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Sintering effect on mechanical properties of composites of natural hydroxyapatites and titanium

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Abstract

This study presents the fabrication and characterization of composite materials of hydroxyapatite and Ti. Hydroxyapatite (HA) powder was obtained from bovine bones (BHA) and human enamel (EHA) via calcination technique. Fine powders of HA were admixed with 5 and 10 wt.% fine powder of metallic Ti. Powder-compacts were sintered at different temperatures between 1000 and 1300 °C. Compression strength, Vickers microhardness and elastic modulus as well as density were measured. SEM and X-ray diffraction studies were also conducted. The experimental results showed that addition of Ti to EHA and BHA decreases the elastic modulus, comparing to samples of pure BHA. The best mechanical properties for BHA–Ti composites were obtained after sintering in the range of 1200–1300 °C and for EHA–Ti composites in the range of 1100–1300 °C.

Keywords: A. Sintering; B. Microstructure; C. Mechanical properties; Hydroxyapatite; Titanium

1. Introduction

Living in the era of life control and prolongation, artificial implants of hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) are very popular in hard-tissue (e.g. bone) restorations because they accelerate bone growth around the implant. Biological apatites attract special interest since it is believed that the several substitutions at the Ca^{2+}, PO_4^{3-} and OH^- sites of HA and the presence of several trace elements play an important role in the overall physiological functioning and in the osseointegration process. The poor mechanical properties of biomaterials made of pure HA have directed HA-biomaterials' design to tissue-engineering approaches [1].

In particular, HA has received considerable attention as an implant material over the past two decades due to its excellent biocompatibility [2]. HA has been widely used for bone replacements in restorative dentistry and in orthopedic implants, due to its chemical and crystallographic structure, which is similar to bone mineral. HA is biocompatible [3], well accepted in human body and it features osteoconductive properties. Nevertheless, the mechanical properties of HA are poor, especially in wet environment. Therefore, ceramics of pure HA cannot be suggested for use in heavy-loaded implants, such as artificial bones or teeth. They can only be used at non-loading applications, such as graft materials. To improve mechanical reliability of HA-ceramics, i.e. to increase their fracture toughness, incorporation of metallic materials, ceramic oxides [4,5], whiskers, or fibers, have

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been suggested. Nevertheless, whiskers are not recommended in biomedical applications because of their potential carcinogenicity [6].

Titanium (Ti), which is the most biocompatible metal, is often combined with HA to improve mechanical properties [7]. Furthermore, the mechanical properties of Ti and its alloys are superior to bioceramics (e.g. HA), other ceramics and glasses. In order to develop high performance biomaterials for bone and teeth replacements, composites consisting of HA and Ti have been considered among the most promising groups of biomaterials [8].

There are several reports on HA that is plasma-sprayed on Ti and titania [9–11], but very few on sintered HA–Ti composite bodies. With regard to the latter case, Goller et al. [7] have suggested that the mechanical properties of sintered HA-composites do not improve with Ti-doping. On the other hand, recent studies have shown that Ti-containing HA-bioceramics where HA was derived from tooth-dentine (DHA), exhibit very good bioactivity. It has been postulated that Ti may induce increasing bioactivity in DHA [12,13].

In this study we present the production and characterization of HA–Ti composites, produced via sintering of powder compacts. Two different types of HA were used: bovine derived HA and tooth human enamel HA, designated as BHA and EHA, respectively. Ti-doping was 5 and 10 wt.%. Measurements of compression strength, microhardness, elastic modulus and density, along with microstructure observations and crystallographic analysis were carried out in the produced samples.

2. Materials and experimental procedure

The powders of HA, namely BHA and EHA, were obtained from bovine bones and human enamel, respectively, according to the methodology described in our earlier studies. To eliminate any risk of diseases' transmission, the powders were calcined at 850 °C in air. Accordingly, the biologically derived HA-powders used are very safe because they are produced via high temperature calcination method. Beyond safety, that production method is also very economic comparing to other time- and energy-consuming methods [14,15]. In the case of teeth, enamel matter was easily separated from dentine after calcination (human tooth comprises 40% enamel and 60% dentine [15]).

