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Biomaterials 19 (1998) 2015–2029

Biomaterials

# Plasma sprayed hydroxyapatite coatings on titanium substrates Part 1: Mechanical properties and residual stress levels

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Received 1 September 1997; accepted 3 March 1998

**Abstract**

Hydroxyapatite (HA) coatings have been sprayed on to substrates of Ti–6Al–4V, using a range of input power levels and plasma gas mixtures. Coatings have also been produced on substrates of mild steel and tungsten, in order to explore certain aspects of the mechanical behaviour of HA without the complication of yielding or creep in the substrate. Studies have been made of the phase constitution, porosity, degree of crystallinity, $OH^-$ ion content, microstructure and surface roughness of the HA coatings. The Young's moduli in tension and in compression were evaluated by the cantilever beam bend test using a tungsten/HA composite beam. The flexural Young's modulus was determined using a free-standing deposit under the same test. Adhesion was characterised using the single-edge notch-bend test; this is considered superior to the tensile bond strength test in common use. Measured interfacial fracture energies were of the order 1–10 $J\,m^{-2}$. Stress levels were investigated using specimen curvature measurements in conjunction with a numerical process model. The quenching stress for HA was measured to be about 10–25 MPa and the residual stress level in HA coatings at room temperature are predicted to lie in the approximate range of 20–40 MPa (tensile). These residual stresses could be reduced in magnitude by maintaining the substrate at a low temperature (possibly below room temperature) during spraying and it may be worthwhile to explore this. Ideally, the HA coating should have low porosity, high cohesive strength, good adhesion to the substrate, a high degree of crystallinity and high chemical purity and phase stability. In practice, such combinations are rather difficult to achieve by just varying the spraying parameters. 

*Keywords:* Plasma spraying; Hydroxyapatite; Young's modulus; Adhesion; Residual stresses

## 1. Introduction

HA-coated implants have been widely used in orthopaedics [1, 2] and dentistry [3, 4]. This cementless fixation technique combines the strength, ductility and ease of fabrication of metallic implants with the increased biocompatibility associated with HA. Once HA is implanted, it has the ability to bond directly to the bone [1], to achieve earlier and greater fixation strength [2, 5, 6] and to reduce healing time [7] and pain levels. The reason for its acceptability lies in its having a composition similar to the mineral phase of bone and tooth enamel [8]. In an implanted prosthesis, the stability and the adherence of implant/coating and coating/bone interfaces strongly affect its performance. While the former bond is largely mechanical and the latter is mainly physiochemical in nature, the performance of both interfaces is closely related to the coating properties.

HA coatings have been applied by a variety of methods: dip coating [9, 10], electrophoretic deposition [11, 12], hot isostatic pressing [9], ion-beam sputtering [13], ion beam dynamic mixing [14], plasma spraying [15], conventional flame spraying [16, 17] and high-velocity oxy-fuel (HVOF) combustion spraying [18, 19]. Among these, plasma spraying appears to be the most favourable one in terms of chemical control, biocorrosion resistance [20], process efficiency [15] and the degree to which the substrate fatigue resistance is reduced [21].

The ideal HA coating for orthopaedic implants would be one with low porosity, strong cohesive strength, good adhesion to the substrate, a high degree of crystallinity

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0142-9612/98/$—See front matter 
*PII* S0142-9612(98)00103-3

and high chemical purity and phase stability. Amorphous HA tends to dissolve rapidly in the physiological environment, so that coatings with low crystallinity quickly become weak and may promote inflammatory responses. There may be benefits in tailoring the chemistry of the coating surface in some way so as to promote bone growth. It is possible that a thin reprecipitated amorphous HA layer on the surface could thus be advantageous, but the details of this are not yet clear. While a number of studies [19, 22–29] have been devoted to characterising the changes induced by plasma spraying in chemical composition and crystallinity, studies on the mechanical behaviour of HA coatings are rare. It is well known that the Young's modulus of a plasma sprayed coating is usually much lower than its corresponding bulk value. This can be attributed to the presence of pores and microcracks inside the coating. There are virtually no data available on the Young's modulus of sprayed HA, which is essential in predicting the residual stress levels presented inside the coatings and in determining their fatigue behaviour under cyclic loading.

