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Mechanical performance of bioceramic coatings obtained by high-velocity oxy-fuel spray for biomedical purposes

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ABSTRACT

Plasma-sprayed hydroxyapatite coatings were used for many years to improve the osseointegration of joint implants. However, it was observed that their mechanical properties did not meet the requirements. Consequently, as in previous studies, an HAp–TiO_2 mixture was considered. But, contrarily to these studies, where TiO_2 is the majority phase (80–90 wt.% into the mixture), in this work the feasibility of coatings containing only 20 wt.% of TIO_2 is proposed. Composite coatings were obtained via high-velocity oxy-fuel (HVOF) spray at four different sets of conditions. Bond strength tests, fracture toughness calculations and scratch tests together with preliminary cell viability tests were performed and compared with those of pure hydroxyapatite coatings and a powder mixture of 60wt.%HAp–40wt.%TiO_2 (considered in previous studies and which showed mechanical and biological limitations, respectively). Results showed that one of the proposed 80–20 cases displayed a best combination of mechanical and biological properties than the proposed alternatives.

1. Introduction

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) has been used for biomedical applications for decades, due to its well-known osteoconductive properties [1,2]. As its mechanical behavior is poor, the material was found to be unsuitable for large bone or load-bearing replacements [3]. However, in the early 1980s a new use was envisaged: as coating on metal substrates, in order to combine the mechanical properties of the metal alloys with the biological properties of the HAp in prosthetic or dental devices [4]. Industries soon took up the idea and started to produce HAp coatings using plasma-spray [4] to resolve aseptic loosening, which is the main cause of early failure in joint replacements after short implantation times [5].

Further studies in the following years showed the problems inherent in the plasma-spraying procedure. Although the physiological behavior of the coated prosthesis is better than that of the uncoated one, the high temperatures reached during the plasma process lead to a degradation of the initial phases of the HAp powder [6]. As a consequence, unwanted phases with poor mechanical properties appear, either in the coating–substrate interface or across the coating. In addition, hydroxyapatite is a brittle material [7], with a tendency to delaminate easily. Therefore, micrometric parts of the coating may separate from the prosthesis and damage tissues [8].

One way to solve these problems is by combining, within the coating, hydroxyapatite with another compound with better mechanical performance. Different possibilities have been considered in literature, such as carbon nanotubes to improve toughness and abrasion resistance [9,10], silicon oxide to improve adherence and corrosion resistance [11,12], and ceramic (TiO_2 for example) interlayers [13].

The addition of TiO_2 as the majority phase (≈80%) has been considered in many studies, using a nanometric titania [14]. The nanostructure allows a good proliferation and adhesion in vitro, but the lower amount of calcium into the coating would lead to a lower differentiation than for HAp coatings, because of the essential role of this ion in this biological process [15,16]. Furthermore, according to some authors [17,18], TiO_2 surfaces are bioinert when in vivo conditions are tested, and could lead to the formation of a fibrous capsule between them and the surrounding tissues. Previous preliminary studies performed in the Thermal Spray Centre with 100%HAp coatings and 60wt.%HAp–40wt.%TiO_2 pointed their possible limitations (low adherence in the first case, low bioactivity in the latter). For these reasons, an intermediate composition (80wt.%HAp–20wt.%TiO_2) was explored, in order to find out a compromise between good mechanical properties and the well-known biological properties of HAp. This mixture was considered the starting material, comparing it with the other two. Plasma-spray technique, the most common technique, was substituted by HVOF (high-velocity oxy-fuel spray), using lower temperatures and, subsequently, resulting in a lower degradation of the coating. Adhesion, delamination and crack growth were studied using bond strength tests, scratch testing and indentations, to assess the influence of TiO_2

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and HVOF. A preliminary viability test was also performed to evaluate the biological behavior of the studied samples.

2. Experimental method

2.1. Raw materials and thermal spray conditions

The starting powder was a mechanical mixture of a Sulzer-Metco TiO_2 powder and a Plasma-Biotal Ltd. hydroxyapatite powder.

The morphology and structure of the two powders, HAp and TiO_2, were first characterized by Scanning Electron Microscopy (SEM) using a Jeol JSM-5310 equipment. A Beckman Coulter LS13320 Laser Spectrometer was used to study granulometric dispersion. Finally, a Siemens D500 X-ray diffraction Bragg–Brentano type $\theta/2\theta$ apparatus, with Cu $K_{\alpha 1+2}$ radiation with $\alpha_1 = 1.54060$ and $\alpha_2 = 1.54443$ at 40 kV and 30 mA, was used to analyze their purity and crystallinity.