Each of the HA-powders (i.e. BHA or EHA) was mixed with 5 and 10 wt.% Ti fine powder. The HA/Ti mixtures were well homogenized in a planetary ball-mill. For comparison purposes (i.e. only for SEM observations), similarly prepared DHA/Ti mixtures were also produced. The powder mixtures were pressed in hardened steel dies, according to the British Standard 7253. The obtained powder compacts (in form of cylinders with diameter of 11 mm and height 11 mm) were sintered at different temperatures, i.e. 1000 °C, 1100 °C, 1200 °C and 1300 °C in a laboratory electric furnace (Protherm, Alserteknik Inc., Ankara, Turkey) in air for 4 h (heating and cooling rates were 4 °C/min). The DHA-Ti reference-samples were sintered at slightly different temperatures.

The measurements of the mechanical properties comprised compression-strength tests, carried out with a universal test machine (Instron-85111, UK), and Vickers microhardness (Leica VHMT, UK), which was also employed to determine the elastic moduli of the sintered composites (microhardness tester unit CSM, USA). The densification of the sintered samples was estimated with density measurements, conducted with a sensitive pycnometer (Quantachrome Ultrapycnometer 1000, USA). The set of characterization also comprised observation of the microstructure at randomly fractured surfaces (SEM, Jeol-JSM-5410, Japan, equipped with EDS elemental analysis equipment) and crystallographic analysis with X-ray diffraction (XRD, D8 Advance, Bruker-AXS, Germany).

3. Results and discussion

3.1. Densification and microstructure

The influence of sintering temperature on the density of the produced samples is presented in the plots of Fig. 1: (a) for BHA–Ti and (b) for EHA–Ti. According to the plots, one cannot point out a clear conclusion with regard to the influence of sintering temperature on densification of HA–Ti. The big difference between the density of Ti and HA may obscure the true trend of density over increasing sintering temperature in the plots of Fig. 1. Direct observation of the

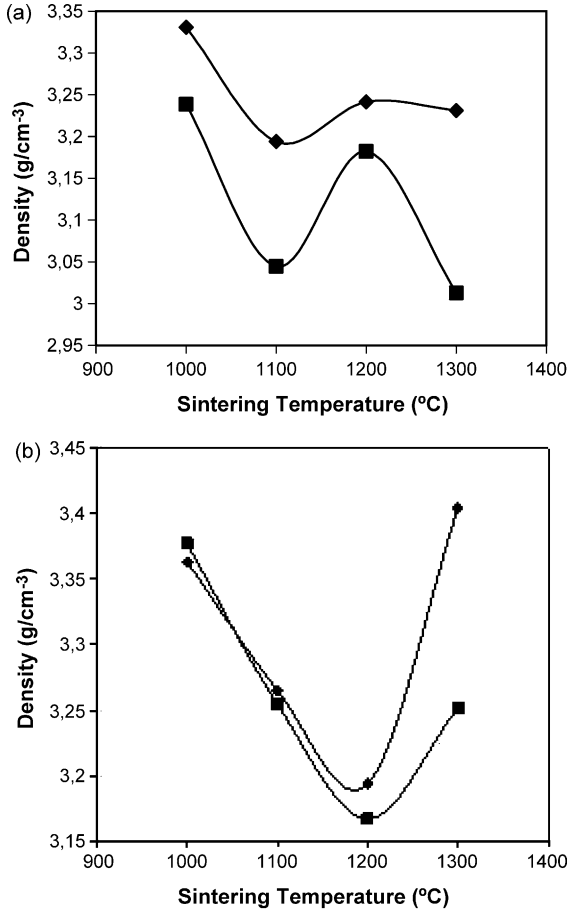

Fig. 1. Influence of density on sintering temperature for (a) BHA–Ti and (b) EHA–Ti composites with different Ti-contents (5% Ti (-■-) and with 10% Ti (-◆-)).

