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Dilatometric and Microstructural Study of Particle and Functionally Graded Composites Based on Hydroxyapatite and Crystalline Bioglass

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Abstract:

Hydroxyapatite (HA) and bioglass (BG) ceramics have become of prime importance in bone tissue engineering. Besides the appropriate composition, the microstructure of bone replacement plays a crucial role. In the present work, particle composites and functionally graded material (FGM) based on HA and BG prepared by electrophoretic deposition were thoroughly characterised in terms of the preparation method, sintering process, phase composition and microstructure. The sintering was monitored by high-temperature dilatometry in two directions, the sintering rates were calculated, and the overall sintering process was discussed. The SEM showed the continuous change in the microstructure of FGM with gradual interconnected porosity favourable for bio-applications. The fundamental fractographic analysis proved the crack development in FGM related to the sintering process, and the recommendations for the reduction of the crack development were given. The phase transformations during thermal treatment were analysed using X-ray diffraction analysis and deeply discussed.

Keywords: Hydroxyapatite; Bioglass; Functionally graded material; Sintering; Microstructure.

1. Introduction

Functionally graded materials (FGMs) are a special kind of composite in which the material properties vary smoothly and continuously from one surface to the other. The variation of the properties is attained by the gradual change of the material composition. FGMs attract great attention today in the materials science and engineering society because conventional composites do not achieve the necessary properties appropriate for many challenging applications [1]. FGMs are successfully applied in automobile, military, energy, machinery, aerospace or medical areas where a continuous chemical and structural change over the material is demanded [2]. In particular, regarding the medical area, the most important examples of FGMs are directly located in a human body. Bones or teeth have a gradual change in their structure and properties.

The most common strategy for hard tissue regeneration after some kind of trauma is to heal the bone by autograft or allograft. In the case of allograft, the utilisation of synthetic bioactive material with low risk of immune reaction is a highly discussed topic in the

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literature. Hydroxyapatite (HA) is being considered as a candidate for hard tissue substitution because of its 65% chemical similarity of the mineral constituent with the natural bone and excellent biocompatibility, bioactivity and cytocompatibility [3, 4].

Although the biocompatibility of HA is high, it can be improved further. It has been proposed that the addition of silicon to the apatite structure influences the material in biological environments [5]. The enhancement of HA bioactivity is due to the substitution of $SiO_4^{4^-}$ for $PO_4^{3^-}$ ions that affect HA surface chemistry or local bioavailable Si release [6]. The favourable results of the substitution were reported by several authors [7-9]. Therefore, the using of Bioglass[®] (BG) together with HA seems to be justified. Moreover, the addition of more bioactive BG [10] into HA composite can accelerate its dissolution rate because the dissolution rate of HA is relatively low [11], corresponding to ionic substitutions into the HA lattice and crystallinity [12].

Many studies have been made to describe HA/BG composite systems [5, 13-16]. The authors mainly focused their efforts to show manufacturability, microstructure and properties of the composites. However, it is hard to maintain the BG in an amorphous structure. The BG has a high crystallisation ability and it crystallises by a surface crystallisation mechanism, so that the material is highly crystalline even a low temperature (600-750 °C) [17]. Crystalline phase may affect its bioactivity and dissolution profile [18, 19]. Therefore, tailoring of manufacturing method with applied pressure [13, 14, 16] or thermal conditions [13, 14] has to be done.

Probably for these very reasons, only a few studies are available in the literature aiming on FGM from HA and BG [20-24]. Most of these studies deal preferably with coatings instead of bulk material. Moreover, all these works report specific types of multi-layered functionally graded HA/BG rather than FGM with continuous microstructural change. It is attributed to the fabrication techniques used, i.e. Spark Plasma Sintering (SPS) [20], plasma spraying [21, 22], pulsed laser deposition [23] or enamelling technique [24].

