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Selection of the implant and coating materials for optimized performance by means of nanoindentation

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ABSTRACT

Mechanical compatibility between a coating and a substrate is important for the longevity of implant materials. While previous studies have utilized the entire coating for analysis of mechanical compatibility of the surface, this study focuses on the nanoindentation of a uniformly thermally sprayed splat. Hydroxyapatite was thermally sprayed to create a homogeneous deposit density, as confirmed by microRaman spectroscopy, of amorphous calcium phosphate. Substrates were commercially pure Ti, Ti–6Al–4V, Co–Cr alloy and stainless steel. Nanoindentation revealed that splats deposited on the different metals have similar hardness and elastic modulus values of 4.2 ± 0.2 GPa and 80 ± 3 GPa, respectively. The mechanical properties were affected by the substrate type more than residual stresses, which were found to be low. It is recommended that amorphous calcium phosphate is annealed to relieve the quenching stress or that appropriate temperature histories are chosen to relax the stress created in cooling the coating assembly.

1. Introduction

The load-bearing requirement of biomedical implants has led to the choice of metals that can sustain large forces and retain their shape after patient physical activity. Metal alloys used in artificial joints (i.e. hip, knee and shoulder), dental implants and orthopaedic screws include commercially pure titanium (CP Ti) [1–3], a titanium-based alloy (i.e. Ti–6Al–4V) [4,5], a cobalt based alloy (i.e. Co–Cr alloy) [6,7] and stainless steel [8,9]. The selection of these metals is based on the properties, cost, manufacturing ability and ease of making surface modifications for improved bone growth and attachment.

Titanium-based alloys offer a high strength to weight ratio, low modulus, high biocompatibility and resistance to corrosion [10]. Ti–6Al–4V is the most widely used titanium alloy for surgical and odontological applications due to its lightness (4.5 g cm^{-3}) compared with stainless steel (7.9 g cm^{-3}) and Co–Cr alloy (8.3 g cm^{-3}).

One of the main applications for Co–Cr alloys is in dental skeletal structures. These biomaterials have shown superior wear resistance over a long time in vivo, uniform surface finishing and a high resistance to bone debris formation [11]. Stainless steel finds wide use in orthopaedic applications because of its cost effectiveness, availability and process ability.

On the other hand, the release of ions (see Table 1) from metals, as well as their high elastic modulus compared with bone (see Table 2), are major concerns. Studies have shown that the release of aluminium and particularly vanadium ions may cause long-term health problems due to adverse tissue effects [12–15]. The introduction of foreign ions into the body arises from surface film dissolution and corrosion [16,17]. These reactions and the side effects of these products in the human body must top the list of considerations during material selection. The toxicity of metal ions, ranked in order from least to most toxic, is as follows: Cr < Mo < Al < Co < Ni < Fe < V [13]. Aluminium has been associated with dementia [18], while vanadium is considered to be an essential element in the body, becoming toxic at excessive levels [19]. Titanium forms a 1–4 nm thick oxide layer resulting in high corrosion resistance [20]. This protective TiO_2 film forms particularly quickly for Ti alloys [21,22], however, it may break down on contact with physiological fluids [23]. Overall, CP Ti causes the minimum amount of side effects and has received increasing interest for the fabrication of fixed and removable restorations [24]. Alloys such as Ti–6Al–4V are the preferred biomedical alloys because the second generation titanium orthopaedic alloys (i.e. Ti–12Mo–6Zr–2Fe, Ti–15Mo–5Zr–3Al, Ti–15Mo–3Nb–3O, Ti–15Zr–4Nb–2Ta–0.2Pd, Ti–15Sn–4Nb–2Ta–0.2Pd and Ti–35Nb–5Ta–7Zr) [25] are not yet widely available.

Another key problem that has been reported is loosening of the prosthetic device, a consequence of low adhesion between metallic implants and bone and insufficient load transfer [26]. This phenomenon could be attributed to the mismatched elastic moduli of bone and the artificial joint replacement, which is exacerbated

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Table 1
Elemental composition (mass%) of metal alloys.

Substrate	Ti	Al	V	Fe	O	Si	Co	Cr	Ni	Mo
CP Ti	Balance				0.10	0.16				
Ti–6Al–4V	Balance	6.24	4.19	0.18	0.17					
Co–Cr alloy				0.44		0.71	Balance	29.92	0.25	5.96
Stainless steel				Balance		0.47		19.72	10.46	2.38

Table 2
Elastic moduli of metallic implants.

Material	Elastic modulus (GPa)
Bone	7–30 [49], 10–40 [25]
CP Ti	98 [50], 103 [51], 105 [25]
Ti–6Al–4V	105–110 [52], 110 [53], 114 [51]
Co–Cr alloy	200–230 [25], 230 [52], 240 [54]
Stainless steel	193 [51], 200 [52], 205 [53]

by using Co–Cr and stainless steel (see Table 2). Furthermore, these metals are not bioactive in their native state and do not bond directly with bone. Therefore, there is concern about the long-term use of metallic implants.

