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Original scientific paper

FABRICATION OF COMPOSITES BASED ON $Ca_{10}(PO_4)_6(OH)_2$ AND SiO_2

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The aim of the work described in this paper was to make a composite consisting of hydroxyapatite as bioactive matrix and SiO_2 as bioinert component. Five different systems were formed where the content of SiO_2 in the hydroxyapatite matrix were 10, 30, 50, 70 and 90 wt%. Consolidation of the composites was made by pressing (P = 15 MPa) and sintering (T = 1200 ^oC/1h). Dilatometer investigations of the composites show that composites with 10, 30 and 50 wt% are in thermal equilibrium. The increasement of SiO_2 content is reflected in decreasement of the density of the sintered composites. The E-modulus and shear modulus of the composites with 10, 30 and 50 wt% SiO_2 are 32 ± 1 GPa and 18 ± 3 GPa, respectively.

The equations given by several authors like Turner, Kerner, Thomas, Tummala & Friedberg and Taya were used to predict the coefficient of thermal expansion of the composites as a function of E-modulus, shear modulus, module of compressibility, Poisson's ratio and volume fraction of the constitutive phases. According to the coefficients of correlation, the equations given by Turner and Kerner give the best approximation of the experimental data.

Key words: hydroxyapatite; SiO_2; thermal expansion coefficients; mechanical properties; porosity; model equations

ДОБИВАЊЕ НА КОМПОЗИТИ БАЗИРАНИ НА $CA_{10}(PO_4)_6(OH)_2$ И SIO_2

Целта на овој труд беше добивање на композити составени од хидроксиапатит како биоактивен матрикс и силициумдиоксид како биоинертна компонента. Добиени беа пет различни системи во кои содржината на SiO_2 во хидроксиапатитниот матрикс изнесуваше 10, 30, 50, 70 и 90 mas.%. Консолидацијата на композитите беше реализирана со пресување (P = 15 MPa) и синтерување (T = 1200 ^oC/1h). Дилатометриските испитувања на композитите покажаа дека композитите со 10, 30 и 50 wt% се наоѓаат во термичка рамнотежа. Модулот на еластичност и модулот на смолкнување на композитите со 10, 30 и 50 wt% SiO_2 се 32 ± 1 GPa и 18 ± 3 GPa, соодветно.

Равенките дадени од неколку автори како што се: Turner, Kerner, Thomas, Tummala & Friedberg и Taya беа користени за предвидување на коефициентот на термичка експанзија на композитите во функција од модулот на еластичност, модулот на смолкнување, компресиониот модул, Поасоновиот број и волуменската фракција на конститутивните фази. Според коефициентите на корелација, равенките дадени од Turner и Kerner покажуваат најдобра апроксимација со експерименталните резултати.

Клучни зборови: хидроскиапатит (биоактивен матрикс); SiO_2 (биоинертна компонента); коефициенти на термичка експанзија; порозитет; моделни равенки

INTRODUCTION

Calcium-phosphate-based ceramics are highly biocompatible with hard tissues such as bone, and their biodegradation depends on their composition [1]. Among the several compositions of calcium phosphate systems, hydroxyapatite (HA) has been highlighted as a bone replacement material. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) belongs to the group of bioactive ceramics that has an ability to promote

a direct physical-chemical bond between the implant and new bone tissue. Due of the bonding ability, hydroxyapatite ceramics are widely used in medicine in bone-fillers, coating elements, artificial bones, etc. [2, 3].

In an effort to prepare a material with proper biodegradation and improved bioactivity approximating more closely that of an ideal bone replacement material, HA/α-wollastonite composites were selected. Siriphannon et al. [4, 5] indicated α-wollastonite ($CaSiO_3$) as a representative material among several calcium silicate compounds. Ruy et al. [6] showed that incorporation of silicon into HA ceramics enhanced the bioactivity of calcium phosphate ceramics by forming calcium silicate. According to other work [7, 8, 9], the different amorphous and crystalline phases of calcium silicate exhibited different microtextures and specific surface areas of the powders.