Another suitable method for preparation of non-composite [25, 26] or composite materials (particle [27] and fibre reinforced composites [28] or laminates [29]) including FGM [27, 30] is electrophoretic deposition (EPD). It is a versatile technique allowing fabrication of complicated objects from suspensions containing charged ceramic particles through their movement in an electric field applied between two electrodes. Contrary to previously mentioned methods, EPD offers the possibility of preparing FGM with continuous change of composition without any sharp phase interphase. Although, the EPD is widely used to prepare HA and BG composites [31, 32], but it has not yet been used to fabricate the FGM from these biomaterials. However, products of electrophoretic deposition are subsequently processed by conventional sintering, therefore crystallisation of BG in HA/BG composite is inevitable. Crystallisation of BG could consequently be suppressed by combining EPD with following SPS or Hot Isostatic Press methods (HIP).

Another challenging issues associated with the HA/BG FGM materials is coefficients of thermal expansion (CTE) of HA and BG and sintering shrinkage if the prepared green bodies do not have the same density and undergo phase changes during sintering. In the first case, the CTE of HA and BG are 15.9 and $9.7 \times 10^{-6} \text{ K}^{-1}$, respectively, indicating the possible development of cracks during cooling from the sintering temperature. In the second case, the structural change during sintering, i.e. variation of grain or pore morphology and size, phase transformations are accompanied by volume change (a shrinkage). Generally speaking, the shrinkage of BG is considerably high (60 % at 1050 °C [17]) compared to HA (13 % at 1050 °C [33]), which may lead to crack development in the FGM as well. This situation is very well documented in the work of Luginina et al. [20]. Therefore, a deep description and understanding of the sintering process of FGM based on HA and BG are needed.

Present work as the first describes the preparation of bulk FGM based on HA and BG with continuous phase change using EPD. To accomplish this goal, the various bulk (several millimetres thick) HA/BG particle composites had to be prepared and evaluated as well. Since

conventional sintering of the prepared composites was chosen, the article brings original information about densification, crystallisation of bioglass and phase changes in HA/BG and FGM composites during sintering determined by high-temperature dilatometry and X-ray diffraction analysis.

2. Materials and Experimental Procedures

Two commercial powders, i.e. hydroxyapatite (HA, 99.95%. Nanografi Nanotechnology, Turkey) and bioglass 45S5 (BG, Schott AG, Germany) with mean particle size of 50 nm and 10 µm, respectively, were used to prepare functionally grade and particle composite materials as well as standards (pure HA or BG). The fine HA particles were chosen in order to use the lowest possible sintering temperature. The suspensions designed to prepare FGM consisted of 15 wt % HA or BG, 0.85 wt % of monochloroacetic acid (Merck, Germany) and 84.15 wt % of 2-propanol (Lachner, Czech Republic). The suspensions related to fabrication of the two standards and three particle composites had the same compositions of ingredients, but the ceramics loads had different weight ratios of powders (HA:BG): 100:0, 75:25, 50:50, 25:75, 0:100. After mixing all components, the suspensions were homogenised mechanically and ultrasonically for 30 minutes. The electrical conductivity of the suspensions was measured using a SevenCompact Conductivity S230 conductometer (Mettler Toledo AG, Switzerland).



Fig. 1. Scheme of the flow rate of suspension change during fabrication of FGM.

The EPD apparatus was assembled from a glass cell, two stainless steel electrodes placed in vertical positions with 26 mm distance between them and a stable power source with applied constant current of 5 mA (current density of 0.27 mA/cm²). The depositions of the pure ceramics and particle composites were interrupted each 5 minutes and the suspensions were stirred to avoid a sedimentation of the particles at an electrophoretic cell bottom (described elsewhere [25, 26, 28]). At the same time, a weight yield on the deposition electrode was monitored to obtain data about deposition kinetics required for preparation of FGM. The deposition time was up to 40 minutes to obtain robust set of kinetic data and thick enough deposits. Based on that, the FGM could be prepared using the continuous mode of EPD. The suspension containing only BG was drained continuously from the glass cell, and the fresh suspension with HA was fed into at the same rate. The flow rate was increased during the deposition process to respect the evolution of the deposition kinetics given by

materials change in the suspension, thickness and resistivity of the growing deposit. The schemes of the EPD apparatus and flow rate during the deposition (23 minutes) are given in Fig. 1.

