Calcium Phosphate-Titanium Composites for Articulating Surfaces of Load-Bearing Implants

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Abstract

Calcium phosphate (CaP)– titanium (Ti) composites were processed using a commercial laser engineered net shaping (LENS™) machine to increase wear resistance of articulating surfaces of load-bearing implants. Such composites could be used to cover the surface of titanium implants used in total arthroplasty procedures and potentially increase the lifetime of the joint replacement without any harmful metal ion release. It was hypothesized that adding calcium phosphate to commercially pure titanium (CP-Ti) and Ti6Al4V alloy via laser processing would decrease the material loss when subjected to wear. This added protection would be due to the *in situ* formation of a CaP tribofilm; which acts as a solid lubricant and a protective barrier. Different amounts of CaP were mixed by weight with pure titanium and Ti6Al4V in powder form. The mixed powders were then made into cylindrical samples using a commercial LENS™-750 system. Microstructures were observed and it was found the CaP had integrated into the titanium metal matrix, while causing the formation of columnar grains in the Ti6Al4V. Compression test revealed that CaP significantly increased the 0.2% offset yield strength as well as the ultimate compressive strength of CP-Ti. After conducting wear tests, it was found that the addition of CaP to pure titanium reduced the material loss and increased wear resistance. This was due to the formation of CaP tribofilm on the articulating surface. The *in situ* formed tribofilm also lowered the coefficient of friction and acted as a solid lubricant between the two interacting metal surfaces. Overall, CaP addition to Ti and its alloy Ti6Al4V is an effective way to minimize wear induced damage due to the formation of *in situ* tribofilm, a strategy that can be utilized in various biomedical devices.

Key words: Calcium phosphate-Ti composites, wear resistance, tribofilms, metal ion release, load-bearing implants.

1.0 Introduction

Commercially pure titanium (CP-Ti) and its alloy Ti6Al4V (Ti64) have been used in the biomedical industry for a long time, primarily for replacing or repairing hard tissues. This is due to the alloys biocompatibility, corrosion resistance, and fatigue resistance (Bose and Bandyopadhyay, 2013). Though titanium and its alloys have proven to work well in many medical applications, one of the issues these materials face is poor wear resistance. An application where this is prominent includes articulating surfaces of hip, knee or shoulder joint replacements. Wear induced metal ion release can cause implant failure or metallosis due to toxic metal ions *in vivo* (Andreietelli et al., 2009). Much research has been done on reducing wear of materials used in the ball and the cup implant design in order to increase its lifetime. Some methods that have been tested to do this are adding surface coatings of materials with excellent wear resistance such as zirconia and alumina ceramics (Samuel et al, 2008; Yen et al., 2001). This gives the head of the implant a barrier that will reduce the overall material loss from the implant and act as a passive layer that significantly reduces metal ion release. However, if we consider biomimetic design concepts, instead of a hard coating, a softer layer equivalent to cartilage should be used to minimize friction coefficient and wear induced damage. Moreover, it will be ideal to have the coating surface such that if it degrades, the degradation product is resorbable in the body and non-toxic. A possible solution to this problem could be found by adding calcium phosphate (CaP) to reinforce the metal matrix of the titanium alloy. This approach has the potential to form an *in situ* tribofilm of CaP on the articulating surface *in vivo*. Once formed, this tribofilm acts as a solid lubricant and minimizes wear damage and metal ion release from articulation. Manufacturing CaP-Ti composite can be achieved through the use of a variety of techniques including freeform Laser Engineered Net Shaping (LENSTM), a commercially available additive manufacturing technique.

It was hypothesized that addition of CaP in commercially pure Ti (CP-Ti) or Ti64 alloy would enhance wear resistance of Ti/Ti64-CaP composites due to the formation of tribofilms at the articulating surface. To validate the hypothesis, CP-Ti-CaP and Ti64-CaP composites with

different amounts of CaP using a commercial LENSTM system have been processed. Microstructural examination, mechanical property evaluation and wear studies were conducted to understand the influence of different amounts CaP addition in CP-Ti and Ti64 matrices.

