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COMPARATIVE STUDY OF THE SYNTHESIS AND PROCESSING OF HYDROXYAPATITE

M. de Campos[1,2], A. H. Bressiani[2]

[1]Technological Research Center-University of Mogi das Cruzes, Av. Dr. Cândido Xavier de Almeida Souza 200, 08780-911, Mogi das Cruzes, S.P, Brazil.

[2]Department of Materials Engineering, IPEN - DMC, Travessa R 400, Cidade Universitária Armando Salles Oliveira, 05508-900, São Paulo, S.P, Brazil

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Abstract. The HAp is a biomaterial applied as dense, porous or coating bioceramics, in the medical and odontological areas. The aim of this work was obtain hydroxyapatite with characteristics that allow its application as dense or porous bodies, and coating studying three methods of syntheses: precipitation, neutralization and sol-gel in alcoholic media. Precipitation and neutralization showed the best results for thermal spraying stability, being thereafter reproduced in a pilot scale, in an open and closed system. Nitrogen atmosphere was used to avoid the formation of hydroxyapatite carbonate. The powders obtained by neutralization were used for coating titanium alloy substrate. Plasma spraying technique was used for deposition. On coating layer HAp was the main phase detected, showing a good adherence to the substrate. Porous ceramic bodies were obtained by gel casting foam with the HAp from the neutralization method in an inert atmosphere. The main techniques used on the characterization of powder, metallic substrates, coatings, porous and dense ceramic bodies were: particle size distribution (D), scanning electron microscopy (SEM) and X-ray diffractometry (XRD). The HAp phase was detected as the majority in all conditions and results are no cytotoxicity.

Introduction

Hydroxyapatite (HAp), $Ca_{10}(PO_4)_6(OH)_2$, exhibits high potential for applications in the fields of medicine and dentistry, because of its similarity with the mineral phase of bone tissues. HAp belongs to a group of materials that is not toxic or adverse to tissues surrounding the implant. The HAp is able to promote chemical bonds with live bone tissue, promoting thereby, bone integration by ontogenetic bonding. It has been widely applied as a biomaterial in the form of powder, granules, dense or porous bodies and oral and cranio-maxillofacial reconstructive surgery, and dent alveolar surgery [1]. The use in the orthopedic field is however limited, due to the low tensile strength. To overcome this lack of strength metallic prosthesis are coated with a thin HAp layer. HAp coatings increase the rate of fixing of implants to bone, by bone integration. The properties of the hydroxyapatite powders such as crystal morphology, crystallinity, thermal stability, and solubility have shown to be dependent greatly on the route of fabrication. In this work, there different methods of hydroxyapatite synthesis were compared, including the precipitation, neutralization and sol-gel in alcoholic media. The influence of powder properties on processing of dense, porous bodies and coatings was investigated [2,3].

Materials and Methods

Powder synthesis: Three different routes were used to prepare Hydroxyapatite: (1) precipitation from calcium acetate, $Ca(CH_3COO)_2$, and ammonium hydrogenophosphate $(NH4)_2HPO_4$. This method

consisted of drop wise addition of 0.20M $Ca(CH_3COO)_2$ and 0.11M $(NH4)_2HPO_4$ to a stirring of ammonium acetate, 0.40M NH_4CH_3COO in water. The temperature of precipitation was 90°C. (2) neutralizations of calcium hydroxide $Ca(OH)_2$ and phosphoric acid H_3PO_4; This method consisted of drop wise addition of 0.3M H_3PO_4 to a stirring of 0.1M $Ca(OH)_2$ in water. The temperature of precipitation was 25°C. (3) sol-gel route from calcium acetate $Ca(CH_3COO)_2$ and phosphoric acid H_3PO_4 in alcoholic medium. This method consisted of drop wise addition of H_3PO_4 to a stirring of 1.8M $Ca(CH_3COO)_2$ in 2-ethylhexanol with 6.2M ammonium hydroxide NH_4OH. The temperature of precipitation was 25°C. The HAp precipitates were separated from the suspension using vacuum filtration technique. The filtered cake was placed in an oven at 40°C, and the temperature was raised gradually up to 80°C over 24 hours. The powders surface area, particle size distribution, mineralogy were characterized by X-ray diffraction analysis and FTIR. Crystal morphology was studied by SEM.
Cytotoxicity tests: The most thermally stable powders were evaluated for cytotoxicity by producing extracts of the powders and exposing them to RPMI-FCS culture medium (RPMI 1640 containing 10% if fetal calf serum, 1% penicillin solution e streptomycin). The number of cell colonies was counted for various extract concentrations, and compared to positive and negative controls. *Powders Processing*: selected powders were processed by dry pressing to produce dense bodies, foaming of ceramic suspensions to produce porous bodies [2] and plasma spraying to produce coatings on Ti-6Al-4V alloys substrate [3]. Due to the low thermal stability of sol-gel derived powders, theses were not tested for all techniques.

Results and Discussion

Powders obtained by precipitation and neutralization exhibited the best results in terms of crystallinity and thermal stability. The powders processed by sol-gel in aqueous medium presented mainly HAp phase with traces of tetra calcium phosphate (TTCP) and tri calcium phosphate (β-TCP). In alcohol, this route produced significant amounts of secondary phases.

The crystals of powders produced by precipitation had an acicular shape and a surface area of 2.4 m^2/g, whereas the other had heterogeneous angular shape and a surface area of 3.0 m^2/g. The sol-gel route led heterogeneous angular shape with surface area in the range of 6.0-7.0 m^2/g. The influence of synthesis method on morphology is shown in Fig.1.

Fig. 1. SEM micrographs of HAp powders after calcination at 1000°C for 3 hours. (a) precipitation; (b) neutralization, and (c) sol-gel method.

