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Crystallinity and structural changes in HA plasma-sprayed coatings induced by cyclic loading in physiological media

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In this study hydroxyapatite plasma-sprayed Ti-6Al-4V was characterized by X-ray diffraction (XRD) after being cyclically loaded, while immersed in two different testing environments: Hank's balanced salt solution (HBSS) and an isotonic saline solution (0.15 M NaCl). An original method was developed to test these systems under cyclic bending, while immersed in the testing solution. The crystallinity of the coating was calculated, before and after testing. Crystallinity changes were related to coating dissolution rates, measured by atomic absorption spectroscopy (AAS) and by a photocolourimetric method using ascorbic acid. Structural changes induced either by the plasma-spraying procedure or due to corrosion-fatigue tests, namely a preferential dissolution of the coating's amorphous phase, were also found in X-ray diffraction patterns. Long-term immersion tests, without any applied load, were carried out for assessing cyclic loading effects. An immersion for 2 years in static conditions was found to be equivalent to a cyclic test of 27.8 h in the same solution, as measured by the changes on the coating structure and by the amount of coating material lost to the solution.

1. Introduction

The clinical application of bioactive hydroxylapatite (HA) coated implants is attracting considerable interest, with emphasis on the use of plasma-sprayed coatings to combine the superior mechanical performance of the metal component with the excellent biological responses of HA [1]. In fact, the application of titanium alloys coated with hydroxyapatite by plasma-spraying has been growing over the last few years. More than 150 000 HA-coated orthopaedic prosthesis have been implanted [2]. However, some doubts remain on the long-term stability of these coatings [3], as they are porous and should be degradable to promote cementless bone fixation of the prosthesis [4].

Some authors [1, 5] claim that HA may act as a biological barrier to reduce toxic responses caused by the release of metallic ions from the metal substrate into the bone. Furthermore, the release of metal ions from the substrate may influence the coating's dissolution behaviour, and as a consequence the implant *in vivo* performance [6]. On the other hand, Ducheyne and Whitehead [7, 8] claimed that degradation of the coating may induce higher metal ion release levels and that localized corrosion may occur under physiological cyclic loading. A study by J. de Bruin *et al.* [9] has highlighted, in more detail, that the bone-bonding properties of HA coatings seem to be associated with dissolution of the coating.

The simultaneous action of cyclic loads and aggressive fluids from the physiological media is potentially very dangerous. As a consequence, corrosion-fatigue is of some concern, and may lead to catastrophic fracture [10], metal ion release [11] and accelerated coating dissolution [12]. For instance, Kummer and Jaffe [12] have tested Ti-6Al-4V coated systems under cyclic loading in physiological media. They concluded that degradation under cyclic loading occurs much faster than under static conditions, specially in acid solutions.

In previously published works [13–16] the development and application of an innovative testing method for studying these systems under cyclic loads while immersed in physiological media has been reported. The proposed method is based on a different testing concept. The imposed stress levels are intended to simulate the cyclic physiological loads that implants must withstand in service, and are the lowest that may cause coating cracking, without leading to metal substrate corrosion-fatigue failure. Both coating degradation and ion release levels induced by concomitant

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action of physiological stresses and fluids must be characterized under these conditions. The main principles involved in the testing methodology [13, 14] and the electrochemical behaviour of the metal substrate [14–16] when tested in this way have been published previously.

In this present work the same testing approach has been used to study the action of physiological fluids and cyclic loads on coating behaviour. Special importance has been given to changes in the coating structure, its degree of crystallinity, possible roughness variations and dissolution rates.

2. Materials and methods

Hydroxyapatite (HA) coatings with a thickness of 50 ±10 μm on Ti-6Al-4V substrates were produced by plasma-spraying. Samples were beam shaped (180 × 30 × 6 mm or 30 × 20 × 6 mm), and coatings performed by Plasma Biotal Company, Tideswell, UK. Before coating, samples were annealed at 750 °C for 2 h, air cooled, blasted with alumina grit and passivated in nitric acid (30% v/v, 60 °C, 60 min). An $\alpha + \beta$ microstructure was produced, giving a yield strength of 865 MPa and 16% elongation at fracture, under tensile loading.

An original method previously described [14–16] was used for the cyclic loading of specimens while immersed in physiological media. Two different testing environments, namely a Hank's balanced salt solution (HBSS) and an isotonic saline solution (0.15 M NaCl) were used. The composition of the testing solutions is presented in Table I. Some experiments were also done under cyclic loading in dry conditions (air).