2.0 Experimental Procedure

2.1 LENSTM processing: Commercially pure titanium (CP-Ti) and Ti6Al4V (Ti64) powders were purchased from Crucible Research (Pittsburg, PA) with a particle size between 44 and 212 µm. Commercially available food grade CaP powder was purchased (Monsanto, CA), ball milled, and sieved in the lab until it had a particle size between 47 and 212 µm. **The food grade CaP was >97% pure with non-toxic impurities due to it being made for human consumption. This purity of CaP was deemed suitable for this study that is a proof of concept experiment and analysis.** CP-Ti was mixed with CaP in proportions of 3.3, 6.8 and 10 % CaP powder by weight. The same was done for Ti64 but in proportions of 2% and 5% CaP by weight. Mixing of higher fraction of CaP in Ti64 proved to be quite challenging to make reproducible structures using LENSTM, and therefore 2 and 5 wt. % CaP was used for all of our studies. Thorough mixing was a very important step to minimize heterogeneity in the metal and ceramic phases with very different density. In the remainder of this article samples are referred to by their CaP content. These pre-mixed powders were then loaded into the LENSTM and samples were directly processed into different shapes having various compositions. **All samples were made homogeneous by using the pre-mixed powder to build the parts, as opposed to in situ mixing the powder using the LENSTM machine. No part was made with a gradient or coating of different amounts of CaP.**

CaP and titanium samples were then processed using a commercial LENSTM -750 (Optomec Inc., Albuquerque, NM) system. LENSTM works by depositing feedstock powder on the build material at the focal point of a continuous wave Nd:YAG laser. As laser melts the substrate material, the feedstock powder is added to the melt pool to increase the melt pool volume. The substrate moves along the x and y directions and that creates liquid metal lines. By moving multiple times, these lines create a layer based on the computer aided design file of the desired part. Once the layer is done, the deposition nozzle along with the laser on the z-axis moves up and repeats the same process. Figure 1 shows a schematic of the LENSTM system.

Further description of this process is given in our previous references (Balla et al., 2007; Bandyopadhyay et al., 2010). All samples were processed in an argon gas environment maintaining an oxygen level below 10ppm to prevent any oxidation of Ti during processing. For the CP-Ti with CaP, 8 mm diameter cylinders were fabricated for compression testing. For all other tests 14.5mm square samples and 12mm diameter cylindrical samples were fabricated. A scan speed of 7.6 mm/sec and a laser power of 400 watts were used to prepare these samples.

2.2 Physical characterization: For microstructural analysis, samples surfaces were polished successively with 120, 300, 600 and 1000 grit silicon carbide sandpapers. Then sample surfaces were polished with 1, 0.5 and 0.3 micron alumina powder on a felt disc until all surfaces had a mirror-like surface finish. Polished surfaces were then etched with Kroll's reagent (92ml DI water, 6ml nitric acid, 2ml hydrofluoric acid). Each sample was then examined in a field emission scanning electron microscope (FEI Quanta 200, OR).

Surface energy of the samples was measured using a sessile drop method. Polished surfaces were cleaned with their respective testing fluids - water or diiodomethane prior to analysis and air dried (Das et al., 2007). Contact angles were measured using ASTM standards D7334-08 (ASTM International, 2008). Five separate tests were conducted on each sample and averages were reported.

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

The measured contact angle for water and diiodomethane along with the known polar γ_l^p and dispersion γ_l^d components of the surface tension γ_l of the liquid were used in the Owens-Wendt-Kaelble equation.

$$\frac{\gamma_l(1 + \cos \theta)}{2} = (\gamma_l^d \gamma_s^d)^{1/2} + (\gamma_l^p \gamma_s^p)^{1/2}$$

The result was a system of two equations with two unknowns. By solving the equations, the polar γ_s^p and dispersion γ_s^d components of the solid could be calculated. The polar and dispersion components of the solids were then added together to find the surface energy of the material in dynes/cm.

