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Study of the microstructure and mechanical properties of beta tricalcium phosphate-based composites with alumina addition produced by powder metallurgy

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Abstract

The use of alumina as a reinforcement in metallic and ceramic matrix is well-known. The purpose of this study was to investigate the effect of alumina addition according to its amount on the microstructural and mechanical behavior of tricalcium phosphate ceramic (TCP), more specifically the β-TCP. Although β-TCP has excellent bioactive and biocompatible properties, it presents low fracture resistance and load bearing capacity, which limits its use in the monolithic form. The route used for the β-TCP/alumina composite production was powder metallurgy. The powders were milled in a high energy ball mill with the following parameters: 5, 10, 15 and 20 hours, mass/sphere relation of 1:20 and speed of 150 rpm. After the milling process, the powders of both compositions were uniaxially pressed and sintered. Two of the compositions were processed containing 90% and 50% of β-TCP, respectively. The results indicated that composition 1 with a smaller percentage of alumina in its microstructure presented 62.4 % smaller particle size after the high energy ball milling process, which provided higher densification after pressing and sintering. These results implied in increased mechanical resistance, with 4.6 GPa of elastic modulus and 140 MPa of compressive strength, against 3.6 GPa of elastic modulus and 117 MPa of compressive strength obtained in composition 2.

Keywords: beta tricalcium phosphate, alumina, composites, powder metallurgy.

1. Introduction

The calcium phosphate ceramics (CPCs) are a class of biocompatible and bioactive materials often used as synthetic bone substitute. It happens due to the great similarity that they have with the mineral phase of the bone. The four CPCs more commonly used are: Hydroxyapatite (HAP), amorphous calcium phosphate (ACP), biphasic calcium phosphate (BCP) and tricalcium phosphate (TCP). The TCP occurs in two different phases, α and β. However, β-TCP is more widely used in bone regeneration than α-TCP (Parent *et al*., 2017; Dorozhkin and Epple, 2002).

Despite the excellent bioactive and biocompatible properties, the CPCs have low fracture resistance and load bearing capacity, which limits their use in the monolithic form. While the CPCs present Young's modulus corresponding to a range of 35-120 MPa, the bone tissue has superior value of 300 MPa. Since CPCs must have mechanical resistance as similar as possible to the surrounding tissue, it is recommended to increase its mechanical properties to avoid failure. Thus, to increase the CPCs load bearing capacity and resistance, other biocompatible materials are used as reinforcement. In short, most imitations of bioactive CPCs powders refer to its low fracture toughness which can restrict its biomedical application as, for example, in the production of load bearing implants (Canillas *et al*.,2017; Shirazi *et al*., 2015).

Therefore, an approach to increase the CPCs mechanical properties is to incorporate alumina as a second ceramic phase dispersed in the matrix. The alumina in its α phase is a bioinerte

material widely used as reinforcement, especially as a result of its high hardness combined with good flexion resistance, excellent dynamic, impact fatigue, subcritical cracking and compression resistance. In fact, the alumina particles can increase the HAP hardness, demonstrating the role of reinforcement (Bhattacharyya and Behera, 2017; Yan *et al.*, 2017; Askari *et al.*, 2012).

The powder metallurgy (PM) is a suitable technique for metallic matrix composite fabrication. Also, it can be used in the confection of ceramic matrix composites. In comparison with the traditional melting process, one of the most prominent advantages related to PM is the low process temperature, which prevents the formation of undesirable phases between the matrix and the reinforcement. In addition, the reinforcement particles can be found homogeneously distributed in the matrix, providing better mechanical results. Other advantages of PM include less cost for large scale production, the possibility to create workpieces in various shapes, and practically no waste of materials, being also considered a clean process. The process includes the powders obtainment, compaction of those powders in a die and sintering over a controlled atmosphere. Through sintering, the powders acquire mechanical strength through atomic diffusion (Bolzoni *et al.*, 2017; Kuffner *et al.*, 2015; Suryanarayana, 2001; Nassar and Nassar, 2017).