Hydroxyapatite (HAp) coatings on metals are considered effective coatings for orthopaedic devices, [27,28] achieving minimum side-effects and maximum performance. Hap-coated implants provide both mechanical and biological compatibility to biomedical implants. The ideal HAp/metal combination should exhibit a low elastic modulus to transfer the applied load to the skeleton. The major issue identified with current coated implants is the inadequate implant-coating interface properties, in which the first layer of the coating plays a significant role.

Applying HAp to a metallic implant (especially by means of the thermal spray method) results in an anisotropic structure due to the formation of amorphous and calcium phosphate phases [29]. A fully formed HAp coating is a complex structure consisting of in excess of 200,000 droplets per cubic millimeter. Therefore, initial consideration is given to these single solidified droplets rather than the complete coating, in order to better understand its intrinsic behavior rather than extrinsic characteristics.

This study examines the influence of the substrate on the micromechanical properties of single solidified HAp drops. The metallic substrate and HAp powder are not unique. The composition depends on the raw material and manufacturer. The HAp powder and substrates are first measured separately. Then, the micromechanical properties of HAp coatings on substrates are determined and the interplay of mechanical properties examined.

2. Materials and experimental methods

2.1. Powder classification and characterization

HAp powder exhibits a high electrostatic potential and readily absorbs moisture and, therefore, agglomerates to lower the powder flowability. Agglomeration needs to be avoided, for better control of the separate particles and to facilitate the collection of single isolated splats. Thus, the spray dried HAp powder used in this study (CAM Implants, Leiden, The Netherlands) was sieved to 40–60 μm and dried prior to flame spraying.

The powder was analyzed using grazing incidence X-ray diffraction (GIXRD) with a Panalytical X'Pert using Cu$K\alpha$ radiation at 40 kV and 30 mA. The diffracted signal was collected through a fine slit at a step size of 0.02° over a 2θ range of 10–90° (20–60° shown here). The incident beam was fixed from the source at 2° relative to the powder surface, with an X'Pert position sensitive detector (PSD) and collimating slits. The powder pattern was peak matched to confirm the presence of HAp and the absence of other calcium phosphate compounds.

2.2. Flame spraying

The substrates were ground with 800, 1000 and 1200 SiC paper and then polished on a Dur surface (Struers, Denmark) with 3 and 1 μm diamond suspensions. Bataille et al. [30] found that slightly roughened sandblasted stainless steel is significantly less biocompatible than the polished condition. Therefore, polishing was followed by another 3 min final step using MD Chem cloths with OPS suspension (Struers, Denmark). The same task was carried out to observe cross-sections of HAp particles after mounting in epoxy.

The powder was fed through a Metco 3MP powder feeder (Sulzer Metco, Wohlen, Switzerland) with air to a Metco 5P flame spray torch (Sulzer Metco) operated with acetylene and oxygen. The polished substrates were mounted 10 cm from the torch and preheated to ~200 °C to avoid a tendency for droplet splashing. Only one traverse was performed to collect single solidified droplets.

2.3. Morphology, microstructure and chemistry

Splat topography and morphology were examined using an XL30 Philips scanning electron microscope at 20 keV. Samples were sputter coated with gold using an Edwards S150B sputter coater before examination. Scanning electron microscopy (SEM) line analysis was used to reveal the chemical composition of the substrates (Table 1).

The topography of the single solidified droplets was examined using an Asylum MFP-3D atomic force microscope (Asylum Research, Santa Barbara, CA) in combination with an optical microscope (Eclipse TE2000-U, Nikon, USA).

Chemical analyzes were conducted using microRaman spectroscopy (Raman Renishaw RM1000 microspectrometer) with an excitation wavelength of 514 nm at a spectral resolution of 1 cm^{-1}. Spectra were recorded within the range 500–1200 cm^{-1} (800–1100 cm^{-1} shown here). To ensure the reliability of the data two different positions on 12 splats (centre and edge) were tested randomly.

2.4. Nanoindentation

Nanoindentation was performed using a NanoTest instrument (Micro Materials Ltd., Wrexham, UK). A Berkovich indenter (a three-sided pyramid with a face angle of 65.3°) was used. Depth sensing indentation tests were carried out on a reference sample of fused silica (FS) with a Poisson ratio of 0.17. Fused silica is usually chosen as a reference sample since its modulus is load independent. Load-controlled, load-partial unload experiments of several cycles were executed, with depths from 50 up to a maximum of 1500 nm (Fig. 1). Other experimental conditions were preset: loading and unloading rate of 20% of maximum load and 30 s holds for thermal drift correction. The results reveal a well-calibrated diamond area function (Fig. 1).