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Production and Characterization of Bioglass®-Titania Reinforced Hydroxylapatite Composite

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Abstract. Hydroxylapatite, titania and Bioglass 45S5 are the components generally used for the production of bioactive biomaterials for years. In literature, although the binary composites with the permutation of three components exist, a ternary composite has not yet been tried. Primarily, Bioglass 45S5 was cast, its thermal analysis (Differential thermal analysis (DTA), dilatometric analysis), phase analysis (X-Ray Diffraction (XRD)), microstructural characterization (Scanning Electron Microscopy (SEM)) were performed. Then Bioglass 45S5 powder was ground to fine powder to make its particle size closer to the hydroxylapatite and the titania powders. The particle size of the powders were determined using the laser particle sizer. The DTAs of the 3 components, separately and mixed, were performed. They were then mixed, and ball-milled during 24 hours for a better homogenization. Following drying for 24 hours, pellets of 1 inch diameter were obtained using unaxial manuel press and sintered at 1000, 1100, 1200 ^{o}C. Mechanical testing (compression and microhardness), porosity measurement (The Archimèdes Method), phase determination (XRD) and microstructural characterization (SEM) of the composites were then performed. As a conclusion, when sintering temperature was increased, the porosity in the structure was decreased. Between 1100 ^{o}C and 1200 ^{o}C, a phase transformation occurred. The results of microhardness (24.6, 38.99, 316.2 HV (500gf for 15 sec) for the composites sintered at 1000, 1100, 1200 ^{o}C, respectively) and subsequent compression tests (93.023±10.5, 298.14±78.074, 371.9684±38.36 MPa, respectively) approved the possible phase transformation between 1100 ^{o}C and 1200 ^{o}C along with the XRD results.

Introduction

The accomplishments of bioactive ceramics, such as bioglass and dense hydroxyapatite –or hydroxylapatite- (HA) have attracted attention in the field of biomedical applications because of their ability of forming strong bonding with surrounding bone tissue when implanted [1, 2, 3]. However, as their mechanical properties are not good enough for load bearing applications, some reinforcement materials such as titania were used as additives in the studies both with HA and Bioglass® 45S5. Regarding these cases, titania comparing to other ceramic reinforcements in the ceramic matrix was a better choice for its capacity of combining good mechanical properties with the ability of forming an apatite layer when exposed to body fluids [1, 4, 5].

In one of the study based on the effect of Bioglass® 45S5 reinforcement on the mechanical properties of HA, naturally produced HA from human teeth was sintered with various addition of bioglass at 1200 and 1300 ^{o}C for 4 hours. As a result, the average hardness value of 383±60 HV (200 g load), average density of 2,72±0,01 g/cm^3 and compressive strength value of σ_{avr} = 83,03±33 MPa were achieved by sintering at 1200 ^{o}C with addition of 10 wt % bioglass in HA [6]. In an other study, in order to obtain the optimal matching mechanical and bioactivity properties; bioactive glass 45S5 was reinforced by introducing titania in anatase form and treated at 1000 ^{o}C to form new bioactive glass/titania biocomposites. The bioglass 45S5 powders mixed in weight ratios 75, 50, 25 % with TiO_2 powder and sintered at 1000 ^{o}C withstood to an average compressive strength of 36,87; 72,31; 122,31 MPa, respectively [7].

The HA-titania biocomposite coatings were applied onto several different substrates [8, 9] with several different techniques such as sol-gel [8], thermal spray [10,11], hydrothermal-electrochemical method [12]. In one of the most recent studies, researchers worked on the fabrication and characterization of porous bioceramic composite based on hydroxyapatite and titania [13]. The optimal titania content in the composite was 15 wt % and the mechanical properties of the porous composite (Young Modulus; 1,7±0,2 GPa, bending strength; 2,1±0,3 MPa, compressive strength; 7±1 MPa) was found close to cancellous bone whose Young Modulus was 0,05-0,1 GPa and compressive strength was found as 5-10 MPa [13].