However, little research has been destined to investigate the effective role of bioinert materials as an addition in bioactive materials in terms of mechanical behaviour. As a result, this work evaluated the influence of alumina addition and its amount in the microstructure and mechanical properties of β-TCP based composites produced by powder metallurgy.

2. Materials and methods

For the biocomposites production used were: Beta tricalcium phosphate (β-TCP) and alumina (Al_2O_3), both as powder. Table 1 details the materials percentage for each composition.

Composition	β-TCP	Al_2O_3
1	90%	10%
2	50%	50%

Table 1
Compositions used in the biocomposites production.

In the high energy ball milling process of the compositions, a Noah Nuoya® 0.2 L planetary ball mill was used. The parameters used in the milling include mass/sphere relation of 1:20, speed of 150 rpm and times of 5, 10, 15 and 20 hours. After the milling process, the powders were uniaxially pressed with 175 MPa of pressure in a cylindrical matrix with diameter of 12 mm and sintered in a Fortelab® conventional atmosphere oven. The heating rate used was 5°C/minute until 1200°C, with 2 hours of permanence.

For the powders and sintered samples characterization, a Microtrac® Turbotrac SDC laser granulometer, a Carl Zeiss® Evo MA 15 scanning electron microscope in the back-scatter mode, a Panalitycal® X Pert PRO x-ray diffractometer with copper tube (λ = 1,5418 Å) with scanning of 0.02° and 2θ = 10° a 90° and a EMIC 23-30 universal testing machine were used.

3. Results and discussion

Figure 1 shows compositions 1 and 2 after 5 hours of milling. It is possible to observe that composition 1 with 90% β-TCP (Figure 1a) presented particles located in a range of 8 – 0.4 µm, while composition 2 with 50% β-TCP (Figure 2a) presented a range of 11 – 0.5 µm. Both compositions obtained predominantly irregular particle morphology, with cluster formation, being this more pronounced in composition 2.

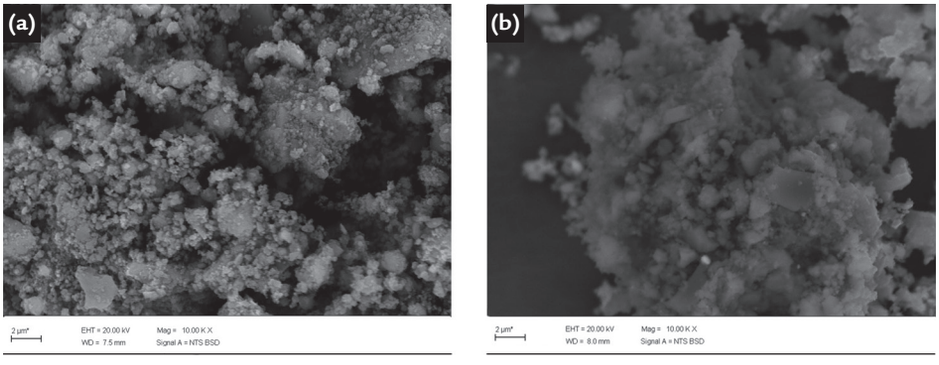

Figure 1
Photomicrographs of compositions 1 (a) and 2 (b) after 5 hours of milling.

After 10 hours of milling, it is observed that the particles of composition 1 (Figure 2a) suffered granulometric reduction, changing their size from a range of 8 – 0.4 µm (5 hours of milling) to 7 – 0.3 µm (10 hours of milling). Composition 2 (Figure 2b) also obtained reduction, from a range of 11 – 0.5 µm (5 hours of milling) to 9 – 0.5 µm. The particle morphology maintained irregular for both compositions, being observed in composition 1 a higher volume of clusters in comparison with composition 2 which had significantly reduction in this volume.