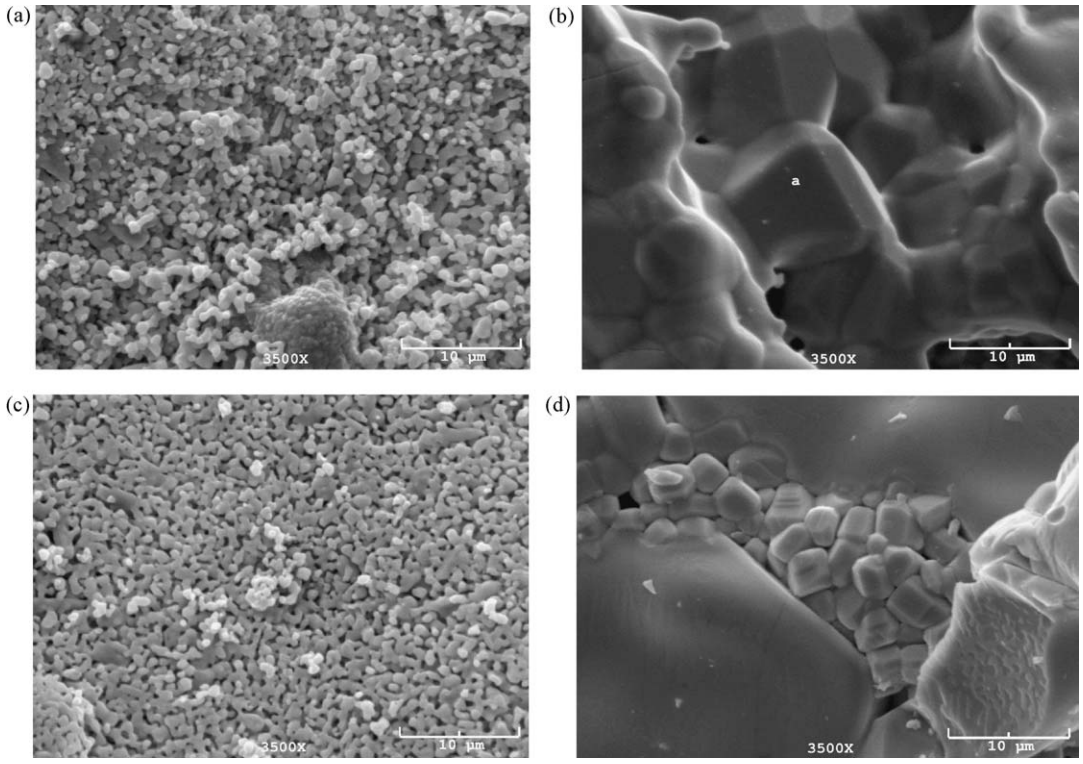

Fig. 2. SEM images of the 5% Ti–BHA composites sintered at 1000 °C (a), and 1300 °C (b), and 10% Ti–BHA composites sintered at 1000 °C (c) and 1300 °C (d).

microstructure of the sintered samples, typically presented in the SEM images of Figs. 2 (for BHA–Ti) and 3 (for EHA–Ti) (for BHA–Ti) and 3 (for EHA–Ti), reveal that trend. Specifically, a high densification regime is suggested after sintering at 1300 °C whereas rather poor densification characterizes the samples sintered at 1000 °C. These results agree fairly well with earlier similar studies on sintered HA composites with other dopant materials.

