

MECHANICAL PROPERTIES OF MACROPOROUS SILICON NITRIDE-BASED CERAMICS DESIGNED FOR BONE SUBSTITUTES

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Porous silicon nitride preforms designed for bone substitutes were prepared by two different forming methods: by introduction of semolina as pore forming agent and by template method with polyurethane sponge. Silicon nitride-based green bodies were sintered in air at two different temperatures, while the Si + 20 % Si₃N₄ samples were sintered by reaction bonding process in nitrogen. Template method yields samples with interconnected macroporous structure comparable to the bone structure while introduction of semolina results only in isolated macropores formation. All sintered samples were characterized in terms of phase composition and microstructure. Moreover, some of the mechanical properties (hardness, elastic modulus, bending strength) were measured and compared to the bone properties in order to select the most suitable method for the preparation of trabecular bone substitute. Despite of relatively low strength, the template method with subsequent sintering in air appeared to be the most promising way for the preparation of trabecular bone-like silicon nitride-based porous ceramic structures, whereas the hardness and elastic modulus of as prepared samples were in perfect accordance with bone characteristics.

INTRODUCTION

A superior combination of high fracture toughness and hardness together with excellent wear resistance and inertness enables the application of silicon nitride ceramics in many areas [1]. These excellent properties combined with verified biocompatibility make the material an apt candidate also for high-load medical applications. Therefore the aim of several studies focusing on dense silicon nitride is to replace metal alloys for hip and knee prosthesis [2-5]. Moreover, porous silicon nitride ceramics are also applied in medicine. A cancellous-structured porous silicon nitride composite ceramic is already commercially used as a spinal fusion implant and the bone ingrowth rates are similar to those reported for porous titanium. This indicates that porous silicon nitride is applicable for implants requiring direct, biological skeletal fixation [2, 6] what makes the preparation of highly porous silicon nitride very attractive.

The microstructure of materials designed for bio-applications, mainly for bone substitution is of great importance, besides non-toxicity and inertness or resorbability. In principle three-dimensional (3-D)

interconnected porous network with interconnected large pores (more than 100 µm) enabling tissue ingrowth and nutrition delivery are required [7]. Additionally, pores smaller than 50 nm, promoting cell adhesion and adsorption of biologic metabolites are needed. Under suitable conditions the bone grows into such porous structure at a rate of ~1 µm per day [8-10].

There are several methods reported for the preparation of ceramic material with macroporous structure, e.g. introduction of different pore-forming agents which can be burnt out by calcinations [11], replica method using polymeric sponge or other porous materials [12], suspension foaming or the production of gas bubbles [14].

Sintering of silicon nitride requires high temperatures because of its covalent character. However, oxidation bonding of Si₃N₄ enables sintering at significantly lower temperatures (1200°C - 1500°C) and yields remarkable decrease of costs [15]. Moreover, the presence of silicon oxide in this air-sintered silicon nitride (ASSN) ceramics may be advantageous in terms of improved biological properties. Silicon oxide is known as a main component of bioactive glasses [16], and also bioactive properties of silicon oxide coatings were reported [17].

On other hand, reaction bonding of silicon nitride gives advantages due to using low cost silicon powder and the near-net shape capability [18]. Reaction bonded silicon nitride (RBSN) is prepared from green compact of Si powder which is then reacted in a nitrogen atmosphere in accordance with a specific temperature-time cycle [19]. Sintered RBSN (SRBSN) could be prepared by a following post-sintering step at higher temperatures which diminishes the considerable porosity (15-25 %) which still exists after reaction-bonding [20].

Despite of relatively low density and high porosity, bone should form tough and protective load-bearing framework of the body. Therefore, characterization of the mechanical properties of bone, such as elastic modulus, strength, and fracture toughness are crucial not only in the field of medicine, but also in material research dealing with a development of bone substitutes.

The aim of this work is the preparation of silicon nitride-based ceramics suitable for bone implants by two different forming methods and two different sintering routes. Phase composition, microstructure and mechanical properties of sintered samples have been investigated. Moreover, the most promising method for the preparation of porous materials suitable as bone substitute regarding the microstructure and the mechanical properties has been selected.

