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Wear Performance of Laser Processed Tantalum Coatings

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Abstract

This first generation investigation evaluates the *in vitro* tribological performance of laser-processed Ta coatings on Ti for load-bearing implant applications. Linear reciprocating wear tests in simulated body fluid showed one order of magnitude less wear rate, of the order of $10^{-4}\text{mm}^3(\text{N.m})^{-1}$, for Ta coatings compared to Ti. Our results demonstrate that Ta coatings can potentially minimize the early-stage bone-implant interface micro-motion induced wear debris generation due to their excellent bioactivity comparable to that of hydroxyapatite (HA), high wear resistance and toughness compared to popular HA coatings.

Keywords

Laser deposition; Wear; Biomaterial; Tantalum, *In vitro*

1. Introduction

Over the last few decades researchers have attempted to find a ‘bioactive’ metal with high mechanical strength that can simultaneously bond chemically with surrounding bone on one side and provide hard/wear resistance surface on the other side for orthopedic applications. As it is quite difficult to achieve both the bioactiveness and wear resistant properties in one material, the most popular approach is to fabricate implants with adequate biological properties followed by a special treatment to enhance their surface properties such as wear resistance. Furthermore, the surface properties can be selectively modified to enhance site-specific biological and/or tribological performance of the implants for a variety of orthopedic applications. Because of these reasons, research on surface modification of metallic biomaterials has attracted much attention to improve multifunctionality, tribological and mechanical properties, as well as biocompatibility of artificial metal implants while obviating the need for large expenses and long time to develop brand new metallic biomaterials.

A number of different surface modification techniques have been employed for the preparation of metallic implants to improve biological [1–4] and tribological properties [5–8]. Among these techniques laser surface modification can offer high degree of process controllability and flexibility. There is a growing list of published work that testifies to the potential of lasers for altering the surface properties of metallic biomaterials in order to

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improve their biological and tribological properties [9]. Recently there has been renewed interest in tantalum due to its excellent ductility, toughness, corrosion resistance, and bioactivity [10, 11]. However, relatively high cost of manufacture and inability to produce a modular all tantalum implant limited its wide spread applicability. Further, high affinity for oxygen and extremely high melting temperature (3017°C) make it very difficult to process tantalum-based coatings or implant structures via conventional processing routes. Nevertheless, recently we have demonstrated fabrication of dense Ta coatings on Ti [1] and bulk porous Ta structures [12], with total porosities between 27% and 55%, using high-power lasers in LENS™ – a solid freeform fabrication technology. Excellent cell survivability, cellular attachment and spreading in terms of high living cell density, intensity and distribution of vinculin expression, respectively, demonstrated superior biocompatibility of laser processed Ta than Ti [1, 12]. In other studies [13, 14] it has also been shown that laser processed dense Ta coatings provide comparable *in vitro* and *in vivo* cell-materials interactions to that of bioactive hydroxyapatite (HA) coatings, however, with superior interfacial characteristics and mechanical stability. These results demonstrate that Ta structures offer a favorable biological environment for adhesion, growth and differentiation of human osteoblasts, which can promote biological fixation. Although, HA coatings perform equally well in terms of biological fixation, the low fracture toughness, wear resistance and rough surface morphology of these coatings can generate high wear debris as a result of micro motions at the bone-implant interface during early stages of surgery. These particulate wear debris has been recognized as one of the major challenges for long-term viability of load bearing implants [15, 16]. Above problem can be alleviated if HA coatings are replaced with bioactive Ta coatings, as the metallic Ta coatings have high fracture toughness and can be polished to achieve a smooth surface. Therefore, in this study the *in vitro* wear performance of laser processed Ta coatings on Ti was evaluated and compared with commercially pure (CP) Ti and CoCrMo alloy.