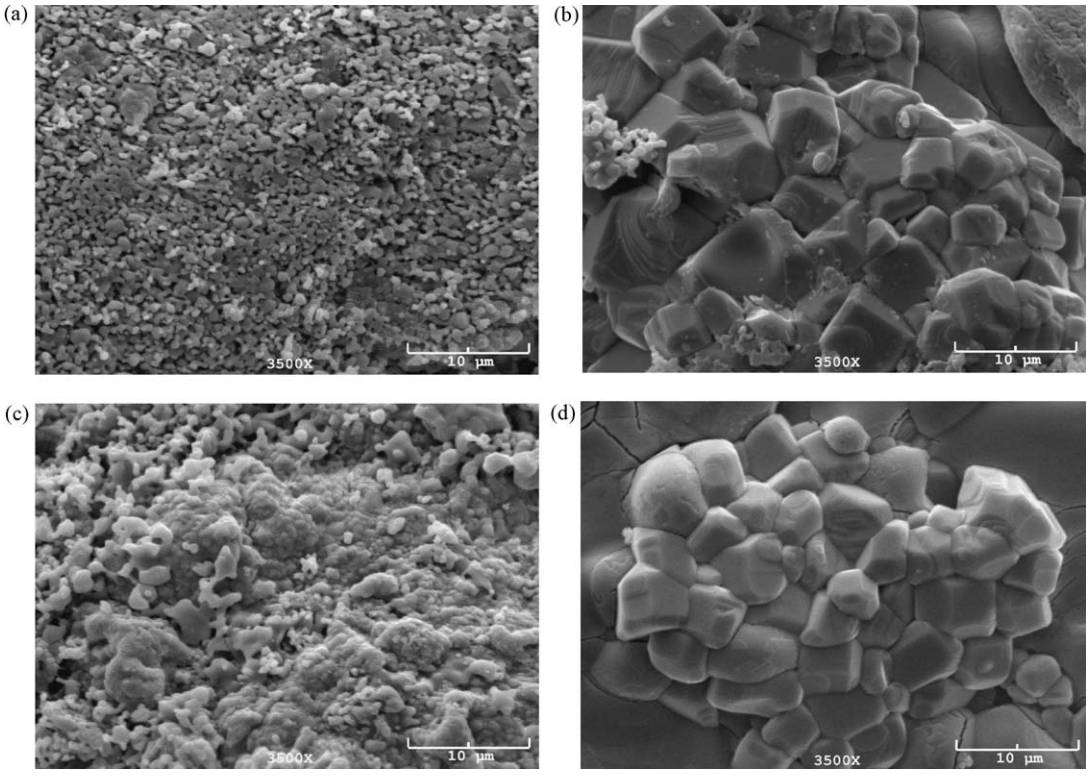

Fig. 3. Microstructure of 5% Ti-EHA composites sintered at 1000 °C (a) and 1300 °C (b), and 10% Ti–EHA composites sintered at 1000 °C (c) and 1300 °C (d).