Thermal stability, the correlation between mechanical properties and coefficients of thermal expansion for the composite hydroxyapatite – SiO_2 has not been investigated so far. Several equations have been proposed to predict the thermal-expansion coefficient of the composites depending on the properties of the constituents, their mechanical properties, and the volume fraction of each phase. The most popular equations for the spherical geometry of the included phase are given by: Turner [10], Kerner [11], Thomas [12], Tummala & Friedberg [13], and Taya [14]. Taya et al. [14] have proposed an equation for the internal stresses in composite materials where the average internal stress depends on Young's modulus, Poisson's ratio, the thermal-expansion coefficient of the constituents, the temperature gradient and the volume fraction of the inclusions.

The aim of this paper was to obtain composites containing a bioactive (biohydroxyapatite) and a bioinert component (SiO_2) in different ratios, and to investigate their mechanical and thermal-expansion characteristics. Using several model equations, depending on the thermal properties of the constituents, their elastic properties and the volume fraction of each phase, it is possible to predict the thermal-expansion properties of the composites in relation to the experimentally obtained results.

EXPERIMENTAL

The commercial powder biohydroxyapatite (HA) from Merck, Germany, was used in the investigations. Tetraethylorthosilicate (TEOS) was the precursor for obtaining SiO_2. The specific surfaces of the powders were determined using the BET method (Micromeritics Gemini 2370).

To produce the composite powder, based on the commercial HA and SiO_2 produced by hydrolysis method, the schematic diagram presented in Fig. 1 was followed.

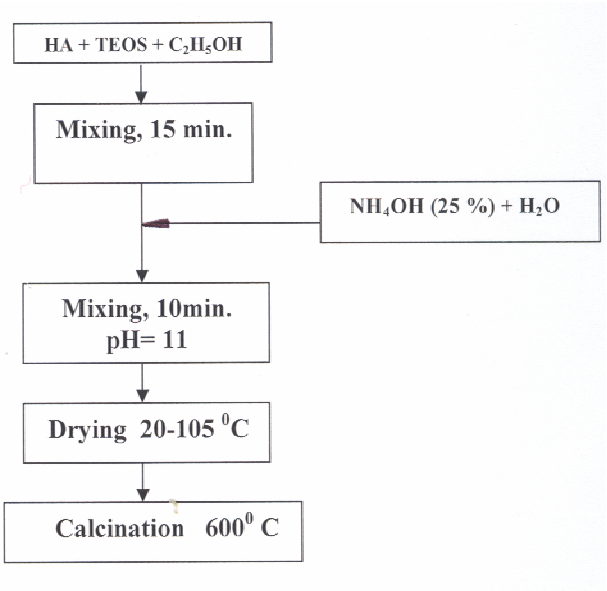

Fig. 1. Schematic diagram for producing hydroxyapatite – silica powder

The content of SiO_2 in the composites varied from 10 to 90 wt%. Five different composites were obtained with the following composition: HA : SiO_2 = 90 : 10 %, HA : SiO_2 = 70 : 30 %, HA : SiO_2 = 50 : 50 %, HA : SiO_2 = 30 : 70 %, and HA : SiO_2 = 10 : 90 %.

Consolidation of the composites was performed by uniaxially pressing (Weber pressen KIP 100) at 15 MPa using PVA as a binder and sintering at a temperature of 1200 ^oC, in an air atmosphere, with a heating rate of 5 ^oC/min. The isothermal period at maximal temperatures was 1 hour.

The microstructure of the fractured surface of the sintered composites was investigated by scanning electron microscopy (Leica S440).

The density of the sintered compacts was determined by the displacement method using water as liquid medium.

The phase composition of the sintered material was analyzed by X-ray diffraction method (DRON – 3 diffractometer), operating at CuKα-radiation in the interval of 2θ from 10 to 75°.

Thermal-expansion characteristics were investigated using the dilatometer (NETZSCH 402 E). Dilatometric investigations was performed at the temperature interval of RT-1000-RT, in an air atmosphere, and a heating rate in the heating /cooling cycle of 2 °C/min.