Experimental Procedure

45S5 Bioglass® (45 wt % SiO_2 , 24,5 wt % Na_2O, 24,5 wt % CaO, 6 wt % P_2O_5) was obtained from SiO_2 , Na_2CO_3 , CaO and P_2O_5 powders. The powders were weighed, mixed and melted in a Pt crucible for 3 h over 1400 ^{o}C using a bottom loading furnace (Carbolite BLF 1700) . The melt was then quenched in water and ground to a finer powder for a better homogenization of the glass and then remelted. This process was repeated until the glass became uncolored, transparent and visibly homogenous. Quenching was fast enough to retain a completely amorphous material, similar to other studies made in this area [14, 15]. To make the particle sizes of the batch's components close to each other the Bioglass® 45S5 powders were then ground using firstly mortar and pestle for one hour, then mortar grinder (Fritsch Pulverissette 2) for one and half hour. The same process was repeated for titania and hydroxylapatite powders, too. The particle size and its distribution for 3 powders were measured using a Malvern MU 2000 laser diffraction particle sizer.

Our blend whose ratio deducted from literature survey [6,7,13]; HA (75 wt%),- Titania (15 wt%)- Bioglass® (10 wt%) was weighed and mixed with water to prepare a proper slurry and then put into HDPE bottles. Each bottle contains 1/3 of the slurry, 1/3 of grinding media (99,5 % pure alumina spheres) and 1/3 of free space. The bottles were placed on ball milling rollers and rolled for 24 h to provide a better homogenization. Following drying for 24 hours, pellets of 1 inch diameter were obtained using unaxial manuel press and sintered at 1000, 1100, 1200 ^{o}C for 3 h.

Differential thermal analysis (DTA) was performed for biocomposite batch, bioglass, HA and titania powders at a heating rate of 10 ^{o}K.min^{-1} using Netzsch STA 409 CD . Dilatometric measurements (Netzsch DIL 402 C) of the composites obtained were conducted from room temperature to 1200 ^{o}C at a heating rate of 10 ^{o}K.min^{-1}. XRD measurements were carried out using a Rigaku vertical diffractometer with Cu K_α radiation, using step size of 0.02° (2θ), with 2 s intervals and under conditions of 40 mA and 20 kV. The diffraction lines were identified using the program «JADE 6» . Scanning electron microscopy (SEM) (Jeol JSM-5910 LV –Low Vacuum Scanning-) and energy dispersive spectroscpoy (EDX) (Oxford Inca Energy 200) were used to characterize the microstructure of the biocomposite. The hardness measurements of the samples were done using FM-ARS 7000 (Future Tech Corp Tokyo, Japan) Full-Automatic Microhardness Testing System, 500 g load for 15 s contrary to the scientific survey [6], because any trace couldn't be seen for 100 g load and 200 g load, so this load and time can be a standard for this material. The compression tests were performed using Instron Universal Testing.

Results and Discussion

The results of the particle size measurements of the biocomposite composites are given in Table1.

Table 1. The average of particle size of the components**.**

Component Name	Average Particle Size [μm]
45S5 Bioglass®	14,5685 *
HA	6,554
TiO_2 (as provided)	59,833
TiO_2 (ground to finer powder by mortar grinder)	0,2895

*Its refractive index is taken as 1,55 according to references [16].

The results of DTA measurements for each powder component were summarized in Table 2.

Table 2. The critical endothermic peak temperatures of the Bioglass® 45S5, titania, and hydroxylapatite powders determined by the differential thermal analysis.

Component	Endothermic peak temperature [^oC]
45S5 Bioglass®	950,8
HA	949,8
TiO_2 (as provided)	902,5

Microhardness, density, porosity and compression test results depending on reinforcement content for HA–titania-bioglass composites are listed in Table 3. Results indicated that the physical and mechanical properties of the biocomposite are improved with increasing sintering temperatures. Beyond this deduction, comparing to previous studies, average compressive strength and microhardness values were improved.

Table 3. Average microhardness, density, porosity and compression strength variation depending on sintering temperatures.

Temperature (^oC)	$D_{(bulk)}$ (Ave.) [g/cm^3]	Compression Strength [MPa]	Microhardness [HV]
1000 ^oC	1,729879	93.023±10.5	24.6±2,271563
1100 ^oC	2,111734	298.14±78.074	38.99±12,45909
1200 ^oC	2,735928	371.9684±38.36	316.2 ±52,1795

With the increase of sintering temperature, the compression strength and the microhardness of the material increases taking account of standard deviations. The microcracks (formed during cooling) present in the material's microstructure drops down the first cracking resistance according to Griffith Law. Even this causes the sudden collapse at the bending test, this isn't observed at the compression tests as the material can absorb more energy because of the sample position and vertical loading.