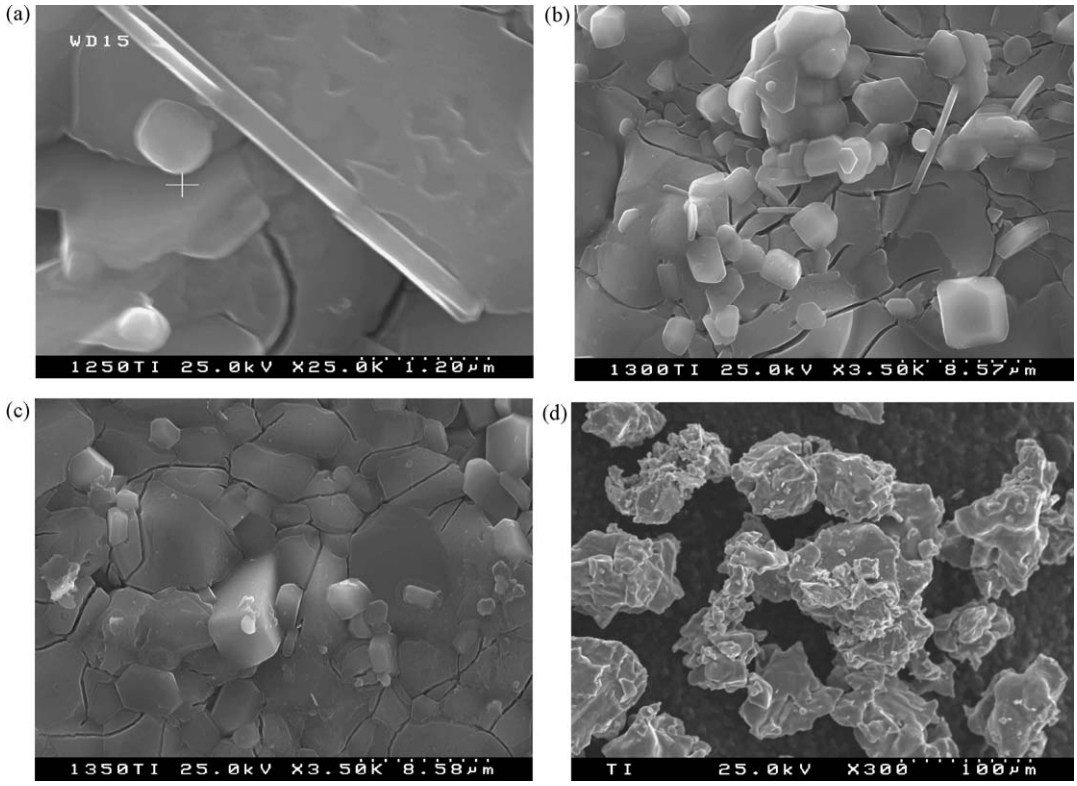

Fig. 4. SEM images of the 5% Ti–DHA composites sintered at 1250 °C (a), 1300 °C (b) and 1350 °C (c). Ti powder particles, used for the production of the BHA–Ti, EHA–Ti, and DHA–Ti composites, are shown in (d).

A peculiar microstructure was observed after sintering at 1300 °C (Figs. 2 and 3). In particular, at that high temperature, cubic-like configurations developed. Similar configurations were also observed in the SEM images of Fig. 4a–c, which correspond to DHA–Ti powder-compact composites sintered at 1250 °C, 1300 °C, and 1350 °C, respectively. An EDS elemental spot-analysis at the middle area of a cube of Figs. 2 and 3 yielded (in wt.%) O 41.39, Ca 26.89, and Ti 31.71. The (apparently glassy) matrix has an elemental composition of O 33.28, P 23.33, Ca 42.64, and Ti 0.75. EDS analysis near the rounded particles of Fig. 4c yielded O 62.31, Al 1.05, P 2.32, Ca 19.04, and Ti 15.27, while the analysis at the elongated structures was O 60.92, Al 2.60, P 4.00, Ca 19.69, and Ti 12.78. Accordingly, the observed cubes are Ti-rich and their development should be related to the presence of Ti in the matrix of HA. To the knowledge of the authors, there is no study reporting a similar extensively formed configuration, including the Refs. [7,16]. In the light of the results of earlier studies and also taking into account the totally different shape and size of the Ti-particles of the Ti-powder shown in Fig. 4d, it might be suggested that the observed Ti-rich cubes likely form in the HA-matrix at temperatures higher than 1200 °C.

3.2. Mechanical properties

The experimental results of compressive strength and Vickers microhardness of the samples of the BHA–Ti and EHA–Ti composites are listed in Table 1. Using the results of Table 1, the influence of sintering temperature on compressive strength and Vickers microhardness is plotted in the four plots of Fig. 5. For comparison purposes, the corresponding values of DHA–Ti composites as they have been reported in an earlier

Table 1
Experimental results of compression strength (σ in MPa) and Vickers microhardness (in HV) of the samples of the composites of BHA–Ti and EHA–Ti sintered at different temperatures.

T (°C)	BHA–Ti				EHA–Ti				DHA-Ti [7]			
	5% Ti		10% Ti		5% Ti		10% Ti		5% Ti		10% Ti	
	σ	HV	σ	HV	σ	HV	σ	HV	σ	HV	σ	HV
1000	17.12	14.49	23.90	13.44	19.39	39.76	15.65	40.13	–	–	–	
1100	20.49	17.51	24.01	27.09	41.70	60.10	41.56	53.70	–	–	–	
1200	44.65	69.77	48.83	93.43	43.30	97.90	39.96	74.70	16.96	80	11.31	91
1300	50.47	166.4	53,29	235.44	46.81	135.00	48.18	123.20	17.56	149	32.10	204

For comparison purposes, similar results of DHA–Ti composites, reported in an earlier study [7], are also presented.