Mechanical characteristics such as Young's modulus, shear modulus and Poisson's number were determined using an ultrasonic method (Krautkramer USD 15) on specimens (10 pieces, 50×5×5 mm) polished with 9 μm diamond paste and subjected to the 3-point bending tester Netzsch 401/3 with 30 mm span and 0,5 mm/min crosshead speed.

RESULTS AND DISCUSSION

The ratio of Ca/P in hydroxyapatite was 1.64 which is near to that of human bone (1.67). The specific surface area for biohydroxyapatite and SiO_2 was 90 m^2/g and 11.05 m^2/g, respectively. The average particle size of HA was 2.5 ± 0.5 μm, but for the composite consisting of hydroxyapatite and SiO_2 it increased with the increase of the content of SiO_2 from 4.3 ± 0.5 to 8.5 ± 0.5 μm.

The relative density of HA sintered at an optimal temperature of 1200 °C [15] was 95 ± 1 % TD. The technical coefficients of thermal expansion for HA and SiO_2 were $14.78\cdot10^{-6}$/°C and $4.00\cdot10^{-6}$/°C, respectively.

The mechanical properties, i.e. Young's modulus, the shear modulus, and Poisson's ratio for HA [15] were 88 ± 10 GPa, 36 GPa and 0.31, respectively, but for SiO_2 the above mentioned mechanical characteristics were 74 ± 5 GPa, 27 GPa and 0.17, respectively.

The XRD analysis of the composites containing 10, 30 and 50 wt% SiO_2 in the matrix of hydroxyapatite showed the presence of hydroxyapatite, tricalcium phosphate, silica, CaO and $CaSiO_3$ (α wollastonite).

The presence of $Ca_3(PO_4)_2$ is a result of decomposition of hydroxyapatite according to (2) which occurs when HA is heated to elevated temperature [16]:

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 3Ca_3(PO_4)_2 + CaO + H_2O\uparrow \quad (2)$$

Part of the formed CaO reacts with SiO_2 forming α-$CaSiO_3$ which is in agreement with the phase diagram [17].

SEM microphotographs of fractured surface of the compacts sintered at the temperature of 1200°C are presented in Figs. 2–6.

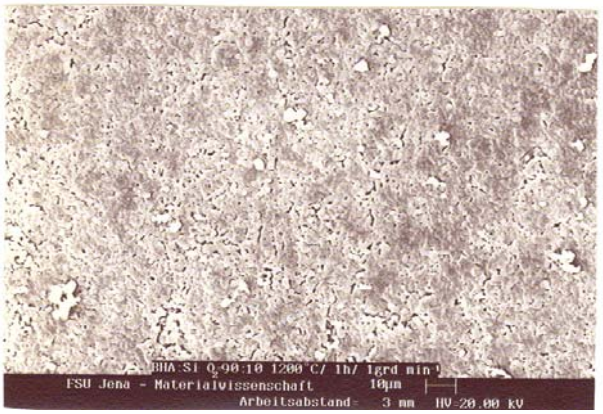

Fig. 2. SEM micrograph of HA : SiO_2 = 90 : 10 % (bar 10 μm)

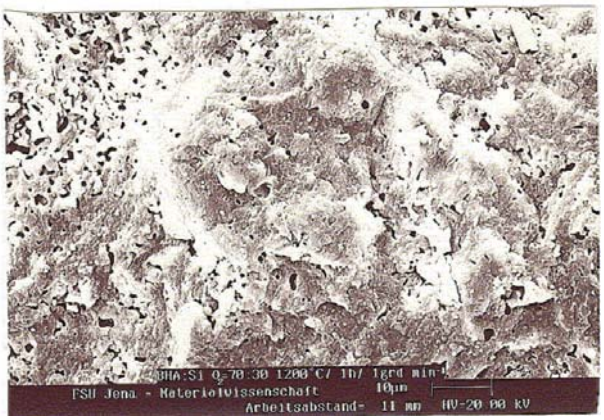

Fig. 3. SEM micrograph of HA : SiO_2 = 70 : 30 % (bar 10 μm)