Cyclic loading was performed under the following conditions: four-point bending loading scheme, under imposed deflection, initial stress ratio $R=0$, initial applied stress range $\sigma_r(t=0) = 80$ MPa, frequency of cyclic loading $f = 10$ Hz, testing period 10^6 cycles. Further details on the testing procedure, and on the electrochemical behaviour of the samples may be found elsewhere [13–15]. Some samples were immersed in HBSS at 37 ± 1° C without any load being applied for periods ranging from 6 months to 2 years.

TABLE I Composition of the testing media: Hank's balanced salt solution (HBSS) and isotonic saline solution (0.15 M NaCl)

Compound	0.15 M NaCl concentration (g/dm^3)	HBSS* concentration (g/dm^3)
NaCl	9.0	8.0
$CaCl_2$	—	0.14
KCl	—	0.40
$NaHCO_3$	—	0.35
$MgCl_2 \cdot 6H_2O$	—	0.10
$Na_2HPO_4 \cdot 2H_2O$	—	0.06
KH_2PO_4	—	0.06
$MgSO_4 \cdot 7H_2O$	—	0.06
Glucose	—	1.0

*Gibco 041-04025 M *w/o phenol red*, Life Technologies Ltd, Paisley, Scotland, UK.

X-ray diffraction (XRD) studies were performed with a SIEMENS D-5000 X-ray Diffractometer. Peak search databases and DOS-DIFFRACT-AT® software were also used. Tests were performed with CuK_α radiation (WL1 =1.5406; WL2 =1.5443; WL3 =1.3924; WL ratio = 0.5140) at (40 kV; 40 mA), using a graphite monochromator and a copper anode. The 2θ angles were scanned from 5 to 110°, at 0.05°/min scanning rate. Coating crystallinity (%) was estimated using five different parameters: full-width half medium (FWHM), integral width (IW), and peak heights of the three main peaks (100% Int. (2 1 1), 60% Int. (1 1 2) and 60% Int. (3 0 0)). These five parameters were used to compute crystallinity. The calculation was based on comparing the values obtained for the coatings with pre-determined figures for several mixtures of a 100% crystalline HA powder with a 100% amorphous HA powder, using 10% steps. Five linear correlations were attained and the final coating crystallinity figure was then taken as the average of the calculated values, for each one of the correlations.

The concentrations of calcium and phosphorous released to the solutions were analysed by atomic absorption spectroscopy (AAS) and a photocolourimetric method using ascorbic acid. Coating thickness was determined by scanning electron microscopy (SEM) using a Jeol JSM 35-C microscope equipped with a Noran Instruments energy dispersive spectroscope (EDS). The roughness of the different surfaces was measured using a Perthometer S4P laser roughness meter. Both the mean roughness (R_A) and the mean roughness depth (R_Z) were measured, according to DIN 4762 and DIN 4768 standards, respectively.

3. Results and discussion

Fig. 1 presents XRD patterns for two original spray powders (a and b) and a control coated sample (c). It may be seen that all powder peaks match perfectly the JCPDS 9-0432 standard file for hydroxyapatite. However, coating peaks corresponding to the (0 0 2) and (0 0 4) plans show a much higher intensity than expected. These peaks correspond, respectively, to d = 3.4420 (2θ =25.86°) and d =1.7210 (2θ =53.18°). In order to verify these results tests were carried out with sample rotation to eliminate any sample positioning effect, but results were always consistent. These preferential

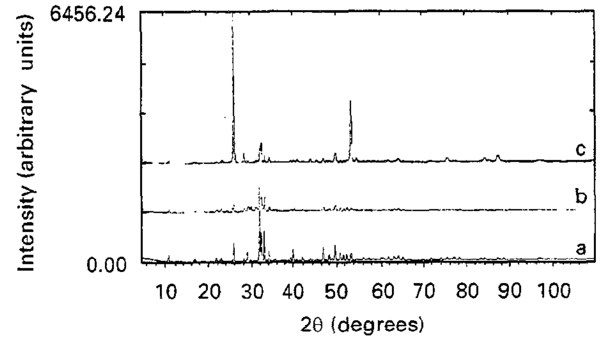

Figure 1 XRD patterns for two different spray powders (a and b) and a control coating (c).

