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CHARACTERIZATION OF CALCIUM PHOSPHATE REINFORCED TI-6AL-4V COMPOSITES FOR LOAD-BEARING IMPLANTS

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ABSTRACT

Titanium alloys such as Ti6Al4V have been popular choices as bulk materials for load-bearing orthopedic implants due to their resistance to corrosion and excellent biocompatibility. To enhance the biological properties and wear resistance of Ti6Al4V, samples of the titanium alloy were tested against titanium composites formed with Ti6Al4V with 2 and 5wt. % tricalcium phosphate. Results show that the calcium phosphate tends to form along the grain boundaries of the titanium alloy matrix, which causes the surface hardness to rise from an average of 177 HV to as high as 542 HV. The increased strength of the material also significantly reduced the amount of material removed during wear testing and preserved a relatively smooth wear track surface to reduce frictional forces from shear. Contact angle measurements with distilled water decreased as the concentration of TCP increased, implying greater hydrophilicity with the composite materials. Simulated body fluid testing for three days show that the presence of TCP in the material accelerated the growth rate of apatite crystals. The results from the contact angle measurements along with the SBF study show that the TCP composite can enhance biological responses of the composites within the body.

1. INTRODUCTION

When choosing a bulk material for load-bearing orthopedic implants, some of the important properties to consider are its long term wear resistance and biocompatibility. The hardness of CoCrMo alloy allows the material to withstand high mechanical wear environments, but there is a present concern of hypersensitive biological responses from the body due to metallic ions [1]. Although titanium alloys are softer than CoCrMo, the improved biochemical compatibility makes it desirable as an implant material [2]. Moreover, concerns are raised related to metal ion release, particularly Co and Cr ions, *in vivo* from metal-on-metal implants. Use of Ti alloy will be ideal if we can improve the wear resistance. Ti-TCP composites are a potential group of materials to accomplish that goal.

Since compressive stresses are essential for proper bone regeneration around the site of injury, it is preferred for an implant to have an elastic modulus close to that of natural bone tissue to prevent stress shielding, where the implanted material carries the majority of the compressive stress away from the bone. Although all of the elastic moduli of popular implant alloys far exceed the modulus of bone, titanium has the lowest elastic modulus ~ 110 GPa compared to 210-250 GPa of CoCrMo alloys [1]. Due to these factors, Ti6Al4V along with other titanium alloys has been growing in popularity compared to their cobalt-based alloy counterparts [3, 4, 5].

Although Ti6Al4V alloys are more mechanically suitable for applications such as prosthetic joint replacements, it is biologically inert, and surfaces cannot effectively bond with the host tissue on its own. Without recognition from the host tissue in the body, the implant will eventually loosen inside the patient.

Current methods of addressing the issue of metallic implant fixation involve the use of calcium phosphates, since they are similar in composition and structure to bone materials [6]. Calcium phosphates can either be applied as bone cement or as a coating on the metal surface of the implant. Studies have shown that with the assistance of osteoconductive calcium phosphates such as hydroxyapatite, the rate of osseointegration improves [7, 8]. To predict how bone tissue will respond to a TCP reinforced titanium composite, the samples can be submerged in simulated body fluid (SBF), which contains ion concentrations similar to that in blood plasma. The amount of apatite that forms on the surface will help determine how well bone tissue will be able to grow on the material surface, assuming there will be no antibody or toxic reactions [8]

This present study will investigate how the material properties of Ti6Al4V will react when TCP is mixed with it during the forming process. Three batches of samples containing 0%, 2%, and 5% TCP by weight are fabricated and compared to one another after testing. Hardness and wear testing are a first step in comparing the changes in mechanical properties, while contact angle measurements and a short simulated body fluid (SBF) study can compare the potential biological response of the TCP samples. Metallography through electron microscopy is also done to correlate the hardness, wear resistance, and apatite growth rates of these materials on how the titanium alloy matrix is changed and to how the TCP particles are distributed within that matrix.

