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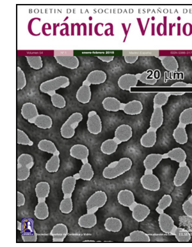

Processing and in vitro bioactivity of a β-$Ca_3(PO_4)_2$–$CaMg(SiO_3)_2$ ceramic with the eutectic composition

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ABSTRACT

In this study, a dense bioactive ceramic, with nominal composition (wt.%) 40 $Ca_3(PO_4)_2$–60 $CaMg(SiO_3)_2$, was prepared by solid state sintering of homogeneous compacted mixtures of fine synthetic $Ca_3(PO_4)_2$ and $CaMg(SiO_3)_2$ powders. The results obtained by X-ray diffraction and field emission scanning electron microscopy with microanalysis indicate that the ceramic composite showed a fine grained and homogeneous microstructure consisting of diopside ($CaMg(SiO_3)_2$) and whitlockite (β-$Ca_3(PO_4)_2$ss) grains with very small amounts of apatite.

The flexural strength and elastic modulus values of the composite are similar to those of cortical human bone.

Bioactivity was experimentally evaluated by examining in vitro apatite formation in simulated body fluid (SBF). In addition, a simulation of the dissolution properties of the different phases present in the material in SBF was carried out by thermodynamic calculations, with the purpose of understanding the in vitro results obtained.

The experimental results demonstrated that, during soaking in SBF, the grains of whitlockite dissolved preferentially than those of diopside, leaving a porous surface layer rich in diopside. Subsequently, partial dissolution of the remaining diopside occurred and the porous surface of the ceramic became coated by a bone-like apatite layer after 7 days in SBF.

This bioceramic containing β-$Ca_3(PO_4)_2$ and $CaMg(SiO_3)_2$ is expected to be useful to fabricate scaffolds for bone repair.

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Procesamiento y bioactividad in vitro de cerámicas de β-$Ca_3(PO_4)_2$ – $CaMg(SiO_3)_2$ Con composición eutéctica

Palabras clave:
Fosfato tricálcico
Diópsido
Bioactividad
Suero fisiológico simulado
Bioceramicas

R E S U M E N

En este estudio se han preparado un material cerámico denso, con una composición nominal (% en peso) de 40 $Ca_3(PO_4)$ – 60 $(SiO_3)_2$, mediante sinterización en estado sólido de polvos finos de $Ca_3(PO_4)_2$ y $CaMg(SiO_3)_2$ sintéticos. Los resultados obtenidos por DRX y microscopia electrónica de barrido de emisión de campo con microanálisis indican que los materiales obtenidos presentan una microestructura homogénea, con un tamaño de grano fino, compuesta por granos de diópsido ($CaMg(SiO_3)_2$) y whitlockita (β-$Ca_3(PO_4)_2$ss) junto con muy pequeñas cantidades de apatita.

Los valores de tensión de fractura y el módulo de elasticidad del material optimizado son similares a los del hueso humano.

La bioactividad del material se ha evaluado experimentalmente estudiando la formación *in vitro* de apatita en suero fisiológico simulado. Con el objetivo de comprender los resultados obtenidos en los estudios *in vitro* se ha simulado la disolución de las diferentes fases presentes en el material en SFA mediante cálculos termodinámicos.

Durante el experimento in vitro en SFA los granos de whitlockita se disuelven más rápidamente que los de diópsido lo que origina una superficie porosa rica en diópsido. Posteriormente, tiene lugar la disolución del diópsido remanente en la superficie del material de β-$Ca_3(PO_4)_2$-$CaMg(SiO_3)_2$ que, después de siete días en SFA, queda recubierta por una capa de apatita.

Se espera que este material biocerámico de β-$Ca_3(PO_4)$ y $CaMg(SiO_3)_2$ sea útil para la fabricación de andamiajes para reparación ósea.

Introduction

Calcium phosphate based bioceramics have been in use in medicine and dentistry for 30 years. They are used in a wide range of applications, including coatings of implants, alveolar ridge augmentation, maxillofacial surgery and scaffolds for bone growth and as powders in total hip and knee surgery [1]. In the last years many efforts in artificial bone engineering have involved the use of synthetically obtained tricalcium phosphate [2] ($Ca_3(PO_4)_2$, TCP), as a bioresorbable compound in clinical use for bone-repair [3,4]; however the control of its bone-bonding ability, i.e. bioactivity, and bioresorbability is not easy [5–8]. On the other hand, Si and Mg have received great attention as substitutes in the $Ca_3(PO_4)_2$ network, to improve osteogenesis, bioreabsorption rate, strength, and phase composition of the resulting bioceramics [9]. Diopside ($CaMg(SiO_3)_2$, D) is a potential candidate as Mg- and Si-containing source for bioceramics because it has been found to be non-cytotoxic, biocompatible and bioactive in vitro (slightly in SBF, and fully in human parotid saliva) and in vivo [10]. On the other hand, dense diopside ceramics show high mechanical strength and toughness, as compared to TCP ($K_{IC} \approx 3.5$ and 1.1 MPa $m^{1/2}$ and $\sigma_f \approx 300$ and 180 MPa for D and TCP [11], respectively; and low biodegradability [12]). Diopside has also been reported to be able to closely bond to bone tissue when implanted in rabbits.

Control of the surface reactivity of bioactive ceramics to surrounding body fluids is essential in the design of novel bone-repairing materials, because apatite formation on bioactive materials is governed by the dissolution of constituents from the materials and the nucleation of hydroxyapatite on the resultant surface.

The combination of a resorbable ceramic compound as $Ca_3(PO_4)_2$, with low strength, with a high strength bioactive one, such as $CaMg(SiO_3)_2$ would led to novel designs of bioactive and bioresorbable materials for use as bone regeneration materials. Moreover, bone formation will be stimulated by the presence of silicon and magnesium [13,14].

Ashizuka et al. [15] reported that the glass-ceramics prepared from glasses with the eutectic composition (wt.%) of 38 $Ca_3(PO_4)_2$-62 $CaMg(SiO_3)_2$ could reach flexural strength values of about 200 MPa. However the bioactivity of this material was not analysed by the authors. Kamitakara et al. [16] investigated the fundamental parameters of preparation of dense and porous glass ceramics by devitrification of the parent glass with eutectic composition of the system $Ca_3(PO_4)_2$-$CaMg(SiO_3)_2$. These authors observed that both porous and dense diopside-β-tricalcium phosphate glass-ceramics show bioactivity and bioresorbability in a simulated body fluid.

In a previous work, Carrodeguas et al. [17] reported a preliminary study of the in vitro behaviour of dense ceramics of $Ca_3(PO_4)_2$-$CaMg(SiO_3)_2$ (60:40 wt.%). These authors observed the formation of a bone-like apatite layer on the interface between the simulated body fluid and the material.

Recently Guerrero-Lecuona et al. [18] in an *in vitro* study about the influence of the structure and microstructure on the bioactive behaviour of a ceramic and a glass-ceramic with composition (wt.%) 45 CaO, 22 SiO_2, 28 P_2O_5 and 5 MgO