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Improved bonding strength of bioactive cermet Cold Gas Spray coatings

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ABSTRACT

The fabrication of cermet biocompatible coatings by means Cold Gas Spray (CGS) provides prosthesis with outstanding mechanical properties and the required composition for enhancing the bioactivity of prosthetic materials. In this study, hydroxyapatite/Titanium coatings were deposited by means of CGS technology onto titanium alloy substrates with the aim of building-up well-bonded homogeneous coatings. Powders were blended in different percentages and sprayed; as long as the amount of hydroxyapatite in the feedstock increased, the quality of the coating was reduced. Besides, the relation between the particle size distribution of ceramic and metallic particles is of significant consideration. Plastic deformation of titanium particles at the impact eased the anchoring of hard hydroxyapatite particles present at the top surface of the coating, which assures the looked-for interaction with the cells. Coatings were immersed in Hank's solution for 1, 4 and 7 days; bonding strength value was above 60 MPa even after 7 days, which enhances common results of HAp coatings obtained by conventional thermal spray technologies.

1. Introduction

The development of biomedical devices and their demand have been rising driven by factors such as aging population or degenerative joint diseases. Besides, life expectancy and active lifestyle has fostered an increasing number of reconstructive procedures. This synergy has led to a global orthopedic prosthetics market which is expected to reach US$23.5 billion by 2017 [1]. In this scenario, titanium alloys (Ti6Al4V) have been widely used as implants because of their mechanical properties, superior biocompatibility and enhanced corrosion resistance [2]. Nevertheless, the limited bioactivity together with possible cytotoxicity of aluminium and vanadium restricts their application [3]. Thus, coated titanium alloy prostheses with bioactive materials able to enhance cell adhesion, proliferation and differentiation are promptly welcomed. Given this framework, Hydroxyapatite (HAp: $Ca_{10}(PO_4)_6(OH)_2$), which is a Ca-based bioceramic with favorable osteoconductive and bioactive properties, has been extensively selected for solving this issue [4].

Among the different coating procedures and the outstanding industrial necessity of coated implants with excellent mechanical properties through rapid manufacturing and cost-effective techniques, thermal spray (TS) processes appeared as an excellent alternative for filling this yielding requirement. Actually, TS has been reviewed as the adequate group of technologies in terms of cost and process efficiency for achieving bioactive coatings onto implants ahead of other coating processes such as sol–gel, dip-coating, pulsed laser deposition or sputtering [5]. Concretely, atmospheric plasma spray (APS) has broadly dealt with the deposition of HAp coatings; the obtained results and product via APS technology have led to the development of a defined market with some established companies [6–8]. APS accelerates powder particles in their melted state towards a substrate by means of a plasma jet at temperatures above 15,000 °C [9]. Overall scientific criteria conclude that APS HAp coatings increase the biocompatibility of different prosthetic materials such as metallic and polymeric implants [10,11]. Nevertheless, the main disadvantages in these coated biomaterials are caused by: i) possible lack of bonding strength between the substrate and the coating; ii) certain delamination between sprayed layers; iii) brittleness of APS thick ceramic coatings; and iv) changes in the composition and microstructure of HAp feedstock material due to the temperatures involved in the APS process.

Other thermally-activated TS processes such as suspension plasma spray (SPS) and high velocity oxygen fuel spray (HVOF) have also led to interesting results. Nevertheless, temperatures involved in plasma jets and combustion flames partially carry out the same drawbacks above mentioned. Therefore, despite the large success of TS HAp coatings and their application, conventional TS technologies may be overcome notably. Cold Gas Spray (CGS) has positioned itself as the technology that represents the most significant strengths of TS but avoids their undesired features that source from thermal degradation; composition and microstructure of the starting raw material are maintained. CGS technology propels powder particles at supersonic velocities and the coatings are built-up due to the plastic deformation of the particles in solid state when impacting onto the substrate [9].

The main target of this research is to provide HAp/Ti coatings onto Ti6Al4V substrates with enhanced bonding strength after immersing

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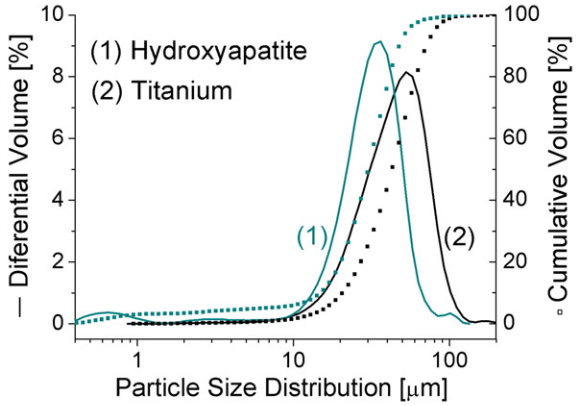

Fig. 1. Particle size distribution of Ti and HAp powders.

the coatings in Hanks' solution compared to benchmark HAp coatings. Different percentages of feedstock blends have been prepared and the relation between the ratios of particle diameter has been studied; a bonding mechanism related to non-deformable HAp particles and ductile Ti particles has been described. In this way, cermet-based CGS coatings have been obtained, which combine high-performance osteointegrative features with exceptional mechanical properties similar to CGS metallic Ti coatings.

