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Stoichiometry, crystallinity, and nano-scale surface morphology of the graded calcium phosphate-based bio-ceramic interlayer on Ti-Al-V

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ABSTRACT

A plasma-assisted concurrent Rf sputtering technique for fabrication of biocompatible, functionally graded CaP-based interlayer on Ti-6Al-4V orthopedic alloy is reported. Each layer in the coating is designed to meet a specific functionality. The adherent to the metal layer features elevated content of Ti and supports excellent ceramic-metal interfacial stability. The middle layer features nanocrystalline structure and mimics natural bone apatites. The technique allows one to reproduce Ca/P ratios intrinsic to major natural calcium phosphates. Surface morphology of the outer, a few to few tens of nanometers thick, layer, has been tailored to fit the requirements for the bio-molecule/protein attachment factors. Various material and surface characterization techniques confirm that the optimal surface morphology of the outer layer is achieved for the process conditions yielding nanocrystalline structure of the middle layer. Preliminary cell culturing tests confirm the link between the tailored nano-scale surface morphology, parameters of the middle nanostructured layer, and overall biocompatibility of the coating.

INTRODUCTION

Calcium phosphate-based bio-ceramics have recently attracted a great deal of interest as functional surface coatings in dental and orthopedic implants because of excellent bio-activity, bio-compatibility, chemical and mechanical properties [1-5]. In particular, hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, Ca/P=1.67) coatings reveal inspiring clinical advantages in promoting efficient implant fixation and implant-to-bone adhesion shortly after the implantation, as well as faster bone remodeling due to enhanced bi-directional growth and formation of a bonding interlayer between bone and implant [1]. Furthermore, calcium phosphates with apatite-like structure are the major constituents of the bone mineral phase, are compatible with various soft and muscular tissue types, and can efficiently sustain protein attachment and growth [1]. Clinical applications of CaP-based bio-ceramics for improved fixation between bone and implant pose a number of challenges for tailoring the coating quality specifications. The key quality factors include stoichiometry, crystallinity, microstructure, metal-implant interfacial stability and several others [6]. In addition, a successful technique for fabrication of a viable biocompatible

coating would intrinsically imply a certain degree of replication of biological apatites, featuring nano-crystalline structures in bone and dentin materials. Above all, surface morphology with nano-scale features and excellent island uniformity, appears to be a critical factor in promoting bio-molecule/protein - surface interactions.

Thus, fabrication of a graded bioceramic-implant structure capable of simultaneously satisfying the basic requirements for the interfacial stability at the coating-implant interface, controllable stoichiometry and crystallinity in the bulk, and the optimized, from the point of view of sustained protein attachment and growth, nano-scaled surface morphology, is a critical problem in the biomaterials research. In particular, a large number of the existing techniques for CaP-based films (including HA) deposition suffer from poor coating-metal implant interfacial bonding strength, excessive amorphosity or larger, than in natural apatites, crystal size in the bulk, as well as irregular surface morphology features typically in the micrometer range.

EXPERIMENTAL DETAILS

Here, we report on a new and efficient technique for synthesis of a graded CaP-based biocompatible interlayer on orthopedic alloy Ti-6Al-4V, consistently satisfying all the above requirements. The essential part of the method is a concurrent low-temperature plasma-assisted Rf magnetron sputtering (PA-RFMS) of crystalline HA and metallic titanium targets in low-pressure discharges of reactive gas mixtures of argon and water vapor sustained in PSAC/PA-RFMS facility. The titanium target has purposely been introduced to create a titanium-rich layer adjacent and stronger adhering to the implant-simulating metallic sample. The discharges were sustained in the range of Rf powers of $P_{in} = 300 - 700$ W applied to a water-chilled Rf magnetron electrode with several rows of concentrically positioned permanent magnets with specific polarities. The working pressure p_0 was typically maintained in the range of 10 to 70 mTorr. In this pressure and power range, large DC sheath potentials near the HA/Ti target surface, promoting high sputtering yields, and eventually high film deposition rates, can be achieved. An electrically floating substrate heater powered by an external temperature controller supports the Ti-6Al-4V samples, with the surface being coated facing downwards, approximately 6 cm above the HA/Ti sputtering target. In the experiments, the substrates were negatively biased with $V_b = 25 - 200$ V. Chemical composition and elemental bonding states in the interlayer were studied by VG ESCALAB 220i-XL spectrometer (XPS). The crystal structure was characterized using SIEMENS D5005 X-Ray diffractometer (XRD) in a lock coupled ($\theta - 2\theta$) mode with an incident x-ray wavelength of 1.540 Å (Cu $K\alpha$ line). Cross-sectional structure of the functionally graded structure was examined with the Field Emission Scanning Electron Microscopy (FESEM). Nano-scaled features of the surface morphology were studied by the Atomic Force Microscope in a contact mode (AFM). Bio-ceramic-metal interfacial bonding strength was assessed via a Micro-scratch teste. Further details of the PSAC/PA-RFMS sputtering facility, routine steps in pre-deposition substrate treatment, as well as film characterization instruments and techniques, can be found elsewhere [7,8].

