Improved Biomaterials

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Zirconia Protective Coating on Ti6Al4V Bio-alloy to Improve Corrosion and Wear Resistances

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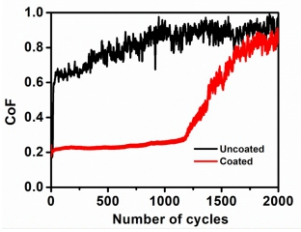

CoF versus number of cycle

ABSTRACT

Methods to limit wear and corrosion of artificial implants is crucial to reduce inflammation, allergies and implant failure. Pulsed laser deposition of zirconia thin film at a substrate temperature of 400 ^{0}C has been shown to work as protective layer on Ti6Al4V bio-alloy and improve its wear and corrosion resistances. A reduction in corrosion rate from 4.55 mil/yr to 2.89 mil/yr was observed for Ti6Al4V bio-alloy after thin film coating of zirconia. Tribological analysis indicated a reduction in wear rate of Ti6Al4V by 0.5 x 10^{-3} mm^3/Nm after zirconia coating.

KEYWORDS: *Biomaterial, Ti6Al4V, Zirconia, Pulsed laser deposition, Tribology, Corrosion*

Introduction

In an era of ever-increasing demand for artificial implants, the search for most suitable biomaterials that can be converted into desired implants such as, bone plates, screws, orthopaedic and dental devices is an ongoing effort. As defined by American National Institute of Health *"a substance or combination of substances, other than drugs, synthetic or natural in origin, which can be used for any period, which augments or replaces partially or any tissue, organ or function of the body are considered as biomaterial"* and biocompatibility of that material is its potential to perform the expected activities related to a particular remediation without producing any adverse effect locally or to the body [1]. In this regard, numerous materials such as stainless steel, titanium, cobalt, nickel and magnesium based alloys have already proven their biocompatibility [2]. Of late, Ti6Al4V-alloy of titanium has been identified as one of the most useful biomaterial for dental and orthopaedic applications because of its biocompatibility, mechanical properties, high strength-to-weight ratio and elastic modulus [3]. However, in the body environment comprising of aqueous medium, ions and biological molecules, the passivation oxide layer on the surface of Ti6Al4V is weakened causing release of harmful ions from the material due to wear and corrosion. Accumulation of wear debris and diffusion of corrosion products into the adjacent host tissue can cause inflammation, hypersensitivity and toxicity in patient body [2]. Since initial interactions and the subsequent acceptance of an implant by human body are governed by its surface properties, researchers have been working towards suitably altering the surface properties of existing biomaterials so as to make them more biocompatible. Laser induced surface modification is a method to improve tribological and corrosion properties of biomaterials [4-5]. On the other hand, coatings of oxides and carbides have also been found effective in improving corrosion and wear resistance of biomaterials [6-7]. Various coating techniques e.g., chemical vapour deposition [8], sol-gel [9], plasma based coatings [10] have been tried by many groups. Thin film coating by pulsed laser deposition (PLD) method has gain interest as the process gives control on various parameters such as, laser fluence, substrate temperature, target-substrate distance and deposition time.

In the work being presented here, PLD technique has been used for coating of zirconia thin film on Ti6Al4V bio-alloy to improve its tribological and corrosion properties. A nanosecond pulsed Nd:YAG laser was employed for PLD and the coating was performed at 400 ^{0}C substrate temperature as a uniform coating over a larger area was obtained at this substrate temperature in comparison to coating done at room temperature and at 200 ^{0}C substrate temperature. The change in morphology and wettability of the sample after coating was confirmed by surface characterization. The corrosion measurement was carried out using three electrode cell in simulated body fluid (SBF) to mimic body condition. The open circuit potential (OCP) was recorded for 2h followed by recording of electrochemical potential and impedance data. Corrosion rate of the Ti6Al4V decreased from 4.56 mil/yr to 2.89 mil/yr after zirconia coating as estimated from Tafel curve and larger radius of curvature in the Nyquist impedance curve of coated sample indicated superior corrosion resistance of the sample [4]. The tribological behavior of the uncoated and coated samples was studied in terms of coefficient of friction (CoF) and wear rate at 2N normal load using stainless steel counterpart in dry sliding condition. The wear rate of the Ti6Al4V sample decreased from 1.9 x 10^{-3} mm^3/Nm to 1.4 x 10^{-3} mm^3/Nm after zirconia coating.

