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# ION BEAM MIXING OF TITANIUM OVERLAYERS WITH HYDROXYAPATITE SUBSTRATES

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## ABSTRACT

The mixing of titanium overlayers with hydroxyapatite (HA) substrates via ion irradiation has been demonstrated. Analysis via secondary ion mass spectroscopy (SIMS) indicates an interfacial broadening of titanium and calcium of the implanted sample compared to that of the unimplanted sample. Attendant to the observed ion beam mixing of titanium into the HA, the oxygen signal of the titanium overlayer increases as a result of ion irradiation. It is supposed that this change is evident of diffusion through the metal layer and possibly from titania formation at the free surface and perovskite formation at the film/substrate interface. This possibility is consistent with thermodynamic predictions. Additionally, the force required to separate the film from the substrate increased as a result of ion irradiation, validating the continued study of ion beam processing of Ti/HA systems towards the improvement of long term fixation of implant devices.

## INTRODUCTION

Porous hydroxyapatite (HA) coatings hold promise towards overcoming aseptic loosening of implant devices, an outstanding issue in biomaterials technology [1,2]. Current HA coating technology includes radio frequency (RF) sputtering and plasma spray [3]. RF sputtering can produce very thin coatings (~20  $\mu\text{m}$ ) with improved adhesion, but the coatings are amorphous and phosphorous deficient. Plasma spray is presently the only practical commercial method to date that produces relatively thick (50-200  $\mu\text{m}$ ) porous HA coatings onto irregular shaped prostheses. However, plasma sprayed HA films have been shown to have poor mechanical adhesion resulting in premature separation and subsequent implant failure [3-6]. In addition, plasma spraying lacks control of HA microstructure which results in suboptimal tissue responses.

Since present HA coating techniques appear to have limited lifetimes, we have been developing a thin film deposition and ion beam-modified HA coating methodology. This approach can potentially offer improved HA coating/substrate mechanical adhesion and optimal bone/implant integration.

In this paper we focus on the feasibility of using ion beam processing, in the form of ion beam mixing, towards improving the mechanical adhesion of HA and titanium. Since we are solely interested in ion mixing of HA and titanium, we have eliminated the variability of HA coating techniques through a reversal of the system of interest. Here we investigate the susceptibility of titanium overlayers on hydroxyapatite substrates to ion beam mixing.

Although dynamic ion mixing of HA with titanium substrates has been observed [7], our interest lies in the observation of ion mixing effects using a chemically inert gas species

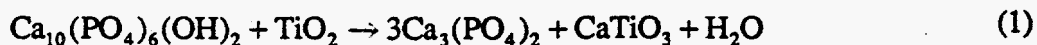
implanted into fully dense, polycrystalline hydroxyapatite in a process that is applicable to industrial production, through the use of plasma source ion implantation, for example.

Ion beam mixing is a technique whereby the components of a thin film are displaced either by thermal, chemical and/or ballistic inducement into an underlying film or substrate via ion irradiation [8]. The formation of a 'bridging' layer of intermediate composition has been correlated with improved adhesion in various metal-on-oxide systems [9].

Thermal annealing studies have demonstrated that equilibrium thermodynamics is a useful tool in predicting the outcome of an ion mixing experiment [10]. In general two layers for which it is favorable to form a compound, as indicated by a negative enthalpy of reaction, will do so under ion irradiation. Should the constituents form continuous solid solutions then only ballistic mixing will be observed, where species have merely been displaced by the incident ion and the resultant collision cascade. Further if the system exhibits neither behavior (i.e. positive enthalpies of reaction) then the appearance of segregated agglomerates is possible under ion irradiation.

The application of the "enthalpy" rule is justified through the consideration that the track of the incident ion is surrounded by a region of high effective temperature, known as a thermal spike, whereby mobile species can diffuse in the prevailing potential gradient [8]. Further, the general invariability of thermodynamic quantities with temperature permits consideration of the enthalpy of reaction at room temperature.

Based on these ideas a prediction can be made for the system at hand, titanium overlayers on HA substrates. A thermal decomposition of HA in the presence of titanium in its oxide form at 1100°C has been observed by Weng et al. [11] according to the following reaction:



The negative enthalpy of reaction along with the observation of this reaction by Weng et al. [11] predicts that ion beam mixing should occur.