2.3 Mechanical characterization: As a part of mechanical characterization, hardness, compressive strength, wear rate, and coefficient of friction (COF) measurements were done on LENSTM processed samples. Hardness values were measured using a Vickers micro hardness tester (HMV-2T, Shimadzu, Kyoto, Japan). For microhardness measurements, a 4.9N load was applied for 60 sec maintaining a gap of at least 1 mm between each indent. A total of 10 tests were conducted on each sample with three samples per composition. The mean Vickers hardness values and standard deviation were reported for each composition.

Compression tests were done with 8 mm diameter and 16 mm long samples. This was done to maintain the height to diameter ratio of 2:1. These samples were placed in a 222kN MTS servo-hydraulic universal testing machine. Each sample was compressed quasi-statically at a rate of 0.2 mm/min. From the stress-strain plots, ultimate compressive strength and 0.2% compressive yield strengths were determined.

A Nanovea Series tribometer (Microphotonics Inc., CA. USA) was used to measure wear damage in CP-Ti and Ti64 with CaP composites. All wear tests were conducted in linear reciprocating mode with spherical pin on disc with a 10mm stroke length. A 3mm chrome steel ball (100Cr6, 58-63 HRC) was used as pin, and a 5N load was maintained during the test duration. Testing was done for 1000m distance at 1200mm/min stroke rate. 1000m was chosen to calculate a stable coefficient of friction (COF) and achieve enough material loss to have a observable wear track, and quantifiable wear rate. All tests were conducted while fully immersed in a simulated body fluid (SBF) environment being heated at 37°C. Simulated body fluid was prepared according to previously published methods (Bodhak et al., 2010). Wear track images were taken using optical microscope followed by image processing to measure the wear track width at approximately 15 locations for each samples. From the average width, wear volume was calculated. For coefficient of friction (COF) measurements, force sensor data from the tribometer was utilized, which recorded the force at the contact point approximately every 100ms. The COF data is a sinusoidal plot due to the pin moving back and forth, changing the direction of the resistance with the pin head. The values were averaged to determine the zero value or baseline of the sin like data. The absolute value of the variance from zero is then taken to make all the COF data positive. For every 5000 values, the largest 50 were averaged. The result was divided by the 5N load to normalize it and get the static COF.

3.0 Results

Microstructural examination, mechanical property evaluation and wear studies were conducted on CP-Ti and Ti64 alloy with varying amount of CaP to understand the influence of CaP addition in metallic matrices. It was hypothesized that the addition of CaP in both CP-Ti and Ti64 would enhance wear resistance of the composites due to the *in situ* formation of tribofilms at the articulating surface. FESEM images of the microstructures can be seen in Figure 2. Figure 2a shows the microstructure of LENS processed CP-Ti without any CaP. It has fine acicular α grains, which is common in LENS processing and has been reported earlier (Balla et al., 2007; Hosford, 2010). Figures 2b and 2c show the influence on microstructure due to the addition of CaP to CP-Ti. It appears that the grain size increased slightly with the addition of 10% CaP. Figure 2d shows the LENS processed pure Ti64. It has the appearance Widmanstätten structure with fine acicular α grains that are oriented in different directions with small amount of β phase similar to published literature (Collins et al., 2003). Again the fine acicular α in these grains are due to the fast cooling rate of the LENS processing (Balla et al., 2012; Balla et al., 2014). Figures 2e and 2f show the Ti64 with the addition of CaP that lead to the disappearance of the Widmanstätten structure and the grains became columnar with CaP ceramics in the grain boundaries. It can also be seen that with the increase in CaP amount, the columnar grains become finer.