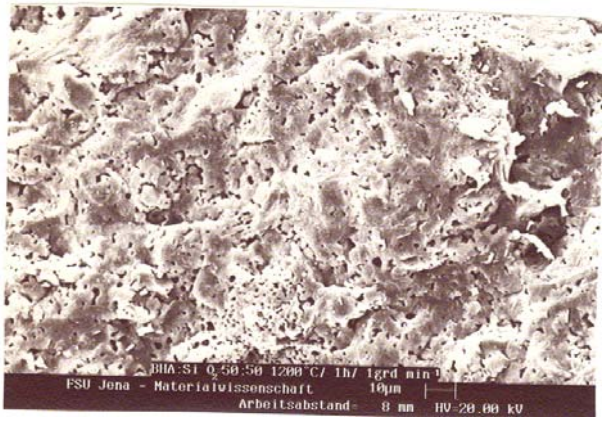

Fig. 4. SEM micrograph of HA: SiO_2 = 50 : 50 % (bar 10 μm)

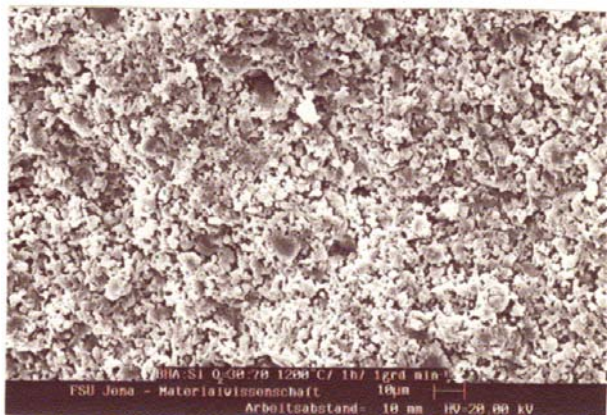

Fig. 5. SEM micrograph of HA : SiO_2 = 30 : 70 % (bar 10 μm)

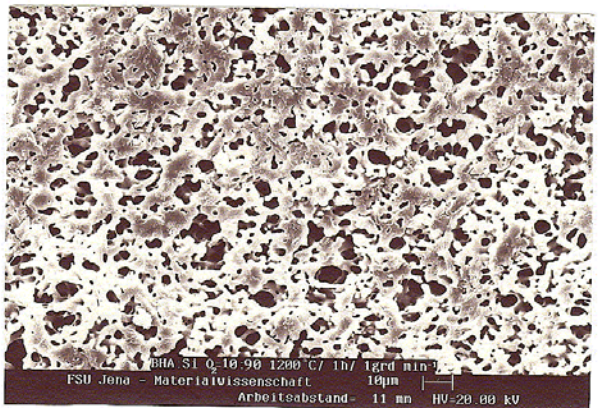

Fig. 6. SEM micrograph of HA:SiO_2 = 10:90 % (bar 10 μm)

From the micrographs it is evident that the composite consisting of 90 wt% HA and 10 wt% SiO_2 (Fig. 2), possesses the most homogenious microstructure. The density of the composite was 88 ± 2 %TD. The size of the grains and pores are 1.5 – 2.5 μm and 0.4 – 6 μm, respectively. The density of the composite containing 70 wt% hydroxyapatite and 30 wt% SiO_2 was 83 ± 1 % TD. The closed pores are with size of 0.6 to 4 μm. The composite with composition 50 wt% hydroxyapatite and 50 wt% SiO_2 has density of 80 ± 1 % TD. One part of the pores are interconnected into caverns with sizes of 5 – 18 μm. The density of the composite containing 30 wt% hydroxyapatite and 70 wt% SiO_2 was 76 ± 1 % TD. The size of the pores is from 3 to 20 μm. The biggest part of the pores are interconnected into canals /caverns with sizes from 8 to 25 μm. The density of the composite made of 10 wt% hydroxyapatite and 90 wt% SiO_2 was 71 ± 1 % TD. The pore sizes are in range from 5 to 18 μm. The biggest part of the pores are closed.

It is clear that by increasing the content of SiO_2 in the composite, the porosity is also increasing.

