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Preparation and Characterization of Stainless Steel 316L/HA Biocomposite

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The austenitic stainless steel 316L is the most used metallic biomaterials in orthopedics applications, especially in the manufacture of articulated prostheses and as structural elements in fracture fixation, since it has high mechanical strength. However, because it is biologically inactive, it does not form chemical bond with bone tissue, it is fixed only by morphology. The development of biocomposites of stainless steel with a bioactive material, such as hydroxyapatite – HA, is presented as an alternative to improve the response in the tissue-implant interface. However significant reductions in mechanical properties of the biocomposite can occur. Different compositions of the biocomposite stainless steel 316L/HA (5, 20 and 50 wt. (%) HA) were prepared by mechanical alloying. After milling the powders for 10 hours, the different compositions of the biocomposite were compacted isostatically and sintered at 1200 °C for 2 hours. The mechanical properties of the biocomposites were analyzed by compression tests. The powders and the sintered composites were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Keywords: *biocomposite, stainless steels 316L, hydroxyapatite, mechanical alloying*

1. Introduction

Metallic materials are often used as biomaterials for replacing structural components of the human body because when are compared to ceramic and polymeric materials, they have superior mechanical properties. Among the metallic biomaterials, Co-Cr alloys, Ti pure and Ti alloys and stainless steel 316L are the most used[1-3]. They have tensile modulus very high (112 GPa and 220 GPa, respectively) compared to the cortical bone (15 to 30 GPa). Studies have been made to reduce this difference in elastic modulus[4].

Stainless steels are characterized by corrosion resistance higher than other steels due to the formation of a passive oxide film. That film reduces the corrosion rate by blocking the transport of metallic ions and electrons. The stainless steels are classified into three categories according to their microstructures: ferritic, martensitic and austenitic. Among them, the austenitic stainless steels (face centered cubic structure, nonmagnetic) which contains Cr (16-18 wt. (%)) and Ni (12-15 wt. (%)) in its composition are responsible for increasing corrosion strength and ensure the stability of the austenitic phase, respectively[5,6].

According to the interfacial response caused by biological interactions between the implant material and adjacent tissue, stainless steels are classified as biotolerable material being not able to form chemical bond with the bone. When the materials is implanted, occurs the formation of a fibrous tissue capsule around the implant with variable thickness, which depending on the amount of relative movement can lead to deterioration of the implant functions or damage in the tissue at interface[7].

An alternative to improve the response at the tissue-implant interface is the development of stainless steel 316L biocomposites with a bioactive material, such as hydroxyapatite (HA: $Ca_{10}(PO_4)_6(OH)_2$)[8-10]. The HA has been widely used for biomedical applications, such as synthetic bone graft and scaffold for tissue engineering. The HA has an excellent biocompatibility and bioactivity due to its chemical composition and crystallographic structure which are similar to the mineral phase of the bone. However, its poor mechanical properties are the main limitation to its use as a load-bearing implant[11].

Several composites of HA, including metal–HA have been studied[12-14]. A biocomposite based on HA reinforced with Ti particles[14], fabricated by hot-pressing, showed a higher fracture toughness, bending strength, work of fracture and lower elastic modulus, when compared to pure HA bioceramics manufactured under the same conditions. This is more suitable for biomedical applications. Furthermore, this biocomposite could be partially integrated with newborn bone tissues and fully osteointegration was obtained. The addition of stainless steel to HA has resulted in improvement of toughness and strength of pure HA. The addition of HA to stainless steel increased the biocompatibility, corrosion resistance and especially hardness and wear resistance of stainless steel[9].

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One of the routes used to obtain biocomposites metal-ceramic it is a powder metallurgy (PM) route. The products obtained by PM have mechanical strength, chemical and physical properties equal or higher than those obtained by other techniques[15,16]. The porosity obtained in materials produced by PM route can be seen as a positive factor because allows the growth of tissue on the surface of the pores or through the implant. Thus, better mechanical properties can be obtained since it is possible occur the interlacement between implant and new tissue[7].

This work aims to prepare the composite stainless steel 316L/HA by powder metallurgy route and to characterize its microstructure and mechanical properties.

