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Production of hydroxylapatite based titania biocomposite as porous bone-like scaffold

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ABSTRACT

Purpose: In this study titania-rutile phase- was proposed as reinforcement material with Bioglass 45S5® due to its high biomcompatibility and to bioactive glass's induced effect on fast cell regeneration and profileration.

Design/methodology/approach: Porous bioinert-bioactive composite ceramics were fabricated using HA and different composition of TiO_2 mixtures. Firstly 75 wt. % HA – 15 wt. % TiO_2 – 10 wt. % Bioglass® 45S5 composition was prepared and another batch with changing Bioglass® content was also tried for 75 wt. % HA – 10 wt. % TiO_2 – 15 wt. % Bioglass® 45S5 and H_2O_2 as pore former.

Findings: The sample with 15 wt % TiO_2 has higher hardness values and the sample with 10 wt % TiO_2 have higher compressive strength values than the reference study. HA/Bioglass®/TiO_2 composites are potential biomaterials to be used in bone filling and bone regeneration techniques.

Practical implications: These biocomposites can be good substitute for missing or damaged bones after supplementary in vivo testing. It is also suggested to evaluate these specimens in vitro tests in SBF (Simulated Body Fluid) solution where temperature is held constant at 37°C with continuous stirring to measure if weight gain will occur by time.

Originality/value: The development of improved biocompatible materials and ultimately bonelike mechanical properties is continuous task in the bioceramics research field. The use of HA is limited due to its poor mechanical properties in load-bearing applications and porous HA structures has tendency in mechanical failure. The reinforcement of HA with several inert ceramics has beneficial effect ın its mechanical properties.

Keywords: Ceramics and glasses; Biomaterials; Bioceramic composites; Mechanical properties

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PROPERTIES

1. Introduction

The use of HA is still rather limited in load-bearing applications because this material does not combine good mechanical properties with an open porosity and thus highly porous HA structures are prone to mechanical failure. This can lead to instability and unsatisfactory duration of the implant or scaffold in the presence of body fluids and under local loading [1,2]. Furthermore, the mechanical strength of porous HA structures is further reduced, considerably, by fatigue loading [3]. In recent years, many reinforcements, including metallic particles [4], ceramic whiskers [5], nanoparticles (nanocomposites) [6], bioactive glass [7,8] as well as inert ceramic phases such as Al_2O_3, TiO_2 nanotubes [9], SiO_2, ZrO_2 have been used in HA materials. These HA composites possess higher mechanical properties in relation to pure HA ceramics. Amongst the different HA based composites developed, those with addition of TiO_2 as second phase seem to merit further consideration [10], due to the well-known biocompatibility of TiO_2 [11,12].

TiO_2 has been suggested as porous cell carrier material whose properties, such as good permeability and high biocompatibility, serve to enhance cell vitality [11]. The efficacy of different titanium dioxide materials on cell growth and proliferation has been studied [12,13].

The present paper describes the processing of bioactive-bioinert composites consisting of HA and different composition of TiO_2 mixtures. Firstly 75 wt. % HA – 15 wt. % TiO_2 – 10 wt. % Bioglass® 45S5 composition was prepared [14] and another batch with changing Bioglass® content was also tried for 75 wt. % HA – 10 wt. % TiO_2 – 15 wt. % Bioglass® 45S5 and H_2O_2 as pore former.

2. Materials and method

Porous bioinert-bioactive composite ceramics were fabricated from hydroxylapatite (HA), titania, Bioglass® 45S5 powder mixtures using H_2O_2 as pore former. Bioglass® 45S5 was prepared using conventional technic [15]. Next, a ternary biocomposite with composition 75 wt. % HA – 15 wt. % TiO_2 – 10 wt. % Bioglass® 45S5 were disposed as seen in Fig. 1. Same procedure was repeated for 75 wt. % HA – 10 wt. % TiO_2 – 15 wt. % Bioglass® 45S5 [16].