In order to investigate the thermal equilibrium of the composites, i.e whether the composites in the course of the heating/cooling cycle showed any chemical, physical and structural changes, dilatometric investigations were performed in a temperature interval of RT – 1000 ^{0}C – RT. Based on the absence of hysteresis effect of the dependence $\Delta L/L = f(T)$, it was concluded that the systems consisting of 10, 30 and 50 wt% SiO_2 were in thermal equilibrium.

The technical coefficients of thermal expansion for the composites containing 10, 30 and 50 wt% SiO_2 are as follows: $13.87\cdot10^{-6}$; $11.22\cdot10^{-6}$ and $9.01\cdot10^{-6}/\,^{o}$C, respectively. These systems were subject to further investigations. The temperature dependence on the thermal expansion in the interval RT-1000 ^{0}C can be presented by the third order polynomial form:

HA:

$$\Delta L/L = -0.02007 + 0.00122\ T + \\ +4.3744\cdot10^{-7}\cdot T^2 - 1.9132\cdot10^{-10}\cdot T^3$$

SiO_2:

$$\Delta L/L = -0{,}015 + 3{,}968\cdot 10 - 5\cdot T + \\ + 4.666\cdot10^{-8}\cdot T^2 - 3{,}446\cdot10^{-11}\cdot T^3$$

HA: SiO_2 = 90:10 %:

$$\Delta L/L = -0.048 + 0.011\cdot T + \\ + 9{,}657\cdot10^{-6}\cdot T^2 - 6{,}821\cdot10^{-9}\cdot T^3$$

HA: SiO_2 = 70:30 %:

$$\Delta L/L = -0{,}134 + 0.012\cdot T + \\ +2{,}475\cdot10^{-6}\cdot T^2 - 3{,}300\cdot10^{-9}\cdot T^3$$

HA: SiO_2 = 50:50%:

$$\Delta L/L = -0.055 + 0.002\cdot T + \\ + 2.164\cdot10^{-6}\cdot T^2 + 1.07\cdot10^{-10}\cdot T^3$$

Relationships regarding to the temperature dependence of the physical coefficient of the thermal-expansion are presented in the second order polynomial form:

HA:

$$\alpha = 0.00122 + 8.7488\cdot10^{-7}\cdot T - 5.73\cdot10^{-10}\cdot T^2$$

SiO_2:

$$\alpha = 3.968\cdot10^{-5} + 9.332\cdot10^{-8}\cdot T - 10.338\cdot10^{-11}\cdot T^2$$

HA: SiO_2 =90:10 %:

$$\alpha = 0.011 + 19.314\cdot10^{-6}\cdot T - 20.46\cdot10^{-9}\cdot T^2$$

HA:SiO_2 =70:30 %:

$$\alpha = 0.012 + 4.95\cdot10^{-6}\cdot T - 9.900\cdot10^{-9}\cdot T^2$$

HA:SiO_2 =50:50%:

$$\alpha = 0.002 - 4.328\cdot10^{-6}\cdot T + 3.21\cdot10^{-9}\cdot T^2$$

The mechanical properties, i.e. Young's modulus of elasticity, Poisson's ratio, shear modulus, and compressive modulus, were determined for the composites which were in a thermal equilibrium. The mechanical properties for the pure constituents and for the thermally stable composites are presented in Table 1.

Table 1

E-modulus, shear modulus, Poisson's ratio and compressive modules of HA, SiO_2 and their composites

	Relative density %	*E* GPa	*G* MPa	μ	*K* GPa
HA	97	88.0	36.0	0.31	77.19
SiO_2	99	74.0	27.0	0.17	37.37
HA:SiO_2= 90:10 %	88 ± 1	33.7	16.88	0.33	47.8
HA:SiO_2= 70:30 %	83 ± 1	33.5	18.00	0.30	37.0
HA:SiO_2= 50:50 %	80 ± 1	30.7	21.68	0.31	26.9

As it can be seen from Table 1, the mechanical properties of the composites are lower than those of the pure components – hydroxyapatite and SiO_2. The density of the hydroxyapatite and SiO_2 are 97 % TD and 99 % TD, respectively, while the density of the composites are from 88 ± 1 to 80 ± 1 % TD. The composites from Table 1 show very low variation of E-modulus with SiO_2 content. For all investigated composites the E-modulus is 32 ± 1,5 GPa. The same can be said in regards to the shear modulus, whose values are 18 ± 3 GPa. The compressive modulus decreases with increasing of SiO_2 content from 47.8 to 26.9 GPa.