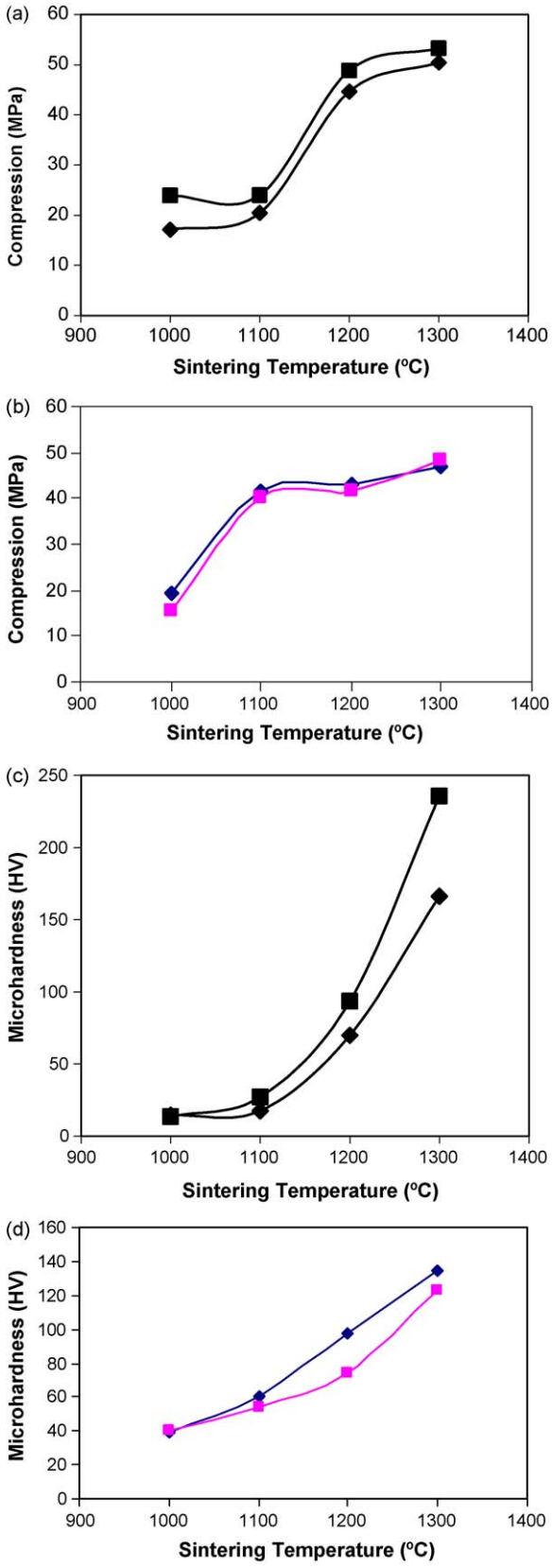

Fig. 5. Influence of sintering temperature on the compression strength (a and b) and Vickers microhardness (c and d) of samples of BHA–Ti (a and c) and (b) EHA–Ti composites (b and d) (5% Ti (-◆-) and with 10% Ti (-■-)).

study [7] are also presented in Table 1. To shed light in the influence of Ti on the mechanical properties of HA-matrix, Table 2 presents the corresponding mechanical properties of BHA and HA samples sintered at the same temperatures, as they have been reported in earlier studies [20–25]. Table 3 completes the experimental results of the mechanical properties of this work and presents the values of E modulus of BHA–Ti and EHA–Ti composites together with the values of pure BHA samples, used as a control-group.

The experimental results show that the compression strength of the BHA–Ti composites is nearly 5% higher than the EHA–Ti for all cases after sintering at 1200–1300 °C. Similar conclusions can be also drawn out for the microhardness of the samples sintered at 1300 °C (for 10% Ti). However, the results of the present work are much better (i.e. more than twice) than the reported values for DHA–Ti composites [7]. With respect to pure BHA, the presence of Ti in the BHA and EHA matrices causes a decrease of elastic modulus of the resultant composite materials. Accordingly, the experimental results of this study qualify the investigated BHA–Ti and EHA–Ti composites for further *in vitro* experimentation by means of cell-cultures.

Several studies have aimed at reinforcing of HA with the aid of various metallic particles and fibers. Zhang et al. have used silver particles for toughening HA [17], but the biocompatibility of silver in human body may be a question mark. Miao et al., Pernot and Rogier, and De With Corbijn have also used various metallic fibers [6,18,19].