The electrodes covered by deposits were allowed to dry in a desiccator for 24 hours at 25 °C. After then the several millimetres thick deposits were removed from electrodes, and the organic residues were burnt out at 600 °C for 1 hour. The samples were sintered at 1050 °C for 2 hours with heating rate of 10 °C/min, whereas the linear dimensional changes were recorded using a high-temperature dilatometer L70/1700 (Linseis, Germany) in longitudinal (parallel with electrode) and transversal (in the direction of deposition) direction. The samples for longitudinal direction had the shape of the prismatic bar with dimensions (length × width × thickness): $10 \times 4 \times 1-5$ mm. The samples for transversal direction had the shape of a cylinder with dimensions (diameter × thickness): $5 \times 1-5$ mm. The thickness of the measured sample depended on the thickness of the deposit. The theoretical shrinkage based on the knowledge of green (ρ_{gb}) and final (ρ) densities of the ceramic body was calculated using equation [34]:

$$\varepsilon_{calc} = 1 - \sqrt[3]{\frac{\rho_{gb}}{\rho}}.$$
 (1)

The density and pore size distribution of the samples were determined using the Archimedes method (EN 623-2) and an automatic pore size analyser (PoreMaster 60, Quantachrome Instruments, USA) equipped with low (1-340 kPa) and high (0.1-330 MPa) pressure stations with a measurable range of pores of 0.004-1000 μ m, respectively. The phase composition of the samples was determined using X-ray diffraction analysis (XRD, SmartLab, Rigaku, Japan). Based on the phase compositions, the theoretical density of individual composites was calculated. The microstructures were observed using a Lyra3 scanning electron microscope (SEM, FEG/FIB, Tescan, Czech Republic).

3. Results and Discussion3.1 Electrophoretic deposition

To determine a correct manufacturing process for preparation of FGM, the deposition kinetics of the pure HA and BG ceramics and their mixtures were studied first. Fig. 2a represents dependence of electrical conductivity on BG amount in the suspension. It is clearly evident that the electrical conductivity of the suspension increased with the BG amount. The suspension containing HA powder only had the electrical conductivity of 0.2 μ S/cm. The addition of 25 and 50 wt % of BG in suspensions led to the electrical conductivity increase to 4.8 and 11.5 μ S/cm, respectively, which was the highest measured value. The subsequent increase in BG concentration resulted in the electrical conductivity of the suspensions on the similar level. This behaviour can be explained in two ways. An adsorption capacity of individual material compositions in suspensions had a different ability to bind the MCCA molecules on the surface of ceramic particles and thus cause their dissociation [25]. The second phenomenon that may have occurred in BG-containing suspensions is slight dissolution of the BG due to the presence of MCAA because the conductive ion release from BG occurs significantly faster at lower pH [35].

The electrical conductivity of the suspensions markedly affected the EPD kinetics. The kinetic curves are given in Fig. 2b. It can be seen from the figure that the fastest deposition was achieved at the lowest electrical conductivity of the suspension. A high voltage is generated between the electrodes in suspension with low electrical conductivity, which causes the particles to move faster. Moreover, this also results in a very rapid depletion of the ceramic particles from the suspension and the deposition is completed in a relatively short time. In the extreme case, the deposited particle applied pressure on the surface of the

already created deposit, which can be separated from the electrode due to the development of cracks [36, 37]. In our case, HA:BG 100:0 and HA:BG 75:25 depositions had to be terminated soon, i.e. 10 and 15 minutes. The results described in Fig. 2b also corresponds to the measured thickness of the deposits, which decreased with increasing electrical conductivity of the suspension from 5.3 mm (HA:BG 100:0) to 0.9 mm (HA:BG 0:100). It is clear from the figure that the kinetic curves obtained from suspensions containing HA:BG 50:50 to HA:BG 0:100 are very similar, which corresponds to the measurement of the electrical conductivity shown in Fig. 2a.