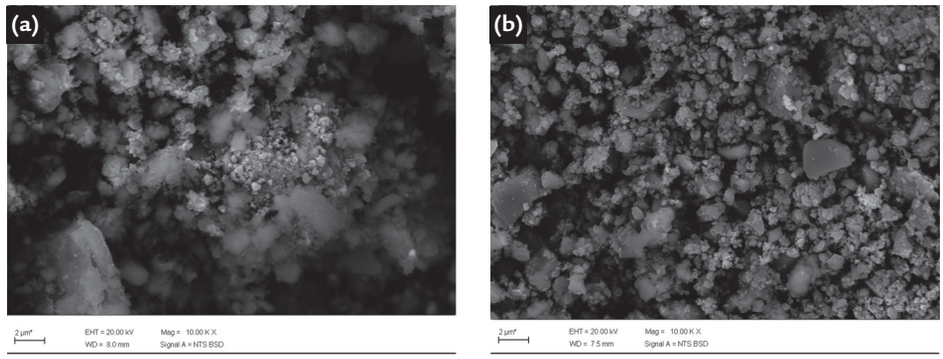

Figure 2
Photomicrographs of compositions 1 (a) and 2 (b) after 10 hours of milling.

Increasing the milling time to 15 hours, it is observed that the particle size of both compositions continued to reduce. In composition 1 (Figure 3a), the particle size was located in a range of 3 – 0.3 µm, smaller than the range of 7 – 0.3 µm with 10 hours of milling. Composition 2 (Figure 3b) obtained a particle size in a range of 4 – 0.3 µm, also smaller than 9 – 0.5 µm obtained with 10 hours of milling. The morphology was maintained irregular for both compositions, being composition 1 the composition that still obtained higher cluster volume. However, a higher homogeneity is noted in the particles distribution for both compositions, in comparison with 5 and 10 hours of milling.

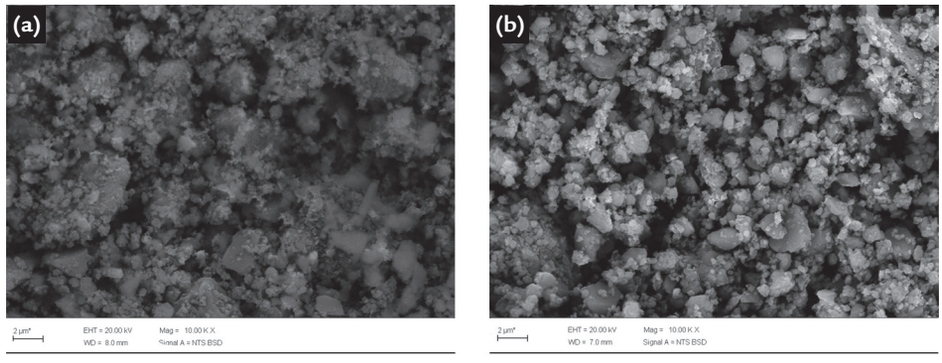

Figure 3
Photomicrographs of compositions 1 (a) and 2 (b) after 15 hours of milling.

For the last milling time, corresponding to 20 hours, it is possible to observe that composition 1 (Figure 4a) obtained a final particle size in a range of 3 – 0.1 µm and composition 2 (Figure 4b) obtained a final particle size in a range of 4 – 0.3 µm. This result evidences the efficiency of the high-energy milling process to reduce the granulometry of both compositions, being very notable the difference of particles size from 5 hours to 20 hours of milling time (from 8 – 0.4 µm to 3 – 0.1 µm in composition 1 and from 11 – 0.5 µm to 4 – 0.3 µm in composition 2). The particle morphology was maintained irregular and composition 1 presented a higher volume of clusters during the whole process