As further evidence of this possibility, Torrisi and Foti [12] have observed altered bonding configurations of an HA film on a Ti substrate following electron irradiation. There the increase of the Auger signal of oxygen bonded to titanium relative to the signal of apatite-bonded oxygen does not preclude the formation of calcium titanate. Although Ohtsuka et al. [7] surmise formation of a Ti-P compound at the interfacial region upon thermal annealing of the implanted HA/Ti system, the data there also does not refute the occurrence of the reaction in equation 1.

## EXPERIMENTAL

A pellet of HA was formed from commercially available pure HA powder which was pressed at 8.5 MPa and heat treated at a heating and cooling rate of 200°C/hr in a 3 zone tube furnace according to the following steps. First the pellet was heated to 800°C where it remained for 1 hour and then cooled to room temperature. Upon reaching room temperature the pellet was then heated to 1400°C, where it remained for 12 hours, and finally cooled to room temperature. A flat surface was polished on the pellet, 1 cm in diameter to an average roughness of 20 nm.

A titanium film of 140 nm thickness was deposited on the sample via electron beam deposition. Half of the sample was masked using aluminum foil. The half-masked sample was subsequently ion implanted using 290 keV Ar to a dose of  $5 \times 10^{16}$  Ar/cm<sup>2</sup> at a dose rate of  $5 \times 10^{12}$  Ar/cm<sup>2</sup>/s at room temperature. The implanter has a base pressure of  $3 \times 10^{-4}$  Pa. The

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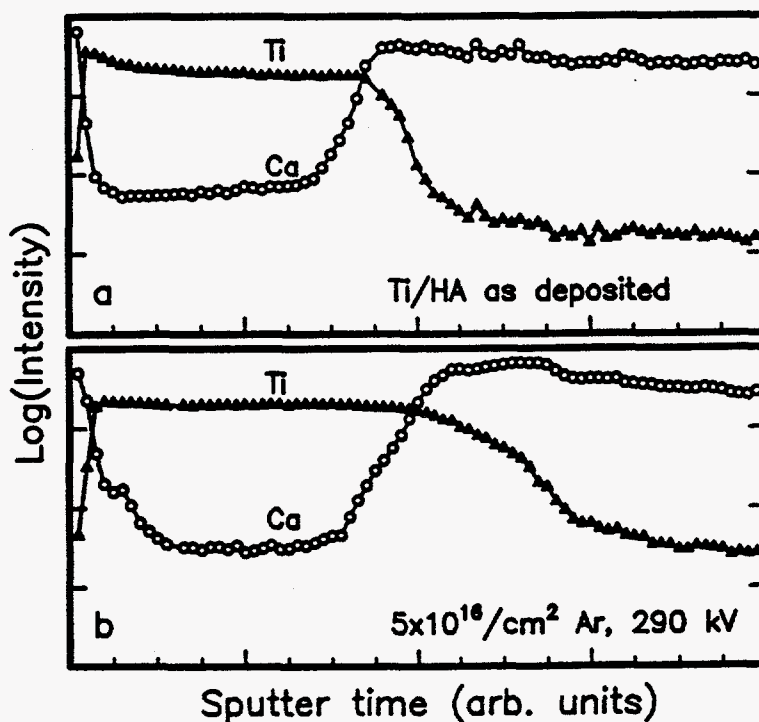
ion energy was chosen to yield maximum nuclear energy deposition at the film/substrate interface, as given by a TRIM calculation [13].

SIMS was performed using a Cs<sup>+</sup> source, with an energy of 5.5 keV. Besides of the following masses were detected: 149, 164, 173, and 179 amu. The analysis beam had a current of 10 nA and a beam spot size of 30 μm diameter rastered over a 250 μm<sup>2</sup> area.

Adhesion was tested using a "poor man's scratch tester" as described elsewhere [14]. The applied force was increased in 10g increments from 10g to 70g.

