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X-RAY PHOTO-EMISSION AND ENERGY DISPERSIVE SPECTROSCOPY OF HA COATED TITANIUM*

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#789 X-ray Photo-Emission and Energy Dispersive Spectroscopy of HA Coated Titanium. JL DRUMMOND, AD STEINBERG*, AR KRAUSS, and RA GIORDANO (University Illinois-Chicago, Argonne National Lab, and Boston University).

ABSTRACT

The purpose of this study was to determine the chemical composition changes of hydroxyapatite (HA) coated titanium using surface analysis (x-ray photo-emission) and bulk analysis (energy dispersive spectroscopy). The specimens examined were controls, 30 minutes and 3 hours aged specimens in distilled water or 0.2M sodium phosphate buffer (pH 7.2) at room temperature. Each x-ray photo-emission cycle consisted of 3 scans followed by argon sputtering for 10 minutes for a total of usually 20 cycles, corresponding to a sampling depth of $\sim 1500 \text{ \AA}$. The energy dispersive spectroscopy analysis was on a $110 \times 90 \text{ }\mu\text{m}$ area for 500 sec. Scanning electron microscopy examination showed crystal formation ($3\text{P}_2\text{O}_5 \cdot 2\text{CaO} \cdot ?\text{H}_2\text{O}$ by energy dispersive spectroscopy analysis) on the HA coating for the specimens aged in sodium phosphate buffer. The x-ray photo-emission results indicated the oxidation effect of water on the titanium (as TiO_2) and the effect of the buffer to increase the surface concentration of phosphorous. No differences in the chemical composition were observed by energy dispersive spectroscopy analysis. The crystal growth was only observed for the sodium phosphate buffer specimens and only on the HA surface. Supported in part by G. Matula Fund, UIC.

INTRODUCTION

The success of implants may depend on the initial contact of the proteins involved in the clotting process. The surface of plasma sprayed hydroxyapatite (HA) has been characterized as to composition and crystallinity, but limited knowledge is known about the surface before and after blood cells and proteins contact. It has been reported that some dissolution of the HA coating may occur and be transformed into other calcium phosphate phases when exposed to a variety of ionic conditions which simulate body fluids (1,2). After implantation, most studies report that a calcium-rich phosphate layer or coating is formed at the interface of the HA with bone (3-8). This first stage appears to be induced through rapid interaction of ions on the HA implant (especially calcium) and in the surrounding tissues (phosphate source). Dissolution of the soluble

components at the interface and precipitation of an amorphous calcium phosphate may follow (2). Dissolution from the HA surface may produce solution-mediated events affecting cellular activity, organic matrix deposition or mineral precipitation which may lead to a bone-like apatite crystal formation and subsequent bone tissue bonding (9). Most investigators suggest that this layer appears to form a chemical bond with the bone bonding to the HA implant surface (1, 10). Since the ceramic surface initially reacts with surrounding extracellular fluid, the nature of the solids formed on the surface is determined not only by the crystal chemistry of the ceramics, but also by the chemical constituents of the surrounding fluid. The intent of this initial project was to characterize the surface layer of plasma sprayed hydroxyapatite on Ti-6Al-4V after exposure of 30 minutes and 3 hours to different solutions and the relationship to surface crystal formation.

MATERIALS AND METHODS

Rectangles 2mm x 2mm x 6 mm were sectioned from a plate of Ti-6Al-4V plasma sprayed with hydroxyapatite (Calcitek Inc, Carlsband, CA.). These specimens were treated in the following manner by exposure for either 30 minutes or 3 hours at room temperature to: distilled water or 0.2M sodium phosphate buffer (pH 7.2. The specimens were then examined using scanning electron microscopy (SEM), surface analysis (x-ray photo-emission), and bulk analysis (energy dispersive spectroscopy). Each x-ray photo-emission cycle consisted of 3 scans followed by argon sputtering for 10 minutes for a total of usually 20 cycles, corresponding to a sampling depth of ~1500 Å. The energy dispersive spectroscopy analysis was on a 110 by 90 µm area for 500 sec. The x-ray photo-emission and energy dispersive spectroscopy comparisons are shown in Table 1 and the x-ray photo-emission analysis in Figures 1-5.

RESULTS AND DISCUSSION

In previous studies, we observed crystal growth upon HA coated Ti surfaces incubated in 0.2M sodium phosphate buffer (unpublished experiments). Investigation into this phenomenon revealed that crystal growth could be observed using SEM as early as 30 minutes after incubation in the 0.2M sodium phosphate buffer and increased crystal growth and different crystal morphology after 12 hours. Cacodylate buffer (pH 7.2) did not induce the crystal growth.

It appears that this process begins immediately upon the HA surface making contact with the sodium phosphate buffer. The created crystals are most likely a form of calcium phosphate with the calcium coming from the HA surface while the phosphate comes from the sodium phosphate buffer. Plasma spraying the HA onto Ti results in a highly reactive HA surface. Thus, the presence of available calcium on the reactive HA surface coming into contact with a high concentration of phosphate may induce crystal formation.

The analyses, Table 1, clearly showed a marked difference between the bulk and the surface of hydroxyapatite as would be expected. Scanning electron microscopy examination showed crystal formation ($3\text{P}_2\text{O}_5 \cdot 2\text{CaO} \cdot \text{H}_2\text{O}$ by energy dispersive spectroscopy analysis) on the HA coating for the specimens aged in sodium phosphate buffer. The x-ray photo-emission analysis of the HA coated titanium control showed carbon contamination, Figure 1. The HA-titanium control also shows the individual peaks for calcium and phosphorous, but no titanium. After aging in water, the main difference is the appearance of two titanium peaks at ~453.8 and 458.5 eV, corresponding to the $2p_{3/2}$ peaks for Ti and TiO_2 (Figures 2 and 3). The relative intensities of the two peaks indicate that Ti is present primarily as the oxide. The phosphate buffer results in an increase in the phosphorous content and the presence of chlorine which is used to maintain the pH of the buffer, Figures 4 and 5. The analysis of a material providing only the bulk analysis is not representative of the surface and the region where the success of the implant will be determined. Future work will involve the expansion of this project to include short term interaction with clotting blood.

In conclusion, only surface changes were observed from these analyses and crystal growth appears to be associated only with the HA coating.

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TABLE 1: XPS and EDS Compositions in Percent of Elements

Element	Control	30m Water	3h Water	30m Buffer	3h Buffer
XPS Analysis					
O	37.2	58.1	56.9	58.1	57.8
P	9.2	12.8	13.3	16.2	17.4
Ca	22.9	29.1	25.3	25.7	24.8
Ti	0.0	0.0	4.6	0.0	0.0
C	30.8	0.0	0.0	0.0	0.0
EDS Analysis					
O	60.0	60.8	60.8	60.7	61.0
P	13.3	14.3	14.4	14.3	15.0
Ca	26.6	24.9	24.7	24.6	23.1
Ti	0.2	0.1	0.1	0.3	0.1
Na	0.0	0.0	0.0	0.0	0.8

FIGURE 1: CONTROL HA TITANIUM SURFACE

**FIGURE 2: HA-TITANIUM SURFACE AFTER
30 MINUTES DISTILLED WATER**

**FIGURE 3: HA-TITANIUM SURFACE AFTER
3 HOURS DISTILLED WATER**

**FIGURE 4: HA-TITANIUM SURFACE AFTER
30 MINUTES Na_3PO_4 BUFFER**

**FIGURE 5: HA-TITANIUM SURFACE AFTER
3 HOURS Na_3PO_4 BUFFER**