Ti6Al4V alloy was used as the substrate, and was alumina grit-blasted before the spraying process to obtain roughness values of over 5 μm, which guarantee good coating adhesion.

All the coatings were sprayed with an HVOF Sulzer-Metco Diamond Jet Hybrid (DJH)-2700 system under different spraying conditions (Table 1). Four main conditions are applied to 80wt.%HAp–20wt.%TiO_2 coatings, and pure HAp and 60wt.%HAp–40wt.%TiO_2 samples were also sprayed in their optimal spraying conditions for comparison purposes (for the tests not previously performed with these combinations in the own research group, such as fracture toughness, scratch test, and cell viability). Table 1 shows also the description of each one of the samples along with the name used to refer to them all over the text.

2.2. Microstructural analysis and phase identification

Studied coatings were cut, ground, polished and sputtered before being observed by SEM. Matrox Inspector software was used to obtain thickness and porosity values. Phases were identified by X-ray diffraction using the Rietveld method.

2.3. Mechanical characterization

Bond strength tests were carried out according to the ASTM F1147-05 (2011) standard [19], with the testing machine SERVOSIS ME-402/10. Three samples were tested for each case, to produce enough results to calculate the desired statistics.

Fracture toughness was measured using indentation analysis with a Matsuzawa MXT-CX microhardness tester at 300 gf. Two tests based on Vickers indentation were performed: the Vickers indentation fracture (VIF) test, in the middle layers of the coatings; and the interface indentation fracture (IIF) test, to analyze fracture toughness at the interface. The samples were observed by SEM to obtain sufficiently precise micrographs, and the Matrox Inspector image analysis program was used to measure dimensions and cracks.

Two steps are needed in the VIF test [20,21] to calculate fracture toughness. The first step, which is required to calculate the Young's modulus, employs Knoop indentations and Eq. (1):

$$\frac{b'}{a'} = \frac{b}{a} - \alpha\frac{H_k}{E} \tag{1}$$

where b′ and a′ are the dimensions of the Knoop diagonals after elastic recovery, b/a is a known value of 1/7.11 that corresponds to the indenter geometry, and α is a constant value of 0.45. H_k is considered the hardness measured by the Knoop indentation.

Once the Young's modulus has been calculated, the Anstis equation [21], Eq. (2), can be applied:

$$K_c = 0.016\sqrt{\frac{E}{H}}\left[\frac{P}{c^{3/2}}\right] \tag{2}$$

where P is the applied load of 300 gf, c is the surface trace of the crack measured from the center of the indent, E is the Young's modulus and H is the hardness measured by Vickers indentation. This fracture toughness calculation provides a qualitative comparison of results for biomaterials [22].

The method developed by Becher et al. [23] was applied for the IIF test to obtain a qualitative and comparative measure [22] of interface toughness. The interfacial debonding response was evaluated using cracks generated by a Vickers indents performed at various angles. In this regard, weaker interfaces display interfacial debonding at angles close to 90°. Indents were performed at 300 gf considering a ratio of the intersecting crack length to nominal crack length of around 0.5 [22,23].

For both tests, VIF and IIF, three samples were analyzed for each studied condition and ten indentations were performed in each sample.

The adhesion strength of the TiO_2–HAp coatings on the Ti6Al4V alloy was also evaluated by the single-point scratch technique (ASTM C1624-05 [24]). The tests were performed using a CSM-Revetest scratch testing instrument at a constant speed of 10 mm/min, with a progressive increase to a normal force of 1 to 140 N. The critical scratch load (L_c) was defined as the load which caused adhesive failure, i.e., detachment and separation of the coating from the substrate by cracking and debonding at the coating–substrate interface. Scratch tracks and induced damage were examined by means of laser confocal scanning microscopy (LCSM), using an Olympus LEXT OLS 3100 microscope. Five scratch tests were performed on three different samples for each case studied in order to obtain an average value and a standard deviation.

2.4. Cell culture and viability tests

Osteoblasts were obtained for culture following the protocol described by Nacher et al. [25] from knee trabecular bone obtained after prosthesis replacement with patients' prior written informed consent. The entire study was conducted in accordance with the 1975

Table 1
Spraying conditions.

Sample description	100%HAp	80%HAp–20%TiO_2				60%HAp–40%TiO_2
Sample designation	HAp	80–20				60–40
		A	B	C	D	
O_2 (l/min)	278	253	240	278	265	253
Propylene (l/min)	81					
Compressed air (l/min)	203	203	264	203	264	203
Oxygen/propylene	3.96	3.65	3.65	3.96	3.96	3.65
Number of layers	7	5				5
Distances (mm)	240	200–220–240				200