EXPERIMENTAL

Three different methods have been used for the preparation of Si_3N_4 based ceramics: i) air-sintered Si_3N_4 with semolina as pore forming agent, ii) air-sintered Si_3N_4 prepared by template method with polyurethane sponge and iii) sintered reaction bonded Si_3N_4 (SRBSN) prepared by template method with polyurethane sponge.

Air-sintered Si_3N_4 with semolina were prepared from the mixtures of Si_3N_4 powder (Yantai, Tomley Hi-Tech Ind. & Tra. Co., Ltd., D_{90} : 10.0 μm , O: < 1.5 %) and 10 vol. % or 30 vol. % semolina (density 1.4 $\text{g}\cdot\text{cm}^{-3}$, max. particle size 350 μm). The powders were homogenized in a polyethylene jar in isopropanol (pure, Sigma Aldrich) with high purity Si_3N_4 milling balls for 24 h. The solvent was removed in vacuum rotary evaporator. The green bodies were prepared by uniaxial pressing of powders at 100 MPa with subsequent cold isostatic pressing at 250 MPa. Then semolina was burned out on air at 600°C (heating rate 1°C min^{-1}) for 1 hour. The sintering experiments were carried out in an electrical furnace (NETZSCH GmbH, Selb, Germany) with MoSi_2 heating

elements in air. The samples were sintered at 1150°C or 1250°C for 1 hour; the heating rate was 10°C $\cdot\text{min}^{-1}$ and the cooling rate 20°C $\cdot\text{min}^{-1}$. The samples were denoted according to the volume content of semolina (10S or 30S) and according to the used sintering temperature 1150°C or 1250°C (Table 1).

Air-sintered Si_3N_4 was also prepared by template method with polyurethane sponge. Suspension with 35 vol. % of Si_3N_4 powder (Yantai, Tomley Hi-Tech Ind. & Tra. Co., Ltd., D_{90} : 10.0 μm , O: < 1.5 %) was prepared in deionized water and for optimum dispersion 0.022 g of dispersant was added per gram of Si_3N_4 powder. The suspension was homogenized for 24 h on roller with Si_3N_4 milling balls. The polyurethane sponges were dipped into slurry and compressed while submerged, to fill all the cells in the sponge. Then, the excess of suspension was removed by traditional roll-press processing. After drying, the sponge was burnt out with the same process as the semolina. Likewise the sintering was performed in air at 1250°C; the heating rate was 10°C $\cdot\text{min}^{-1}$ and the cooling rate 20°C $\cdot\text{min}^{-1}$.

Sintered reaction bonded Si_3N_4 (SRBSN) was prepared by template method with polyurethane sponge. Suspension with 48 vol. % of solid content was prepared from the mixture of silicon (grade 4D, Sicomill, Vesta Ceramics AB, Sweden) and $\alpha\text{-Si}_3\text{N}_4$ (SN-E10, Ube Industriels, Japan) in weight ratio of 3:1. Deionized water was used as a dispersion medium and for optimum dispersion 0.07 g of dispersant was added per gram of powder. The suspension was homogenized for 24 h by ball milling with Si_3N_4 milling balls. The polyurethane sponges were dipped into slurry and compressed while submerged, to fill all the cells in the sponge. Then, the excess of suspension was removed by traditional roll-press processing. After drying the sponge was burnt out and the nitridation of Si-based porous structure was carried out in graphite resistance furnace at 1400°C for 3 h followed by sintering at 1750°C for 2 h in nitrogen atmosphere.

