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Fine structure analysis of biocompatible ceramic materials based hydroxyapatite and metallic biomaterials 316L

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ABSTRACT

The aim of this paper was to obtain and characterize (surface morphology and fine structure) two types of materials: $Ca_{10}(PO_4)_6(OH)_2$ hydroxyapatite powder (HAp) as biocompatible ceramic materials and AISI 316L austenitic stainless steels as metallic biomaterials, which are the components of the metal–ceramic composites used for medical implants in reconstructive surgery and prosthetic treatment. The HAp was synthesized by coprecipitation method, heat treated at 200 °C, 800 °C and 1200 °C for 4 h, analyzed by X-ray diffraction (XRD) and scanning electron microscope (SEM). The stainless steel 316L type was made by casting, annealing and machined with a low speed (100 mm/s) in order to obtain a smooth surface and after that has been studied from residual stresses point of view in three polishing regimes conditions: at low speed polishing (150 rpm), at high speed polishing (1500 rpm) and high speed-vibration contact polishing (1500 rpm) using wide angle X-ray diffractions (WAXD). The chemical compositions of AISI 316 steel samples were measured using a Foundry Master Spectrometer equipped with CCD detector for spectral lines and the sparking spots of AISI 316L samples were analyzed using SEM. By XRD the phases of HAp powders have been identified and also the degree of crystallinity and average size of crystallites, and with SEM, we studied the morphology of the HAp. It has been found from XRD analysis that we obtained HAp with a high degree of crystallinity at 800 °C and 1200 °C, no presence of impurity and from SEM analysis we noticed the influence of heat treatment on the ceramic particles morphology. From the study of residual stress profiles of 316L samples were observed that it differs substantially for different machining regimes and from the SEM analysis of sparking spots we revealed the rough surfaces of stainless steel rods necessary for a better adhesion of HAp on it.

1. Introduction

In recent years increasing researches to develop new materials used for medical implants in reconstructive surgery and prosthetic treatment have been done. Metallic (316L, Ti–6Al–4V, unalloyed Ti, Co–(Ni)–Cr–Mo, Co–Cr–W–Ni, AZ31 Mg alloy), ceramic (alumina, zirconia, carbon, calcium sulphate, calcium phosphate like hydroxyapatite) and polymeric (ultra high molecular weight polyethylene, polyurethane) materials and combination of them (metal–ceramic composites as 316L/hydroxyapatite, Ti/hydroxyapatite, polymer–ceramic composite material, such as hydroxyapatite–polyethylene) are known and widely used in medicine [1–10].

One of the major constituents of inorganic components of human hard tissues, bone, teeth and tendon, which are responsible for the stability and function of these organs, is hydroxyapatite biocompatible ceramic [1].

$Ca_{10}(PO4)_6(OH)_2$ hydroxyapatite (HAp) shows excellent biocompatibility not only with hard tissue but also with soft tissue. This material is capable of integrating biologically when directly implanted into a bone defect; furthermore, it produces no harmful effect on the immune system, is not toxic, and features an osteoconductive behavior [2].

Clinically, HAp may be used in a variety of physical forms: as a sintered ceramic powder, block or porous forms, coating applications, particularly, bioactive coatings on a bio-inert implant or as filler phase in case of bone graft substitute. In this latter case, calcium phosphate compound serves as a matrix [1–10].

Hydroxyapatite synthesized by chemical precipitation leads to obtaining a HAp characterized by high specific surface area and small particles size distribution. In most cases deviations from the stoichiometry will occur, and at the same time, the amorphous structure is obtained [7].

The disadvantages of ceramic biomaterials are the low resistance to impact and fracture. For that reason, the biocompatible

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ceramic materials are necessary to be used as replacement implants in combination with the metallic components (stainless steel, titanium, etc.) for increasing the mechanical properties such as strength, bend strength and fatigue resistance [1–11].

The austenitic stainless steels 316L are the most used metallic biomaterials (for hip joints, artificial knee, etc.) because of: (a) their high corrosion resistance in marine and industrial atmospheres, in continuous service up to 930 °C; (b) for the good mechanical properties (tensile strength 860–1100 MPa and 0.2% proof stress 690 MPa, in cold worked condition); (c) they have relatively low cost and (d) it is easy to be processed. Biocompatible steels type AISI 316L cannot be hardened by thermal treatment, but the strength and hardness can be increased substantially by cold working, with subsequent reduction in ductility.

By mechanical processing, cold working, etc. different internal stresses and second order residual stresses arise but it is very important that they do not initiate and propagate cracks in these materials [12].

The appearance of second order residual stresses in biocompatible samples AISI 316L strongly depends on technological processing operations that are carried out on samples before their introduction in use. So, we must pay special attention to choosing the best technique for processing such metallic materials [11–18].