Fig. 2. Dependence of electrical conductivity on bioglass amount in suspension (a) and dependence of deposited weight on time of deposition during preparation of pure ceramics and HA:BG composites (b).

Based on the knowledge of the deposition kinetics for various HA and BG compositions it was possible to estimate an increment of ceramic deposit on the electrode (described in detail for different materials in [29]) and subsequently adjust the correct flow rate of the suspension during the preparation of FGM.

3.2 Physical properties of green bodies

The dependence of relative density on BG amount in the pure and composite green bodies is shown in Fig. 3a and Table I. The relative density increased with concentration of the BG in the HA structure from 25.8 % t.d. up to 47.5 % t.d. It is evident that the value of the relative density was affected mainly by the value of the electrical conductivity of the suspensions from which the pure HA and BG ceramics and HA:BG composites were prepared (see Fig. 2a). The higher values of the electrical conductivity in the suspensions led to the slower deposition rates resulting to better arrangement of ceramic particles to the most advantageous positions in the deposit, thereby increasing the density of the samples [38].



Fig. 3. Dependence of relative density on bioglass amount in annealed deposits (a) and pore size distribution of pure ceramics and HA:BG composites (b).

	Relative density (%)			Shrinkage (%)			
Sample	ρ _{gb} (at 600 °C)	ρ _L (at 1050 °C)	ρ _T (at 1050 °C)	$\epsilon_{L calc}$	ε _L	E _{T calc}	ε _T
100:0	25.8 ±0.1	38.1 ±0.1	37.9 ±0.2	12.2	14.2	12.0	16.1
75:25	36.7 ± 0.1	50.7 ± 0.0	48.9 ± 0.2	10.2	16.4	9.1	22.1
50:50	$44.0\pm\!\!0.1$	54.0 ± 0.1	54.0 ± 0.1	6.6	19.1	6.6	24.2
25:75	43.5 ± 0.1	95.0 ± 0.3	92.1 ±0.7	22.9	32.6	22.1	38.6
0:100	47.5 ± 0.1	92.7 ± 0.4	91.4 ±0.6	20.0	59.0	19.6	67.7
FGM	-	-	-	-	21.2	-	38.9

Tab. I Summary of relative densities and shrinkages of HA:BG composite and FGM samples measured in longitudinal (L) and transversal (T) directions.

Green density of the samples did not change linearly with concentration. An explanation could be the different size of the HA and BG particles causing different porosity of deposits, whereby the small HA particles could fill the large pores between the big BG particles and thus reduce the overall porosity of the composite. The pore size distribution of these samples is displayed in Fig. 3b. The pure HA ceramic sample (HA:BG 100:0) showed a trimodal pore distribution with most frequent pore sizes of 0.04, 0.08 and 0.16 μ m. As the content of the BG in the HA increased, the most frequent pore sizes increased as well. The HA:BG 75:25 composite also showed a trimodal pore size distribution with most frequent pore size of 0.03, 0.13 and 0.25 μ m. Bimodal pore size distributions with most frequent pore sizes of 0.15, 0.21 μ m and 0.19, 0.36 μ m were measured for HA:BG 50:50 and HA:BG 25:75 samples, respectively. The measurement of HA:BG 0:100 pure ceramics showed an unimodal

pore size distribution with most frequent pore size of $1.21 \ \mu\text{m}$. In contrast to the pure and composite materials, a broad distribution of pores in FGM was determined. This result can be expected as a superposition of performed measurements on the aforementioned samples. The broad size distribution in FGM may imply significant influence on physical, microstructural and mechanical (not studied here) properties.