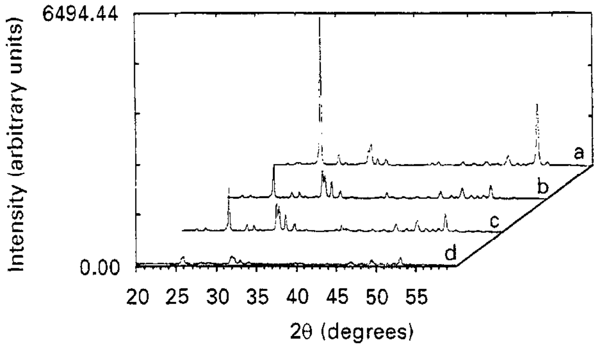

Figure 2 XRD spectra for samples: (a) non-tested controls; (b) cyclic loaded in NaCl 0.15 M NaCl; (c) in HBSS; and (d) in air.

coating orientations might have been generated by the plasma-spraying procedure, due to a preferential heat flow direction during cooling.

Fig. 2 shows XRD spectra for a control coated sample (a), compared with samples cyclically loaded in 0.15 M NaCl (b), in HBSS (c) and in dry conditions (d). After cyclic loading there is no peak shift and the relative position of all peaks is maintained. However, a marked decrease was detected in the peak intensity, specially for the dry (air) tested samples. This must be related to the coating thickness decrease reported in Table II. The increase of this effect on the dry tested samples must be attributed to the fact that during cyclic fatigue there was a preferential dissolution of the amorphous phase of the coating. This effect, again clearly presented in Table II, tends to increase the signal derived from samples tested in HBSS and 0.15 M NaCl when compared with samples tested in air.

A preferential dissolution of the coating's amorphous phase during tests under cyclic loads was detected in both solutions. This favoured dissolution of amorphous calcium phosphates in plasma-sprayed HA coatings has also been found by several other authors [1, 8, 17, 18].

Furthermore it was clear that this dissolution occurred much faster than during long-term static immersion tests. After two years immersion in HBSS the amounts of Ca and P released to the solution are almost the same as were found after 27.8 h under cyclic loading conditions in the same solution. Nevertheless, the levels of Ca and P released to the solution, as presented in Table II, are not critical. This is especially true in the case of HBSS (78 ppm and 11 ppm) as they are augmented around 15 and 30 times, respectively, in the 0.15 M NaCl solution. Studying the same system, Whitehead *et al.* [8] found values of 1 ppm of Ca released to the solution after a 1-week test in HBSS and a maximum of 16 ppm after 6 weeks.

A bigger increase in relative crystallinity (% Cryst., see Table II) corresponds to more intense coating dissolution. The crystallinity of the coatings increased by 13% after tests in HBSS, and by 17% after tests in NaCl 0.15 M. The higher dissolution rate of the amorphous phase in the latter case may be due to a gradient generated by the absence of Ca and P in the isotonic solution [12]. The coating tends to the equilibrium Ca/P ratio when tested under cyclic loads in physiological solutions as shown in Table II. However, tests did not cause large changes in Ca/P ratios (Table II). Initially the Ca/P relationship was around 1.70. This Ca excess with respect to stoichiometry has been reported in plasma-sprayed coatings [1, 12]. After tests in HBSS, Ca/P ratio tended to the equilibrium value of 1.67 indicating that the upper layers, with an excess of Ca, were dissolved. In fact some authors [12, 17] claimed that there is an incremental change of Ca/P ratio in the direction (metal interface) --> (surface).

The integrity of the coating was significantly affected by the cyclic loading, with remarkable decreases in the thickness. As an example Fig. 3 presents a degraded coating surface after a test in HBSS. Hank's solution seems to be more aggressive and the presence of the solution induces coating decohesion.

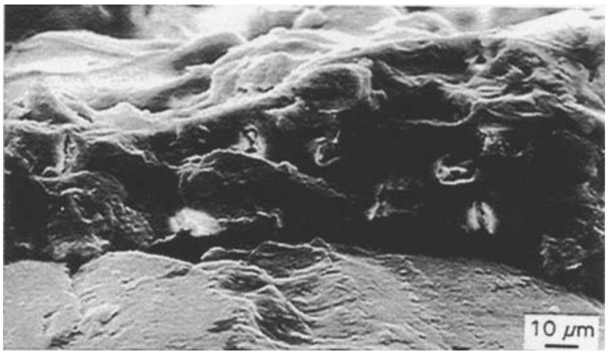

Figure 3 SEM photomicrograph showing a degraded coating surface after being tested under cyclic loading in HBSS.