The density of sintered specimens was determined on the basis of Archimedes' principle in distilled water. The porosity was calculated based on the assumption that the theoretical density of Si_3N_4 is 3.2 $\text{g}\cdot\text{cm}^{-3}$. In the case of oxidized samples the ratio of compounds estimated from X-ray diffraction pattern was used to calculate the theoretical density. The phase composition of sintered silicon nitride-based samples was investigated by powder X-ray diffraction (Bruker AXS D8 Discover X-ray diffractometer). Quantitative evaluation from X-ray diffraction patterns was made by software TOPAS (based on Rietveld method) which allows also the estimation of the amount of amorphous phase. The oxygen and carbon content in the samples was measured using elemental analyzers EMIA-320V2 AC and EMGA 830 AC (Horiba Jobin Ivon). The pore size distribution of smaller pores was determined by mercury intrusion porosimetry (Pore Master 60).

Table 1. Densities and porosities of prepared samples.

	10S	30S	10S	30S	sponge	sponge
	1150	1150	1250	1250	1250	SRBSN
Density ($\text{g}\cdot\text{cm}^{-3}$)	1.57	1.56	1.75	1.63	1.16	0.81
Porosity (%)	51	52	43	45	63	75

Regarding the investigation of mechanical properties the elastic modulus, hardness and four-point bending strength have been measured. The hardness and elastic modulus were determined by indentation techniques using a micro/nanoindentation system (TTX/NHT2 CSM Instruments). Surface of samples were polished using successively finer grades of diamond suspension with final diamond suspension of 1 μm . The samples were washed, dried and stored under laboratory conditions. Using a calibrated Berkovich indenter, force-displacement load-unload curves were recorded for each porous material at maximum loads of 100 mN with the holding time 10 s at maximal load. At least 30 indents were made on each sample. The elastic modulus and hardness were calculated using the Oliver-Pharr method [21]. According to finite element calculations performed by Roberts et al. [22] the Poisson's ratio of porous ceramics does not change significantly with the porosity of material, therefore a constant value of Poisson's ratio 0.25 was used in all calculations.

A four point bending test has been used for the strength measurements. The specimens were cut into the rectangular test bars with the dimensions of $3 \times 4 \times 25$ mm. The surface of the specimens was ground and polished using diamond suspensions up to 3 μm . The specimens were tested on the universal testing machine Lloyd 5Kplus with inner and outer spans 8 and 16 mm, respectively and cross-head speed of 0.5 mm/min. The maximum load at the fracture point was recorded and four point bending strength was calculated according to following equation:

$$\sigma_{4p} = \frac{3P(S_1 - S_2)}{2BW^2} \quad (1)$$

where P is maximum load, S_1 and S_2 are the outer and inner spans, W and B are the height and width of the specimen, respectively.

Mechanical properties of prepared samples were compared to the mechanical properties of trabecular bone measured in the same way. The samples of human trabecular bone were obtained from tissue bank (Associated Tissue Bank in Košice, Slovakia). Trabecular bones were received in the form of rectangular specimens with dimensions of $10 \times 10 \times 10$ mm. Samples were polished using SiC papers (800, 1200 and 2400 grit) with final polishing by 4000 grit SiC paper corresponding to the grain size of 5 μm . The donor was approximately 40 years old without any grave disease in anamnesis.

RESULTS AND DISCUSSION

Porosity, microstructure

All sintered samples were porous with density in the range of 0.8 to 2.0 $\text{g}\cdot\text{cm}^{-3}$ and porosity from 43 to 75 % (Table 1). In the case of samples with semolina the porosity increased slightly with increased semolina content (10S vs 30S). Generally, the density of samples prepared by sponge infiltration ranges from 0.8 to 1.5 $\text{g}\cdot\text{cm}^{-3}$, for both air sintered Si_3N_4 samples and RBSN samples. In the sponge infiltration method the density is significantly influenced by the amount of suspension remaining in sponge. The other parameters which could influence the final density such as solid loading of suspension and sintering temperature are rather limited in practice. The first parameter is controlled by the availability of the suspension for infiltration process [12]. It is known that only strict interval of viscosities corresponding to narrow interval of appropriate solid loading is possible to use by this process in order to attain complete infiltration and to avoid suspension leakage. Likewise, the sintering temperature especially by air-sintered samples is limited because of considerable surface oxidation of Si_3N_4 which will be discussed later.

