Spark plasma sintered Hydroxyapatite/Bioactive glass based products for Biomedical Applications

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Highlights

- SPS to obtain dense HA/BG samples with diverse grains size and crystallization degree.
- Osteoblasts cultivated on HA samples generate an apatite layer with trabecular structure.
- Apatite formation is promoted in crystallized BG/45S5 samples compared to the amorphous.

1. Introduction

Hydroxyapatite (HA) has a composition ($Ca_{10}(PO4)_6(OH)_2$) similar to that of biological apatite, the main inorganic component of hard human tissues [1-2]. Thus, the obtainment of synthetic HA for orthopedic and dentistry applications has been widely investigated. One of the main problems associated to the consolidation of HA powders is related to their thermochemical instability. Indeed, when they are exposed to high temperature conditions, HA tends to decompose to form $Ca_3(PO_4)_2$ (TCP) or other undesired phases, whose presence negatively affects mechanical and biological characteristics of the material.

Thanks to their positive response shown when interacting with biological tissues, also bioactive glass (BG) materials have attracted significant attention in the biomedical field [3-4]. Specifically, when suitable glass compositions are considered, a bone-like hydroxycarbonate apatite (HCA) layer is produced on the BG-physiological fluids interface, so that a strong bond between the substrate and the surrounding tissues can be established [3-4]. Thus, the classical 45S5 Bioglass® (BG/45S5), consisting of 45 % SiO_2-24.5 % Na_2O-24.5 % CaO-6 % P_2O_5 (wt. %), as well as other glass formulations developed more recently, have been employed by orthopedic surgeons and dentists. It should be noted that the occurrence of crystallization phenomena in glass-ceramic products is generally found convenient to improve mechanical properties. In contrast, controversial findings were reported in the literature on the effect of the crystallization from the parent glass on the material bioactivity. In this regard, the BG/45S5 system exhibits a rapid tendency to crystallize at temperature values in the range 550-650°C, whereas innovative CaO rich glass compositions was reported to preserve its amorphous nature at temperatures even above 800°C [3].

In this context, the SPS technology is a suitable route either for the consolidation of HA powders, because decomposition phenomena can be avoided/mitigated due to the mild sintering conditions to be adopted, as well as for the preparation of highly dense BG products with controlled crystallization degree. In this work, various HA/BG-based systems are investigated under different SPS conditions and the resulting dense materials characterized in detail, particularly from the bioactivity point of view.

2. Methods

Commercial HA and BG/45S5 powders as well as lab-made CaO-rich glass (BG/CaMiX) are used as starting materials in the present work [1-6]. HA and BG were consolidated individually or combined in suitable proportions in the form of cylindrical disks by Spark Plasma Sintering (SPS 515S model, Sumitomo Coal Mining Co Ltd) under vacuum conditions. The effect of the dwell temperature, the holding time, and the mechanical pressure on the product characteristics was systematically investigated. Bioactivity of the sintered samples was evaluated through in-vitro test in Simulated Body Fluid (SBF) solution or using human SAOS-2 osteoblasts cultivated on their surface for different time periods.

3. Results and discussion

Completely dense products consisting of sub-micrometer sized apatite grains without secondary species are obtained by SPS at 900 °C using highly pure HA powders with relatively small sized particles (7 μm). On the other hand, temperatures up 1200 °C are needed to fully consolidate, with no HA decomposition, coarser pure powders (33 μm).

The latter SPS condition is also required when using fine powders (6 μm) which contain secondary phases like CaHPO4. Correspondingly, products with coarser microstructures and mainly consisting of TCP are obtained. Furthermore, in vitro tests using human osteoblasts evidenced that an apatite layer with a trabecular microstructure is deposited on the materials surface in samples entirely consisting of HA (Fig. 1a). In contrast, the formation of the new apatite phase is markedly suppressed, when cells are seeded on sintered samples composed of TCP.

Completely dense and 75 wt.% amorphous products were obtained from BG/45S5 powders sintered at 550°C, while full crystallization occurred when the temperature was raised at 600°C or higher levels. In contrast, the amorphous character of BG/CaMiX was entirely preserved when powders were wholly densified at 730°C. Moreover, a temperature of 830°C is needed to induce crystallization in the parent glass.

In-vitro experiments evidenced that a relatively lower amount of HCA apatite is formed on the surface of mainly amorphous 45S5 samples, whereas, a more extensive apatite layer with trabecular structure (Fig. 1b) is generated on fully crystallized specimens, consisting of 20 nm grains. Such biological behaviour is likely ascribed to the large grains boundary area made available by such nanocrystallites, which determines an intensification of ion-exchange phenomena and, in turn, the formation of the HCA layer.

HA/BG composites were also investigated [5-6] to overcome the disadvantages associated to the use of pure HA, i.e. the high sintering temperatures and its rather low reactivity at body temperature and physiological pH. Indeed, BG acts as sintering aid for the consolidation of HA powders. In addition, by properly combining the two constituents, it is possible to control the bioactivity and the dissolution rate of the resulting material, so that tailored biological properties can be obtained.

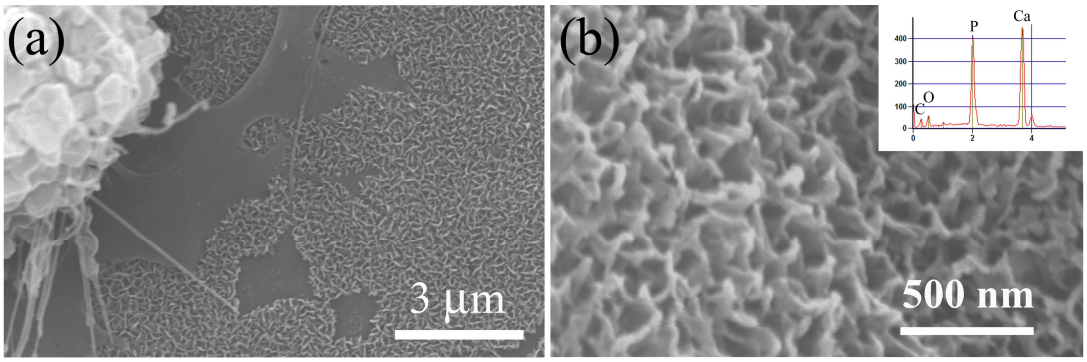

Figure 1. (a) Interaction of osteoblasts with the surface of a HA specimen and (b) microstructure and related EDX spectra of the surface of 45S5 BG sample immersed in a SBF solution

4. Conclusions

The possibility offered by the SPS technique to avoid or limit HA decomposition and/or suitably control crystallization phenomena in BG systems is examined in this work. Both these aspects are quite relevant to determine the biological response of bulk HA/BG-based bioceramics.

References

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Keywords
Hydroxyapatite; Bioactive glasses; Spark Plasma Sintering; Bioactivity.