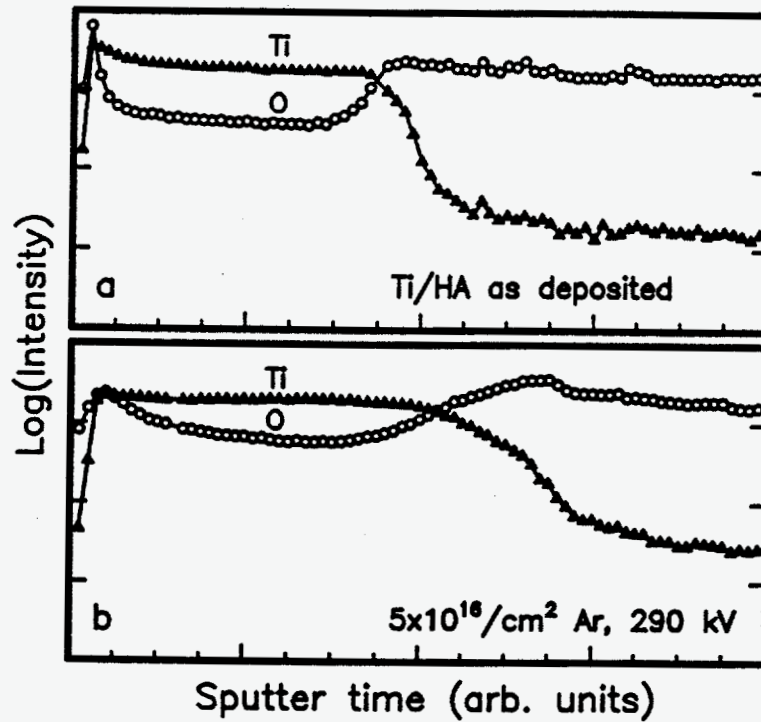
## RESULTS/DISCUSSION

Figs. 1a and b show the SIMS depth profile signals of titanium and calcium of the as-deposited and implanted samples. Although sputter rates vary with local composition and ionization probability, it is a reasonable assumption that the sputter rates of the as-deposited and the implanted sides of the sample are identical. Further while it is true that ion beam mixing phenomena are attendant to SIMS depth profile studies, the energy of the sputtering ion beam is approximately one tenth that of the implanted ions at the interface. In this way a comparison of SIMS depth profiles between the as-deposited and implanted samples should confirm or deny the prevalence of mixing from implantation. Given this, it is evident from the change in slope of the Ti signal and to a lesser extent by that of the Ca signal in Fig. 1 that the Ti/HA interface has been broadened as a result of ion-beam mixing. That neither the Ca or Ti signal approach zero in regions far from the interface that are necessarily deficient in each species stems from the isotopic similarity of titanium and calcium. The effect on mixing of the sputtering ion beam may be the result of the shift of the calcium trace with respect to the titanium trace.



Figures 1a and b. SIMS depth profile traces of titanium and calcium signals of as-deposited sample and implanted sample.

There are some interesting features offered by the oxygen SIMS depth profile, plotted separately in Figs. 2a and b. The titanium trace is plotted also in Figs. 2a and b for reference. The most notable change from irradiation is the increased oxygen level through the titanium overlayer. Additionally there appears to be a buildup of oxygen at both the free surface and the film/substrate interface. It is possible that oxygen diffuses through the titanium overlayer forming titania at the free surface and ion mixed titanium forms perovskite at the film/substrate interface according to Eqn. 1.



Figures 2a and b. SIMS depth profile traces of oxygen and titanium signals of as-deposited sample and implanted sample.

The force required to separate the Ti film from the HA substrate increased upon ion irradiation. At a force of 40 g, neither the as-deposited nor the implanted Ti films were observed to delaminate as shown in Fig. 3.

However, upon increasing the force to 70 g, the maximum of the tester, the as-deposited film completely failed as shown in Fig. 4, whereas partial adherence was observed in the implanted film. The high degree of contrast exhibited in the wear track of the unimplanted film is indicative of substrate exposure; the lesser degree of contrast in the wear track of the implanted indicates that the substrate has not been exposed.