2. Experimental

The HA powder was prepared by wet precipitation using reagents calcium-nitrate – $Ca(NO_3)_2.4H_2O$ and phosphoric-acid – H_3PO_4. The acid solution of 0.4 mol.L^{-1} was added with flow control to the basic solution of 0.6 mol.L^{-1} previously heated to 30 °C under constant agitation. The solution pH was controlled by the addition of NH_4OH and remained around[8,9]. The precipitate was aged for a period of 24 hours, subsequently the solution was filtered and the precipitate was dried at 80 °C. Then, the dry powder was calcined at 900 °C for 2 hours. All reagents used in the synthesis were from VETEC Química Fina, Brazil. The stainless steel powder was produced by gas atomization and supplied by Hoganas company. The HA powder was mixed with 316L stainless steel in the following proportions 95:5 wt. (%), 80:20 wt. (%) and 50:50 wt. (%). The homogenization of the powders was performed in a planetary ball mill (Fritsch®, model Pulverisette 5), at 120 rpm for 10 hours with a ball to powder weight ratio of 10:1. The milling was performed using steel balls with 18 mm diameter and stainless steel vessel (250 mL). The solution of zinc stearate lubricant 0.5% vol. in relation to the material added in the jar for grinding. The powder mixture was consolidated by uniaxial compression under constant pressure of 32 MPa, (in order to provide a pre form in the specimens to be submitted to hydrostatic pressing) and subsequently by isostatic pressing with 200 MPa. The scanning electron micrographs of the powder particles of HA and 316L stainless steel are shown in Figure 1, respectively.

The compacted samples were sintered at 1200 °C/2 hours in vacuum with heating rate of 10 °C/min in a resistive furnace. Cooling was performed to room temperature at rate of 30 °C/min at room temperature (25 °C)

The apparent density of investigated samples was calculated from the mass and dimensions of six samples for each composition of the biocomposite. Total porosity (ε) was estimated from relation between the theorical density of the powders ($\rho_{t\text{-}HA}$ = 3.16 g.cm^{-3} and $\rho_{t\text{-}316L}$ = 8.0 g.cm^{-3}) and the apparent density according to Equation 1.

$$\varepsilon = (1 - \rho_G/\rho_t) \quad (1)$$

where ρ_G and ρ_t are the apparent density (g.cm^{-3}) of the powders and the theorical density (g.cm^{-3}), respectively.

The HA powder and 316L stainless steel were characterized by X-ray diffraction (Shimadzu® XRD-6000) using Cu-Kα radiation (λ = 1.5406 A) employing a scanning rate 0.2 s^{-1} and 2θ ranging from 10 to 80°. The morphology of the powders after grinding and microstructural features of sintered samples was analyzed by scanning electron microscopy-SEM (Zeiss® microscope model EVO-MA10). For mapping analysis, it was used the technique of EDS (Energy Dispersive Spectroscopy).

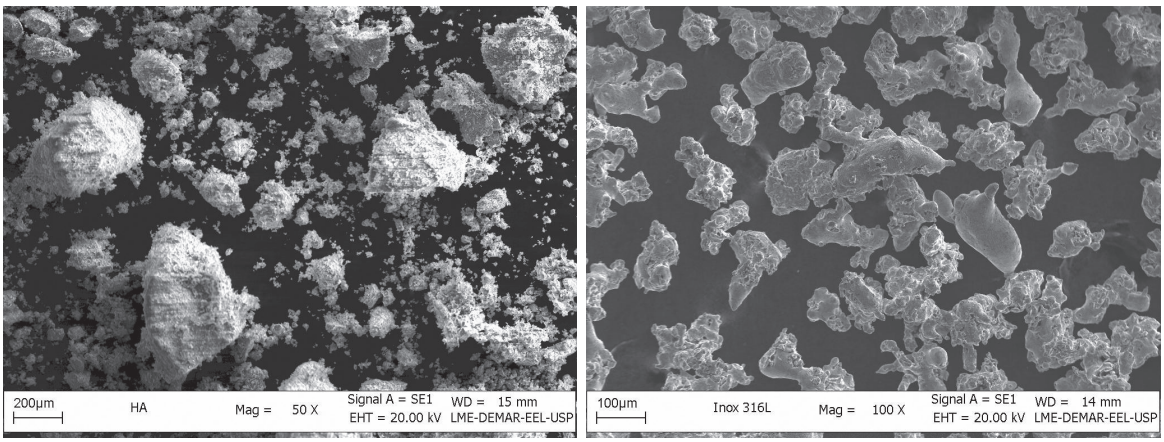
The mechanical strength was determined using the diametral compressive strength, according to ASTM C 496-90 standard, in a universal test machine-MTS® with loading speed of 0.5 mm/min. For each composition it was used six cylindrical samples (10 mm diameter and 4 mm height). The stress fracture was calculated by Equation 2