Results from the surface energy measurements revealed that CaP had little effect on the surface energy. In CP-Ti matrix composites, there was some fluctuation observed in the surface energy due to the addition of CaP. A slight increase in surface energy was measured for 3.3%CaP while the same for 10%CaP showed a decrease. When considering the possible experimental errors, all samples were in the same relative range. The Ti64 followed the same trend and experienced little to no change.

The 0.2% compressive yield strength (YS) and ultimate compressive strength (UTS) of the CP-Ti with CaP are shown in Table 1. It can be seen that there was a significant increase in both 0.2 % compressive YS and UTS as more CaP was added to the CP-Ti. A 10% addition of CaP increased the yield strength by four times. The UTS did not show as significant of increases when CaP was added in quantities of 3.3% and 6.8% wt. Yet upon addition of 10% CaP, the UTS increased from 1230MPa to 2070MPa, nearly a 70% increase. Figure 3 shows

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4 corresponding stress-strain plots from these tests. As more CaP was added to the CP-Ti, the
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6 metal matrix became more brittle and lost some of its ability to plastically deform before failure.
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8 The results from the hardness tests and the calculated wear rate of different samples can
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10 be seen in Table 2. The data shows that the addition of the CaP to the CP-Ti considerably
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12 increased the hardness and decreased the wear rate. This trend was also seen when the CaP was
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14 added to Ti64. Upon addition of 10% CaP to CP-Ti, the wear rate decreased by 92% while the
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16 hardness increased by 388%. Figure 4 shows images of the wear tracks from the wear tests. The
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18 tracks of the CP-Ti and Ti64 with no CaP addition have a much larger width than the alloys that
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20 have CaP in the metal matrix. Also as more CaP was added, the surface became harder and the
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22 wear track became narrower, visually showing that less material was lost. From these results, it
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24 can be concluded that addition of CaP to CP-Ti and Ti64 can minimize wear induced damage
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26 during articulation.

27 Figure 5 is a graph of the static coefficient of friction (COF) data calculated from the
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29 wear test. As CaP was added to CP-Ti, the COF consistently decreased as well. It was also found
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31 that the CP-Ti have a gradual increase in COF with an increase in wear distance. Addition of
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33 CaP stabilizes the COF, and both the 6.8% and 10% CaP samples show a consistent COF for the
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35 duration of the wear test. Figure 5 also shows the COF of all the Ti alloys compared to CoCrMo
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37 alloy, a commonly used alloy for articulating surfaces, under similar test condition. The CoCrMo
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39 alloy has a lower COF than the CP-Ti with and without CaP.

40 Figure 6 shows high magnification images of the wear tracks of the CP-Ti and Ti64
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42 samples. Figures 6a and 6d show pure CP-Ti and Ti64 wear tracks without any CaP addition.
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44 Both of those images show the wear track being rough with jagged layer edges present from the
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46 metal being worn away. The addition of 3.3% CaP to CP-Ti, shown in Figure 6b, shows a small
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48 reduction in these edges and the surface appears to be smoother. In the case of Ti64 alloy, this is
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50 even more apparent when comparing Figures 6d and 6e. Adding 2% CaP significantly reduced
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52 the roughness and the wear track looks almost uniform and flat. Upon the addition of more CaP,
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54 this trend continues and the jagged rough surface features disappear, as shown in Figure 6c and
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56 6f. There is a somewhat of an uneven texture that does not resemble how the metal was wearing
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58 when no CaP was added. The added layer is a tribofilm of CaP that has formed during
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60 articulation, which is the main reason for the minimized wear damage.
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Figure 7 reveals the tribofilm that has formed on the surface. Figure 7a is an image of the microstructure of the 2%CaP in Ti64. The CaP has mixed in the metal matrix of the Ti64. Figure 7b presents the smooth surface of the wear track after 500m articulation. The smooth surface is the result of the CaP tribofilm. Then Figure 7c shows the wear track after the tribofilm had been etched away, revealing the metal substrate with no visual evidence of the fracturing or damage as seen in the wear track images of Ti64 with no CaP addition.