Knowing the exact chemical compositions and fine structure of biocompatible components is considered one of the major requirements for predicting the behavior of the body implant. The desired chemical, physical, structural and mechanical characteristics to be obtained for each component involved in composite for biomedical applications are: (i) chemical composition, (ii) phase-composition, (iii) fine structure of the polymorphic phase, (iv) distribution and preferred orientation of grains (texture), (v) synergistic effects on mechanical and electrical properties, (vi) essential biocompatibility [1–19].

Because of the specific characteristics mentioned above, studies and experimental investigations (surface morphology and fine structure, including second order residual stresses) of this work were focused on the following groups of materials: (a) hydroxyapatite powders (HAp) obtained by coprecipitation method and (b) 316L stainless steel obtained by casting and annealing for homogenization.

Corroborating the results of investigations on the two types of materials, we can elucidate many structural aspects of them and we can improve the bonding at interface HAp-316L stainless steel by obtaining a rough microscopic morphology of stainless steel melted surfaces, and implicit to allow a better adhesion by coating of an adherent bioactive HAp on AISI 316L.

2. Materials and experimental procedure

2.1. Hydroxyapatite synthesis

For the synthesis of hydroxyapatite 0.1 M calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) and 0.16 M diammonium hydrogen phosphate $(NH_4)_2HPO_4$ have been used according to the procedure presented in other paper [20].

The equation of chemical reaction is:

$$10Ca(NO_3)_2{\cdot}4H_2O + 6(NH_4)_2HPO_4 + 8NH_4OH \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 20NH_4NO_3 + 46H_2O$$

From the reaction between the two solutions based on calcium and phosphorus a precipitate has been obtained. The resulting slurry was filtered. The filter product was dried at 110 °C for 24 h and heat treated at 200 °C, 800 °C, respectively, 1200 °C for 4 h.

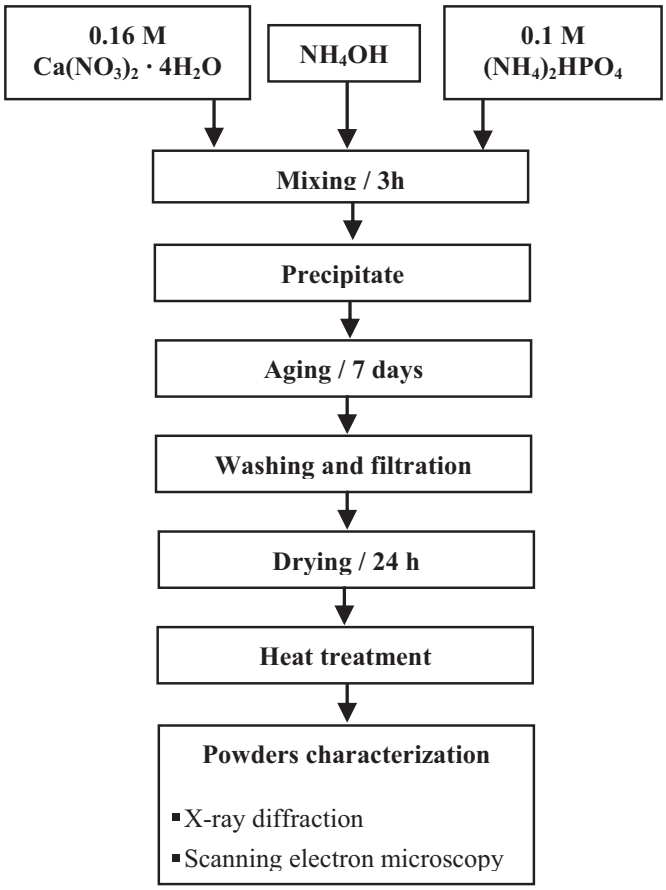

Fig. 1. Chemical coprecipitation route for hydroxyapatite powder preparation.

The procedure for preparing hydroxyapatite powder, according to above described procedure, is schematically illustrated in Fig. 1.

2.2. AISI 316L stainless steel preparation

The stainless steel AISI 316L was made by casting techniques followed by annealing. The experimental procedure was presented in previous works [13].

We obtained gross ingots and rods from homogeneous alloy with chemical composition required for AISI 316L standards, presented in Table 1.

From this stainless steel we cut samples at 50 mm × 40 mm × 10 mm dimensions. The alloy samples chosen for analysis are homogeneous and representative. One of the two faces of 50 mm × 40 mm was machined with a hard alloy "widia" head at a low speed (100 mm/s) in order to obtain a smooth surface.

The AISI 316L cylindrical samples of 40 mm in diameter were spectrometrically tested in repeating conditions to assess its elemental composition and the standard uncertainty of mass concentration. The standard uncertainty was estimated by the experimental standard deviation (STDEV) calculated according to SR EN 130005:2005. We consider that relative experimental standard deviation (RSD) is more relevant for experimentalists [13,18].

2.3. Hydroxyapatite powder analysis

The X-ray phase analysis of powders was carried out by X-ray diffraction using a Bruker AXS D8 ADVANCE diffractometer Cu-K_α radiation (1.5405 Å) working at voltage and current settings of 40 kV and 30 mA. XRD diagrams were recorded in the