2. EXPERIMENTAL PROCEDURE

2.1 Sample Preparation

Sample preparations started with milling TCP particles to reduce the particle size of the powder. The powder was filtered through two sets of sieves to have the final particles in the ranged between 50 and 186 μm. The TCP powder was mixed with Ti6Al4V powder in ratios of 0, 2, and 5 wt.% TCP. The containers containing TCP powders were shaken well to mix the ceramic particles throughout. Due to the difference in mass densities within the mix, the container had to be shaken vertically, side to side, and occasionally upside down if too much of the titanium powder sank at the bottom. Samples were processed via Laser Engineered Net Shaping (LENS™) at 400W to create rough cylindrical rods with a circular cross section of about $0.8cm^2$. Samples of each composition were cut with a diamond saw into thicknesses of approximately 3mm each. The surfaces of each sample were polished down to 0.05μm prior to testing.

2.2 Microstructure Analysis

A polished Ti6Al4V, 2% and 5 wt.% TCP samples were taken for microstructural analysis. The surfaces were etched using Kroll's reagent which was a mixture of 2% hydrofluoric acid, 6% nitric acid, and 92% de-ionized water by volume. The etchant was swabbed on the sample surfaces for three to five seconds each and promptly rinsed off with de-ionized water. The surfaces were checked using optical microscopy, and additional etching was performed, if necessary. The etched samples were observed under an FESEM to document differences in microstructure among different compositions.

2.3MicrohardnessMeasurements

Microhardness testing was done using a Shimadzu HMV tester with 9.807N of applied force. Three polished samples from each composition were used for testing, and ten measurements were taken on each. The positions of measurements were taken along a linear path across the surface starting close to the outer edge and progressing towards the center of the samples. This was done to ensure the results accurately represented the overall hardness of the samples rather than a local area, and to see if there would be a hardness gradient across the sample.

2.4 Wear Testing

Two polished samples from each composition were used in wear testing. Each sample was submerged under 200mL of SBF solution heated to 37°C to simulate a biological environment. A 3mm diameter chrome-steel ball with 5N of applied force ran over the sample surface linearly at a rate of 1200mm/min over a track length of 10mm and continued to oscillate for a final distance of 1km. One sample from each TCP concentration ran an additional 3km wear test. The remaining SBF from each test, typically between 90 and 100mL, was collected and preserved in a mixture of 2mL of HNO_3 with 5mL of HCl and split between two 50mL plastic tubes for future studies on the wear debris.

2.5 Simulated Body Fluid (SBF) Testing

Two samples from Ti6Al4V and 2 wt.% TCP were selected to be put through SBF testing. The samples were placed in a culture plate and submerged under 3mL of simulated body fluid in each cell. The plate was placed in an oven controlled at 37°C. After 3 days, the SBF solution was removed from two cells, one containing a sample of Ti6Al4V and the other containing 2wt.% TCP. The removal of the SBF solution was done carefully with a pipette pressed against the side of the culture plate well to avoid as much contact with the surface of the samples as possible. The SBF samples were analyzed under the FESEM to check for apatite growth on the surfaces.

2.6 Contact Angle Measurements

Contact angle measurements were taken on polished samples across all sets of composition. Samples were thoroughly dried prior to testing. Distilled water and diiodomethane were used to characterize the polar and dispersion components of the total surface tension. From the contact angle measurements, the surface tension was calculated using the equation:

$$\frac{n(1+\cos\theta)}{2} = \left(\gamma_l^d \gamma_r^d\right)^{1/2} + \left(\gamma_l^p \gamma_r^p\right)^{1/2}$$

Given:

	γ_l	γ_l^d	γ_l^p
Distilled Water	72.8	21.8	51.0
Diiodomethane	50.8	49.5	1.3

Where γ_l is the surface tension of the test liquid and γ_l^d and γ_l^p are the dispersion and the polar components of the liquid surface tension respectively in dynes/cm. From this information, the dispersion and polar components of the solid surface (γ_s^d and γ_s^p) were calculated. [9]

3. RESULTS AND DISCUSSION

3.1 Microstructural Analysis

The microstructure of the Ti6Al4V etched sample appears to consist of two phases as seen in Figure 1. These are expected to be primarily made up of α phase with regions of β [10]. The structure for Ti6Al4V changes significantly with the introduction of 2% TCP content as seen in Figure 2. Upon closer inspection, the tricalcium phosphate seems to prefer to integrate into the grain boundaries of the titanium alloy in a continuous phase. As the TCP concentration is increased to 5 wt%, the calcium phosphate distribution within the metal matrix seems to become less homogeneous and more localized along the titanium alloy grain boundaries as seen in Figure 3. With TCP appears thicker and growth of larger circular patterns have also emerged. Laser absorption coefficients for calcium phosphates (CaP) are very low, and most of the laser energy actually pass through CaPs. When Ti and CaP are hit by laser, it is the Ti that absorbs laser energy and melts. During solidification of Ti, some CaP particles break and some goes into solid solution, but the remaining particles accumulate at the grain boundary area. Having this ceramic form along the grain boundaries will increase the strength of the material, while providing areas for live tissue to bond with the material through osseointegration.