2. Materials and Methods

Tantalum (Ta) metal powder (Grandview Materials Inc., Columbus, OH) of 99.5% purity and with particles size between 45 and 75 μm was used. Ta coatings of $15 \times 15 \times 2.0$ mm were deposited on a substrate of 3 mm thick rolled CP Ti plates using a LENS™-750 (Optomec Inc., Albuquerque, NM) equipped with a 500 W continuous wave Nd:YAG laser. Detailed descriptions of LENS™ operation and capabilities can be found elsewhere [17, 18]. All coatings were fabricated in a glove box containing an argon atmosphere with O_2 content of less than 10 ppm to limit oxidation of materials during processing. Dense Ta coatings were prepared using a laser power of 450 W, a scan speed of 7 mm s^{-1} and a powder feed rate of 106 g min^{-1} [1]. For comparison, CoCrMo alloy powder (Stellite Coatings, Goshen, IN) with 50 to 100 μm particle size was used to make 15 mm square blocks with 30 mm height at 450 W laser power, 22.5 mm s^{-1} scan speed and 46.5 g min^{-1} feed rate [6]. These blocks were removed from the substrate and disc samples of 2 mm thick were then cut using a water jet for further testing and characterization.

For *in vitro* wear testing Ta coatings, CP Ti substrate and CoCrMo disc samples were abraded using successive grades of 400, 600, and 1200 grits of silicon carbide paper and then ultrasonically cleaned in distilled water and dried at room temperature. Final polishing was done using a cotton polishing cloth with a $0.05 \mu\text{m}$ alumina suspension and the samples were cleaned and used for wear testing. Finally, just before wear testing, all samples were ultrasonically cleaned in an alcohol bath. The surface roughness of each test sample was measured using a surface profilometer (SPN Technology, Goleta, CA). Linear reciprocating ball-on-disc wear testing, according to ASTM G133, was performed using a tribometer (NANOVEA, Microphotonics Inc., CA, USA) with ϕ 3 mm hardened chrome steel ball (100Cr6, 58 to 63 HRC) rubbing against test samples. A linear oscillatory motion 10 mm in

length (the full cycle represents 20 mm of travel) with a speed 1200 mm/min was used. The wear tests were performed with a normal load of 5 N for sliding distance of 1000 m. The width of the wear track was measured using SEM images of test samples, and from the known curvature of the ball and linear oscillatory stroke length, the wear track volumes were calculated. Average wear rate from three tests on each test sample was reported in $\text{mm}^3\text{Nm}^{-1}$. All tests were carried out in aseptic condition in freshly prepared simulated body fluid (SBF) at $37 \pm 1^\circ\text{C}$ to represent the biological environment in the body. We have selected SBF as a test medium and wear test method/configuration based on earlier reports, where current test method has been used with SBF as an articulating media to simulate wear on joint replacement devices [5, 6, 19, 20]. The ionic concentration of the SBF used in the present study is as follows: 2.5mM of Ca^{2+} , 1.5mM of Mg^{2+} , 142.0mM of Na^+ , 5.0 mM of K^+ , 147.8 mM of Cl^- , 4.2 mM of HCO_3^- , 1.0 mM of HPO_4^{2-} , 0.5 mM of SO_4^{2-} . The top surface hardness of the test samples was measured using a Vickers microhardness tester (Shimadzu, HMV-2T) at 200 g load for 30 s and the average value of 10 measurements was reported. Top surface microstructures of the polished and etched samples were examined using optical microscope and wear track morphology was observed using scanning electron microscope (SEM).