RESULTS AND DISCUSSION

XPS layer-by-layer analysis of the composition and chemical bonding states reveals clear presence of Ca, P, O, and Ti in the film, the concentration of the latter being gradually increased towards the bottom layer of the coating. In addition, varying the DC substrate bias V_b and deposition pressure p_0 , one can efficiently control the elemental composition and Ca/P ratio (Fig.1), which is a key factor defining the phases of apatite. In particular, a near-stoichiometric HA (Ca/P ~ 1.67) can simply be achieved by applying DC bias of $V_b = -100$ V at $p_0 = 70$ mTorr. The elemental presence in the bulk of the coating is measured to be approximately Ca (27 %), P (15 %), O (50 %), and Ti (5 %). Furthermore, most of calcium and phosphorus in the film enter calcium phosphate phase, whereas titanium is predominantly a part of CaTiO_3 and TiO_2 . Formation of the phosphate phases is further supported by the results of FTIR analysis (Perkin Elmer Spectrum I spectrometer) showing the characteristic absorption peaks of PO_4^{3-} . Thus, the results of the XPS and FTIR analysis confirm that stoichiometry, elemental composition, and bonding states in the coating in question can indeed be tailored by varying the substrate bias, and under certain conditions the near-stoichiometric phase of HA can be synthesized.

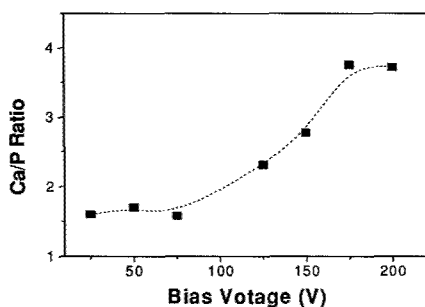


Figure 1. Ca/P ratio versus DC bias voltage

The XRD spectrum of the film prepared at $P_{in} = 700$ W and $p_0 = 70$ mTorr is presented in Fig.2, suggesting preferential crystal growth along (130) or (132) planes depending on deposition parameters. Furthermore, the diffraction pattern suggests presence of monoclinic crystalline tetracalcium phosphate $\text{Ca}_4\text{P}_2\text{O}_9$ (TTCP) structure. It is remarkable that the diffraction pattern is strongly affected by variation of the substrate bias and working pressure. An amorphous phase is observed to be characteristic to weakly biased films. A close examination of the broadening nature of the diffraction peaks reveals that the films prepared at higher negative bias feature clear nanocrystal structures (see, for example, (132) plane), and the (132) direction becomes a preferential crystal growth plane at substrate biases exceeding 150 V. It is also worth noting that a high crystallinity of the coating can be achieved at lower working pressures and moderate substrate biases.

Cross-sectional structure of the graded CaP-based film on Ti-6Al-4V has been analyzed using FE SEM. The total thickness of the CaP-based interlayer appears to be approximately 200 nm, and it contains three major areas namely, adjacent to the implant alloy, bulk area, and outer surface area (the latter to be in contact with bone tissues). Furthermore, cross-sectional SEM imaging (not shown here) suggests about formation of a functionally-graded titanium-embedded CaP-based graded coating on Ti-6Al-4V alloy.

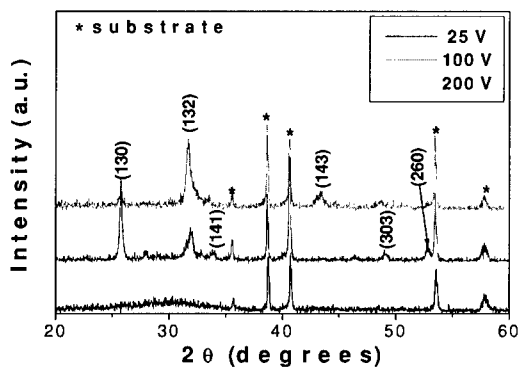


Figure 2. Typical XRD spectra from Ca-P-Ti thin films at different DC substrate bias.

Nano-scaled surface morphology of graded CaP-based crystalline interlayers was analyzed with the Atomic Force Microscopy. Fig.3 demonstrates remarkable changes in surface morphology with variation of the substrate bias. Indeed, V_b affects homogeneity of distribution and architecture (e.g. sharpness) of the elements of morphology as well as inter-element spacing and surface areas in the "humps" and "dips". We note that homogeneous distribution of very much similar by shape and size nano-sized morphology elements over the micro-scaled surface area is ideal for promoting biomolecule/protein attachment and growth. Furthermore, sharp "humps" and smooth "dips" are especially desirable for this purpose, which has recently been confirmed by cell culturing experiments on ordered arrays of sharp pillars. The inspiring conclusion that can be drawn from the AFM analysis is that all the above quality factors of the surface morphology of the outer functional layer are met for the films prepared at $V_b = -100$ V (Fig.3a). The latter suggests direct link between the origin of nano-crystalline structure reflected in Fig.2, and self-organization of the outer functional layer, which can be inferred as a possible reason for preferred nano-crystalline self-assembly of natural apatites in various bone embodiments. The AFM data thus confirm a challenging opportunity of controlling the nano-scale surface morphology of the outer layer of the graded structure by varying the process parameters.