3.2 Microhardness Measurement

As predicted from the microstructural analysis, the hardness of the samples with higher TCP concentrations consistently measured higher, averaging 438 HV with 2 wt.% and 542 HV with 5wt.%, compared to the pure Ti6Al4V alloy due to the TCP reinforcement along the grain boundaries. Without TCP, Ti6Al4V only measured an average of 177 HV as seen in table 1.

Table 1 – Microhardness measurement values

	Ti-6Al-4V		2% TCP		5% TCP	
	HV	HRC	HV	HRC	HV	HRC
Max	185	7.2	512	49.9	597	55.1
Min	168	2.5	373	38.1	489	48.3
Average	**177**	**5.11**	**438**	**44.2**	**542**	**51.8**

The measurements for Ti6Al4V with no TCP content seem to be lower compared to what is expected value for hardness. According to the website of ASM Aerospace Specification Metals Inc., the hardness of Ti6Al4V should be around 350 HV [11]. Although these values resemble more closely to the measurements for the 2 wt.% TCP composite, they are significantly higher than what was measured for the pure titanium alloy. It should be noted however that during the grinding and polishing phases of sample preparation, some pores left from the LENS process were occasionally exposed.

3.3 Wear Degradation

SEM analysis of a wear-tested Ti6Al4V sample is shown in Figure 4a with a rough wear track surface. This correlates with the low hardness measured from the microhardness test. The rough texture from shearing also implies that the coefficient of friction increased over time due to sticking friction and accelerated the wear rate of the material. The calcium phosphate composite materials, however, show a much smoother wear track surface compared to the pure titanium alloy as seen in Figure 4b and c.

As opposed to the rough texture on the titanium alloy sample, a smoother surface on the composite can help minimize the friction and wear rate over time. Overall the volume of material removed from the samples during wear testing is calculated to be 5.24, 2.04, and 1.64 mm^3 for Ti6Al4V, 2wt. % and 5 wt.% TCP, respectively. The average wear rate of the titanium alloy of 0.0063 mm^3/min was significantly reduced to 0.0024 and 0.0020 mm^3/min with 2 wt.% and 5 wt.% TCP, respectively.

3.4 Simulated Body Fluid Testing

After the first three days of SBF testing, the surface of the Ti6Al4V and 2 wt.% TCP samples can be seen in Figure 5. At 1000x magnification, there appear to be more growth of apatite crystals on the 2% TCP surface. The pattern of apatite growth followed the grain boundaries on the unetched surface where the calcium phosphates are located. Although the Ti6Al4V shows signs of apatite growth, the smaller crystal sizes indicate slower apatite growth rates. The 2% TCP sample showed a consistently faster growth rate compared to pure Ti6Al4V. Not only is area fraction of apatite on the surface higher, large apatite crystals roughly 50μm have been observed.

3.5 Contact Angle Measurements

From the contact angle measurements taken with distilled water and diiodomethane test liquids, surface tension results for each sample are given in table 2.

	Total Surface Tension	**Dispersion Component**	**Polar Component**
Ti-6Al-4V	36.37	33.1	3.27
2% TCP	36.11	32.1	4.01
5% TCP	38.23	30	8.23

Table 2 – Dispersion and polar components of the total surface tension in dynes/cm

As the amount of TCP in the composite is increased, the contact angle measurements with distilled water decrease as is reflected by the increase in the polar component of the total surface tension. The increased affinity towards polar molecules resulted in great hydrophilicity and in-turn allowed greater bonding potential between the material and live tissue.