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Figure 4. Micrograph of wear track following test under 70 g load. Both as-deposited and irradiated portions of the sample are visible

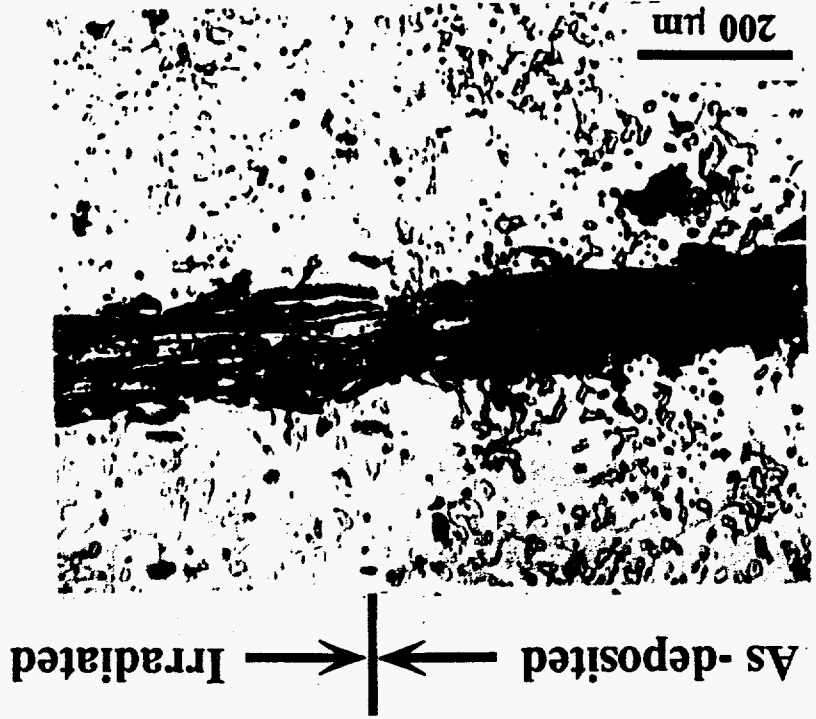
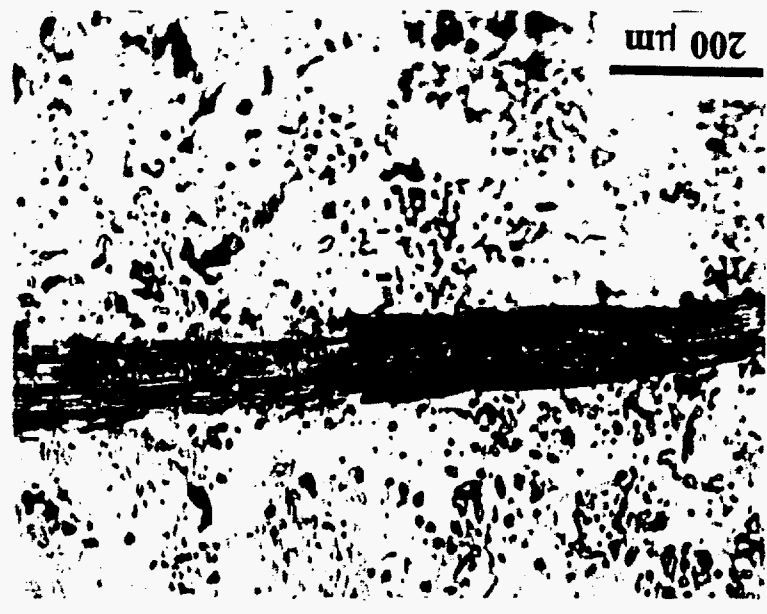


Figure 3. Micrograph of wear track following test under 40 g load. Both as-deposited and irradiated portions of the sample are visible.



## CONCLUSIONS/FUTURE DIRECTIONS

We have demonstrated that titanium overlayers can be ion mixed with hydroxyapatite substrates. The interfacial broadening of the titanium and calcium SIMS signals are attended by a change in oxygen concentration which may be indicative of oxygen diffusion and phase formation at the free surface and film/substrate interface. We can conclude thus that the increased force to separate the film from the substrate arises from ion mixing of the film with the substrate. Since this work verifies that ion beam processing is a useful technique towards enhancing adhesion between titanium and hydroxyapatite, it is necessary now to continue to evaluate systems closer to the real application. Studies include: examining the phase formation in this system explicitly using an appropriate technique; investigating the effect of varying species and energy on the ion beam mixing response of this system; performing similar work on HA deposited and processed via industrially applicable techniques, such as sol-gel methods and plasma source ion implantation, onto titanium-based alloys.

## ACKNOWLEDGEMENTS

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