3.3 Dilatometric evaluation

The sintering shrinkage (ε) of standards, HA:BG composites and FGM, measured in the longitudinal direction, is shown in Fig. 4a. An enormous difference can be seen between sintering shrinkage of pure HA (HA:BG 100:0 sample) and BG (HA:BG 0:100 sample) in both longitudinal and transversal directions. The temperature 1050 °C was selected not to exceed the melting point of the BG. At this temperature, the shrinkage of the BG in longitudinal direction was 59.0 %. A very similar result was reported before in the work of Bretcanu et al. [17]. Table I shows the calculated shrinkage values using Eq. 1. It should be noted that this equation is valid for isotropic shrinkage. Despite the obvious anisotropy of the studied materials, the calculation was performed in individual directions in order to demonstrate the contribution of more than one process to shrinkage. The calculated sintering shrinkage for pure BG is 20.0 % (see Table I) indicating the existence of more internal processes during thermal treatment including first and second glass transition, glass in glass phase separation and crystallisation processes [39, 40]. It is clear from the Table 1 that these processes were applied in all studied materials. Contrary to BG, the shrinkage of the HA was only 14.2 % as a consequence of the low sintering temperature and the low value of green body density. The shrinkage curve of the FGM was close to the measured HA:BG 50:50 composite with similar final shrinkages of 19.1 % and 21.2 %, as could be expected for correctly designed FMG.



Fig. 4. Linear shrinkage of standards, HA:BG composites and FGM in (a) longitudinal and (b) transversal direction; sintering rate of standards, HA:BG composites and FGM in (c) longitudinal and (d) transversal direction.

The sintering shrinkage of standards, HA:BG composites and FGM, measured in transversal direction, is shown in Fig. 4b. It can be seen from Fig. 4b and Table 1 that shrinkage is slightly higher in the transversal direction than in the longitudinal direction for all measured samples. The visibly different sintering shrinkages in the longitudinal and transversal directions compared with density values in Table I, more evident in samples containing the BG, indicate sintering shrinkage anisotropy. The preferential packing of particles during EPD causes probably this phenomenon [41]. Concerning EPD, a similar behaviour was observed recently for the sintering characterisation of deposited alumina [42]. The explanation is strengthened by the fact that higher anisotropy was observed for big non-spherical BG particles.

The two significant sintering steps are often identified during sintering of the pure BG up to 1050 °C. The first densification step is seen to start at 530 °C (T1) and to end at 620 °C (T2), while the second densification step starts at 850 °C (T3), followed by a slight inflexion at 1000 °C attributed to a softening point when viscous flow starts [17]. Contrary to the literature data, our investigations for the same heating rate (10 °C/min) in longitudinal direction showed slight temperature deviations at the beginnings of the densifications steps and their shifting with composition change. The first densification step for HA:BG 100:0 sample started at 490 °C (T1) and ended at 610 °C (T2), while the second densification step started at 770 °C (T3). The shrinkage during the first step was 7.0 %. It should be noted that no inflexion was observed. The typical sharp sintering steps were also observed in HA:BG 25:75 sample, but the beginnings of the steps were recorded at higher temperatures, i.e. T1 was 505 °C. T2 was 620 °C, and the second densification step started at 900 °C with reduced shrinkage of 2.2 % in the first step. Higher content of the HA in the HA:BG 50:50 sample eliminated sharpness of typical plateau (between T2 and T3). In this sample, the densification started at 550 °C, followed by smooth curve descent with substantial bend at 990 °C. The record of HA:BG 75:25 sample shows no plateau with identified densification temperature at 590 °C. The curve of pure HA is smoothly descending as can be expected for this material with beginning of the densification at 640 °C. However, it is clear from this result that the second sintering phase did not develop for pure HA, which was mainly due to the low green body density and low sintering temperature.

The situation for the samples measured in transversal direction was similar to the longitudinal direction. In sample HA:BG 0:100, the first step started at 520 °C and ended at 700 °C. The shrinkage of 21.2 % during this step was much higher when compared to the longitudinal direction. The second densification step started at 790 °C. The beginning of densification of HA:BG 25:75 sample was determined at 530 °C, and the end of the first step was recorded at 640 °C accompanied by shrinkage of 2.8 %. The T3 was 900 °C. From this point of view, the densification in HA:BG 50:50 and HA:BG 75:25 samples began at temperatures about 10°C higher than those measured in longitudinal direction and HA:BG 100:0 sample revealed no change. To conclude, the higher HA content shifts the starts and ends of the individual sintering steps of BG to higher temperatures and reduces the typical plateau.