A number of in vivo studies [1, 2, 7, 30, 31] have indicated that failure mainly occurs at the metal/coating interface. The longer the period of implantation, the higher is the probability of failure at this interface (since the strength of the bone/HA interface tends to increase with time during the early stages of post-operative recovery). Therefore, any anticipated long term benefit is expected to depend on the adhesive and cohesive integrity of the coating, which are strongly dependent on microstructure. To optimise the adhesion of HA coatings on metallic implants, a reliable method is needed for characterisation. The adhesion of HA coatings on metal substrates is frequently determined by the tensile adhesion test. This test has long been regarded as semi-quantitative at best and useful only for ranking purposes. The main problem associated with this test is that failure depends on the distribution of the flaws present at the specimen edge, which results in a wide scatter for the strength values obtained. In addition, there is a danger of significant penetration of adhesive (usually epoxy) into the coatings or even down to the interface if they are thin. To characterise the interfacial adhesion in a systematic way, a fracture mechanics approach should be adopted. The interfacial fracture toughness, $K_{ic}$ (or the closely associated critical strain energy release rate, $G_{ic}$), should be considered, along with the strength, in the overall design of an implant system. There has been very little research in this area concerning biomedical materials. Filiaggi et al. [32] used the short bar chevron notch test and obtained values of $K_{ic}$ equal to 0.60–1.41 $MPa\,m^{1/2}$. Evan et al [33] used the double-cantilever beam test and obtained values of $G_{ic}$ equal to 1 $J\,m^{-2}$ and 4 $J\,m^{-2}$ for bead-blasted and grit-blasted substrates, respectively. It should be noted that both of these sets of values represent relatively brittle interfaces.

In this study, coatings plasma sprayed with different input power levels and different plasma gas mixtures (Ar with $H_2$ or He) have been examined. Free-standing deposits were obtained by pre-spraying a layer of salt before coating deposition, which was followed by immersion in water. Young's moduli were measured by a cantilever beam bending method. Adhesion was measured by a single-edge notch bend test. A numerical model was used to evaluate the quenching stress of the HA coatings in conjunction with the use of an in situ curvature monitoring technique. Some predictions of the residual stress levels in sprayed HA coatings produced under various conditions are presented.

## 2. Experimental procedure

### 2.1. Substrate preparation and plasma spraying

Substrates of Ti–6wt%Al–4wt%V were prepared by pickling in acid (8% HF and 40% $HNO_3$) for 1 min, to remove surface oxide, and degreased by rinsing in acetone. Substrates were then grit-blasted with brown $Al_2O_3$ (−80 mesh) under a pressure of 6 bar for ~30 s. The surfaces were air-blasted to remove any residual grit and finally cleaned with alcohol. Similar substrate preparation procedures were employed with mild steel and tungsten. The substrates were then coated with HA, using the spraying conditions given in Table 1. The spraying equipment employed was a PT VPS system with a F4-V gun. The spraying pattern consisted of a number of cycles, depending on the thickness of the coating required, each consisting of six vertical passes of the gun, followed by an inter-cycle cooling period. This was done to ensure that the substrate temperature remained within a specified range. For spraying onto tungsten (~100−125 μm thick), a mild steel strip (~2 mm thick) with many holes in it was placed at the back of the substrate for support. Argon cooling was applied at the back. For spraying onto mild steel and Ti–6Al–4V, the pre-set minimum temperature between each cycle was ~400°C and that for spraying on tungsten was ~100°C. The input power levels used were between 30 and 42 kW. Hydrogen or helium was used as the secondary plasma gas. The flow rates are shown in Table 1. Coatings of thickness in the range 100 μm–1 mm were obtained.

Table 1
Spraying conditions used for all the specimens

| | |
|---|---|
| Chamber pressure (mbar) | 200 |
| Spraying stand-off distance (mm) | 270 |
| Nozzle internal diameter (mm) | 8 |
| Plasma gas flow rates (slpm) | $Ar = 50 + H_2 = 4–9$ or<br>$Ar = 35–40 + He = 50$ |