4.0 Discussions

Initially a scan speed of 8.5 mm/sec and a laser power of 450 watts were used during LENSTM operation. Those optimized parameters were selected because they had been used before to successfully process CP-Ti and Ti64 samples. A powder feed rate of 13 g/min was used. A faster feed rate had a marginal increase in material deposited but wasted more powder as it passed through the system un-melted. When composite powders, especially those with a higher CaP concentration, were melted using the same parameters, thinner layers were formed. More energy was needed to melt these composites and the scan speed was reduced to 7.6 mm/sec to allow the contour time to build a thicker layer. A reduction in scan speed unfortunately increased the residence time, which led to the absorption of more energy by the bulk material. In order to reduce the excess residual heat, the laser power was reduced to 400 watts. This combination allowed sufficient time for each layer to grow thick enough while keeping the energy input low enough for the part to cool without any visible radiation.

The microstructural analysis shows that the CaP caused little change to the CP-Ti structure. There only appeared to be some larger β grain size in the 10%CaP sample. There also appears to be some possible porosity in the 10%CaP when looking at the grain boundaries. This is due to the powder flow or processing parameters of the LENS with such a high amount of CaP. The grain structure has been found to have some advantages when considering it for load bearing implant applications. In previous studies the acicular α phase has shown to increase the hardness (Balla et al., 2007). This higher hardness value helps to increase the wear resistance of the titanium, which has been seen in other metal-ceramic composite systems (Chen & Wang, 2003). The change in microstructure that the CaP causes has also been found to not affect the biocompatibility of the CP-Ti, leaving it just as functional for use in biomedical applications (Balla et al., 2007). Addition of CaP could possibly be increasing the biocompatibility of the

material due to the fact that adding CaP to CP-Ti on the surface has been studied before in order to increase the biocompatibility and possibly make the surface more bioactive (Roy, et al., 2008 (1); Roy, et al., 2008 (2)).

The Ti64 matrix had a significant change in grain structure due to the addition of the CaP. In previous studies, CaP being added as a surface coating to Ti64 caused the grains to grow in a columnar pattern seen in Figures 2e and 2f (Nag et al., 2013). This is due to fact that the melt solidification front grows towards the opposite direction of the heat dissipating, which was towards the substrate. It appears that there are very distinguishable white colored veins in the structure that are primarily present in the grain boundaries. As reported earlier by Roy et al., those are areas of high CaPs (Roy, et al., 2008 (1); Roy, et al., 2008 (2)). In the same study it was found that in CaP and Ti bonded zones, compounds of $\text{Ca}_3(\text{PO}_4)_2$ and CaTiO_3 were both present. Both of these phases could be present at the grain boundaries and be causing the white areas between the grains. This shows CaP is well integrated into the metal matrix of the Ti64. Also it should be noted that P has been known to be a β stabilizer and has no solubility in the α Ti phase (Nag et al., 2013). The presence of the P could also be helping to retain the β phase and is the main reason why there is little to no visible α phase in the grains.

The surface energy of the LENS processed Ti64 is consistent with what has been found in past studies (Wu et al., 2013). The surface energy of the implant plays a significant role in cellular adhesion and proliferation to the implant (Bodhak et al., 2010; Braga et al., 2007; Das et al., 2007). Addition of CaP did not change the surface energy, therefore the hydrophilicity should remain close to the same, as well as the cells affinity towards the surface (Bose et al., 2013).

CaP caused the yield strength to increase significantly. This increase is ideal for the surface of a hip implant where large loads are being applied. Also it can be seen from the stress strain plot that the slope of the elastic region, i.e., the modulus of elasticity, has increased as more CaP has been added. In previous studies, it has been found that adding phases such as SiC to Ti helps to inhibit plastic deformation which has been found to reduce wear (Das, et al., 2010). In this case, the addition of CaP is causing this same phenomenon. This is ideal for the surface of a load-bearing implant where it is necessary to have it retain its shape for the longevity of the implants life.