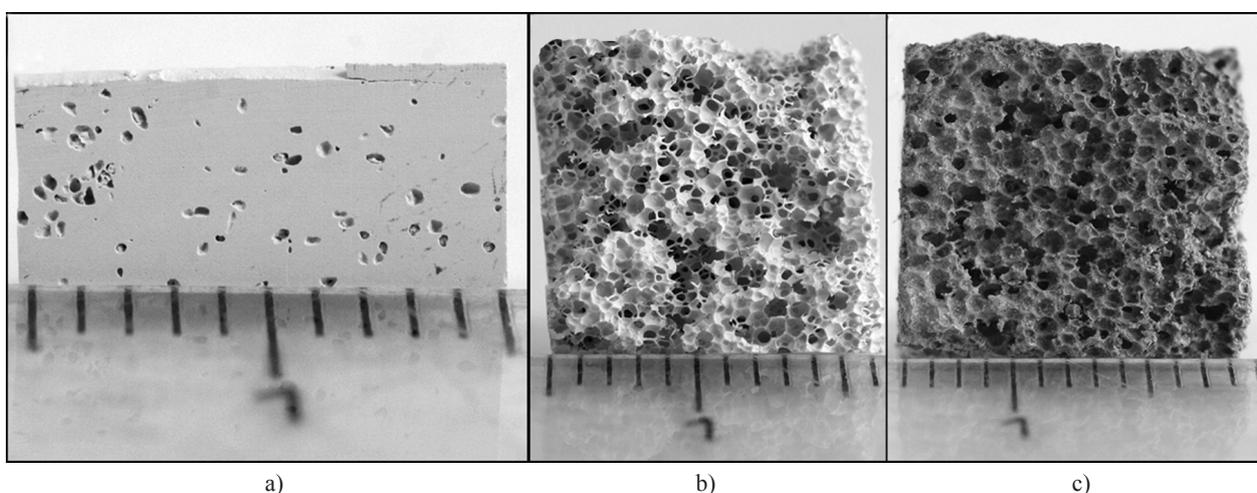


Figure 1. Microstructure of air-sintered Si_3N_4 (ASSN) prepared using 30 vol. % of semolina as pore forming agent (a), ASSN prepared by sponge infiltration (b), and SRBSN prepared by sponge infiltration (c).

The specified microstructure of porous ceramics described in introduction should be obtained in order to ensure biocompatibility of material. In the case of samples with semolina addition the structure consists

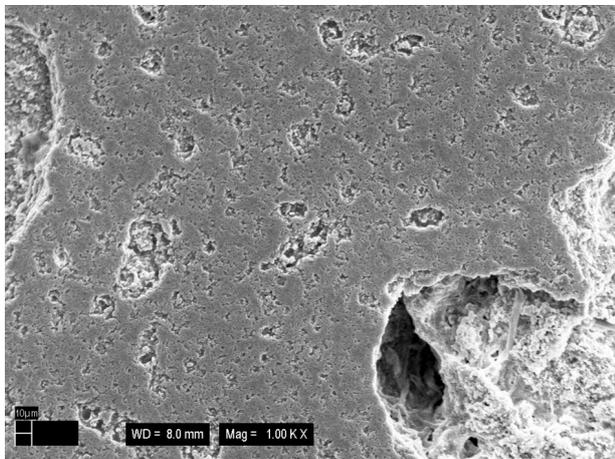
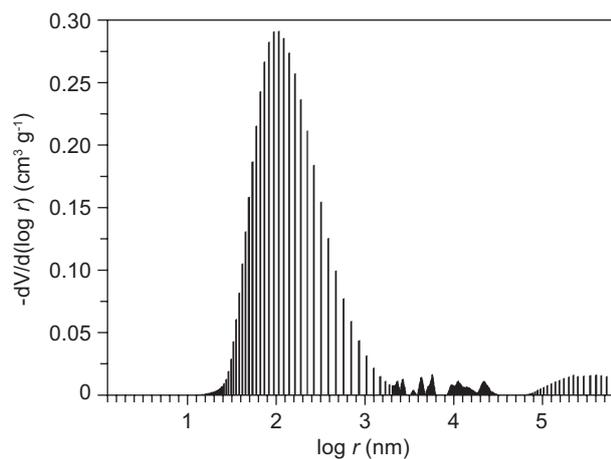
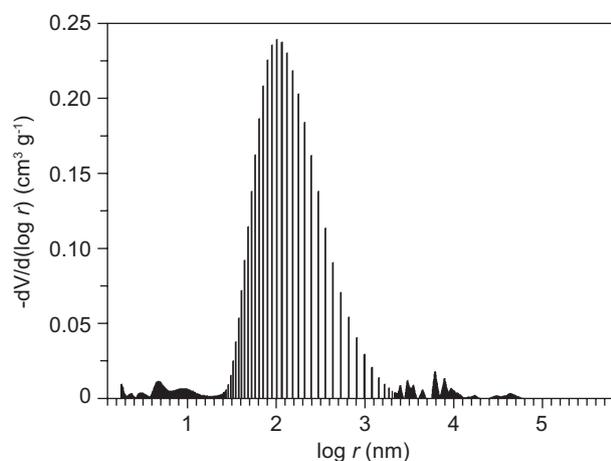


