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### Feature article

# Innovative hydroxyapatite/bioactive glass composites processed by spark plasma sintering for bone tissue repair

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### ABSTRACT

Hydroxyapatite-based composites (HA-C) with bioglass as second phase are usually produced by hot-pressing or pressureless sintering. However, such methods require thermal levels which exceed the crystallization temperature of the glass, with possible negative effects on the bioactivity of the final system. Spark plasma sintering (SPS) is a powerful consolidation technique in terms of both processing time and temperature. In this work SPS has been employed, for the first time, to obtain HA-C with an innovative bioglass as second phase. Such glass was designed to be used whenever a thermal treatment is required, thanks to its low tendency to crystallize. A systematic study is conducted to identify the optimal sintering conditions for preparing highly dense composites and, at the same time, to minimize the crystallization of the glassy phase. The obtained samples are highly bioactive and display higher compactness and hardness with respect to the counterparts produced by conventional sintering methods.

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## 1. Introduction

The repair of osseous defects caused by tumors, traumatic events or inflammatory diseases is a common clinical problem. Current lines of treatment such as autogenous bone grafts, which involve the transplantation of bone from another part of the patient, or allografts, where bone tissue is taken from donors or cadavers, are affected by specific drawbacks, *i.e.*, donor site morbidity, disease transmission risks, high costs and potential complications like infections [1,2]. In the last 40 years several research works have been devoted to develop specific synthetic alternatives for the replacement of damaged or lost bones. In this context, hydroxyapatite (HA), which belongs to the calcium phosphates group, plays a prominent role in oral, maxillofacial and orthopaedic surgery since the 1980s [3,4]. Thanks to its similarity to the biological apatite, which constitutes the mineral phase of hard tissues, HA exhibits excellent biocompatibility and osteoconductivity, as it is able to promote, *in vivo*, bone tissue apposition to its surface. HA has been extensively used in form of cements, powders and granules to produce bone fillers and synthetic bone grafts for biomedical appli-

cations. Unfortunately, the poor mechanical performance of HA (in particular the tensile strength and fracture toughness) makes its use difficult in bulk form when load bearing capacity is required. As a consequence, for such applications, HA utilization is mainly confined to the deposition of bioactive coatings on metallic implants [5–8].

The disadvantages associated to the use of HA also include the high sintering temperatures typically required for obtaining bulk products [9,10]; moreover, the reactivity of this material at body temperature and physiological pH is typically low, consequently the osseointegration rate of HA-based grafts, which should match the rate of growth of the new tissue, is also rather modest [7,11]. This fact can be particularly detrimental for the production of HA scaffolds for bone tissue engineering, which should resorb in a predictable way, at the same rate as the tissue is repaired.

In order to overcome these limitations, several investigations have been addressed to the preparation of HA-based composites with bioactive glasses as second phase. Most of these studies involved the use of 45S5 Bioglass® (45S5), the first bioactive glass developed by Larry Hench in 1969 [12]. 45S5 is a degradable glass in the Na<sub>2</sub>O–CaO–SiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub> system, and it is able to form a chemical bond with soft tissues as well as with bone. In general, bioactive glasses bond to bone more rapidly than other bioceramics. Moreover, *in vitro* studies demonstrated that the dissolution products

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(e.g. Si, P, Ca) of 45S5 stimulate osteoblasts proliferation and seem to induce angiogenesis and neo-vascularization [13].

The production of HA/bioactive glass composites opens intriguing scenarios, since it allows to go beyond the intrinsic limits of the ceramic and glassy phases when considered singularly [4]. On the one hand, by varying the volume fractions of the two constituents, it is possible to control the bioactivity and the dissolution rate of the resulting material, so that innovative systems with tailored biological properties can be obtained. In addition, the use of glasses may be further exploited to incorporate specific ions, such as fluorine, silicon, magnesium or strontium, within the lattice of HA, with the aim to reproduce the composition of the biological apatite, which is intrinsically nonstoichiometric and calcium-deficient with many di- and tri-valent ion substitutions [14]. Furthermore, the glass may act as sintering aid, thus promoting the densification of the composite powders [9,10].

One of the main issues concerning the production of HA/bioactive glasses composites regards the thermal treatment which is necessary to sinter them. The densification of 45S5-based composites by pressureless sintering usually requires temperatures up to 1300 °C, which exceeds the crystallization temperature of the glassy phase. On the one hand, the crystallization of the glass has an adverse effect on the sintering process, thus limiting the densification of the final system which may be prone to unwanted residual porosity. Moreover, the HA decomposition and/or reactions between glass and apatite during the thermal treatment was also observed. Finally, the crystallization of the glassy phase may reduce its bioactivity [3,9,10,15].