The most notable finding was the addition of CaP to both Ti64 and CP-Ti increased the wear resistance considerably. The reason for this is the formation of a tribofilm of CaP on the

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4 surface reducing the COF and acted as a physical barrier which hindered further material loss
5 during articulation. The CaP undergoes preferential wear and forms a thin tribofilm of CaP on
6 the surface as the chrome steel ball rubbed against it. This occurrence has been seen in other
7 systems such as grey cast iron, where graphite exists within the metal matrix. As wear is
8 induced, the graphite undergoes preferential wear and forms a film on the surface (Luo, 2013).
9 Graphite acts as a solid lubricant that helps to reduce wear and material loss. The CaP is
10 behaving in the same manner and is forming a tribofilm where the material is subjected to wear.

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12 The wear tracks of the CP-Ti and the Ti64 in figures 6a and 6d show some layered
13 fracture surfaces. This shows that the material is breaking away as the chrome steel ball rubs
14 against it. This is typical for Ti alloys which have been known to have localized fracture of
15 transfer layers and undergo a microfragmentation process when rubbed against metals or
16 ceramics (Molinari, et al., 1997; Qu, et al., 2005). This is also what is believed to be the cause of
17 the fluctuation in the COF and could contribute to its rise as wear continues. By comparing the
18 wear tracks in figure 6 that have CaP, they show no signs of these fracture planes. It can also be
19 seen the COF remains relatively steady as wear is induced. The tribofilm of CaP that is forming
20 is almost eliminating all apparent fracturing of the surface and is forming a smooth face with a
21 lower COF. This lower COF causes less abrasion and stress induced on the material when two
22 surfaces interact. Figure 7c shows the wear track that had a tribofilm formed on it and had it
23 etched away revealing the Ti64 substrate underneath with little to no noticeable fracturing. This
24 image reveals the Ti64 with the CaP phases dispersed with the metal matrix. The tribofilm has
25 protected the base alloys, reducing localized fracturing and subsequent material loss.

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27 A unique feature of this system is the self-healing ability. The CaP tribofilm develops
28 where the material is subject to wear and the two surfaces interact. As the film forms, it causes
29 the COF to drop and acts as a barrier between the two faces. As more wear is induced, more
30 tribofilm forms and continually protects the metal matrix. CaP is very similar to naturally
31 occurring bone minerals and has excellent biocompatibility (Bandyopadhyay et al., 2006; Bose et
32 al., 2011). This means that if the tribofilm is released over time *in vivo*, it should not be harmful
33 to a patient compared to metal ions coming from the articulating surfaces (Andreiotelli et al.,
34 2009). Though particle release may still cause inflammation, CaP is bioresorbable and over time
35 should resorb into the body unlike metal ions (Bose & Tarafder, 2012; Roy et al., 2008).
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Conclusions

A method for increasing the wear resistance and strength of commercially pure titanium and Ti64 for their use in an articulating surface was studied. This was accomplished by adding CaP to the titanium which increased the strength, hardness, and subsequent wear resistance by making a metal-ceramic composite. It was also found that during tribological studies, the CaP underwent preferential wear and formed a tribofilm which added additional protection and lubrication to the surface. This resulted in a decreased wear rate of 92% when 10% wt. CaP was added to CP-Ti. Similarly, the addition of 5% wt. CaP to Ti64 decreased the wear rate by 70%. The CaP raised the 0.2% offset yield strength, ultimate compressive strength, and increased the hardness. It was found that the CaP had little effect on the surface energy of the titanium. LENSTM processing proved to be an effective method of integrating the CaP and titanium together. This system of adding CaP shows promising results for being able to be applied to surfaces of load-bearing implants to extend their lifetime *in vivo*.