Meanwhile, the entire coating strongly adheres to the Ti-6Al-4V alloy, which has convincingly been confirmed by the interfacial bonding strength measurement with the Mi-

croscratch test. The critical load that the coating can withstand ranges from 2.0 N to 5.7 N. It is notable that the best interfacial strength is achieved for moderately-biased and higher pressure-grown coatings with well-resolved nano-features. We remark that higher gas pressures favor enhanced sputtering of the titanium target, thus eventually improved doping of the bottom layer by titanium/titania in the atomic/molecular or nanocluster states.

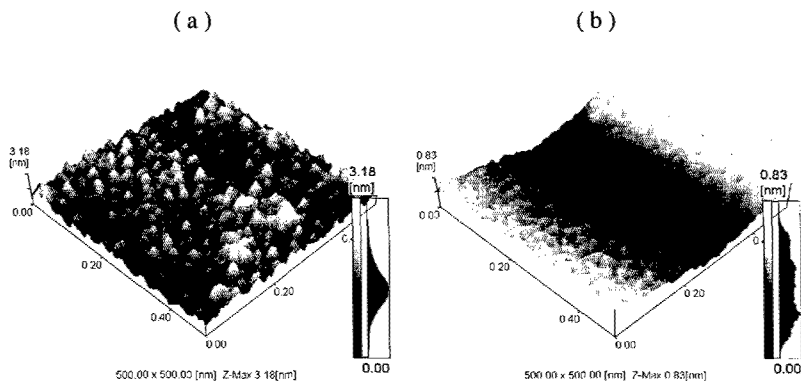


Figure 3. AFM images of the outer nano-sized layer of Ca-P-Ti coating deposited at -100 V (a) and -50 V (b) DC bias.

It is notable that preliminary *in-vitro* cell culturing tests on the graded CaP-based inter-layer suggest promising biocompatibility of the coating. The relevant imaging reveals well-preserved cyto-skeletal structure of COS7 monkey kidney cell series after up to 48 hours after cell culturing. The work is continuing into *in-vivo* assessments of these bioactive HA films.

CONCLUSION

In summary, the plasma-assisted concurrent Rf sputtering in low-temperature, low-pressure reactive environment offers a great deal of control of the major coating quality parameters, including functional grading, stoichiometry, phase purity, chemical composition, crystallinity, crystal size, interfacial bonding strength, as well as of tailoring the nano-scale features of the surface morphology of the outer thin (few nm) layer with specific bio-active functionality. Another unique features of this technique include, but are not limited to, low-temperature, no need for post-treatment, easy deposition process control, etc. From practical considerations, the technique proposed is indeed promising to mimic a number of the basic parameters of natural bone minerals via tailoring certain features at nano-scales, such as nano-crystalline structure and surface morphology. Successful cell culturing tests have demonstrated excellent *in-vitro* biocompatibility, which sounds favorably in view of future *in-vivo* studies. Finally, the results obtained have further supported the usefulness of nano-scale approach for assembly of functionally graded

coatings and give us a hope that such an approach will soon be widely adopted for a wider class of nano- and bio-materials.

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REFERENCES

1. L. Sun, C. C. Berndt, K. A. Gross, A. Kucuk, *Journ. Biomed. Mater. Res.: Appl. Biomater.* **58**, 570 (2001).
2. C. C. Berndt, G. H. Haddad, A. J. D. Farmer, K. A. Gross, *Mater. Forum* **14**, 161 (1990).
3. Y. C. Tsui, C. Doyle, T. W. Clyne, *Biomaterials* **19**, 2031 (1998).
4. C. K. Wang, J. N. Chern Lin, C. P. Ju, H. C. Ong, P. R. H. Chang, *Biomaterials* **18**, 1331 (1997).
5. R. G. T. Geesink, K. D. Groot, C. P. A. T. Klein, *Journ. Bone Jt. Surg.* **70-B**, 17 (1988).
6. J. Gomez-Morales, J. Torrent-Burgues, T. Boix, J. Fraile, R. Rodrigues-Clemente, *Cryst. Res. Technol.* **36**, 15 (2001).
7. S. Xu, J. D. Long, J. H. Lu, K. N. Ostrikov, and C. H. Diong, *IEEE Trans. Plasma Sci.* **30**, 118 (2002).
8. S. Xu, J. D. Long, K. N. Ostrikov, and H. Y. Foo, *Key Eng. Mater.* **240**, 307 (2002).