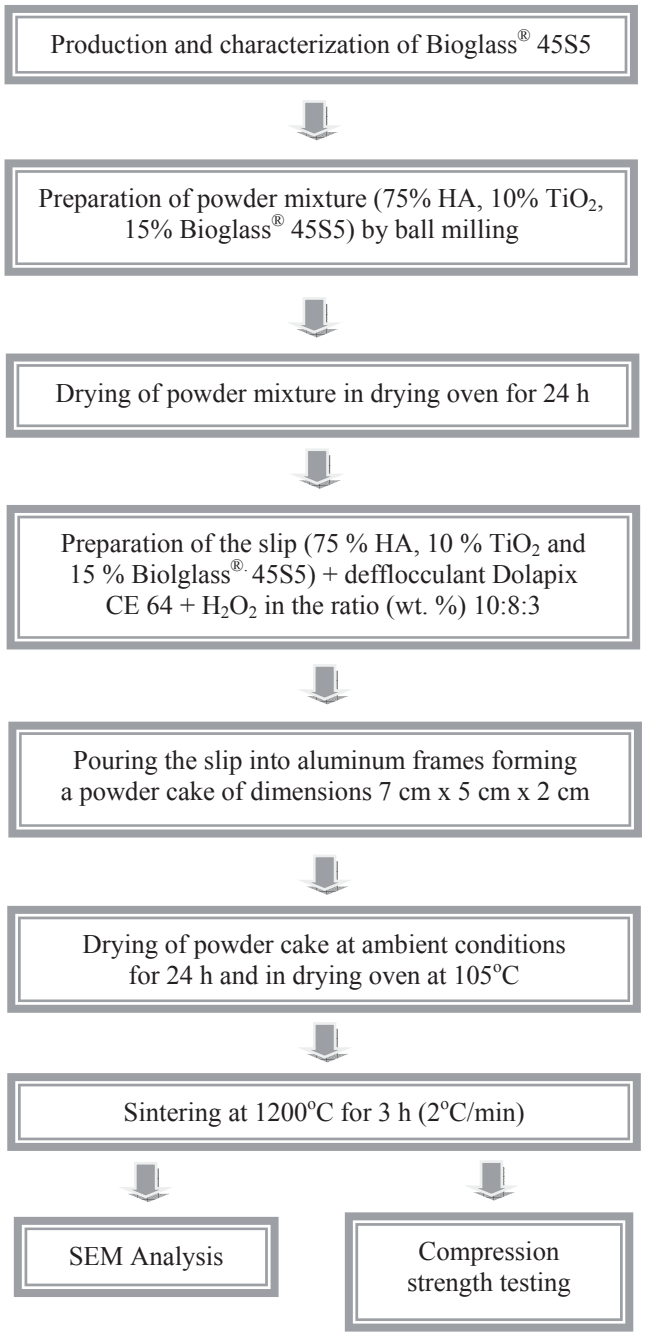

Fig. 1. Summary of the experimental procedure [16]

3. Results and discussion

The phase composition of the composites with 15 wt. % TiO_2 is summarized in Table 1 [16] and shown in Fig. 2 [16].

Table 1.
Phases of the composites with 15 wt. % TiO_2 sintered at 1000 and 1200°C [16]

Sintering temperature	Phases
1000°C	Hydroxylapatite, anatase and whitlockite
1200°C	Whitlockite, rutile, sodium calcium phosphate, calcium phosphate, perovskite, titanite

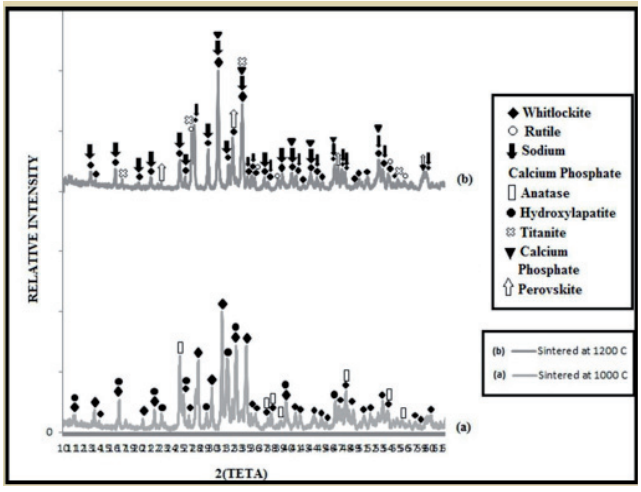

Fig. 2. The result of XRD with 15 wt % TiO_2 [16]

This results show possible reactions during transformation at temperature from 1000 to 1200°C as follows [16];

$$Ca_{10}(PO_4)_6(OH)_2 + TiO_2 \rightarrow 3Ca_3(PO_4)_2 + CaTiO_3 + H_2O \quad (1)$$

$$Ca_{10}(PO_4)_6(OH)_2 + SiO_2 + TiO_2 \rightarrow 3Ca_3(PO_4)_2 + \\ + CaTiSiO_5 + H_2O \quad (2)$$

$$Ca_8(PO_4)_6(PO_2OH) + 3/2Na_2O \rightarrow Ca_3(PO_4)_2 + \\ + Na_2Ca_6(PO_4)_5 + 1/2H_2O + O_2 \quad (3)$$

$$TiO_2\,(anatase) \rightarrow TiO_2\,(rutile) \quad (4)$$

According to phase compositions it is obvious that $CaTiO_3$ is a by-product of the reaction sintering process that takes place between TiO_2 and CaO, the latter is one of the decomposition products of HA. In the 15 wt. % TiO_2 composite the presence of β-TCP is evident, meaning that part of α-TCP had transformed to β-TCP.