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Table 1: 0.2% Compressive yield strength and ultimate compressive strength of CP-Ti and CaP-Ti composites

	0.2% Compressive Yield Strength (MPa) (±5% error)	Ultimate Compressive Strength (MPa) (±5% error)
CP-Ti	368 +/- 4	1230 +/- 60
CP-Ti-3.3% CaP	780 +/- 20	1300 +/- 30
CP-Ti-6.8% CaP	1220 +/- 20	1450 +/- 70
CP-Ti-10% CaP	1470 +/- 90	2070 +/- 70

Table 2: Hardness and wear rates of CaP added CP Ti and Ti64 matrix composites

	Hardness HV	Wear Rate mm³/N m
CP-Ti	177+/-9	$2.85 \times 10^{-4} \pm 0.18 \times 10^{-4}$
Ti64	240+/-7	$2.65 \times 10^{-4} \pm 0.7 \times 10^{-4}$
CoCr	457+/-12	$8.2 \times 10^{-6} \pm 2.4 \times 10^{-6}$
CP-Ti-3.3% CaP	540+/-20	$7.4 \times 10^{-5} \pm 2.5 \times 10^{-5}$
CP-Ti-6.8% CaP	760+/-30	$2.7 \times 10^{-5} \pm 1.0 \times 10^{-5}$
CP-Ti-10% CaP	930+/-50	$2.3 \times 10^{-5} \pm 1.0 \times 10^{-5}$
Ti64- 2% CaP	440+/-70	$1.06 \times 10^{-4} \pm 0.06 \times 10^{-4}$
Ti64- 5% CaP	540+/-50	$7.94 \times 10^{-5} \pm 0.19 \times 10^{-5}$

Table 3: Surface Energy of CaP added CP Ti and Ti64 matrix composites

	Surface Energy dynes/cm
CP-Ti	33.1 +/- 1.2
Ti64	36.4 +/- 1.7
CP-Ti-3.3% CaP	36.7 +/- 1.9
CP-Ti-6.8% CaP	33.8 +/- 1.2
CP-Ti-10% CaP	32.2 +/- 0.5
Ti64- 2% CaP	36.1 +/-1.8
Ti64- 5% CaP	38.2 +/- 2.0

Figure 1: Image of the Laser Engineered Net Shaping (LENS™) set-up at WSU with the laser path shown through the nozzle.

Figure 2: Microstructure of (a) Ti64; (b) Ti64 with 2%CaP; (c) Ti64 with 5%CaP; (d) CP-Ti with 3.3%CaP; (e) CP-Ti with 6.8%CaP and (f) CP-Ti with 10%CaP.

Figure 3. Uniaxial compressive strengths plot for CaP in CP-Ti composites

Figure 4. Low magnification wear track images for (a) CP-Ti; (b) 3.3%CaP in CP-Ti; (c) 6.8%CaP in CP-Ti; (d) Ti64; (e) 2%CaP in Ti64 and (f) 5%CaP in Ti64.

Figure 5: Coefficient of static friction for CoCrMo, CP-Ti and its CaP composites

Figure 6: Pin on disk wear Track for (a) CP-Ti, (b) CP-Ti with 3.3%CaP, (c) CP-Ti with 6.8%CaP, (d) Ti64, (e) Ti64 with 2%CaP and (f) Ti64 with 5%CaP in simulated body fluid at 37°C under a 5 Newton load.

(A)

(B)

(C)

Figure 7. Wear track after etching – showing tribofilm for Ti64 with 2% CaP

- (a) As processed and etched. White areas are **CaP** and dark areas are Ti6Al4V for 2%CaP-Ti64.
- (b) After 500m wear test in DMEM cell media – tribofilm formation covering the metal surface.
- (c) Post wear etched surface exposing the pristine Ti64-**CaP** surface below the tribofilm.