Several investigations have been devoted to understand how to tailor the glass formulation with the aim to prevent crystallization [16–18]. In recent years, a novel class of silicate glasses with lower tendency to crystallize with respect to 45S5 were produced and employed to develop HA-based composites. In particular the so-called BG.Ca/Mix system – a CaO-rich, K<sub>2</sub>O modified glass composition – was specifically formulated as an alternative to 45S5 to be used whenever thermal treatments on bioactive glasses are required [19,20]. A crystallization temperature of 880 °C is reported for BG.Ca/Mix, while 45S5 starts to crystallize at temperatures as low as 610 °C [21]. BG.Ca/Mix powders were recently used to produce various HA-based composites containing up to 70 wt.% of HA [22,23]. Although it was possible to sinter the novel samples at a lower temperature with respect to HA/45S5 composites with the same HA/glass proportion, the composites with higher amounts of HA suffered for some residual porosity and poor mechanical properties. For these reasons, several efforts have been made to identify more efficient powder densification techniques, as an alternative to classical sintering.

In this regard, spark plasma sintering (SPS), also referred to as pulsed electric current sintering (PECS) or field-assisted sintering technique (FAST), represents a more effective consolidation method with respect to conventional pressureless and hot-pressing approaches [24]. Briefly, during SPS, an electric current flows through the graphite mould containing the processing powders, that are therefore heated very fast by Joule effect. The simultaneous application of a mechanical load allows for the rapid obtention of highly dense samples. Compared to alternative sintering methods, SPS has two main advantages: firstly, it makes processing time significantly shorter; secondly, it requires relatively lower temperatures to reach high consolidation levels. Consequently, SPS is beneficial in sintering processes where crystallization phenomena, grain growth, and/or phases decomposition have to be avoided or minimized.

Based on these considerations, two studies aimed to the consolidation by SPS of three different commercial HA powders [25] as well as 45S5 and BG.Ca/Mix bioactive glasses [26] were recently carried out. In particular, the full densification of HA CAPTAL® powders

was achieved after 5 min dwell time at 1200 °C and the resulting product does not present any secondary phase [25]. Moreover, concerning the bioglass powders, completely dense and fully amorphous BG.Ca/Mix materials were produced by SPS at 730 °C in 2 min holding time [26].

In this work, the SPS technique is employed for the first time to produce HA-based composites with BG.Ca/Mix glass as second phase. Specifically, a systematic study is conducted to identify the optimal sintering conditions for preparing highly dense composites by considering three different HA/BG.Ca-Mix proportions. The obtained bulk products are then characterized from the compositional, microstructural and mechanical points of view. Finally, the bioactivity of the composites is investigated *in vitro* in a simulated body fluid solution.

## 2. Materials and methods

### 2.1. Composites preparation

The raw powder reagents (commercial SiO<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> by Carlo Erba Reagenti, Rodano-Milano, Italy) were melted at 1450 °C for 1 h to produce BG.Ca/Mix (composition: 47.3 mol% SiO<sub>2</sub>, 45.6 mol% CaO, 2.3 mol% K<sub>2</sub>O, 2.3 mol% Na<sub>2</sub>O, and 2.6 mol% P<sub>2</sub>O<sub>5</sub>). Subsequently the melt was quenched in room-temperature water to obtain a frit which was dried at 110 °C for 12 h and then milled into powder (grain size <45 μm). BG.Ca/Mix and commercial HA powders (CAPTAL® Hydroxylapatite, Plasma Biot Ltd., UK) were accurately mixed in a plastic bottle using a rolls shaker for 6 h in order to prepare the following set of composites:

- 80 wt.% BG Ca/Mix and 20 wt.% HA powders (“80BG.20HA”);
- 50 wt.% BG Ca/Mix and 50 wt.% HA powders (“50BG.50HA”);
- 30 wt.% BG Ca/Mix and 70 wt.% HA powders (“30BG.70HA”).

Moreover, SPSed pure HA specimens were prepared and subsequently used as a control in the investigation of the composites' bioactivity (see next paragraphs). The sintering conditions for the production of the HA samples have been previously reported and discussed in Ref. [25].

### 2.2. Spark plasma sintering of composite powders

Spark plasma sintering experiments for the consolidation of 80BG.20HA, 50BG.50HA and 30BG.70HA powders were performed by means of a SPS 515S equipment (Fuji Electronic Industrial Co., Ltd., Japan), which is based on the combination of an uniaxial press (50 kN maximum load) with a DC pulsed current generator (10 V, 1500 A, 300 Hz). The 12:2 ON/OFF pulses sequence was adopted, with the characteristic time of each pulse of about 3.3 ms. About 1.49, 1.53 or 1.56 g of 80BG.20HA, 50BG.50HA and 30BG.70HA, powders, respectively, were placed in a cylindrical die (outside diameter of 35 mm, inside diameter of 15 mm, and 30 mm high) equipped with two punches. All the tooling components consisted of AT101 graphite (Atal s.r.l., Italy). To facilitate sample release after SPS, a graphite foil with a 0.13 mm thickness (Alfa Aesar Karlsruhe, Germany) was placed between the pressed powder and the die/plungers walls. In addition, the die was covered with a graphite felt layer (3 mm thick, Atal s.r.l., Italy) to minimize thermal losses during the heating process.

Temperature measurement and control were performed using a K-type thermocouple (Omega Engineering Inc., USA) inserted in a small hole drilled at the die surface. The real-time evolution of a number of parameters, *i.e.*, temperature, electric current, voltage between the machine electrodes, applied load, and vertical sample displacement was recorded. It should be noted that the contribu-

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