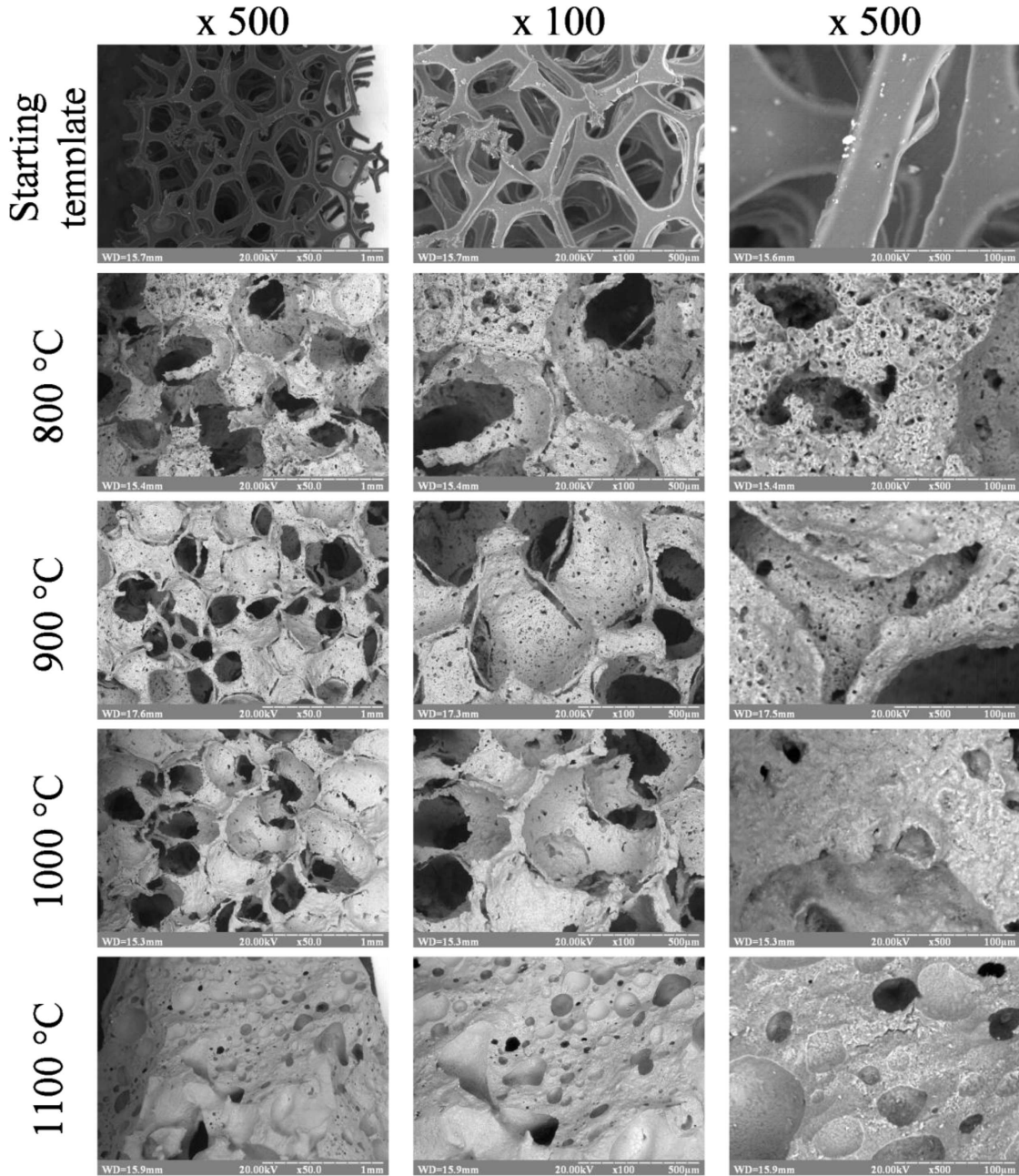


Figure 5. SEM micrographs of the starting template and highly porous glass-ceramics prepared at different sintering temperatures

analysis of it using the Siam PhotoLab program (Fig. 6) revealed that the pore size distribution fell in the 50–700 μm range; with a pore size of 125 μm being the most probable. Besides, 95% pores sized within 50–350 μm . In spite of a broad cell size distribution, the width of isthmuses between large cells is uniform enough and equals 80–100 μm . As can be seen, the structure of material after sintering differs from the template structure. The pores with remained open pore structure are added with arched partitions, which positively affect the total material porosity. However, their number does not permit cells to be completely closed and isolated voids are formed in material; herein a channel structure with an open interconnected pore system remains. Moreover,

such a structure positively affects the specific surface of highly porous materials and makes it possible to create more space for sowing stem stromal marrow cells.