4. CONCLUSIONS

From the tests performed on Ti6Al4V titanium alloy, 2 wt.% and 5wt.% TCP titanium composites, the samples showed very different behaviors. With the addition of TCP, the calcium phosphate appears to prefer moving to the grain boundaries in the titanium microstructure. At 2%, the TCP appears to be well distributed across the matrix, and at 5% TCP, the ceramic becomes more localized at the grain boundaries. The reinforcement along these grain boundaries increased the hardness of pure Ti6Al4V matrix from an average of 177 HV to a significantly higher 438 HV with 2 wt.% TCP and 542 HV with 5wt.% TCP. Wear testing also reflected on the strengthening effects of TCP integration. The wear track surfaces became much smoother and the calculated wear volume and average wear rate also decreased significantly.

Submersion of the samples in simulated body fluid for 3 days showed apatite growth on Ti6Al4V and composite samples. However, it was noted that the growth rate of apatite crystals with the presence of calcium phosphate was increased. Contact angle measurements and calculations for the solid surface tension also showed an increase in the polar component with the increased amount of TCP in the composites. This implies an increased affinity towards polar molecules and greater hydrophilicity on the material surface. The strengthening effects induced by the TCP concentration along the grain boundaries can improve the wear resistance when used in load-bear joint implants. The evidence of improved wear resistance and enhanced biological properties gives this titanium-TCP composite great potential as an implant material.

REFERENCES

[1] R. Pourzal, et al., Characterization of Wear Particles Generated from CoCrMo Alloy Under Sliding Wear Conditions, Wear, Vol. 271, April 2011, pp. 1658-1666.

[2] S.J. Li et al., Wear Characteristics of Ti-Nb-Ta-Zr and Ti-6Al-4V Alloys for Biomedical Applications, Wear, Vol. 257, April 2004, pp. 869-876.

[3] Brunski, John B. "Metals." *Biomaterials Science: An Introduction to Materials in Medicine.* Ed. Buddy D. Ratner, Ed. Allan S. Hoffman, Ed. Frederick J. Schoen, Ed. Jack E. Lemons and Ed. 2nd. San Diego: Elsevier Academic Press, 2004. 143.

[4] M. Niinomi, Mechanical properties of biomedical titanium alloys, Materials Science and Engineering: A, Vol. 243, Issues 1-2, 15 March 1998, pp. 231-236, ISSN 0921-5093, 10.1016/S0921-5093(97)00806-X.

[5] M. Long, H.J Rack, Titanium alloys in total joint replacement – a materials science perspective, Biomaterials, Vol. 19, Issue 18, September 1998, pp. 1621-1639, ISSN 0142-9612, 10.1016/S0142-9612(97)00146-4.

[6] H.L. Dai, Y.H. Yan, Y.F. Wang, X.D. Zhou, G.R. Yu, Biological Evaluation of α-TCP/TTCP Composite Bone Cement, Journal of Wuhan University of Technology: Vol. 17, Issue 3, September 2002, pp. 35-38.

[7] Alexandra E. Porter, PunamTaak, Linn W. Hobbs, Melanie J. Coathup, Gordon W. Blunn, Myron Spector, Bone bonding to hydroxyapatite and titanium surfaces on femoral stems retrieved from human subjects at autopsy, Biomaterials, Volume 25, Issue 21, September 2004, Pages 5199-5208, ISSN 0142-9612, 10.1016/j.biomaterials.2003.12.018.

[8] Tadashi Kokubo, Hiroaki Takadama, How useful is SBF in predicting in vivo bone bioactivity?, Biomaterials, Volume 27, Issue 15, May 2006, Pages 2907-2915, ISSN 0142-9612, 10.1016/j.biomaterials.2006.01.017.

[9] Standard Test Method for Measurement of the Surface Tension of Solid Coatings, Substratres and Pigments using Contact Angle Measurements, ASTM International, Designation: D7490-08.

[10] M. Koike, K. Martinez, L. Guo, et. al, Evaluation of titanium alloy fabricated using electron beam melting system for dental applications, Journal of Materials Processing Technology, Volume 211, Issue 8, August 2011, Pages 1400-1408, ISSN 0924-0136, 10.1016/j.jmatprotec.2011.03.013.

[11] "ASM Material Data Sheet." *ASM.*Web. 13 Dec. 2011. <http://asm.matweb.com/search/SpecificMaterial.asp?bassnum=MTP641>.