Materials and Methods

The Ti6Al4V-alloy sheet of dimension (20 × 20 × 1) mm^3 with average surface roughness ~ 0.52 µm was ultrasonically cleaned in acetone, ethanol, and water. As received zirconia pellet (Merck, KGaA, Germany) of thickness 2 mm and diameter 10 mm were used as PLD target. The PLD of zirconia was performed by employing a nanosecond Nd:YAG laser (λ = 532 nm, pulse duration 6 ns, repetition rate 10 Hz: Ekspla, Lithuania), the experimental set-up is shown in Fig.1a. The laser beam was focused onto zirconia target using a 50 cm focal length lens at an angle of 45 ^{0}. The plume emitted

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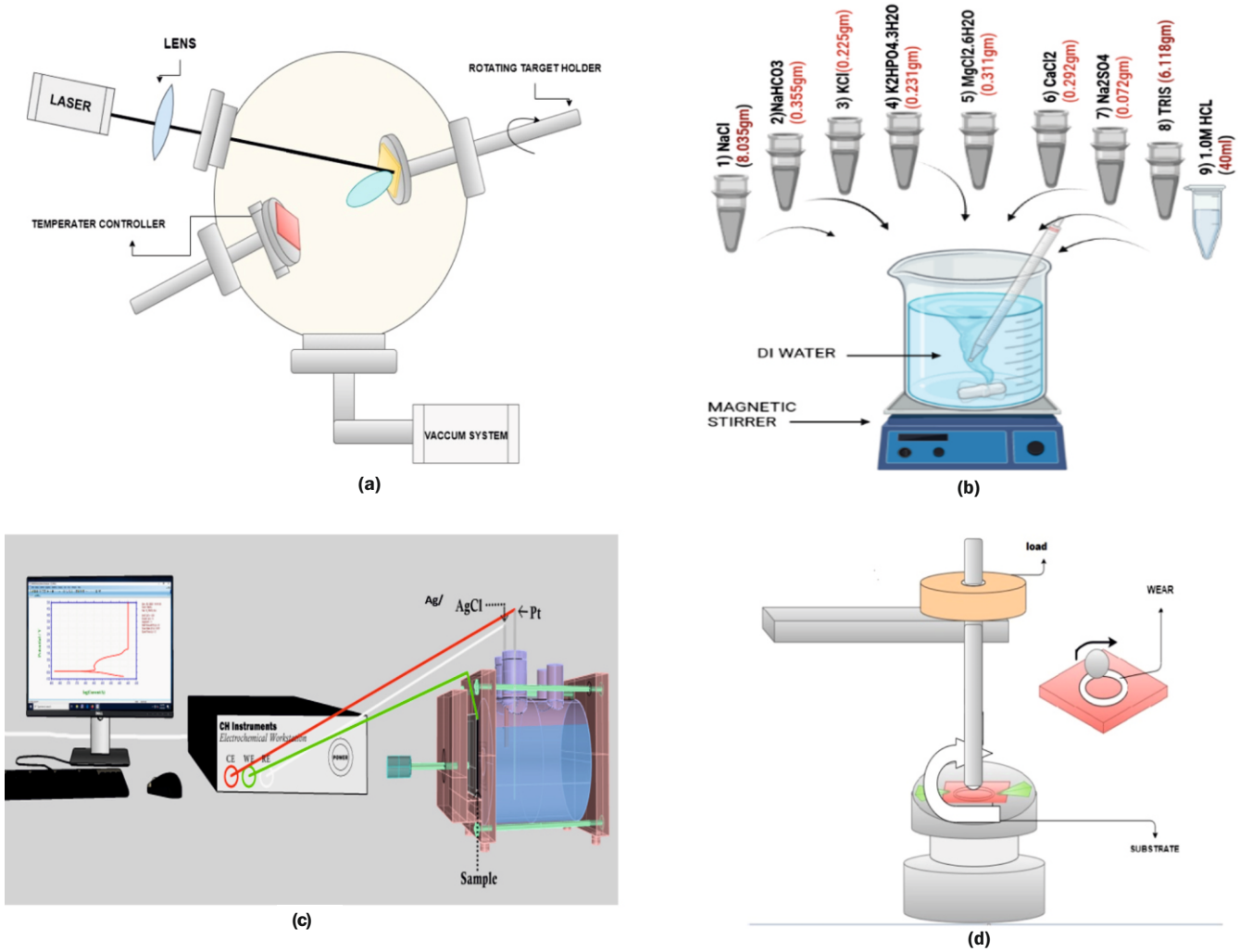

Fig.1: Experimental illustration of (a) PLD set up, (b) SBF preparation, (c) corrosion measurement and (d) Tribological analysis.