The derivate plot vs the temperature for longitudinal and transversal directions is given in Fig. 4c and Fig. 4d, respectively. It was found that the sintering rates of individual materials are similar in both directions. The sintering shrinkage rate of HA:BG 100:0 sample began to increase at 640 °C. The curve had no visible maximum. Such a situation is expected because the maximum densification rate occurs at 1080 °C, as Palard et al. [43] reported for pure HA having an analogous surface area. Moreover, this fact is reflected in all plots of measured samples containing HA, where no primary maxima of sintering rates were observed. Therefore, for samples HA:BG 75:25, HA:BG 50:50 and HA:BG 25:75, the only secondary maxima around 670 °C, 600 °C and 590 °C attributed to the first densification step of BG accompanied by its phase transformation were obtained, respectively. The pure BG sample (HA:BG 0:100) reached the secondary maxima of the densification rate at around

585 °C. Moreover, one more maximum at 650 °C is present in the transversal direction (see Fig. 4d), probably corresponding to the small inflexion visible on the shrinkage curve in Fig. 5b. The FGM started to shrink at 600 °C without distinct primary maximum and one measurable secondary maximum at 815 °C in the transversal direction. Based on the results, it is evident that BG accelerated the sintering rate in the composite materials.



Fig. 5. X-ray diffraction patterns of HA and BG powders.

3.4 XRD analysis

Fig. 5 shows diffraction patterns of commercial HA and BG powders. The red line is a typical pattern for amorphous bioglass with a single flat peak $2\theta = 32^{\circ}$ and other types of glass [44, 45]. The measurement is in good agreement with previously published data [17, 40]. On the contrary, the hydroxyapatite powder exhibited sharp, well-defined peaks, patently indicating the high crystallinity [46]. No secondary phases or impurities were detected during both analyses.

Fig. 6. X-ray diffraction patterns of standards and HA:BG composites annealed at 600 °C.

Further XRD analyses were performed only within standard and composite materials; analysis of FGM was not done for apparent reason. The XRD analyses of standard and composite samples annealed at 600 °C are plotted in Fig. 6. In the pure BG sample, the amorphous structure was completely transformed to a crystalline one, whereas combeite (Na₂Ca₂Si₃O₉) was identified as a dominant phase at the annealing temperature. Additionally, one single peak of the secondary phase identified as silicorhenanite $(Na_2Ca_4(PO_4)_2SiO_4)$ was found. Surprisingly, this secondary phase is usually observed at higher temperatures (800 – 950 °C) [17, 47], and it is considered as a sintering aid because it significantly enhances the sinterability of hydroxyapatite at 1000 °C [48]. It should be noted that many authors identified $Na_2CaSi_2O_6$ phase as the main phase rather than $Na_2Ca_2Si_3O_9$ phase because of better agreement between measured diffraction patterns and calculated ones by the Rietveld refinement method [39, 47, 49, 50]. When BG is mixed with HA (HA:BG 25:75), the pattern shows mainly $Ca_5(PO_4)_3(OH)$ (hydroxyapatite) crystalline phase with secondary phase identified as β -rhenanite (β -NaCaPO₄) and minority phase of Na₂Ca₂Si₃O₉. Hydroxyapatite is a non-stoichiometric compound that accepts many substituting ions in its unit cell [51]. Therefore, it can be assumed that the hydroxyapatite was partially substituted by present ions, such as Na^+ or Si^{2+} , even at this low temperature. In the case of the secondary phase, it is well known that the crystalline phase β -rhenanite exhibits high biocompatibility and bioactivity [48, 52, 53]. The further increasing of the HA content in the composite structure (samples HA:BG 50:50 and HA:BG 75:25) resulted in lower or even negligible content of secondary phases. In the case of HA sample (HA:BG 100:0), the only detected phase was $Ca_5(PO_4)_3(OH)$.