Particle size analysis of starting powders revealed differences in particle size distribution. The powders produced by sol-gel and neutralization has a clear bimodal particle/agglomerate to be around

3 and 15 μm, respectively, while the powders produced by precipitation shows a single maximum at about 15 μm. The powders produced by neutralization and precipitation led to higher density bodies after pressed. Density of HAp processed by precipitation and neutralization is close to the theoretical density, 2.8 and 3.0 $g.cm^{-3}$ respectively. X-ray diffraction analysis of the prepared and calcined powders revealed mainly, the presence of a crystalline phase of HAp. The β-TCP phase was found as secondary phase in the HAp produced by precipitation. The β-TCP and TTCP phases were found in the HAp produced by sol-gel.

During the spray drying step of the plasma spraying process the best results were obtained with HAP powders produced by neutralization route, whereas powders produced by precipitation route caused processing difficulties due to the flow ability of acicular crystals (Fig.2).

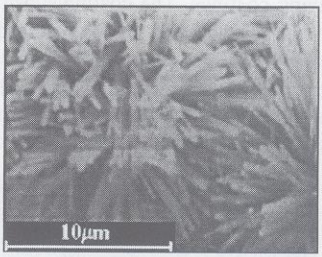


Fig. 2. Micrograph of calcined HAp powders produced by precipitation

Because of the results obtained with neutralization, this process was further implemented in a pilot study, varying the atmosphere conditions, to produce hydroxyapatite with and without carbonate in the structure. The micrograph of the powder without carbonate is shown in Fig.3. The HAp powder consists of agglomerates of small particles. X-ray diffraction analysis revealed mainly, the presence of a crystalline phase of HAp (Fig.4).

The production of porous bodies by dispersion and foaming was successful with the powders produced through neutralization, leading to homogeneous microstructures. Typical structure of foamed ceramics consist of spherical cells interconnected though channels a mainly triangular struts (fig.5). Properties of porous materials depend basically on the strut properties. Therefore, fully densified and flawless microstructures are required [2]. Green densities ranging from 0.42 to 0.44$g.cm^{-3}$ were obtained, leading to post-sintering densities of 22.8 to 23.1% of the theoretical value (3.156$g.cm^{-3}$). X-ray diffraction analysis of porous HAp (after 1250°C/3h) revealed mainly, the presence of a crystalline phase of hydroxyapatite and a small content of β-TCP, however a small peak at 37.4°was also present, indicating the possible presence of CaO.

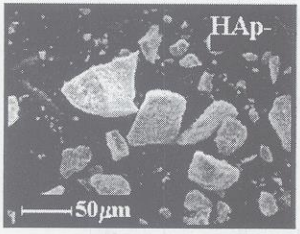


Fig. 3. Micrographs of HAp powders produced by neutralization (1000°C/3h).

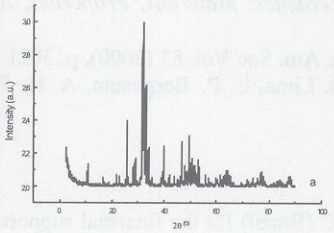


Fig. 4. X-ray diffractogram of HAp powders produced by neutralization process (1000°C/3h).

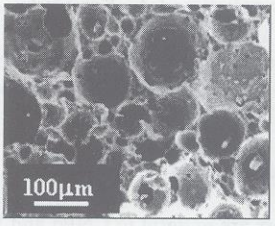
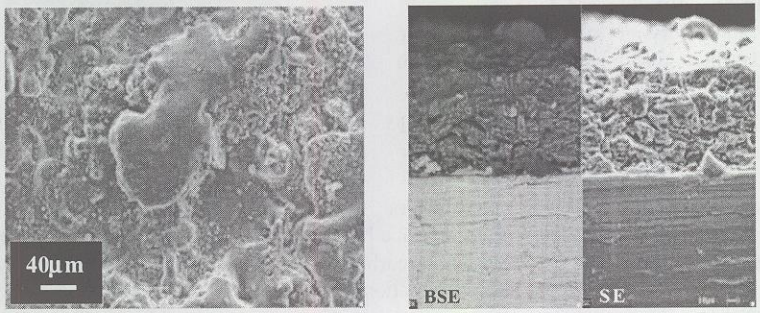


Fig. 5. Micrographs of fracture surface porous HAp (1250°C/3h).

A Ti-6Al-4V alloy was used as the substrate material for coating. Sample surface was grit blasted with alumina particles for roughen prior spraying [3]. Fig.6-a shows the SEM micrograph of plasma sprayed coating surface showing loose particles, splats and cracks. These are typical features in plasma spraying coatings. The coating/substrate interface does not reveal cracks, as can be seen in the micrographs of cross section in Fig.6-b, indicating good adhesion of the coating. The presence of a crystalline phase of HAp and small quantities of a secondary phase β-TCP and CaO were detected by X-ray. Cytotoxicity analysis demonstrated that all powders were non-toxic (IC_{50}>100), showing that the powders were produced under careful processing conditions and using high purity reagents. Further studies are needed to evaluate the behaviour of selected powders "*in vivo*".



a b

Fig. 6. Plasma spraying HAp coating surface produced (a); interfaces Ti-6Al-4V/HAp coating.

Conclusions

Synthesis of hydroxyapatite powders by the methods of precipitation and neutralization produced the best results in terms of thermal stability and crystallinity. The powders produced by neutralization allowed easier processing into dense, porous forms and as coatings.

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Corresponding Author:
Magali de Campos, PhD: Tel: +55-11-4798-7229, Fax: +55-11-4798-7225, E-mail: magali@umc.br