Figure 2. Microstructure of ASSN sample prepared using 30 vol. % of semolina as pore forming agent and sintered at 1250°C.



a) 1150°C



b) 1250°C

of separated large pores with diameter between 100 and 300 μm (Figure 1a) interconnected only by channels of small pores. The microstructure can be seen in Figure 2. In all samples the overall porosity is mostly open and the maximum closed porosity of 7 % was observed in sample 30S1250. On the other hand, both air-sintered Si_3N_4 and SRBSN samples prepared by sponge infiltration exhibited the interconnected macroporous structure with pore size in the range of approximately 300 - 1000 μm (Figures 1b and 1c).

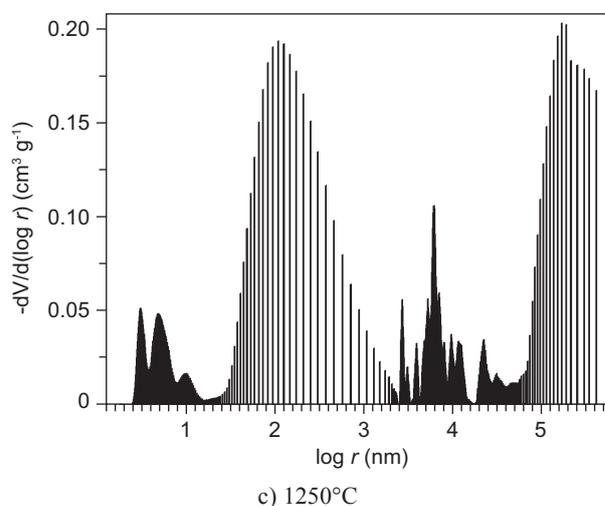
Interconnection of large pores in samples with semolina could be theoretically achieved by enhancing the pore forming agent (PFA) content. However, increasing semolina content to 50 vol. % led to extensive cracking during semolina burn out, even if very slow heating rate was used.

Besides macroporous structure also the presence of pores less than 50 nm is required [7]. The pore size distributions of samples prepared using semolina sintered at 1150°C and 1250°C and of air sintered sample prepared by sponge infiltration are shown in Figure 3. It is evident, that the content of these small pores is minimal in samples prepared with semolina while template method provides samples with relevant amount of such pores.

Considering the pore sizes and pore structure the results suggest that the template method using polyurethane sponge seems to be more suitable method regarding the bio-application requirements on the microstructure of porous ceramics.