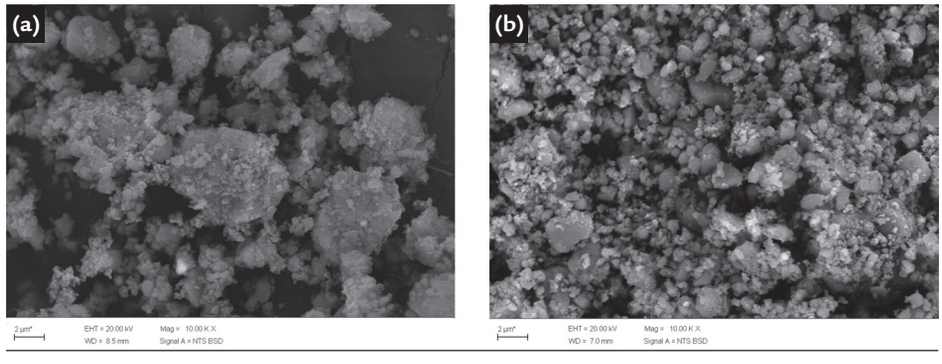

Figure 4
Photomicrographs of compositions 1 (a) and 2 (b) after 20 hours of milling.

At the end of the process, it is verified that the high energy ball milling of both compositions was shown as efficient, since that resulted in significantly granulometric reductions. Over the 20 hours of milling, the particles of larger size got 63% of reduction for both compositions 1 and 2, being that first, composition 2 presented particles in higher scale. For the particles of smaller size, there was observed a reduction of 75 % for composition 1 and 40 % for composition 2. Besides the granulometry, it is also noted through the micrographs that for all milling times, a few particles presented larger size than their medium values, which is attributed to the notable cluster presence formed due to the high tensions and cold welding that the material suffered in the high energy ball milling process (Suryanarayana, 2001). In general, it is verified that composition 1 proved to be more effective in the particles size reduction than composition 2, for presenting smaller granulometry for all milling times. This result is proven also through the laser granulometry test, which shows the volumetric fraction versus particle volume for the final milling time of 20 hours. Figures 5 and 6 show, respectively, the curves of particle size distribution for composition 1 and composition 2.

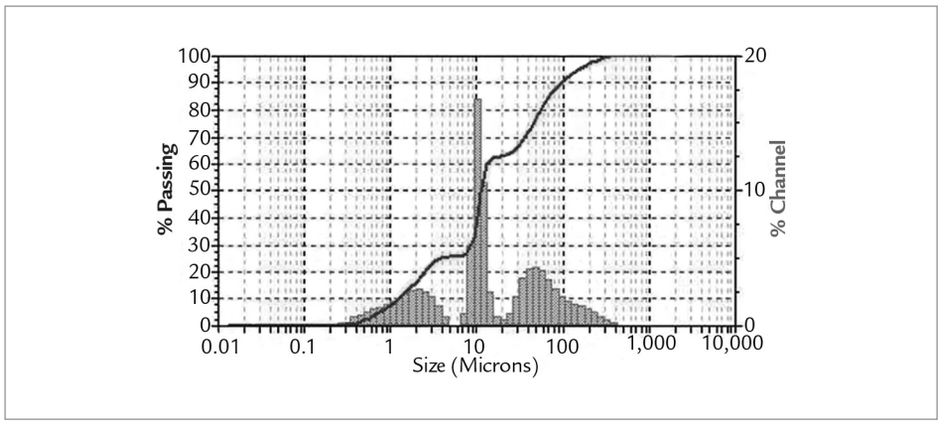

Figure 5
Particle size distribution curve for composition 1 after 20 hours of milling.

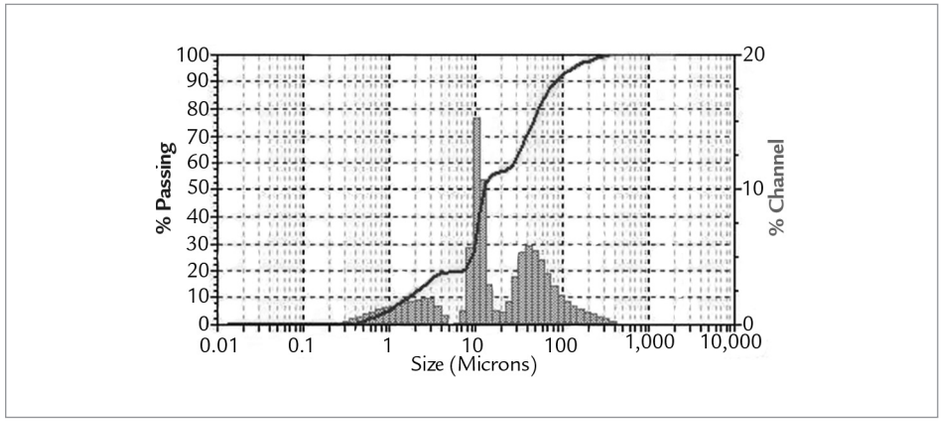

Figure 6
Particle size distribution curve for composition 2 after 20 hours of milling.