perpendicular to the target and deposited on the Ti6Al4V at 400^{0}C placed at a distance of 40mm from the target. The thin film deposition was done at laser fluence of 20 J/cm^{2} for 36000 number of laser shots. For preparing SBF NaCl (8.035gm/L), KCl (0.225 gm/L), $NaHCO_3$ (0.355 gm/L), $K_2HPO_4.3H_2O$ (0.231 gm/L), $MgCl_2.6H_2O$ (0.311 gm/L), $CaCl_2$ (0.292 gm/L), Na_2SO_4 (0.072 gm/L) and $CNH_3(CH_2OH)_3$ (6.118 gm/L) reagents were mixed in 960 ml of deionized water and 40 ml of 1M HCl by following a standard protocol, a pictorial representation is shown in Fig.1(b) [11]. Table-top Scanning Electron Microscopy (SNE, 4500M Plus, M/S. S&C, Korea) and water contact angle (VCA, Optima, India) measurements were performed to understand the topographical modification and change in wettability, respectively of the sample after zirconia coating. Micro-Raman spectrum (AIRIX Corp., Japan) was recorded to know the phase of zirconia thin film on Ti6Al4V. The electrochemical potential of the sample was measured in SBF using a three-electrode cell (CHI604E Electrochemical Analyzer, India), shown in Fig.1(c). About 0.785cm^{2} area of the sample (working electrode) was exposed to electrolyte (SBF). Platinum and Ag/AgCl were used as counter and reference electrodes, respectively. For both samples OCP was measured for 2h, the polarization curves were recorded at a scan rate 0.01V/s, over a potential range of -0.8V to 2.0V and the electrochemical impedance spectroscopy was measured in frequency range 0.1 Hz to 1MHz. The topography of the sample after corrosion studied was analyzed using 3D profilometer (CCI HD, Taylor Hobson, UK). The dry sliding wear tests were

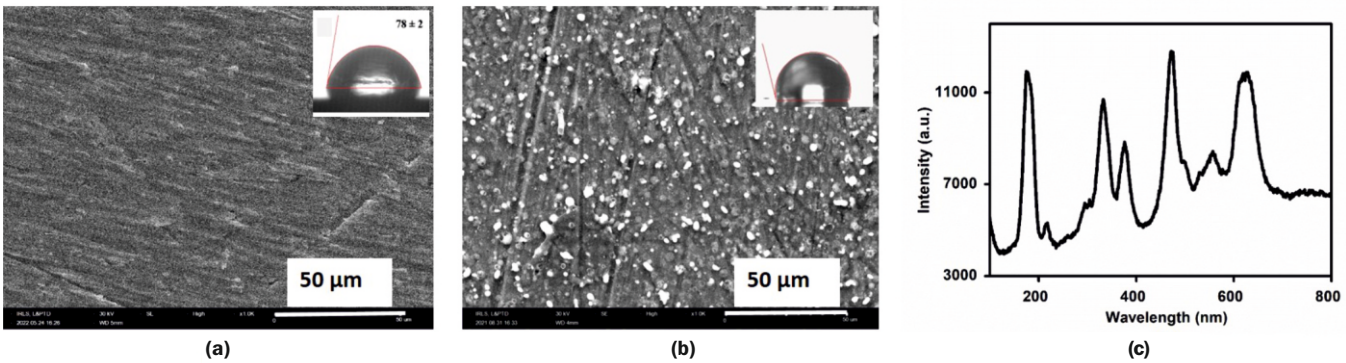

Fig.2: SEM image of (a) uncoated, (b)zirconia coated samples, inset: respective water contact angles and (c) Raman spectrum of coated sample.