Phase composition

Phase composition was observed by X-ray diffraction. The main crystalline phase in all samples is $\alpha\text{-Si}_3\text{N}_4$ and minor $\beta\text{-Si}_3\text{N}_4$ is also present. In samples sintered in air at 1250°C also cristobalite was observed. Silicon



c) 1250°C

Figure 3. Pore size distributions of samples prepared using semolina as PFA sintered at 1150°C (a), at 1250°C (b) and samples prepared by template method and sintered at 1250°C (c).

oxide is formed due to the oxidation process of silicon nitride grain surface and acts as a sintering aid thereby providing sufficient manipulation strength to silicon nitride samples at relatively low sintering temperature. The oxidation extent could be roughly estimated from the X-ray diffraction patterns. At lower sintering temperature (1150°C) there is no evidence of any type of crystalline silicon oxide. Since the oxidation of Si₃N₄ was already evidenced at 900°C [15], we could suppose the presence of either amorphous silica, or a certain amount of crystalline SiO₂ probably below 3 %, which is the approximate detection limit of XRD analysis. At higher sintering temperature the amount of silicon oxide is much higher, moreover the amorphous phase crystallized partially to cristobalite. The presence of cristobalite is undesirable in terms of crack formation during cooling caused by the high thermal expansion coefficient mismatch between this surface/coating phase and Si₃N₄ matrix. Such cracking could lead to the degradation of mechanical properties. The lowest amount of cristobalite was found in samples prepared by sponge infiltration. The possible influence of residual carbon, which content can differ depending on the used types of pore forming agents, was excluded by carbon analysis. The residual carbon content in calcined samples was low and similar in both types of samples (0.2 wt. %). Thus we can only suppose that the conditions for cristobalite crystallization are more advantageous in inhomogeneous dry pressed samples than in more homogeneous microstructure of samples prepared by colloidal way. Finally, from the phase composition point of view the silicon nitride-based ceramics prepared by template method seems to be more suitable for bio-applications because of lower cristobalite crystallization.

Table 2. The crystalline phase content in sintered samples.

Sample	α -Si ₃ N ₄ (wt. %)	β -Si ₃ N ₄ (wt. %)	SiO ₂ * (wt. %)	SiC (wt. %)
10S 1150	92	8	0	–
30S 1150	92	8	0	–
10S 1250	88	8	4	–
30S 1250	78	7	15	–
sponge 1250	91	8	1	–
sponge SRBSN	84	12	–	4

*cristobalite

Table 3. The ratio of all phases in sintered samples including the amorphous SiO₂ phase.

Sample	α -Si ₃ N ₄ (wt. %)	β -Si ₃ N ₄ (wt. %)	SiO ₂ * (wt. %)	SiO ₂ -am. [#] (wt. %)
10S 1250	80	7	4	9
30S 1250	71	7	13	9
sponge 1250	85	7	1	7

*cristobalite, [#] amorphous

In SRBSN samples the presence of SiO₂ was not confirmed. SRBSN samples contain also silicon carbide which is formed due to the high activity of carbon at applied sintering conditions in furnace with graphite heating element. Detailed phase compositions are summarized in Tables 2 and 3.

The amount of SiO₂ in air sintered silicon nitride (ASSN) samples was calculated also from oxygen analysis. The results are present in Table 4. The values are rather high compared to the silica content obtained from XRD analysis. However, it could be again clearly seen that the oxidation degree increases with the sintering temperature. The lowest oxidation of ASSN materials sintered at 1250°C was observed for samples prepared by replica method.

Table 4. SiO₂ content in air-sintered Si₃N₄ samples calculated from oxygen analysis.

Sample	10S 1150	30S 1150	10S 1250	30S 1250	sponge 1250
SiO ₂ (wt. %)	12	12	28	34	18

Mechanical properties

The indentation hardness and elastic modulus were measured from the load-displacement curves recorded continuously during the indentation process using depth sensing method. The results of the indentation hardness and reduced elastic modulus are summarized in Figure 4.

The elastic modulus value of trabecular bone, measured as reference material, was 11.4 ± 0.9 GPa which is in good accordance with the elastic modulus of trabecular bone (11.4 ± 5.6 GPa) reported in the work of Zysset et al. [23]. Samples prepared using semolina and sintered at 1150°C exhibited the values of elastic modulus around 19 GPa which is almost two times higher than the elastic modulus of trabecular bone. The big difference in the elastic modulus between porous ceramic samples and bone could lead to greater stress concentration resulting in fracture at the interface between bone and porous implant material. This is the reason why such material should not be used for the bone substitute application. On the other hand the samples prepared using semolina sintered at 1250°C exhibited the values of elastic modulus 6.3 GPa and 5.4 GPa that are two times lower compared to the value of trabecular bone, excluding their utilization as bone substitute.