$$\sigma = 2F/\pi hD \quad (2)$$

where: σ (ultimate stress) is the rupture tension (Pa), *F* is the rupture load (N), *h* is the height (m) e *D* is the diameter of the test specimens (m).

3. Results and Discussion

Figure 2 shows the X-ray diffraction patterns of raw materials used in the preparation of biocomposites. The



(a) (b)

Figure 1. SEM micrographs shown the morphology of the powder particles of: a) HA and b) 316L stainless steel.

XRD patterns were indexed using the JCPDS. Figures 2a, b are possible to observe diffraction peaks related with crystalline phase of HA (JCPDS card number.09-0432), and stainless steel 316 L (JCPDS card number. 33-0397), respectively.

The scanning electron micrographs of the different powder mixtures milled for 10 hours are shown in Figure 3. The 316L stainless steel particles are rounded and presented a non-homogeneous size, with particle sizing between 5 up to 30 μm. With the increasing amount of HA in the mixture, it is noted that particles of 316L stainless steel are covered by HA particles.

Figure 4 shows the SEM micrographs of different compositions of the biocomposite 316L/HA stainless steel after sintering. For all compositions, there is a homogeneous distribution of HA particles in metal matrix. The addition of 5 wt. (%) HA did not change appreciably the size and pores distribution compared with a pure sintered stainless steel. The addition of 20 wt. (%) HA increased the porosity of biocomposite while in the composite with 50 wt. (%) of HA, the particles of stainless steel 316L were fully involved by HA.

Figure 5 shows the distribution of the elements Fe, P, Cr and Ca obtained by EDS at the interface between particles of steel and HA, in a sample of 50 wt. (%) HA after sintering. The results indicated that there is no diffusion of elements of 316L stainless steel (Fe and Cr) into HA. However there is a little diffusion of elements of HA (P and Ca) in the 316L stainless steel. Increasing the concentration of HA in the biocomposite, the sintering process hinders, since the HA acts as a barrier between the particles of 316L stainless steel.

The values of density and apparent porosity of the different compositions of biocomposite 316L/HA are shown in Figure 6. The density values ranged from 6.54 to 3.05 $g.cm^{-3}$. It can be observed that the density of biocomposites decreased with HA content is increased. This decreasing is more pronounced when the amount of HA increases to 20 wt. (%) and 50 wt. (%) and it can be related to the reduction of compressibility and ductility of the composites. These results are in agreement to results found by Younesi and collaborators (2010) that studied the effect of HA adding on the physical and the tribological properties of nickel free stainless steels[17]. The apparent porosity values ranged from 18.3% to 43.5%. It can be observed an increase in the porosity with the HA addition in the composite.