Typical microstructures of bioglass-titania–HA composites are given in Fig. 1 for a sample containing 10 wt.% bioglass-15 wt.% titania- 75 wt % HA and sintered at 1000, 1100, 1200 ^oC. It seems that amount of porosity is decreased when sintering temperature is increased in accordance with Archimèdes density measurement's results. The X-ray diffraction analysis indicated that main phases of the sample sintered at 1200 ^oC are basically whitlockite, sodium calcium phosphate,

calcium phosphate and perovskite (Fig. 2) whereas only hydroxylapatite, whitlockite and anatase phases existed in samples sintered at 1000 ^{o}C. The thermal transformations occurring during sintering till 1200 ^{o}C between 1000-1200 ^{o}C (1049,5 ^{o}C, 1072,8 ^{o}C, 1102,8 ^{o}C, 1131 ^{o}C, 1150 ^{o}C, respectively) could also be seen in DTA and dilatometer thermograms. At 664,9 ^{o}C there is an exothermic peak indicating the crystallization of 45S5 Bioglass® . An endothermic peak (at 918,7 ^{o}C)similar to bioglass, titania and HA peaks as summarized in Table 2 also exists. These changes could also be detected with the change in the slope of α linear expansion coefficient biocomposite sintered at different sintering temperatures. The α linear expansion coefficient of the biocomposites sintered at 1000 ^{o}C changes between 602-770 ^{o}C and 770-948 ^{o}C showing the crystallization of 45S5 Bioglass® (664,9 ^{o}C) and endothermic peak (918,7 ^{o}C), respectively. The thermal transformations occurring during sintering could also be observed between 919-1041 ^{o}C, 1040-1078 ^{o}C, 1077-1115 ^{o}C, 1115-1147 ^{o}C at the dilatometer thermogram of the biocomposite sintered at 1200 ^{o}C. These thermal coefficient changes and exothermic peaks in both thermograms can be attributed to the phase transformations which occurred between 1000 and 1200 ^{o}C, as approved by XRD results (Fig 2.).

Conclusion

The phase transformation between 1000 ^{o}C and 1100 ^{o}C is the main reason of the change in the microhardness and compression strength. Then the increase in diffracted intensity and new phase formations between 1100 ^{o}C and 1200 ^{o}C indicate phase transformations in the composite. This change is also obvious in the thermograms and the slope of α linear expansion coefficient. Another reason can also be attributed to the densification of the material by increasing sintering temperature as observed in SEM micrographs and measured through the Archimèdes method. Comparing the other studies formerly mentioned [6,7] based on binary composites, the mechanical properties were by far upgraded –from the compressive strength of σ_{avr} = 83,03±33 MPa [6] and 122,31 MPa [7] to 371.9684±38.36 MPa in our study- and this product can also be applicable to porous structure owing to its improved mechanical properties.