According to the results of the elastic modulus measurement performed on the samples prepared using semolina it can be concluded that the increase in the sintering temperature associated with the increase of SiO₂ content caused significant decrease of the elastic modulus values.

The samples prepared by sponge infiltration exhibited elastic modulus of 14.3 ± 1.4 GPa and 92.1 ± 21.3 GPa

for air-sintered and reaction-bonded silicon nitride, respectively. The elastic modulus of air-sintered silicon nitride samples prepared by the sponge infiltration is relatively close to the value of trabecular bone when compared to the other experimental materials. The lower value of elastic modulus of air-sintered material compared to the reaction bonded Si_3N_4 can be explained similarly like for the samples with semolina content, i.e. by the higher amount of silica in the air-sintered material. This indicates that the presence of certain amount of amorphous silica (~ 10 wt. %) in silicon nitride ceramics could shift the elastic modulus of these porous materials close to the values characteristic for the human trabecular bone. The hardness of trabecular bone measured by indentation was 513 ± 67 MPa which is in good accordance with the values measured by Gibson et al. [24]. The porous ceramics prepared using semolina as pore forming agent and sintered at 1150°C exhibited the highest value of hardness, about 700 MPa among all investigated materials (Figure 4). The increase of the sintering temperature to 1250°C resulted in the decrease of nanohardness values due to the increase of the amount of SiO_2 , because its hardness (9 GPa) is significantly lower than the nanohardness of $\alpha\text{-Si}_3\text{N}_4$ (37 GPa) [25]. The air sintered Si_3N_4 sample prepared by sponge infiltration method exhibited the hardness of 456 ± 73 MPa which is similar value to the hardness of trabecular bone.

Taking into account the results of elastic modulus and hardness with the silicon nitride oxidation level it can be concluded that the modification of the amount of SiO_2 could be a useful way to adjust the elastic modulus and hardness of air sintered silicon nitride to bone properties.

The results of bending strength measurements of the investigated porous materials are summarized in Figure 5. The samples using semolina as pore forming agent and sintered at 1150°C exhibited the highest value of strength (around 17 MPa) among all investigated materials. The increase of semolina content to 30 % in the material sintered at the same temperature 1150°C results in the decrease of strength to ~ 5 MPa. A further decrease

of strength was caused by the increase of sintering temperature to 1250°C . In this case the different amount of semolina, i.e. the pore volume did not affect the strength value (samples 10S1250 and 30S1250). Even though the samples sintered at 1250°C exhibited a bit lower porosity than the samples sintered at 1150°C (Table 1) which could assume higher strength, an opposite case was observed. The lower strength of air sintered samples at 1250°C can be explained by the higher silica content in these samples and by lower bending strength of silica compared to that of silicon nitride. Moreover, besides the amorphous silicon dioxide also cristobalite was detected by X-ray analysis (Table 4). As it was mentioned, crack formation can occur during cooling of samples from sintering temperature due to the high thermal expansion coefficient mismatch between cristobalite and Si_3N_4 matrix. On the other hand, Kingetsu et al. [26] observed that the devitrication of amorphous SiO_2 as well as the mismatch of the coefficient of thermal expansion between cristobalite and amorphous SiO_2 might affect the performance of the as-sintered porous Si_3N_4 ceramics, resulting in little improvement of the flexural strength at higher sintering temperatures. However, in the present work the increase of strength with increasing sintering temperature was not observed. In our case the ratio of weaker amorphous silica to cristobalite was too high and cristobalite could not influence positively the strength characteristics of porous ceramic material.