Fig. 7. X-ray diffraction patterns of standards and HA:BG composites sintered at 1050 °C.

The XRD analysis of standards and composite samples sintered at 1050 °C is shown in Fig. 7. The difference between annealed and sintered HA:BG 0:100 sample was in the more complex crystalline phase structure. The major phase was still identified as combeite, but more peaks of silicorhenanite appeared. This result was published many times, and thus it is not surprising [17, 54, 55]. On the other hand, the many published papers ignore the presence of β -rhenanite that was identified in the structure as well. When the HA:BG 25:75 composite is sintered at 1050 °C, no peaks corresponding to hydroxyapatite were detected. The structure was composed of combeite and more significant quantity of β -rhenanite as a product of the chemical reaction between HA and BG [52]. The phase composition of HA:BG 50:50 included β -rhenanite, combeite, β -wollastonite and hydroxyapatite phases. The hydroxyapatite was a dominant phase in HA:BG 75:25 composite, and several peaks of β -rhenanite and combeite were also identified. The structure of HA (HA:BG 100:0) contained beside Ca₅(PO₄)₃(OH) phase also β -Ca₃(PO₄)₂ (TCP) phase, which is not usual at such low temperature [56-58]. Cihlar et al. [59] determined that hydroxyapatite decomposes to tricalcium phosphate at a temperature above 1200 °C. The explanation of this behaviour is in nanoparticle size of HA, which probably accelerated decomposition to TCP [60, 61].

3.5 Microstructure

The microstructure of composite samples was examined on the fracture surfaces, see Fig. 8. Fig. 8a shows microstructures of HA:BG 100:0 where small grain size and open porosity were observed. The considerable porosity can be expected because the closing of pores in HA occurs at a relative density higher than 90 % [62] that was not reached by the used sintering temperature, see Table 1. When the BG was incorporated into the composite (sample HA:BG 75:25 in Fig. 8b), the pores were still interconnected, but the detailed inset shows an increase in the grain size. Such growth is more evident in Fig. 8c, where the microstructure of HA:BG 50:50 is given. Moreover, a gradual decrease in the volume of pores at the expense of their size is clearly visible because of bigger BG particles and promoted the densification process [48]. This fact is quite well documented in other microstructures of HA:BG 25:75 and HA:BG 0:100 samples in Fig. 8d and Fig. 8e, respectively.



Fig. 8. Fracture surface micrographs of standards and particle composites sintered at 1050 °C: a) HA:BG 100:0, b) HA:BG 75:25, c) HA:BG 50:50, d) HA:BG 25:75 and e) HA:BG 0:100.

The microstructure of the prepared FGM is shown in Fig. 9a. The sample had a visually continuous change in the microstructure. In order to examine a microstructure

evolution during the preparation of FGM, several places were investigated; the marks in the FGM correspond with detailed images in Fig. 9b-f. The closer inspection of detailed microstructures indicated a perfect agreement with microstructures presented in Fig. 8, which proves that the FGM with continuous microstructural and chemical change was prepared.

The microstructure without presence of cracks is provided. However, more than one sample was sintered during experiments, and some cracks in transversal or even longitudinal directions were observed occasionally. The longitudinal cracks are most likely caused by too large difference in the shrinkage of the basic materials observed by dilatometric measurements. Related to this, the samples' bending was observed, which probably caused transversal cracks located mainly in the HA rich microstructures. The transversal cracks are often reported as inauspicious results of the material composition at other fabrication methods [20]. To reduce or suppress the crack development, the pure BG layer in the FGM should be thinner, or the final material composition of the FGM should be HA:BG 25:75. On the other hand, the visible crack bridging in Fig. 9a (see white arrows) suggests higher fracture toughness, which is beneficial for this composite material.