With regard to the matrix itself, a recent study has demonstrated the superiority of mechanical properties when the source of HA was EHA, attributed to the F-content of enamel (F ions, accommodated in the lattice of HA, cause reinforcing of the lattice of HA) [23]. As far as the reinforcing phase is concerned (i.e. Ti), there is no study on the influence of Ti on the mechanical properties of HA–Ti sintered bodies, except the study of Goller et al. on DHA–Ti [7]. Ti, which is very popular in dental implant applications [8], can reinforce HA plasma-spray coatings, which exhibit high resistance in tensile strength tests. In an attempt to improve bioactivity, HA–Ti composites were produced with a very high weight ratio of 50:50 [3]. Nakahira and Eguchi [8] have reported results of SEM and XRD analyses of HA–Ti composites sintered at temperatures between 800 °C and 1000 °C, where Ti-content was 20–25 vol.%, but there is no information about the mechanical properties of the produced composites.

3.3. Crystallographic analysis

Beyond densification, the mechanical properties reported in Table 1 should be also a result of the crystalline phases formed after sintering of the BHA–Ti and EHA–Ti composites. The results of the crystallographic analysis of the produced samples, carried out with X-ray diffraction, are summarized in Fig. 6. In all cases, the diffractograms have predominantly registered the phase of whitlockite ($Ca_3(PO_4)_2$, JCPD card no. 09-169). Weaker peaks, assigned to secondary phases of titanium dioxide (TiO_2, JCPD card no. 99-0090) and perovskite ($CaTiO_3$, JCPD card no. 22-053),