The samples prepared by sponge infiltration exhibited the lowest strength values with the largest range of scatter among all studied materials. This is caused by the highest porosity and especially by the presence of very large pores (300 - 1000 μm) compared to the samples prepared using semolina, where the pore size is 100 - 300 μm . Pore in the microstructure can be considered as a defect; larger pore causes larger degradation of the strength value. In accordance with this rule the samples prepared using semolina exhibited higher strength compared to the samples prepared by sponge

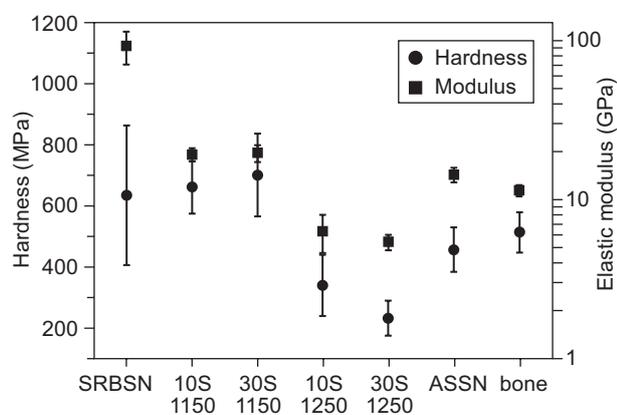


Figure 4. The hardness and elastic modulus of the porous silicon nitride samples in comparison to the bone properties measured by nanoindentation using Berkovich indenter.

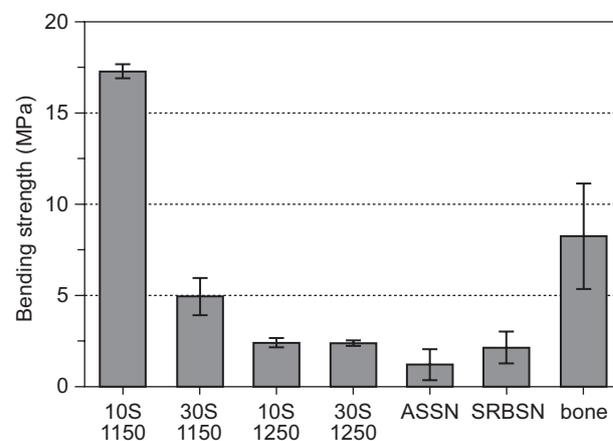


Figure 5. Four-point bending strength of the porous silicon nitride and the trabecular bone.

infiltration. However, results presented above (extensive cracking during the process of burning semolina) insisted the sponge infiltration as a better method for the processing of porous materials. The strength of sponge infiltrated samples can be increased by the decrease of the pore size from 300 - 1000 μm to the value close to 100 μm which is still acceptable for biological application, and/or to increase the content of more elongated $\beta\text{-Si}_3\text{N}_4$ grains in the microstructure, which has a higher strength than $\alpha\text{-Si}_3\text{N}_4$, a major phase in our samples. It should be pointed out that the elongated $\beta\text{-Si}_3\text{N}_4$ grains must be embedded in the sintered body and the presence of whisker-like grains on the surface of porous ceramic body must be avoided due to the toxicity of Si_3N_4 whiskers [27].

CONCLUSIONS

Two forming methods and two ways of sintering were examined for the preparation of porous silicon nitride materials with the aim to select the more suitable method for bone substitute applications. The required interconnected macroporous structure with macropores in the range of 300 - 1000 μm was attained only by the template method. The second method, where semolina was introduced as pore forming agent yields structure with isolated pores in the range of 100 - 300 μm . Hardness and elastic modulus of prepared material were estimated by nanoindentation method and evident dependence on oxidation level was observed. Both material characteristics decrease with increasing amount of SiO_2 in Si_3N_4 matrix. The comparison of obtained ceramic material characteristics with the bone properties shows that the sample prepared by sponge infiltration with ~ 10 wt. % of SiO_2 content exhibits hardness and elastic modulus very close to the bone values. The strength of sample, which was the most similar to the bone in terms of pore-structure and matrix mechanical properties, was markedly lower compared the bone strength, therefore further optimization of strength of porous silicon nitride-based ceramic materials is needed.

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