TABLE II Coating thickness, crystallinity (%), dissolution of Ca and P, and Ca/P ratio, before and after cyclic loading in air, HBSS and NaCl (0.15 M) for an imposed stress level at $t = 0$ of 80 MPa. See also results after immersion for 2 years (no load applied) in HBSS

Testing solution	Coating thickness (μm)	Crystallinity (%)	Ca dissolution (ppm)	P dissolution (ppm)	Ca/P ratio
Control samples (not tested)	50 ± 10	Powder-99.8	HBSS-73 NaCl-430	HBSS-4 NaCl-122	1.70 ± 0.01
Air	40 ± 11	59.0	—	—	1.70 ± 0.01
HBSS	28 ± 11	66.7	78	11	1.67 ± 0.01
0.15 M NaCl	32 ± 14	69.1	1200	310	1.70 ± 0.01
2 years immersion (no load)	34 ± 11	67.8	81	9	1.67 ± 0.01

Table III presents the changes in crystallinity that occur in commercial "crystalline" and "amorphous" coatings after 6 months static immersion in HBSS at 37 °C. As was found under the cyclic loading conditions, there was preferential dissolution of the coating's amorphous phase. The crystallinity of the more crystalline coating was increased by 33% and that of the amorphous coating was increased by around 80%. The corresponding XRD spectra are shown in Fig. 4. Work by de Groot *et al.* [19] demonstrated that the simple immersion of HA plasma-sprayed coatings in distilled water was sufficient to cause a change in their relative crystallinity. This behaviour is interesting for *in vivo* conditions, allowing very strong bioactivity in the first stages of prostheses consolidation, and then a lower dissolution rate assuring that the coating will remain performing its duty for the required time. However, Whitehead [8] claims that in the long term the dissolution of the amorphous phase may be responsible for the degradation of coating adhesion. In fact the metal/coating bonding is assured basically by the amorphous phase near the interface [17].

The roughness values determined in this work (Table IV) are systematically lower than those reported by Delécrin [20], and de Bruijn [21], which were around R_A =5 µm. However, comparisons should be treated with caution, as laser roughness measurements usually give lower values than traditional mechanical measurements.

The coatings tend to attenuate the rough profile of the metal surface after blasting. Tests in air produce a lower value, indicating that more sharp particles at the surface tend to be mechanically released from the surface during cyclic loading. On the other hand, after tests in physiological media the roughness is increased, specially after experiments in NaCl 0.15 M. The preferential dissolution of one of the phases seems to increase the coating roughness. Tests in NaCl 0.15 M give rise to a greater change in crystallinity, and as a consequence generate a rougher surface.

TABLE III Crystallinity changes induced by long-term static immersion tests in HBSS at 37 ± 1 °C, for 6 months. For these tests only commercial "crystalline" and "amorphous" HA coatings were used

Sample reference	Crystallinity %
HA powder	99.8
"Crystalline"coating	54.5
"Crystalline" coating after immersion	72.4
"Amorphous" coating	19.4
"Amorphous" coating after immersion	34.9

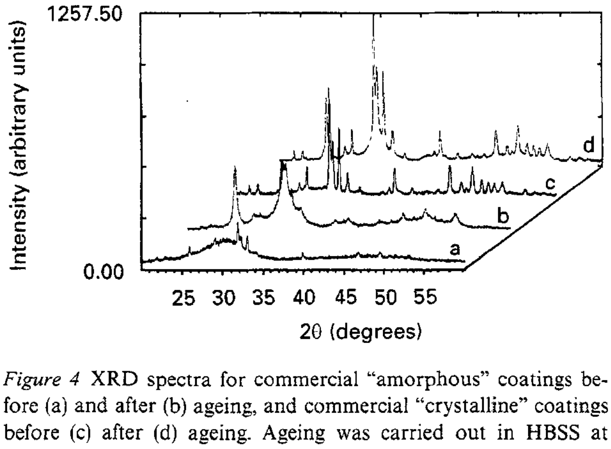

Figure 4 XRD spectra for commercial "amorphous" coatings before (a) and after (b) ageing, and commercial "crystalline" coatings before (c) after (d) ageing. Ageing was carried out in HBSS at 37 ± 1 °C, for 6 months.

TABLE IV Values of roughness parameters: mean roughness (R_A) and mean roughness depth (R_Z)

Sample	R_A (µm)	R_Z (µm)
As-received Ti-6Al-4V	0.65	2.68
Blasted Ti-6Al-4V	1.66	5.61
Control sample	0.57	2.38
Tested in air	0.50	2.14
Tested in HBSS	0.64	2.55
Tested in 0.15 M NaCl	0.68	2.64
2 years immersion (no load)	0.62	2.48

4. Conclusions

Preferential dissolution of the coating's amorphous phase was found in X-ray diffraction patterns. The effects on the coating structure and on material lost after immersion for 2 years in static conditions was found to be equivalent to a cyclic test of 27.8 h in the same solution.

Acknowledgements

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