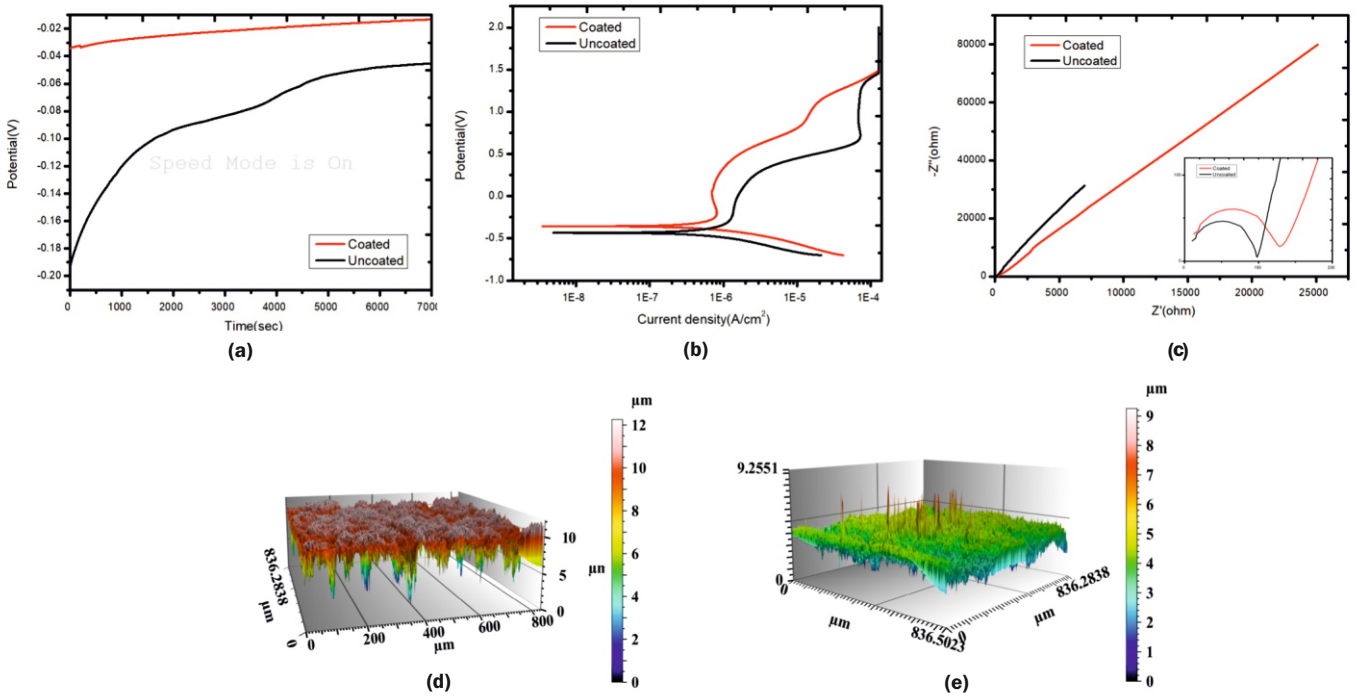

Fig.3: (a) OCP, (b) Tafel, (c) Nyquist plot of uncoated and zirconia coated Ti6Al4V (d-e) 3D Optical Profilometer image of uncoated and coated sample after corrosion measurement.

carried out by a ball-on-disc tribometer (TRB3, Anton Paar, Graz Austria) at normal load of 2N, as illustrated in Fig.1(d). A standard stainless steel ball of a diameter ~ 5 mm was used as counterpart and the measurement was done at 10Hz frequency for 2000 number of sliding cycles.

Results and Discussion

Fig. 2(a)-2(b) shows the SEM images of uncoated and coated Ti6Al4V samples in which change in morphology of the sample can be seen. As shown in the inset of the figures, the sample become hydrophobic after zirconia coating as water contact angle increased from 78^0 to 103^0. Exact thickness of zirconia coating could not be obtained due to inherent surface roughness of Ti6Al4V sample. However, the thickness was estimated to lie within 100-200 nm using 3D profilometer. In Fig.2(c), Raman peaks at 149 cm^{-1}, 224 cm^{-1}, 324 cm^{-1}, 456 cm^{-1} and 636 cm^{-1} represented tetragonal crystal structure of zirconia in the coating [12]. As shown in Fig.3(a), the OCP of coated sample showed an anodic shift in comparison to uncoated Ti6Al4V sample. An increase in OCP potential can attribute to a decrease in the anodic reaction due to growth of a passive film on the surface of the sample which indicated more stability of the coated sample in SBF environment [13]. The Tafel plot in Fig. 3b shows and increase in E_{corr} from -0.4390 V to -0.359V and decrease in I_{corr} from 5.50 x 10^{-7}A/cm^2 to 3.49 x 10^{-7}A/cm^2 for uncoated and coated samples, respectively. Since, sample with lower value of corrosion current density (I_{corr}) and higher value of corrosion potential (E_{corr}) indicates superior corrosion resistance, the zirconia coated sample has superior corrosion resistance than the uncoated sample. Corrosion rates of 4.56 mil/y and 2.89 mil/y were estimated for uncoated and coated sample, respectively. A definite decrease in corrosion rate of Ti6Al4V by half was observed after zirconia coating. In the Nyquist plot shown in Fig.3(c), the increased curvature of coated sample as compared to the uncoated one also indicates superior corrosion resistance of the coated sample. Fig.3(d)-3(e) shows the 3D profilometer images of uncoated and coated samples, respectively taken after electrochemical analysis. The large number of localized variation in depth in the surface profile of uncoated sample penetrating in to the bulk is attributable to pitting corrosion. Absence of such surface profile variations in case of zirconia coated sample shows its increased resistance to pitting corrosion in SBF environment.