Figure 7 demonstrates the dependence of the compressive strength on the sintering temperature. As can be seen, the strength increases with increasing the sintering temperature, which, in its turn, depends on the porous structure of samples. Closed (isolated) pores are known to form the so-called matrix system, and its strength increases with increasing the degree of matrixity. It is therefore expected that the sample strength increases from 0.8 to 10.5 MPa with increasing temperature owing to the formation of closed porosity and vitrification of the sample surface. The obtained strength is

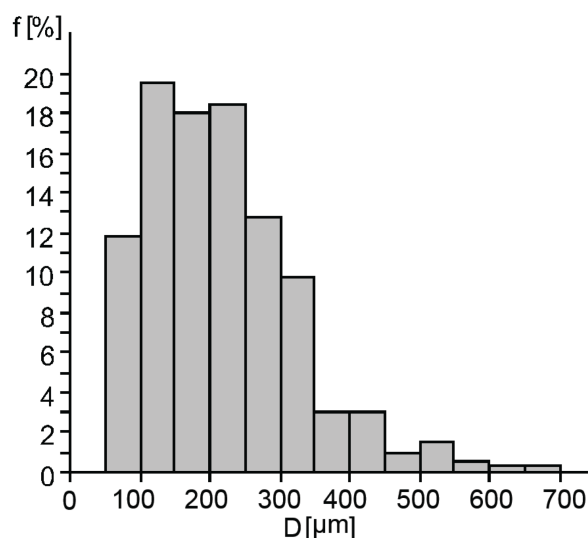


Figure 6. Pore size distribution of highly porous glass-ceramics prepared at 900 °C

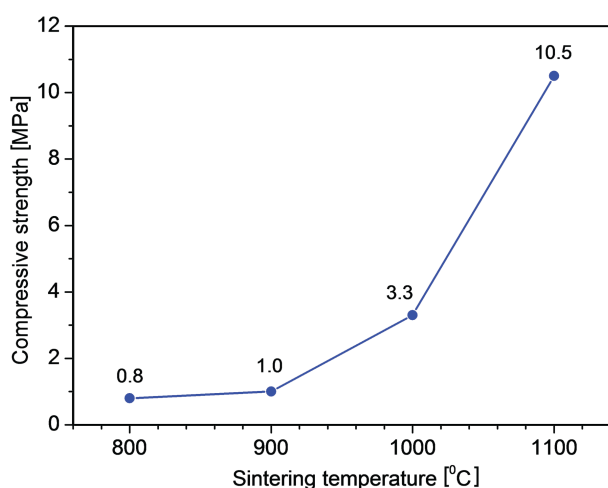


Figure 7. Compressive strength of highly porous glass ceramics prepared at different sintering temperatures

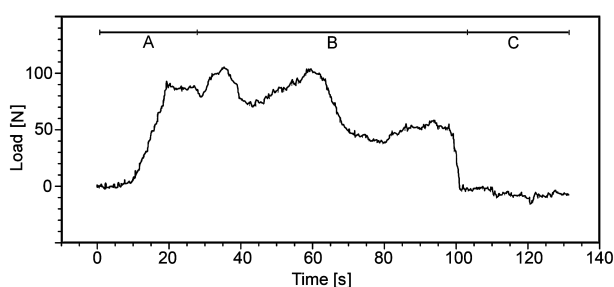


Figure 8. Typical loading diagram for highly porous glass-ceramics samples

high enough to perform the required manipulations during implantation without implant destruction. Also, it is worth mentioning that highly porous ceramics are characterized by a specific mode of destruction, which can be presented with a typical loading diagram in Fig. 8. Three distinct regions could be distinguished in all sample loading diagrams, namely region A of linear elastic deformation, which is related to the resistance of pore

walls; region B of step-by-step brittle crushing of pore walls, and region C of the complete material destruction.

Based on *in vitro* experiments it was established that the bioresorption rate of highly porous ceramics does not depend on the sintering temperature and equals 0.03 mas.%/day.

IV. Conclusions

Highly porous ceramics using biogenic hydroxyapatite and $\text{SiO}_2\text{-CaO-Na}_2\text{O}$ glass as starting materials have been prepared by a replication of the structure of a polymer template in the temperature range 800–1100 °C. It has been established that sintering of samples leads to the decomposition of biogenic hydroxyapatite and interaction with the glass phase, which results in forming of renanit NaCaPO_4 , calcium silicate phosphate $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$, calcium pyrophosphate $\text{Ca}_2\text{P}_2\text{O}_7$ and impurities of hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. The obtained results were confirmed by IR spectroscopy. An increase in sintering temperature over 1000 °C causes marked volume shrinkage to 76% and pore structure transformation from an open into closed type. The samples prepared at 900 °C exhibit optimal structural-mechanical properties. They are characterized by a permeable structure with a predominant pore size of $\sim 125 \mu\text{m}$ and a small volume shrinkage of 12%, which makes it possible to fabricate samples with required shape, size as well as total and open porosity of 78 and 63%, respectively, and a compressive strength of 1.0 MPa. The obtained materials are promising for replacement of defective cancellous bone in orthopedy and traumatology.