Several equations have been proposed to predict the thermal-expansion coefficient of the composites depending on E-modulus, shear modulus, modulus of compressibility, Poison's ratio, and volume fraction.

TURNER's equation [10]:

$$\alpha_c = \frac{\alpha_i f K_i + \alpha_m (1-f) K_m}{f K_i + (1-f) k_m}$$

$$K_i = E_i / 3(1 - 2\nu_i) \quad K_m = E_m / 3(1 - 2\nu_m)$$

KERNER's equation [11]:

$$\alpha_c = \frac{[\alpha_i f K_i /(3K_i + 4G_m)] + [\alpha_m (1-f) K_m / (3K_m + 4G_m)]}{[f K_i /(3K_i + 4G_m)] + [(1-f) K_m /(3K_m + 4G_m}$$

$$G_m = E_m / 2(1 + \nu_m)$$

THOMAS's equation [12]:

$$\alpha_c = \alpha_i^{\,f} \cdot \alpha_m^{\,f}$$

TUMMALA & FRIEDBERG's equation [13]:

$$\alpha_c = \alpha_m - f\frac{(\alpha_m - \alpha_i)(1+\nu_m)}{2E_m \frac{(1+\nu_m)}{2E_m}} + \frac{1-2\nu_i}{E_i}$$

TAYA's equation [14]:

$$\alpha_c = \alpha_m (1-f) + \alpha_i f + 2(1+\nu_m)(\alpha_i - \alpha_m)(I_1 - I_2)$$

where:

α_c, α_i, α_m – thermal-expansion coefficients of the composite, matrix and dispersed phase;

f – volume fraction of the constituents;

K_i – compression modulus of the included phase;

K_m – compression modulus of the matrix;

E_i –Young's modulus of the included phase;

E_m – Young's modulus of the matrix;

ν_i – Poisson's number of the included phase;

ν_m – Poisson's number of the matrix.

Experimentally obtained thermal-expansion coefficients and calculated values applying the above mentioned model equations are presented in Table 2.

Table 2

Experimental and calculated values for the thermal-expansion coefficients

Composite	$\alpha_{exp}\cdot10^{-6}$	$\alpha_{calculated}$				
HA: SiO_2 %	°C	Tumm. and Fried.	Taya	Turner	Kerner	Thomas
90 : 10	13.87	14.25	13.02	13.60	13.60	12.66
70 : 30	11.22	13.18	9.62	11.05	11.16	9.27
50 : 50	9.01	12.12	6.46	8.78	8,91	6.82

Equations which best fit the experimental data for SiO_2 concentration up to 50 % are those given

by Turner nad Kerner, with a coefficient of correlation of cca 98 %.

CONCLUSION

The procedure for producing hydroxyapatite–SiO_2 composite was designed. TEOS was used as a precursor for SiO_2.

The increased content of SiO_2 in the matrix of the hydroxyapatite resulted in increased main diameter of the particles of the non-sintered composites.

The increased content of SiO_2 in the composite sintered at 1200 ^oC/1h resulted in decreased relative density of the compacts.

The composites with 10, 30 and 50 wt% SiO_2 are in thermal equilibrium.

The composites hydroxyapatite–SiO_2 have lower mechanical properties, due to their relative high porosity, in comparison to the pure hydroxyapatite and SiO_2.

The parameters of interconnected porous structure of the composites can be controlled trough the content of SiO_2.

The coefficient of thermal expansion of the composites can be presented in function of E-modulus, shear modulus, compression modulus, Poisson's ratio, and volume fraction of SiO_2 using the model equation given by Turner, Kerner, Thomas, Tummala and Friedberg.

The best approximation of the technical coefficient of thermal expansion in function of E-modulus, shear modulus, compressive modulus, Poisson's ratio, and volume fraction of SiO_2 provides the equations proposed by Turner and Kerner.

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