2. Material and methods

Titanium powder obtained from a fused and crushed process and agglomerated hydroxyapatite were used as feedstock. Different blends of HAp and Ti were prepared: B1 (70 vol.% HAp); B2 (50 vol.% HAp) and; B3 (30 vol.% HAp). The CGS equipment used for obtaining the coatings was a KINETICS® 4000 (Cold Gas Technology, Ampfing, Germany), with a maximum operating pressure of 40 bar and temperature of 800 °C operating with nitrogen as the propellant gas. In addition, KINETICS® 4000 had the possibility of using a pre-chamber of 120 mm in length connected to the nozzle of the gun where powders are heated up for a longer time. The powder and the cross-section area of the samples were observed by Scanning Electron Microscopy, SEM (ProX Phenom). Energy Dispersive Spectroscopy, EDS, (Jeol) was used for identifying HAp and Ti. The phase composition of the powder and coatings was analyzed by an X'Pert PRO MPD diffractometer (PANalytical). In order to determine the bonding strengths of the sprayed samples, adhesion tests were performed on each selected coating following the ASTM F1147 (2005) standard. A testing apparatus SERVOSIS ME-402/10 model was used with a cross-head velocity of 0.02 mm/s, which was controlled by under displacement. Before testing the bonding strength of the coatings, the samples were immersed in Hank's balanced salt solution (HBSS) for 1, 4 and 7 days.

3. Results and discussion

Ti and HAp powder had a particle size distribution between 20 and 90 μm and 10 and 40 μm respectively (Fig. 1). As regards the shape of the particles, Fig. 2 shows that Ti powder was angular while HAp was spherical. The composition of starting feedstock material is of special concern; osteointegration depends highly on the surface crystallinity of the implant. Crystalline composition of bioactive materials such as calcium phosphates favors cell parameters [12]. Thus, XRD analyses from the initial powders were carried out (Fig. 3); phase composition of both ceramic and metallic feedstock was pure crystalline hydroxyapatite and titanium respectively, no presence of other phases or impurities were found.

M. Gardon et al. achieved nanostructured TiO_2 coatings onto polyetheretherketone (PEEK) substrates by means of CGS so as to develop bioactive surfaces [13]. CGS nano-TiO_2 increased cell adhesion, proliferation and differentiation compared to original PEEK prosthesis. The coatings were feasibly built-up because of the breaking down of the agglomerated particles at the impact. Anyhow, HAp selected for this study was not expected to uphold the same bonding mechanism due to its lower hardness compared to TiO_2 previously used. Non-deformable HAp powder was blended with Ti powder with the purpose of enabling the mechanical anchorage of the ceramic particles in the coating.

Spraying conditions were selected from operation parameters typically used in the fabrication of CGS Ti coatings discussed in previous studies [14]. These conditions are usually energetic; high pressure and temperature of the N_2 stream are required for adequately deforming titanium in order to reach high quality coatings. With the aim of understanding the deposition of blended Ti and HAp powders onto Ti6Al4V alloy, gun velocity was increased so as to analyze the obtained splats. As it can be observed in Fig. 4, Ti particles were effectively plastically deformed onto the substrate surface while HAp was mechanically embedded. On the other hand, a considerable amount of craters was found, which may be caused by impacting HAp particles and their subsequent detachment. Thus, the spraying conditions were kept constant and the gun velocity was reduced in order to build-up the coating. B1 and B2 led to some anchored particles without properly depositing the coating, but B3 blend exhibited an outstanding outcome. As shown in Fig. 5, thick homogeneous CGS coatings were obtained. Closer

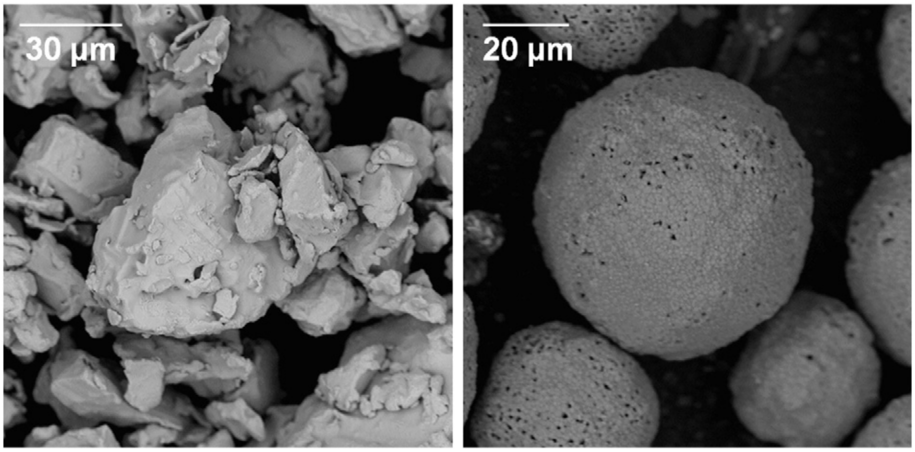

Fig. 2. SEM micrographs of Ti and HAp powders.