

EVALUATION OF CORROSION AND TRIBOCORROSION BEHAVIOR OF 316L STAINLESS STEEL WITH PHYSICAL VAPOR DEPOSITED PURE TI COATINGS

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Abstract— The most common stainless steel that is used in orthopedic implant is AISI 316 stainless steel. Stainless steel is extremely susceptible to pit and groove corrosion. One of the common ways of optimizing the biological adaptability, decreasing metallic ion release, and increasing corrosion resistance in body environment of stainless steel is applying coatings on its surface. Pure commercial Titanium is one of the alternatives for using inside body due to its predictable interaction with biological environment. Therefore, the aim of this study is to investigate corrosion and tribocorrosion resistance of 316L stainless steel with titanium PVD coatings inside Ringer's solutions. Surface characterization analysis revealed thickness of 3.6 μm and hexagonal structure. According to potentiodynamic polarization readings, uncoated and coated specimens showed similar current density but uncoated specimen had higher breakdown potential. The results of tribocorrosion tests at open circuit potential showed a higher potential drop for the coatings due to their more active electrochemical behavior. Optical microscope images and roughness profile graph showed higher groove width and lost mass for coated sample respectively. Thus, our results demonstrated that method of coating and thickness play key roles in improving corrosion and tribocorrosion characteristics of stainless steel coated titanium..

Index terms- stainless steel, Ti, corrosion, tribocorrosion, PVD coating.

I. INTRODUCTION

Corrosion and friction can cause damage and disablement on metallic materials separately [1]. Tribocorrosion phenomenon is incorporation of these two processes [2]. It consists of mechanical and electrochemical reactions that occur between surfaces with a relative movement accompanied by a corrosive environment [3]. Different mechanisms of tribocorrosion including surface characteristics of materials in contact, contact mechanism, and corrosive conditions are not completely defined yet [1]. Meanwhile, corrosion is accelerated by friction and friction is also accelerated inside a corrosive media [3]. Tribocorrosion occurs in industrial, food industries, and body environments. Body

fluid containing chloride, phosphate and bicarbonate ions is considered as a corrosive media [4]. Friction factors can also coexist in joints or orthopedic areas. Coexisting of friction and corrosive factors cause tribocorrosion phenomenon. This can also exist in dental implants because saliva is also considered as a corrosive environment. So, choosing a correct material for such purpose is important and critical. Biomaterials that are used for this purpose should have biocompatibility, good corrosion resistance, and also high friction resistance [5]. In addition, these materials shall have a prolonged durability against tribocorrosion damages [6].

Studies on implants showed that more than 90% of stainless steel implants disablement is due to pitting and groove corrosion attack [7]. Consequently, coating methods are applied for surface modifications. Applying this coating is also very important. It is observed that applying these coatings decreases their corrosion resistance. An intermediate layer between substrate and coating can obstruct porosity and needle-like pits. As a result, corrosive solution cannot penetrate into the substrate and this causes increasing in local corrosion resistant [8].

In this study, according to the mentioned aspects, titanium was coated on 316 stainless steel by PVD method. Corrosion and tribocorrosion behavior of the samples in Ringer's solution (37°C) was investigated.

II. EXPERIMENTAL PROCEDURES

In this study, 316L stainless steel was selected to be used as a substrate. 20×20×3 mm and 10×10×3 mm samples were prepared for examination of corrosion and tribocorrosion behavior respectively. In order to apply the Titanium coating on stainless steel substrate by means of PVD, a Titanium target and high pure Argon gas is needed inside PVD device. 99.95% pure Titanium rod with specific dimensions were used to place inside the instrument.

Ringer's solution with $37^{\circ}\text{C} \pm 2$ was utilized to simulate biological body condition.

To determine the existing phases and diffraction patterns, Philips X'Pert-MPD (XRD) was used. X'Pert High Score software was also utilized to identify phases.

Grain size of the coating was determined using peak broadening related to preferred growth rate of pure Titanium on half height by Debye-Scherrer low and Sigma plot V11.0.0.77 software.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

The surface morphology of the samples were determined using Scanning Electron Microscopy (SEM, Philips XL30). Additionally, thickness of the coating and friction areas in cross section cuts were determined by both scanning electron and Optical microscope.

Roughness was measured by providing a profile from friction surfaces after tribocorrosion test in order to determine mass loss during corrosion-friction phenomenon. This test was done using Mitutoyo-SJ.210 device.

Measurement of potentiodynamic polarization and tribocorrosion were done by a conventional three electrode consisting of a Pt electrode and Ag/AgCl(sat KCl) as reference electrode. Coated and uncoated stainless steel samples were placed as working electrode. Polarization diagrams in 1 mV.s-1 scanning rate starting from 250 mV less than open circuit potentials were obtained.

