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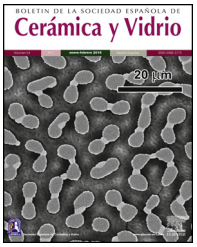

Processing of hydroxyapatite obtained by combustion synthesis

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ABSTRACT

One of the reasons of implants failure is the stress forces appearing in the material–tissue interface due to the differences between their mechanical properties. For this reason, similar mechanical properties to the surrounding tissue are desirable. The synthesis of hydroxyapatite by solution combustion method and its processing have been studied in order to obtain fully dense ceramic bodies with improved mechanical strength. Combustion synthesis provides nanostructured powders characterized by a high surface area to facilitate the following sintering. Moreover, synthesis was conducted in aqueous and oxidizing media. Oxidizing media improve homogenization and increase the energy released during combustion. It gives rise to particles whose morphology and sizes suggest lower surface energies compared with aqueous media. Obtained powders were sintered by using a controlled sintering rate schedule. Lower surfaces energies minimize the shrinkage during sintering and relative densities measurements and diametral compression test confirm improved densification and consequently mechanical properties.

Procesamiento de hidroxiapatita obtenida mediante síntesis por combustión

Palabras clave:
Hidroxiapatita
Síntesis por combustión
Sinterización a velocidad controlada
Módulo de Weibull

RESUMEN

Una de las razones principales de fracaso de los implantes son las fuerzas de estrés que aparecen en la *interface* material-tejido debido a las diferencias existentes entre sus propiedades mecánicas. Por esta razón, es necesario que el implante posea propiedades mecánicas similares a las del tejido circundante. La síntesis de hidroxiapatita por el método de combustión y su procesamiento se han estudiado con el objetivo de obtener cuerpos cerámicos completamente densificados y, consecuentemente, con propiedades mecánicas

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mejoradas. El método de combustión provee de polvos nanoestructurados que se caracterizan por una superficie específica elevada que facilita el siguiente proceso de sinterización. Además, este proceso de síntesis se ha realizado en medio acuoso y oxidante. El medio oxidante homogeniza e incrementa la energía liberada durante la combustión. Esto da lugar a partículas cuya morfología y tamaño indican energías superficiales menores en comparación con las obtenidas en medio acuoso. Los polvos obtenidos se sinterizaron siguiendo un esquema de velocidad de calentamiento controlada. Partículas con bajas energías superficiales dan lugar a menores contracciones durante el proceso de sinterización y las medidas de densidad y los test de compresión diametral confirmaron la mejora de la densificación, así como de las propiedades mecánicas.

Introduction

Most of the calcium in human body is in solid state and stored in bone tissue as nanometric crystals of a calcium phosphate compound with structure and composition similar to hydroxyapatite (HA). Stoichiometric HA is represented by the chemical formula $Ca_{10}(PO_4)_6(OH)_2$, where the molar ratio Ca/P is 1.67 [1]. However, far from the above formula, the calcium phosphate found in the mineral constituent of bones is better described as a non-stoichiometric, calcium-deficient and carbonated apatite [2].

Synthetic HA ceramics are considered as bioactive, i.e. they are able to bond tightly to bone tissue without any intermediate connective tissue. However, HA is the less soluble than other calcium phosphate [3,4] and consequently, it slightly biodegrades when is implanted. This is a problem to complete the regeneration process. Only the surface of the material interacts with bone tissue while the bulk remains unchanged. At the material–tissue interface stress forces are developed due to mismatch of the Young modulus between material and bone [5,6]. This may cause the long term failure of the implant, which usually takes place at the bulk of the ceramic. Thus, HA ceramics with improved fracture toughness [1,5] would be more useful for manufacturing structural load-bearing bone implants.

One way to improve the mechanical behavior is by controlling the sintering process in order to obtain tailored microstructures. Thermal treatments affect the final microstructure and this microstructure affects the mechanical properties. During the thermal treatment, grains connect and close the spaces between them resulting in larger grains. Moreover, mechanical properties such as resistance become worse with porosity increase. If the thermal treatment is realized in harmony with material shrinkage, densification improves by decreasing the porosity. To attempt this challenge, rate controlled sintering (RCS) was suggested. During sintering, porosity can be reduced by controlling the heating rate and shrinkage occurs in synchrony with densification rate.

Particle size of sintered powders plays an important role in the densification process during the thermal treatment. Nanoparticles have higher reactivity and, despite they compact worse, interparticle porosity is smaller and both characteristics should improve densification. Moreover, Nano-HA has great importance in medical applications due to the fact that this small grain size is similar to that of natural HA and showed improved properties with respect to micrometer grain size HA [6].

Solution combustion synthesis (SCS) gives the possibility to produce a big variety of materials, morphologies and sizes [7–11]. Especially in the case for what concerns the size, combustion synthesis is an excellent way to obtain submicronic structured materials. For this reason, SCS method has been chosen to synthesize HA [12–17] in order to obtain nanoparticles and improve densification [18]. During combustion a quick exothermic reaction takes place, delivering high amount of energy [13]. It promotes wide thermal gaps which allow obtain particles in the nanometer size [19].

The objective of this work is the obtaining of dense HA materials with improved mechanical resistance. With this aim a RCS has been carried out on HA nanostructured particles obtained by combustion. Furthermore, it will be demonstrated how mechanical properties can be improved by controlling the conditions synthesis.

Materials and methods

Raw materials employed for solution combustion synthesis were, $Ca(NO_3)_2{\cdot}4H_2O$ (99.5% PA-ACS, Panreac Química S.A.), $(NH_4)_2HPO_4$ (98% PA-ACS, Panreac Química S.A.) and Urea $(NH_2)_2CO$ (99.5% ACS, Panreac Quimica S.A.) as fuel [13]. The quantities employed were calculated to obtain 5 g of final product considering the reaction stoichiometry [13]. A second synthesis was carried out adding 5 cm^3 of HNO_3 (65% Pro Analysis Merck) as internal oxidant or oxidant excess [13] to ensure total fuel combustion and pH control [20].

In both cases, raw materials were separately dissolved in 100 cm^3 of deionized water and put in a porcelain capsules. The capsules were place in a furnace where the mixtures are heated at 500 °C during 30 min to assure the drying and the corresponding combustions.

In order to break down the obtained agglomerates, the synthesis products were passed in an agate mortar and milled by attrition during 8 h. Then, particle size distributions were measured by laser scattering using Mastersizer S (Malvern, UK) after Agatha mortar and after attrition milling. Specific surface area was measured before and after milling in a Monosorb. Mod MS 13 (Quantachrom, EE.UU). Dilatometry was realized

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