The phases of the composites with 10 wt. % TiO_2 sintered at 1000 and 1200°C were shown in Fig. 3 [16] and summarized in Table 2 [16] after XRD analysis.

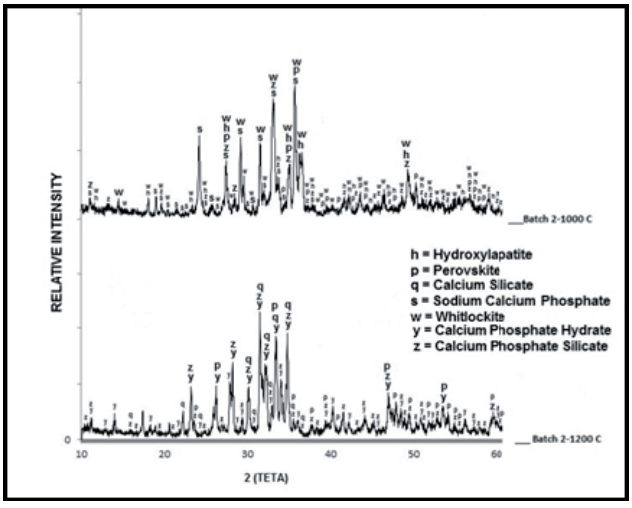

Fig. 3. The result of XRD with 10 wt % TiO_2 [16]

Table 2.
Phases of the composites with 15 wt. % TiO_2 sintered at 1000 and 1200°C [16].

Sintering temperature	Phases
1000°C	Hydroxylapatite, calcium phosphate silicate, perovskite, sodium calcium phosphate and whitlockite
1200°C	Calcium phosphate silicate, calcium phosphate hydrate, perovskite, calcium silicate

Increasing sintering temperature from 1000 to 1200°C, whitlockite, hydroxylapatite, sodium calcium phosphate were transformed to calcium silicate and calcium phosphate hydrate. Perovskite remained unchanged in the phase. In the 10 wt. % TiO_2 composite, the presence of TiO_2 was not been detected as α-TCP or β-TCP.

Dissolution and density increase occurred because of melting of Bioglass® 45S5 and calcium silicate phase was also observed due to HA transformation to whitlockite during transition from 1100°C to 1200°C.

When the results of SEM as depicted in Figs. 4 and 5 [16] are examined, the difference of pore size and structure can be noticed easily and it is also coherent with the results of XRD; in Fig. 5, pores have been decreased and grains have been grown compared to Fig. 4.

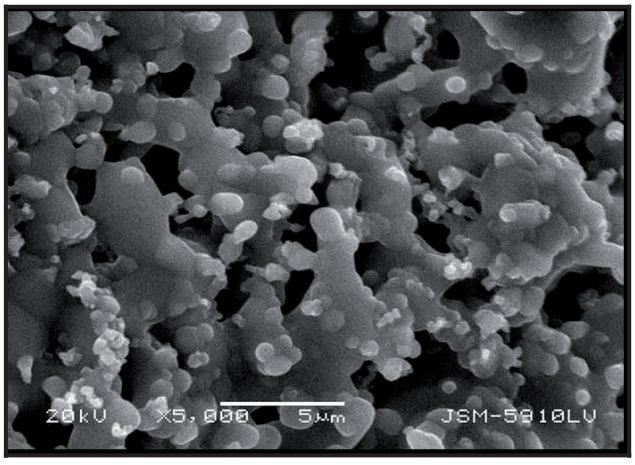

Fig. 4. SEM micrograph with 15 wt. % TiO_2 at 1200°C (x5000) [16]