Fig.4(a) shows variation in CoF of uncoated and coated sample with number of sliding cycles at normal load of 2N.

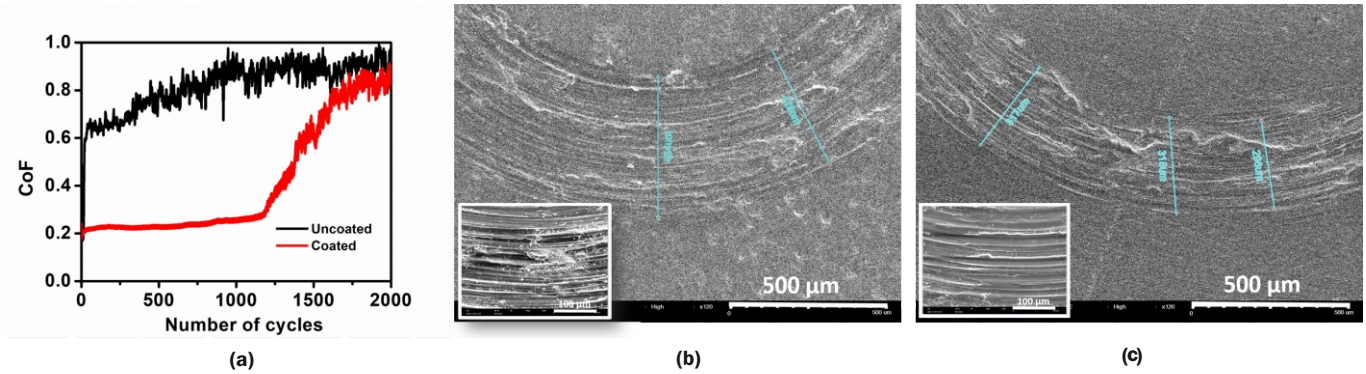

Fig.4: (a) CoF versus number of cycle and (b-c) SEM image of wear trace, inset: magnified SEM image of wear trace of uncoated (wear trace width of ~ 464µm) and coated (wear trace width of ~ 318 µm), respectively.

While CoF exhibited a sharp rise to a high value of 0.63 initially and to a value of 0.92 at the end of 2000 cycles in case of uncoated sample. For coated sample, the initial CoF was relatively low at ~0.21 which remained steady for about 1178 cycles and then, there was a gradual increase to 0.85 at the end of 2000 cycles. The maximum value of CoF in this case was found to be marginally lower than uncoated sample. These results clearly show that the coating could sustain without much alteration for a large number of cycles after which the counterpart wore out the zirconia film and CoF started increasing gradually and when counterpart penetrates the surface of the alloy a similar value of CoF as obtained for the uncoated sample by end of the cycle. The wear rate of uncoated and coated samples was estimated from the Anton-Paar software as 1.9 x 10^{-3} mm^3/Nm and 1.4 x 10^{-3} mm^3/Nm, respectively. Therefore, reduction in wear rate of Ti6Al4V by 0.5 x 10^{-3} mm^3/Nm was observed as a consequence of the protective zirconia coating.

The SEM images of wear trace in Fig.4(b)-4(c) and inset for uncoated and coated samples respectively show the formation of craters, tearing and grooves due to wear ploughing. In case of zirconia coated sample, the dominant wear mechanism is expected to be abrasive initially. As the coating wears out, the counterpart interacts with base material (Ti6Al4V) and adhesive wear mechanism will become dominant. The abrasive and adhesive nature of wear on both the samples is clearly evident from the SEM pictures. The width of wear trace was more on uncoated sample (464 µm) in comparison to coated sample (318 µm), indicating higher wear on uncoated sample as during initial wear cycles the contact area between sample and the ball is minimum and depending upon wear the contact area increases over the cycles.

Conclusion

The pulsed laser deposition of zirconia thin film modified the surface topography and wettability of Ti6Al4V sample. Anodic shift of OCP, increased E_{corr}, decreased I_{corr}, and larger impedance curvature of zirconia coated sample indicate superior corrosion resistance of the sample. Lower CoF, even grooving and lower width of wear trace point to improved wear resistance of the sample as a result of zirconia coating. Superior corrosion and wear resistance are important attributes of an implant material that lengthen its life in the body environment and this study clearly shows that zirconia coating helps improve these properties of a biomaterial.

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