3. Results and Discussion

In metal-on-metal implants, wear of articulating surfaces is the combined effects of adhesive and abrasive wear mechanisms. Fatigue wear is also possible in which repetitive loading of localized regions causes surface and subsurface cracks to propagate thus producing wear debris. Under such conditions, wear resistance of any alloy is primarily governed by the microstructural features such as grain size, the amount and distribution of second phase particles and their morphology in the matrix. Therefore, the initial microstructures of laser processed Ta coatings, CoCrMo alloy and as-received CP Ti substrate were observed using an SEM. Figure 1 shows the typical microstructural features of the three materials used in the present work. The grain size of the samples was measured using linear intercept method. All materials showed equiaxed grains and the laser processed CoCrMo alloy showed very fine carbide precipitates (not shown here) in the interdendritic regions. The grain size of the laser processed CoCrMo alloy was found to be significantly finer than that of laser processed Ta coatings. As shown in Table 1, laser processed Ta coatings exhibited an average grain size of $33.5 \pm 2.0 \mu\text{m}$, which is larger than the grain size of laser processed CoCrMo alloy with an average grain size of $10.3 \pm 0.9 \mu\text{m}$. The CP Ti substrate showed an average grain size of $31.0 \pm 1.4 \mu\text{m}$, comparable to that of Ta coatings. Laser processing is characterized by extremely high cooling rates, of the order of 10^3 to 10^5 K s^{-1} , which influences several aspects of liquid metal solidification. It is well known that the scale of dendritic/grain size is inversely proportional to the solidification cooling rates [21]. In general, lower heat/energy input increases the thermal gradients near the melt zone and therefore high cooling rates can be achieved at lower heat/energy input during laser processing. Therefore, the observed differences in grain size between laser processed Ta and CoCrMo alloy can be directly correlated to the heat/energy input used during deposition. The finer grain size of CoCrMo alloy compared to Ta is attributed to the lower energy put of 17 J mm^{-2} compared to the energy input of 54 J mm^{-2} used for Ta coatings during laser deposition. Although the local cooling rate is not directly measured in the present work, within the melt zone the cooling rate, dT/dt (K s^{-1}), can be expressed as the product of solidification velocity R (mm s^{-1}) and the local temperature gradient G (K mm^{-1}) [22]. Experimentally it has been shown that R is on the order of laser scan speed (v) [23] and G is on the order of $\sim 100 \text{ K mm}^{-1}$ [24]. Thus under the present experimental conditions, the cooling rate in the melt zone is expected to be around $\sim 700 \text{ K s}^{-1}$ and 2250 K s^{-1} , for Ta and CoCrMo alloy deposition, respectively. Therefore, the finer grain size of CoCrMo alloy is a direct consequence of high cooling rates achieved at lower energy input of 17 J mm^{-2} .

Figure 2 shows experimentally determined wear rate of CP Ti substrate, laser processed Ta coatings and CoCrMo alloy discs for a sliding distance of 1000 m at a normal load of 5 N. The average wear rates of CP Ti, Ta and CoCrMo alloy were found to be $1.39 \pm 0.17 \times 10^{-3} \text{ mm}^3 (\text{N.m})^{-1}$, $1.89 \pm 0.4 \times 10^{-4} \text{ mm}^3 (\text{N.m})^{-1}$ and $9.9 \pm 2.9 \times 10^{-6} \text{ mm}^3 (\text{N.m})^{-1}$, respectively. The experimental data clearly indicate that laser processed CoCrMo alloy has superior wear resistance compared to CP Ti and laser processed Ta. It can be seen from the data that, after 1000 m sliding, the CoCrMo alloy exhibited a wear rate that is roughly two orders of magnitude lower than CP Ti substrate and approximately one order of magnitude less wear than laser processed Ta. Similarly, the laser processed Ta showed one order of magnitude less wear rate than CP Ti substrate. The observed *in vitro* wear rate of these materials is further substantiated by their coefficient of friction values, which were found to be 1.42, 0.97 and 0.65 for CP Ti, Ta and CoCrMo alloy, respectively. Under the present experimental conditions, with a normal load of 5 N, the initial maximum Hertzian contact pressure was found to be 1.40 GPa, 1.74 GPa and 1.89 GPa for CP Ti, Ta and CoCrMo alloy, respectively. In spite of the lowest contact pressure used during *in vitro* wear testing of CP Ti substrate, the wear rate of CP Ti was the highest among the materials tested in the present work. The superior wear resistance of CoCrMo alloy is attributed to its high hardness, fine grain size and the presence of fine carbide precipitates [25, 26]. The observed wear rates of these materials correlate well with their respective top surface hardness values. As shown in Table 1, the average top surface hardness of CoCrMo alloy was $358 \pm 17 \text{ HV}$, which is higher than the hardness of Ta ($233 \pm 17 \text{ HV}$) and CP Ti substrate ($160 \pm 4 \text{ HV}$). Generally the wear resistance of a material is directly related to its hardness, i.e., the higher the hardness, the better the wear resistance. Therefore, the wear rate decreased in the order of CP Ti > Ta > CoCrMo alloy. However, it is important to note that the wear rate of laser processed Ta is considerably higher than CP Ti substrate, suggesting that the Ta coatings on Ti can provide better wear protection during implant service.

