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Suspension plasma spraying of optimised functionally graded coatings of bioactive glass/hydroxyapatite

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ABSTRACT

The innovative suspension plasma spraying (SPS) technique was applied to produce a bioactive glass/hydroxyapatite (HA) multi-layered functionally graded coating (FGC). The constituent phases were selected to combine the high bone-bonding ability of bioactive glasses (on the surface of the FGC) with the long-term stability of HA (close to the interface with the metal substrate). The fabrication method was optimised using the suspension feed rates which took into account the different deposition efficiencies of bioactive glasses and of HA. During the deposition process, which was carried out with a SG-100 torch an industrial robot was used to realise the torch movement and the spraying parameters were optimised in view of industrial applications of the coatings. A microstructural investigation was performed on the FGC using Raman spectroscopy and environmental scanning electron microscopy (ESEM) coupled with X-EDS microanalysis. The analysis confirmed that the obtained compositional gradient met the designed one.

The coatings were characterised both in as-sprayed state and after soaking in a simulated body fluid (SBF) for periods ranging from 1 to 14 days. The FGC exhibited a strong reactivity in SBF and a high scratch resistance even after immersion, confirming its potential for biomedical applications.

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1. Introduction

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) and other calcium phosphate ceramic materials are used to produce high-performance biomedical devices for orthopaedic applications, on account of their similarity with the mineral component of human bone [1,2]. Since HA is brittle, it is applied as a bioactive coating on metallic substrates, which provide the required mechanical stability for load bearing prostheses [3–5]. The first clinical trials date back to 1985, when Furlong and Osborn [6] tested the effectiveness of a HA coating on femoral stems. Currently the femoral stem is still the major application for HA coatings; however, other common destinations include knee reconstructions, screws for fixing bone fractures, and dental restorations. For example, Rajaratnam et al. [7] analysed the long-term stability of HA-coated components in total hip replacement and they reported that 21 years after implantation only 2.6% of the HA-coated prostheses failed. Melton et al. [8], who worked on total knee replacements, confirmed these results. In addition, more than 96% of the implants survived up to 18 years without debris-induced failure. These data explain why HA-coated prostheses have replaced to a degree cemented implants.

However, the long-term stability of HA-based prostheses depends on the chemical composition and degree of crystallinity of HA. In fact, stoichiometric and highly crystalline HA is almost stable in a biological environment, but, inversely, poorly crystallised HA and/or nonstoichiometric calcium phosphates undergo quite fast degradation. Other factors, such as the Ca/P atomic ratio, the presence of secondary phases and some microstructural peculiarities such as porosity or crystals size may affect the actual reactivity of HA-based coatings [9–11]. Therefore the achievement of a high degree of crystallinity and a close control of the chemical composition are strictly required to avoid undesired reactions, which may lead to the degradation of the coating and to the failure of the implant [12]. On the other hand, pure crystalline HA has a low dissolution rate, which slows down the bone integration. In order to overcome this drawback, composite coatings, coupling HA with bioactive glasses, may offer a solution. Bioactive glasses are a family of special glasses which are able to bond to bones and, if the glass composition is properly designed, even to soft tissues [13,14]. According to clinical trials, bioactive glasses have the highest, so-called, in vivo bioactivity index (I_B) [15]. For these reasons, the introduction of bioactive glass-HA composites can be an interesting approach to improve the performance of bioactive coatings for orthopaedic devices. In fact, the resorption rate of bioactive glass/HA composites can be controlled by changing the glass volume fraction [16–25].

Plasma spraying is the most widely used process to deposit bioactive coatings, but recently many innovations have been proposed, such as the suspension plasma spraying (SPS) technique [26,27]. In this method, a suspension is used as feedstock instead of dry powder and therefore it is possible to process sub-micrometric or even nanometric powders

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(because they are formulated together with other additives in a suspension). Such feedstock results in coatings having a finer microstructure than that obtained with coarse, dry powders used in conventional plasma spraying [26].