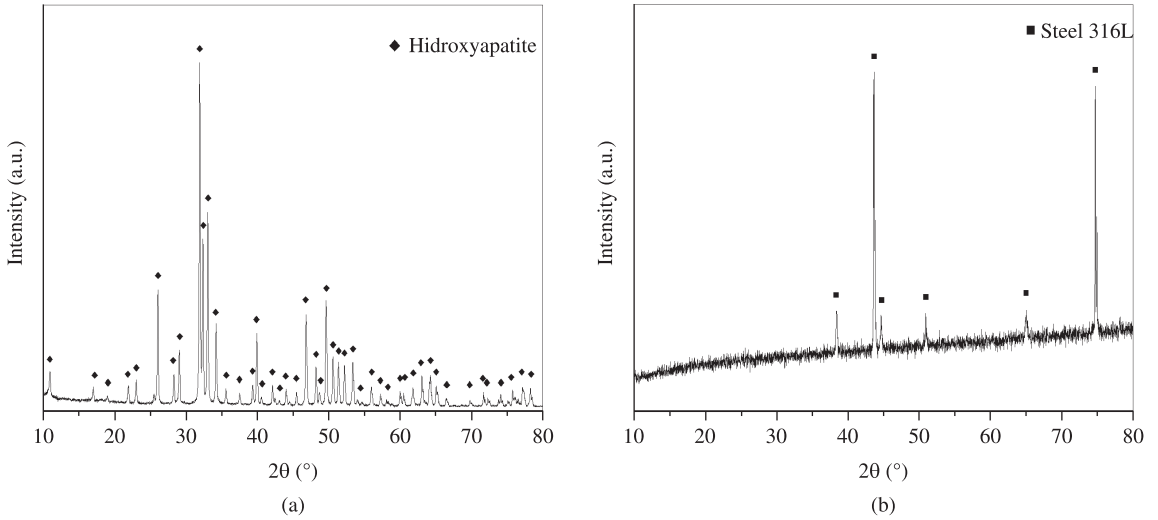


Figure 2. X-ray diffraction patterns of raw materials used in preparation of biocomposite 316L/HA: a) hydroxyapatite powder b) powder of stainless steel 316L.

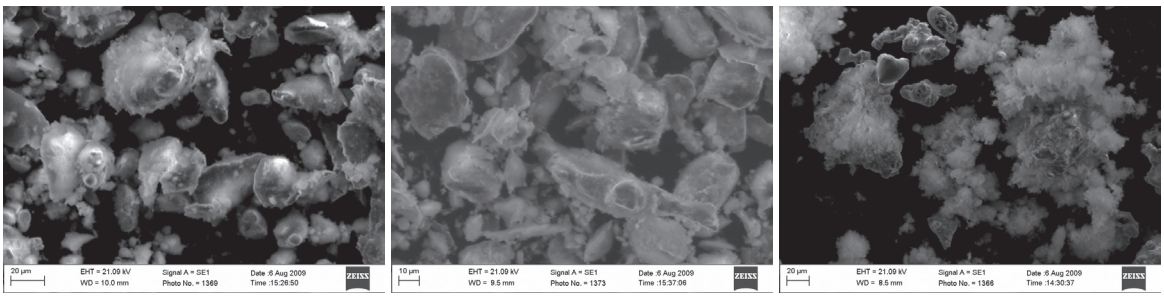


Figure 3. SEM micrographs of the different powder mixtures milled for 10 hours: a) 5 wt. (%) HA, b) 20 wt. (%) HA and c) 50 wt. (%) HA.