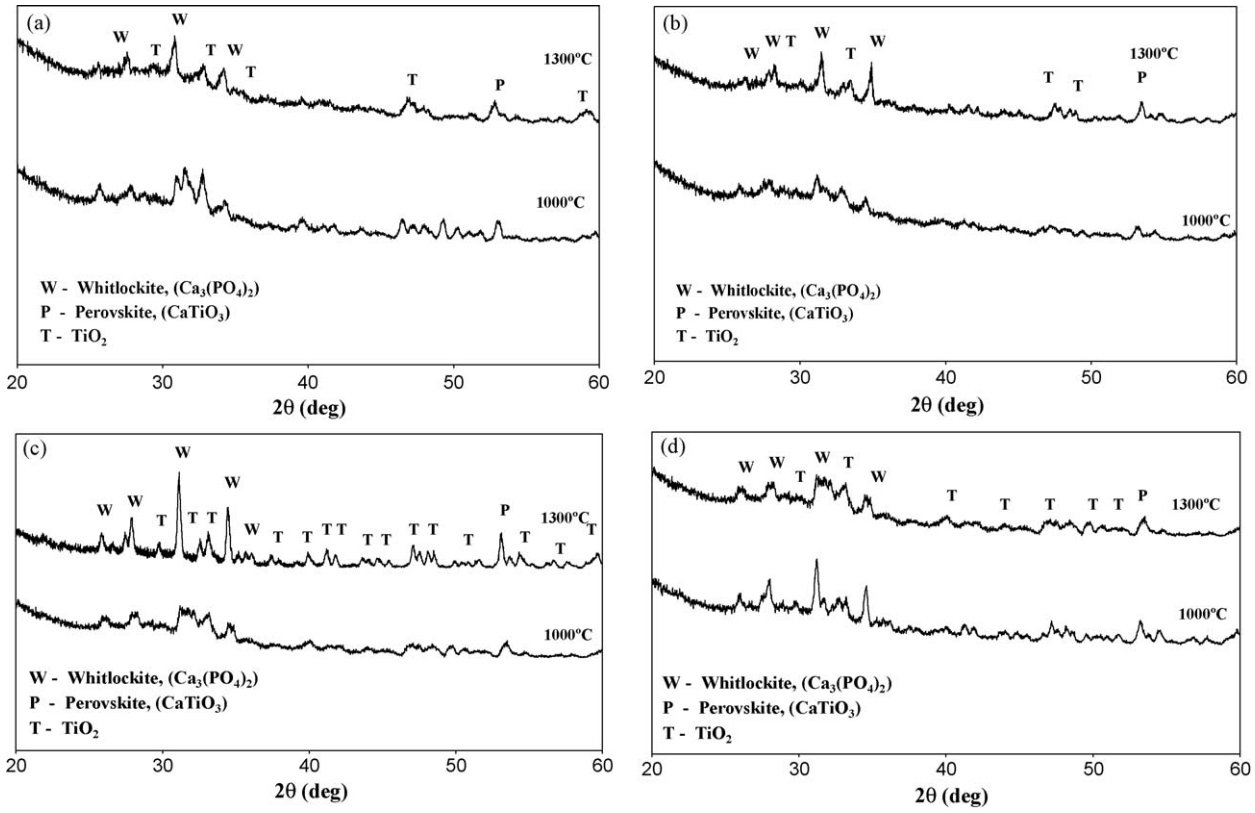

Fig. 6. X-ray diffractograms of (a) 5% Ti–BHA, (b) 10% Ti–BHA, (c) 5% Ti–EHA, and (d) 10% Ti–EHA composites sintered at 1000 and 1300 °C.

Table 2
Experimental results of compression strength (σ in MPa) and Vickers microhardness (in HV) reported in earlier studies [20–22,24,25] for BHA and HA samples sintered at different temperatures.

T (°C)	BHA [20]		BHA [21]		HA [22]		BHA [24–25]	
	σ	HV	σ	HV	σ	HV	σ	HV
1000	12 ± 2	42 ± 2	13.66 ± 0.13	44.14 ± 4.66	18.48	118	48.17 ± 20.02	85.37 ± 9.43
1100	23 ± 3	92 ± 4	20.92 ± 0.51	76.82 ± 2.45	30.42	162	22.16 ± 5.09	74.20 ± 19.80
1200	67 ± 7	138 ± 3	39.22 ± 1.46	147.3 ± 7.28	28.85	336	75.20 ± 18.30	148.50 ± 10.50
1300	62 ± 11	145 ± 3	63.03 ± 1.56	281.8 ± 4.71	29.13	360	65.01 ± 41.57	130.68 ± 17.90

Table 3
Elastic modulus determined from hardness measurements for BHA–Ti and EHA–Ti composites. Samples of pure BHA were used as control group.

T (°C)	BHA	E modulus (GPa)			
		BHA–Ti		EHA–Ti	
		5%	10%	5%	10%
1000	36	15	26	16	9
1100	19	13	13.5	36.8	7.3
1200	7	7	39	34.2	20.2
1300	90	30	22.5	22	29.2

were also registered. Apparently, the former phase should be attributed to the oxidation of Ti and the latter to the reaction of HA with Ti. There was no evidence of remaining intact metallic Ti. The Ti-content slightly affects the intensity of the peaks of the secondary phases. Accordingly, the Ti-rich cube-like configurations of the SEM images of the samples sintered at 1300 °C (Figs. 2 and 3) should be related to the aforementioned secondary phases of TiO_2 and $CaTiO_3$. Valeiro et al. [12] and Sampaio et al. [13] have suggested that some Ti compounds, developed after sintering of DHA powder compacts doped with 5% Ti at 1300 °C, may play a vital role at osteoblast formation.

4. Conclusions

The produced BHA–Ti and EHA–Ti composites exhibited much better mechanical properties, namely compressive strength and microhardness, than the reported values of similarly prepared DHA–Ti composites. The best mechanical properties for BHA–Ti composites were obtained after sintering in the range of 1200–1300 °C and for EHA–Ti composites in the range of 1100–1300 °C. With respect to pure BHA, addition of Ti to EHA and BHA results in decreasing of the elastic modulus of the resultant composite.

The above experimental findings should be result of densification level, the microstructure and the phases developed after sintering. Under that perspective, the produced composites predominantly comprise whitlockite. Secondary phases, associated to the reaction of Ti with HA and the oxidation of Ti, were also registered. Sintering at 1300 °C caused accumulation of Ti in aggregations of cube-like configurations, which should be associated to the secondary crystalline phases registered in the diffractograms.

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