Fig. 9. Fracture surface micrographs of FGM sintered at 1050 °C; a) overall view with marked places corresponding to b) HA:BG 100:0, c) HA:BG 75:25, d) HA:BG 50:50, e) HA:BG 25:75, f) HA:BG 0:100 microstructures.

Therefore, the obtained microstructures of standards, composites and FGM are interesting from a fractographic point of view. The images of the HA rich microstructures show numerous fine ceramic grains connected to their neighbours by thin necks. The crack propagating through these necks caused their decohesion, and completely intergranular fracture-mode occurred. Contrary, the fracture-mode with increasing content of the BG in the microstructure was changed entirely, i.e. transgranular fracture was observed only. A fracture-mode transition from intergranular to transgranular fracture could be attributed to significantly different porosity found in the microstructures. Our conclusion is supported by works of Deng et al. [63] or later Pecqueux et al. [64], who reported that this phenomenon occurs during the transition from higher-porous to lower-porous microstructure.

4. Conclusion

In this paper, the particle composites and functionally graded bulk materials (FGM) based on hydroxyapatite (HA) and bioglass (BG) were studied. First, the kinetics of electrophoretic deposition from variously concentrated suspensions was studied that allowed the preparation of FGM. The key parameter of electrophoretic deposition affecting particle arrangement in deposits and, thus, their green density was identified. The sintering process was evaluated by high-temperature dilatometry in the longitudinal and transversal orientation of the samples. It was found that there exists an enormous difference between the sintering shrinkage of pure HA (14.2 %) and BG (59.0 %). The gradual change in shrinkage was observed related to composition change in composites. The higher content of HA in composite shifts the starts and ends of the individual sintering steps to higher temperatures and reduces the typical plateau. The shrinkage curve of the FGM in the longitudinal direction was close to the measured HA:BG 50:50 composite what indicated correctly designed FMG. The different sintering shrinkages obtained in longitudinal and transversal directions have been attributed to the sintering shrinkage anisotropy originating from ceramic particles' preferential packing during EPD. The sintering shrinkage rate of all samples was calculated. The microstructural inspection of the samples showed interconnected porosity that is favourable for bio-applications and confirmed the continuous material change in FGM. The porosity was also gradually changed in dependence on the corresponding composition. The fractographic analysis of FGM showed that the porosity completely changed the fracture mode from intergranular to transgranular when the material transition from HA to BG occurred. To reduce or suppress the crack development, the pure BG layer in the FGM should be thinner, or the final material composition of the FGM should be HA:BG 25:75, or the preparation route for HA particles must be optimised to provide green bodies with higher density. The X-ray diffraction analyses revealed a fully crystalline structure of all prepared materials changing significantly depending on the starting composition. The phase evolution during changing material composition and dependence on temperature was deeply evaluated. For further experiments, the crystallisation of BG, BG rich particle composites and FGM could consequently be suppressed by combining EPD with following pressure assisted sintering method, e.g. SPS or HIP.

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Сажетак: Керамике на бази хидроксиапатита (ХА) и биостакла (БС) су од највеће важности у инжењерству коштаног ткива. Поред одговарајућег састава, микроструктура коштане замене игра кључну улогу. У овом раду, композити честица и функиионално градирани материјал на бази ХА и БС припремљени електрофоретским таложењем су детаљно окарактерисани у смислу методе припреме, процеса синтеровања, фазног састава и микроструктуре. Синтеровање је праћено високотемпературном дилатометријом у два правца, израчунате су брзине синтеровања и дискутовано је о целокупном процесу синтеровања. СЕМ је показао континуирану промену у микроструктури са постепеном мећусобно повезаном порозношћу погодном за био-апликације. Фундаменталном фрактографском анализом доказан је развој прслине у материјалу у вези са процесом синтеровања и дате су препоруке за смањење развоја прслине. Фазне трансформације током термичке обраде анализиране су анализом дифракције рендгенских зрака и детаљно размотрене. Кључне речи: хидроксиапатит; биостакло; функционални материјали; синтерованје; микроструктура.

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