Figure 3 presents the worn surfaces of the CP Ti, Ta and CoCrMo alloy samples after 1000 m sliding. As shown in Figure 3a, deep worn tracks were observed on the CP Ti substrate compared to relatively shallow and smoother worn tracks on the laser processed Ta surface (Figure 3b). The worn surface of the CoCrMo alloy, shown in Figure 3c, was very smooth with minimum amount of grooves, which are barely visible. From the high magnification SEM images of the worn tracks, shown in Figure 4, parallel arrays of grooves oriented along the sliding direction, were observed on all samples. However, the grooves are very deep on both CP Ti and Ta samples' surfaces indicating abrasive type wear. On the other hand, the smooth nature of worn surface on the CoCrMo alloy suggests adhesive type of wear on this surface. The laser processed Ta coatings and CP Ti samples showed high degree of flaking and wear debris generation, which would have caused third body wear on these surfaces. Present results show that laser processed Ta coatings exhibit superior *in vitro* wear resistance ($1.89 \pm 0.4 \times 10^{-4} \text{ mm}^3 (\text{N.m})^{-1}$) compared to CP Ti substrate ($1.39 \pm 0.17 \times 10^{-3} \text{ mm}^3 (\text{N.m})^{-1}$). Further, present Ta coatings can potentially minimize the early-stage bone-implant interface micro motion induced wear debris generation as a result of their excellent bioactivity comparable to that of HA, high wear resistance and toughness compared to popular HA coatings.

4. Conclusions

For the first time, laser processed Ta coatings have been evaluated for their *in vitro* wear resistance to explore their potential to be used in contact surfaces for load bearing implant applications. The average *in vitro* wear rate of Ta coatings was found to be $1.89 \pm 0.4 \times 10^{-4} \text{ mm}^3 (\text{N.m})^{-1}$, which is one order of magnitude less than CP Ti substrate with a wear rate of $1.39 \pm 0.17 \times 10^{-3} \text{ mm}^3 (\text{N.m})^{-1}$. Although the wear performance of Ta coatings is inferior to that of widely used CoCrMo alloy, its superior *in vitro* wear resistance than Ti

shows their potential to replace current HA coatings on Ti implants with better long-term *in vivo* stability.

Highlights

- *In vitro* tribological performance of laser processed Tantalum coatings on Titanium was evaluated for load bearing implant applications.
- Linear reciprocating wear tests in simulated body fluids showed one order of magnitude less wear rate for Ta coatings compared to Ti substrate.
- Our results demonstrate that laser processed Ta coatings can potentially minimize the early-stage bone-implant interface micro motion induced wear debris generation as a result of their excellent bioactivity comparable to that of HA, high wear resistance and toughness compared to popular HA coatings.

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1a

1b

1c

Figure 1.

Typical microstructures of (a) laser processed Ta coatings, (b) laser processed CoCrMo alloy, and (c) as-received CP Ti substrate.

Figure 2.
Wear rate of CP Ti, laser processed Ta and CoCrMo alloy against hardened 100Cr6 steel ball.

3a

3b

3c

Figure 3.

Wear track morphology after 1000 m of sliding distance (a) CP Ti substrate, (b) laser processed Ta, and (b) laser processed CoCrMo alloy.

4a

4b

4c

Figure 4.
High magnification SEM images of worn areas for (a) CP Ti substrate, (b) laser processed Ta, and (b) laser processed CoCrMo alloy.

Table 1

Grain size (μm), surface roughness (μm) and hardness (HV0.2) of Ta coatings, CoCrMo discs and CP Ti substrate. Laser energy density (J/mm^2) used to fabricate Ta and CoCrMo alloy is also included.

Material	Energy Density	Grain Size	Hardness	Roughness
Laser processed Ta	54	33.5 ± 2.0	233 ± 17	0.008 ± 0.001
Laser processed CoCrMo	17	10.3 ± 0.9	358 ± 17	0.065 ± 0.004
As-received CP Ti substrate	-	31.0 ± 1.4	160 ± 4	0.0074 ± 0.0001