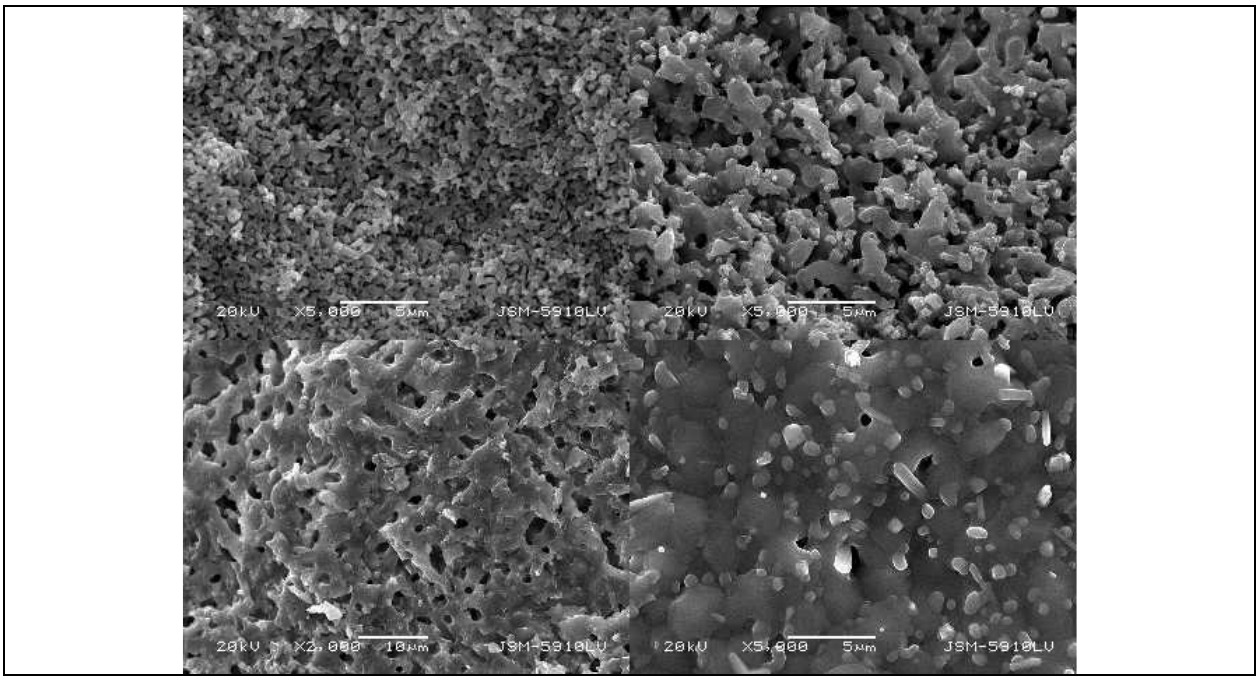

Fig. 1. SEM micrographs with different magnifications of biocomposite sintered at different sintering temperatures. (Upper left: x5000 at 1000 ^{o}C, upper right: x5000 at 1100 ^{o}C, bottom left: x2000 at 1200 ^{o}C, bottom right: x5000 1200 ^{o}C).

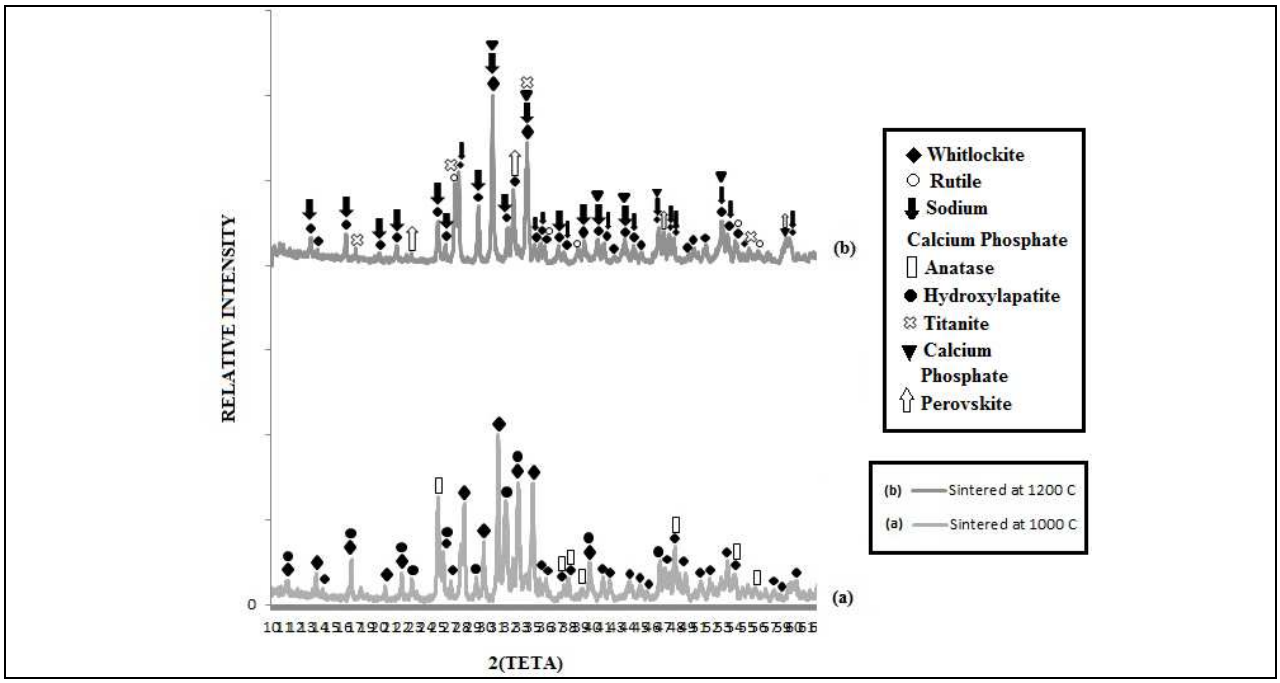

Fig.2. Comparison of XRD pattern at different sintering temperatures.

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