The present contribution aims at exploring the SPS deposition of a multi-layered bioactive glass/HA composite coating, which may be considered as a functionally graded coating (FGC) in which the volume fractions of the constituent phases gradually change from layer to layer, from pure HA at the interface with the metal substrate to pure glass on the outer surface. In particular, the paper describes an advanced approach to produce the bioactive glass/HA FGCs, since the spraying parameters were optimised in view of an industrial application of the coatings. Indeed, this is the third and concluding step of an extensive research dedicated to bioactive glass/HA biphasic coatings produced by SPS. In fact, an introductory contribution aimed at verifying the effectiveness of a thin SPS bioactive glass topcoat onto a standard HA coating obtained by plasma spraying of coarse, dry powders [28]. Subsequently, in a second contribution, various types of bioactive glass/HA biphasic coatings were produced by SPS and the effect of the constituent phases' distribution was analysed [29]. This second investigation included a conventional composite coating (called *Composite* and having a random distribution of the constituent phases), a 50–50 bi-layered coating (called *Duplex* with glass on top of a HA layer) and an initial FGC. The results confirmed that the presence of a bioactive glass layer on top of the coating clearly improved the bone-bonding ability. Indeed, the reactivity in a simulated body fluid (SBF) of both the bi-layered *Duplex* coating and of the initial FGC was definitely superior than that of the pure HA coating (used as a control) and of the *Composite* coating [29]. Nevertheless the presence of an abrupt interface between the glass topcoat and the HA layer undermined the scratch resistance of the conventional bi-layered *Duplex* coating. Hence the FGC emerged as the optimal choice, since it combined a strong apatite-forming ability and a good mechanical reliability [29]. Notwithstanding the good performance of the initial FGC, this preliminary investigation enabled to find out some point to be solved [29]. In fact, the production process was expensive and the real compositional gradient was hard to control, due to the higher deposition efficiency of the glass powder with respect to HA. Moreover residual pores, cracks and other defects could be observed in the initial FGC microstructure [29]. Therefore, with respect to the previous contributions, in the present paper many changes were introduced to finalise the deposition process and, at the same time, to improve the properties of the FGC. First of all, an industrial robot was used to move the torch and the number of sublayers having different compositions in the FGC was reduced. These changes were expected to act in favour of the industrial application. Moreover the percentage of HA was increased to balance the high deposition efficiency of glass. The presence of a higher amount of HA in the sublayers close to the interface was selected to strengthen the stability of the FGC. Finally, very fine (micron-sized) powders were processed aiming at achieving a fine microstructure.

In order to assess their reliability, the coatings produced in this way were characterised using microstructural and mechanical tests. They were also tested in vitro by immersion in SBF to verify their apatite-forming ability. Finally, the adhesion of the coating to the substrate was qualitatively evaluated by means of scratch tests before and after in vitro tests.

2. Materials and methods

2.1. Feedstock materials

The BG_Ca glass (in wt.%, 4.7 Na_2O, 42.3 CaO, 6 P_2O_5, bal SiO_2), with the composition derived from the standard 45S5 Bioaglass® with an important content of CaO to limit the crystallisation at high temperatures [30–32], was produced by a conventional melt-quenching method as described in details elsewhere [27]. The obtained glass was dry milled and, subsequently, attrition milled in ethanol with the addition of 3 wt.% (of dry powder) of the Beycostat C213 dispersant. The final BG_Ca powder had a bi-modal distribution (minor peak at 0.2 μm and major one at 1.8 μm) with a mean diameter of $d_{50} = 1.7$ μm, as determined with a granulometer Partica LA-950V2, Horiba. The feedstock suspension was formulated by dispersing 10 wt.% of solid phase in 90 wt.% of ethanol.

The HA starting powder was a commercial product (Tomita, Japan) with a mean diameter of $d_{50} = 120$ μm. The powder was attrition milled in ethanol adding 3 wt.% (of dry powder) of Beycostat C213 as dispersant. The obtained powder had a bi-modal distribution (minor peak at 0.1 μm and major one at 2.5 μm) with a mean diameter of $d_{50} = 1.7$ μm (data not shown). The feedstock suspension was formulated by dispersing 10 wt.% of solid phase in a liquid solution which was composed of 50 wt.% of water and 50 wt.% of ethanol; this mixture was chosen since previous experiments had proven that it was particularly suitable for the application [29].

2.2. Coating deposition

The deposition process was carried out using a Praxair installation including an SG-100 torch (Praxair, S.T., Indianapolis, IN, USA) configured in subsonic mode. The torch was mounted on a 5-axis ABB IRB-6 industrial robot. The internal injection was used, with a 90° radial injection located at 16 mm from the torch's exit. An injector having an internal diameter of 300 μm was chosen.

A double peristaltic pump system was set up to supply the glass and HA suspensions separately. The suspensions were mixed directly inside the injector, while two non-return valves were mounted to avoid reflux phenomena.

During spraying, the suspensions were continuously stirred to prevent sedimentation and agglomeration of fine solids. As preliminary attempts to deposit glass/HA biphasic coatings revealed problems associated to the flowability of the suspensions, the solid content was reduced to 10 wt.% to avoid clogging the injector and the dispersant content was increased up to 3 wt.% of the dry powders (see [29]). The spray parameters are reported in Table 1.

In order to create the compositional gradient, the FGC was produced in five runs and, thanks to the double peristaltic pump system, the feed rates of the suspensions were separately changed during each run, as shown in Table 2. It is worth noting that the feed rates and the number of passages were adjusted to take into account the low deposition efficiency of the HA powder with respect to the BG_Ca one (as previously observed [29]).

A jet of compressed air was used to limit the temperature of the coating at spraying. The front-side cooling system consists of two jets of air, located on both sides of the plasma. In this way, as the torch moves along the scanning direction, the first cooling jet hits the substrate before the plasma, and the second one after it. The jets are mounted at a distance of about 15 cm from the plasma, in order to avoid interaction with the deposition process. Moreover, between the runs, the samples were cooled down to 80 °C. An optical IN 5 Plus pyrometer (Impac) was used to record the temperature at each spray run; the mean values are reported in the same Table 2.

Table 1
Operational spray parameters.

Parameter		Value
Power [kW]		38
Gases	Ar [slpm]	45
	H_2 [slpm]	6
Distance [mm]		55
Torch speed [mm/s]		750
Scan step [mm]		3
Suspension flow rate [g/min]		20

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