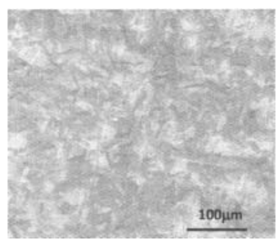

Figure 1. Microstructure of LENS™ processed Ti6Al4V sample at 600x magnification

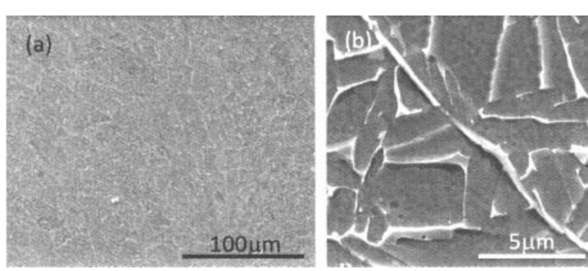

Figure 2. 2% TCP doped LENS™ processed Ti6Al4V composites under different magnifications.(a) Low magnification image and (b) high magnification image.

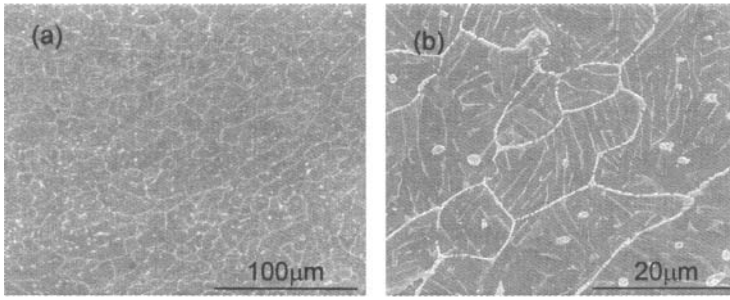

Figure 3. 5% TCP doped LENS™ processed Ti6Al4V composites under different magnifications. (a) Low magnification image and (b) high magnification image.

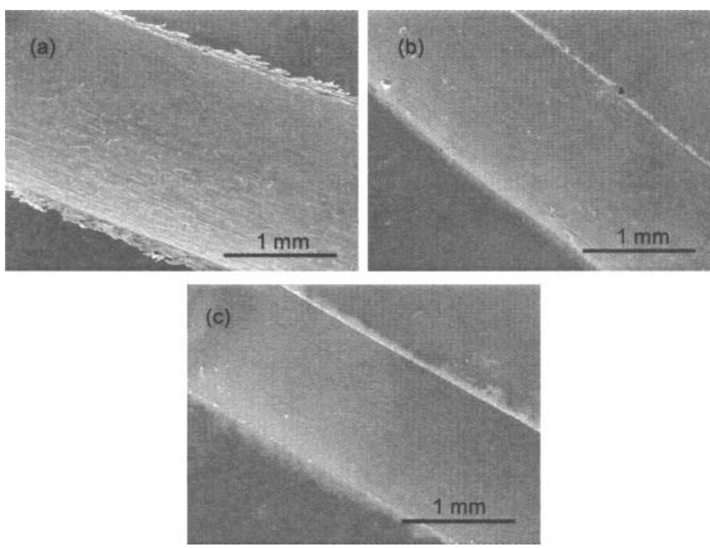

Figure 4. Wear induced damage of (a) Ti6Al4V, (b) 2% TCP doped Ti6Al4V composite and (c)5% TCP doped Ti6Al4V composite.With the addition of TCP in Ti6Al4V, the wear track became smoother and shallow.

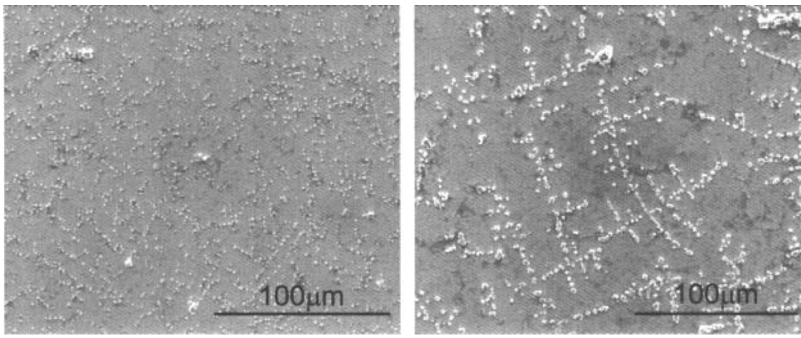

Figure 5. (a) Ti6Al4V sample after 3 days in SBF and (b) 2% TCP doped Ti6Al4V compositeafter 3 daysin SBF.