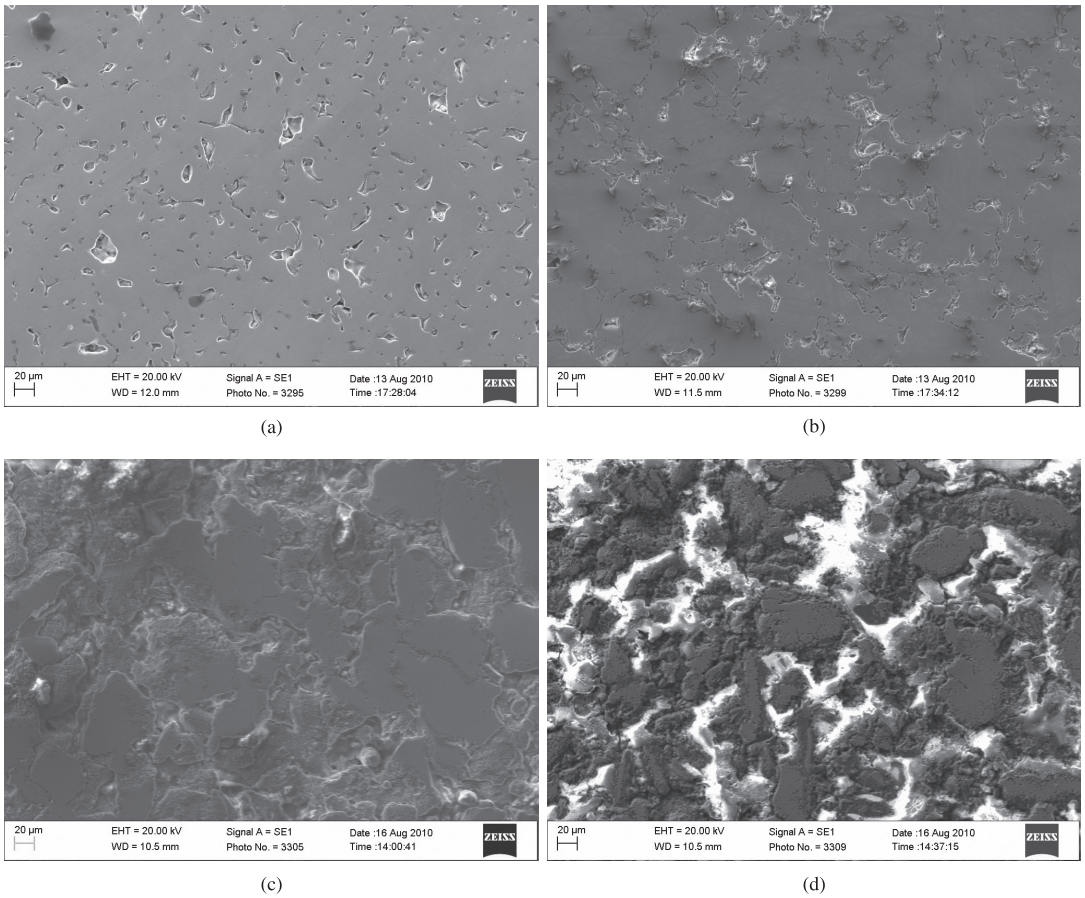


Figure 4. SEM micrographs of different compositions of the biocomposite steel 316L/HA: a) pure stainless steel b) 5 wt. (%) HA, c) 20 wt. (%) HA and d) 50 wt. (%) HA.