References

1. L.-C. Gerhardt, A.R. Boccaccini, “Bioactive glass and glass-ceramic scaffolds for bone tissue engineering”, *Mater.*, **3** [7] (2010) 3867–3910.
2. V. Karageorgiou, D. Kaplan, “Porosity of 3D biomaterial scaffolds and osteogenesis”, *Biomater.*, **26** [27] (2005) 5474–5491.
3. K.H. Zuo, Y.-P. Zeng, D. Jiang, “Effect of polyvinyl alcohol additive on the pore structure and morphology of the freeze-cast hydroxyapatite ceramics”, *Mater. Sci. Eng. C.*, **30** [2] (2010) 283–287.
4. A. Yao, A. Fanrong, X. Liu, D. Wang, W. Huang, W. Xu, “Preparation of hollow hydroxyapatite microspheres by the conversion of borate glass at near room temperature”, *Mater. Res. Bull.*, **45** [1] (2010) 25–28.
5. E.C. Hammel, O.L.-R. Ighodaro, O.I. Okoli, “Processing and properties of advanced porous ceramics: An application based review”, *Ceram. Int.*, **40** [10] (2014) 15351–15370.
6. A.V. Belyakov, E.S. Lukin, T.V. Safronova, M.N. Safina, V.I. Putlyaev, “Porous materials made from calcium phosphates (Review)”, *Glass Ceram.*, **65** [9-10] (2008) 337–339.

7. F. Scalera, F. Gervaso, K.P. Sanosh, A. Sannino, A. Licciulli, “Influence of the calcination temperature on morphological and mechanical properties of highly porous hydroxyapatite scaffolds”, *Ceram. Int.*, **39** (2013) 4839–4846.
8. G. Goller, H. Demirkıran, F.N. Oktar, E. Demirkesen, “Processing and characterization of bioglass reinforced hydroxyapatite composites”, *Ceram. Int.*, **29** (2003) 721–724.
9. R. Ravarian, F. Moztaazadeh, M.S. Hashjin, S.M. Rabiee, P. Khoshakhlagh, M. Tahriri, “Synthesis, characterization and bioactivity investigation of bioglass/hydroxyapatite composite”, *Ceram. Int.*, **36** [1] (2010) 291–297.
10. T. Kokubo, *Bioceramics and their Clinical Applications*, CRC Press LLC, Boca Raton–Boston–New York–Washington, 2008.
11. S.F. Hulbert, L.L. Hench, D. Forbers, L.S. Bowman, “History of bioceramics”, *Ceram. Int.*, **11** [4] (1985) 150.
12. Y. Doi, Shimizu Y., Y. Moriwaki, M. Aga, H. Iwanaga, T. Shibutani, K. Yamamoto, Y. Iwayama, “Development of a new calcium phosphate cement that contains sodium calcium phosphate”, *Biomater.*, **22** [8] (2001) 847–854.
13. W. Suchanek, M. Yashima, M. Kakihana, M., Yoshimura, “ β -rhenanite (β -NaCaPO₄) as weak interface for hydroxyapatite ceramics”, *Key Eng. Mater.*, **132-136** (1997) 2025–2028.
14. T.V. Safronova, D.S. Reshotka, V.I. Putlyaev, E.S. Lukin, V.K. Ivanov, “Phase composition of powdered material based on calcium hydroxyapatite and sodium dihydrophosphate”, *Glass Ceram.*, **66** [7-8] (2009) 293–296.
15. J.S. Sun, Y.H. Tsuang, C.J. Liao, H.C. Liu, Y.S. Hang, F.H. Lin, “The effect of sintered β -dicalcium pyrophosphate particle size on newborn wistar rat osteoblasts”, *Artif. Organs.*, **23** [4] (1999) 331–338.
16. W. Lu, W. Duan, Y. Guo, C. Ning, “Mechanical properties and in vitro bioactivity of Ca₅(PO₄)₂SiO₄ bioceramic”, *J. Biomater. Appl.*, **26** [6] (2012) 637–650.
17. L. Radev, V. Hristov, I. Michailova, M.H.V. Fernandes, I.M.M. Salvado, “Collagen/silicocarnotite composites, cross-linked with chondroitin sulphate: in vitro bioactivity”, *Process. Appl. Ceram.*, **5** [3] (2011) 161–170.
18. S. Callcut, J.C. Knowles, “Correlation between structure and compressive strength in a reticulated glass-reinforced hydroxyapatite foam”, *J. Mater. Sci.: Mater. Med.*, **13** [5] (2002) 485–489.
19. A. Muthutantri, J. Huang, M., “Edirisinghe Novel method of preparing hydroxyapatite foams”, *J. Mater. Sci.: Mater. Med.*, **19** [4] (2008) 1485–1490.
20. G. Tripathi, B. Basu, “A porous hydroxyapatite scaffold for bone tissue engineering: Physico-mechanical and biological evaluations”, *Ceram. Int.*, **38** [1] (2012) 341–349.
21. G. Mestres, C.L. Van, M.P. Ginebra, “Silicon-stabilized α -tricalcium phosphate and its use in a calcium phosphate cement: Characterization and cell response”, *Acta Biomater.*, **8** [3] (2012) 1169–1179.
22. S. L. Seet, “Silicon-substituted calcium phosphate compounds: Synthesis, characterization, and bioactivity evaluation”, *Sci. Asia.*, **35** [3] (2009) 255–260.