The results obtained in both granulometric curves are also resumed in Table 2.

Particle Size	Composition 1	Composition 2
50 – 60 µm	37.6 %	44.5 %
11 µm	36.6 %	35.9 %
1.5 µm	25.8 %	19.6 %

Table 2
Volumetric fraction versus particles volume for each composition.

It is possible to observe by the presented results that composition 1 presented a higher percentage of particle volume in the range of 11 µm (0.7 %) and 1.5 µm (6.2 %) and a smaller percentage of particle volume in the range of 50 – 60 µm (6.9 %) in comparison with composition 2. This is beneficial, since that higher particles volume in submicrometer or nanometric scale implies in better composite densification.

Table 3 shows the values found for density, elastic modulus and ultimate tensile strength. These results prove again that composition 1 presented higher efficiency during the process. Its density was shown as 10.68% higher than the density found in composition 2. In respect to the tensile test, composition 1 presented elastic modulus value of 21.74 % and compressive strength 16.3 % higher than composition 2.

Composition	Density (g/cm³)	Elastic Modulus (GPa)	Compressive Strength (MPa)
1	2.34	4.6	140
2	2.09	3.6	117

Table 3
Mechanical properties values for each composition.

Composition 1 is justified as more effective in terms of mechanical properties as a result of two main factors. First of all, its smaller particle size (higher volume in submicrometer scale) obtained in the high energy ball milling process provided better compaction during pressing and better densification after sintering, since the diffusional process becomes facilitated due to the larger superficial area of the powders and consequently, larger contact between particles. The second factor that occurs is that, increasing the alumina percentage in composition 2, the sintering becomes compromised, since alumina percentages above 10 wt. % result in the worst sintering and consequently, reduction in mechanical resistance. This is attributed to the fact that the alumina sintering temperature (1700 °C) is much higher than the β-TCP sintering tempera-

ture (1050 °C), which forces the composite to be sintered according to the material with lower sintering temperature. The lower temperature creates a pre-sintering phase formed by alumina, which weakens the material. Thus, the composition with a higher percentage of alumina obtains the worst sintering and mechanical behavior (Eskandari *et al*., 2012; Rahimiam *et al*., 2010; Li *et al*., 2017).

Even with these two factors, the alumina addition in different percentages proved to be satisfactory as reinforcement in beta tricalcium phosphate-based composites. Comparing the values obtained in Table 3, it is possible to highlight that the density (2.34/2.09 g/cm³), elastic modulus (4.6/3.6 GPa) and compressive strength (140/117 MPa) of both compositions were smaller from those found in the precursor materials (3.07/ 3.9 g/cm³), (80/400 GPa) and (650/2800 MPa). This is a consequence of higher pore volume that materials produced by powder metallurgy usually have. For biomaterials, porosity is a desirable property. Porous materials present a rough surface, which have been proved to promote higher osseointegration than materials with smooth surface. It happens as a result of the biological response of macrophages over the biomaterial. Macrophages are body cells which induce bone growth, and their response is scientifically proved as better in biomaterials with pores and consequent rough surface, such as those produced by the powder metallurgy route (Silva *et al*., 2014; Silva, 2001; Anderson *et al*., 2016).

4. Conclusions

The powder metallurgy was shown as an effective route to produce beta tricalcium phosphate–based composites with alumina addition. From the two compositions studied in this work, the composition 1 with smaller percentage of alumina presented itself as most effective, since it demonstrated better results for particles size, and consequently, mechanical resistance.

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