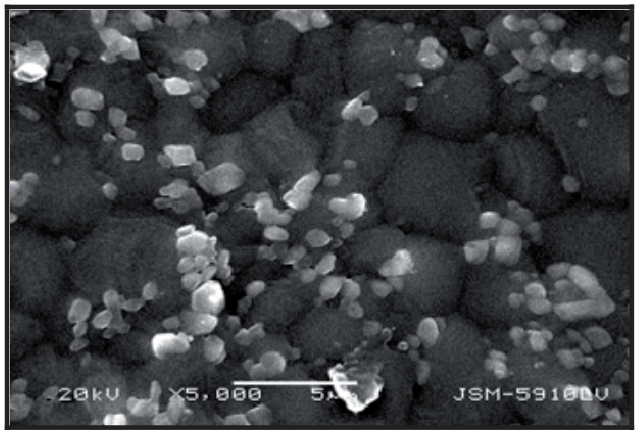

Fig. 5. SEM micrograph with 10 wt % TiO_2 at 1200°C (x5000) [16]

The main reason for this difference is the unlike decomposition behaviour of H_2O_2 in contact with hydroxyapatite and TiO_2. The decomposition of H_2O_2 depends on the geometrical and structural activity of the powder, which in this case is composed of two components. It is known that H_2O_2 decomposes according to relation: $H_2O_2 \rightarrow H_2 + (1/2)O_2$ which is thermally activated. When H_2O_2 is in contact with solids the rate of its decomposition increases and the rate of decomposition depends on the solid surface properties [14].

In Fig. 6 [16], pores possess enough size to create links with alive organism in the body.

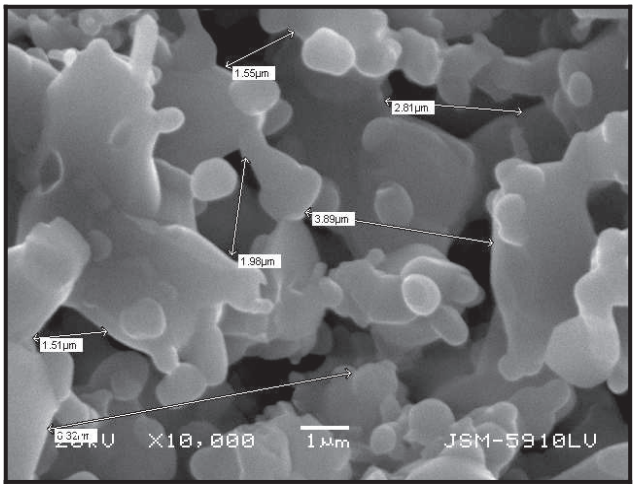

Fig. 6. SEM micrograph with 10 wt % TiO_2 at 1200°C (x10000) [16]

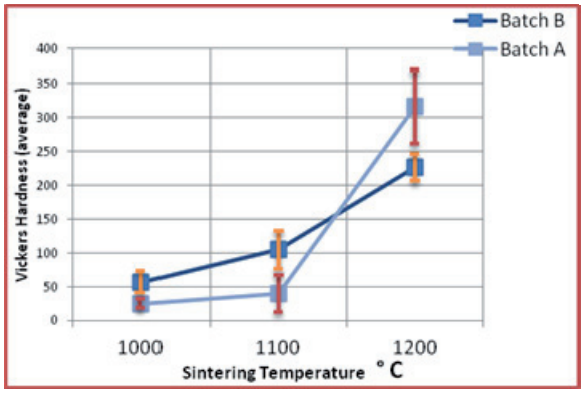

Fig. 7. Vickers Hardness vs. Sintering Temperature of two composition (A: with 15 wt. % TiO_2, B: with 10 wt. % TiO_2) [16]

Vickers hardness results can be seen in Fig. 7 [16] for both batches. At 1200°C, hardness for sample with 15 wt. % TiO_2 had rapidly increased and higher than the

sample with 10 wt. % TiO_2 due to the transformation of TiO_2 (anatase→rutile). However the result of compression strength test was 10 ± 1 MPa 10 wt. % TiO_2 and it was 7 ± 1 MPa for 15 wt. % TiO_2.

4. Conclusions

As conclusion, when all results have been compared, although the sample with 15 wt % TiO_2 has higher hardness values, the sample with 10 wt % TiO_2 have higher compressive strength values than the reference study [14]. HA/Bioglass®/TiO_2 composites are potential biomaterials to be used in bone filling and bone regeneration techniques.

These biocomposites can be good substitute for missing or damaged bones after supplementary in vivo testing. It is also suggested to evaluate these specimens in vitro tests in SBF (Simulated Body Fluid) solution where temperature is held constant at 37°C with continuous stirring to measure if weight gain will occur by time. This will indicate the possible osteointegration of the natural bone with the graft.

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