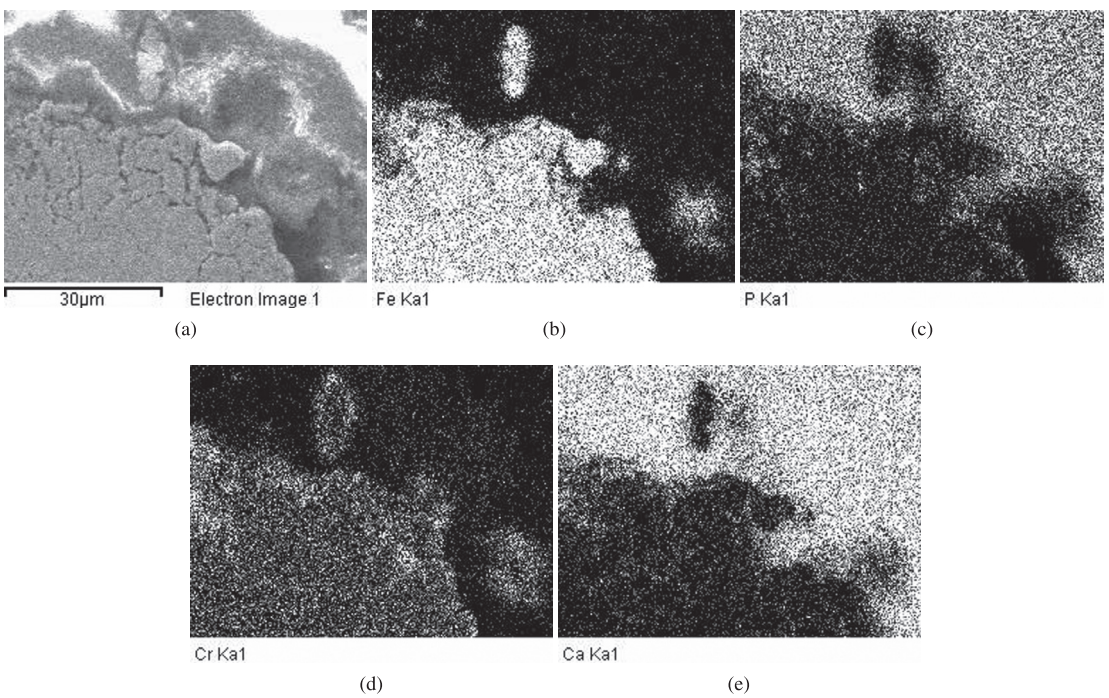


Figure 5. Mapping carried at the interface of the sample with 50 wt. (%) HA after sintering a) analyzed region, b) distribution of Fe, c) distribution of P d) distribution of Cr and e) distribution of Ca.

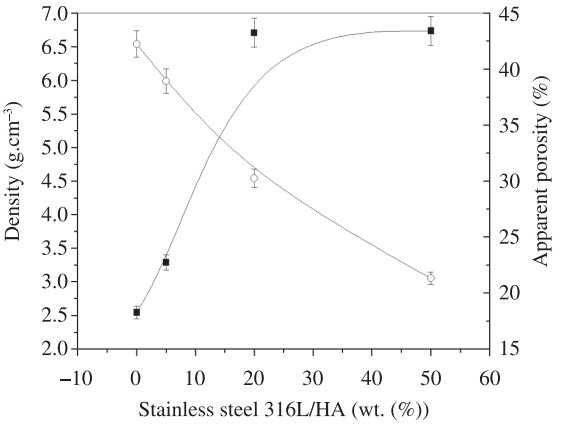


Figure 6. Density and apparent porosity of different compositions of the biocomposite stainless steel 316L/HA (5, 20 and 50 wt. (%) HA).

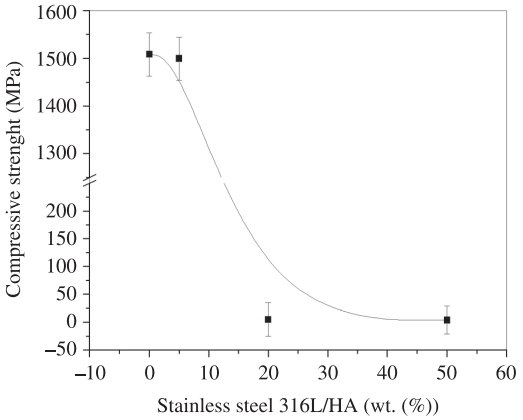


Figure 7. Mechanical properties (compressive strength) of different compositions of the biocomposite stainless steel 316L/HA (5, 20 and 50 wt. (%) HA).

Experimental compressive testing results for distinctive 316L/HA biocomposite samples are shown in Figure 7. It can be noted that the compressive strength of the biocomposites decreased with the increase of the HA addition. Only the composite contend 5 wt. (%) HA showed a mechanical resistance value very close to the value of pure stainless steel, 1499 ± 44.97 MPa and 1508 ± 45.24, respectively. However, for samples containing 20 and 50 wt. (%) HA it was observed a drastically reduction in mechanical strength values (4.9 ± 30.0 and 4.0 ± 25 MPa, respectively). Balbinotti et al.[18], also observed a reduction in the mechanical strength values for titanium/HA composites prepared by powder metallurgy. These mechanical strength values obtained at concentrations of (20 and 50 wt. (%) HA) prevent the use of biocomposites as a structural element in the human body.

4. Conclusions

In this work, different compositions of biocomposite stainless steel 316L/HA were prepared in order to combine mechanical strength of stainless steels with the bioactivity of HA. The results showed that composites with 20 and 50 wt. (%) HA have higher porosity and thus low values of mechanical strength. The mapping of the elements Fe, P, Cr and Ca confirmed the occurrence of a low diffusion between particles of stainless steel 316L and HA. According to the mechanical behavior, to maintain the mechanical strength of the biocomposite is necessary an amount of HA smaller than 20 wt. (%)

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