Tribocorrosion tests on coated and uncoated 316L stainless steel substrate were conducted by a tribometer device with a sweeping movement.

Applying the potential and measuring current density were done by a EG&G (263A) potentiostat/Galvanometer device. Tribocorrosion tests were carried out under open circuit and anodic circumstances. To do so, potential was recorded 1200 sec before starting friction. Then, friction started with a 4.3 mm diameter Alumina ball and a normal 2 N load. Length of test was 10 mm for 1800 cycles and had 1 Hz. All tests were carried out on a constant temperature with controlling it by water bath. Potential was also recorded for 2000 sec after finishing friction. For all experiments, working electrode was kept inside the solution for 1.5 hr to get sure achieving stable conditions. Tests were conducted on a fixed condition. Measurements repeated three times for each samples and average number was reported.

III. RESULTS AND DISCUSSION

A. Characterization of the coating

The SEM image of pure Titanium coated stainless steel is presented in Fig.1, which shows a needle like pores and large particles on the surface of the coating. These defects are common in PVD method. Coating thickness is 1.3 μm .

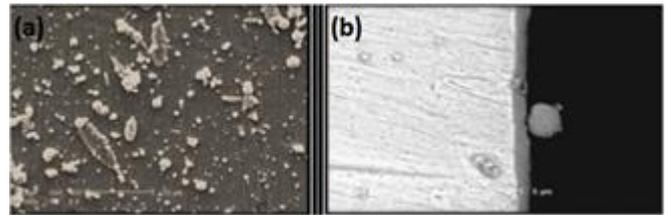


Figure 1- SEM micrograph of a) top view (b) and cross-section of pure Titanium coating on 316L stainless steel

Fig.2 shows the XRD pattern of commercial pure Titanium coating on 316L stainless steel. Strong and Sharp peaks of 74.16 and 62.75 degrees are exhibited in this pattern which indicates pure Titanium with hexagonal crystal structure. Stainless steel 316L with austenite structure peaks are also can be seen.

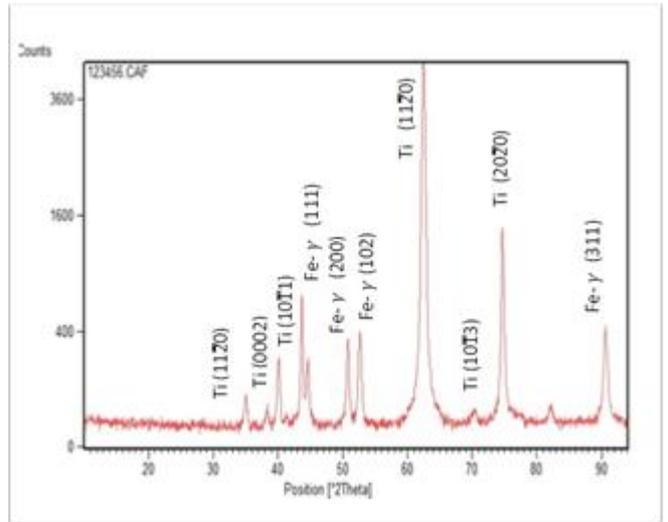


Figure 1- X-ray diffraction patterns of pure Titanium coating on 316L stainless steel

Gaussian function diagram on the (0112) peak for pure Titanium is shown in Fig.3

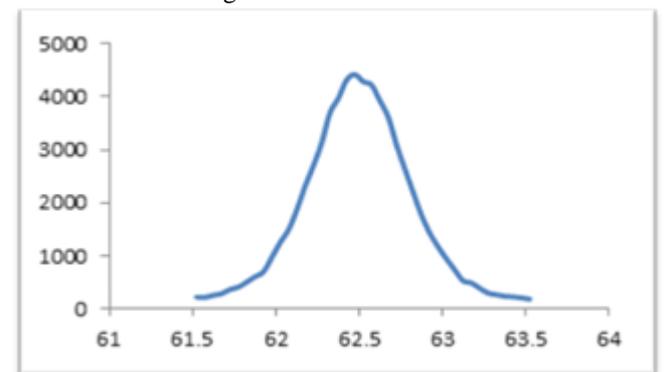


Figure 3- Gaussian function diagram on the (0112) peak for pure Titanium.

Table 1 Shows obtained results from this analysis.

Table 1- Obtained results on (0112) peak analysis

X_0	b	Y_0	A
$6.25 \cdot 10$	$2.8 \cdot 10^{-1}$	$1.615 \cdot 10^2$	$4.183 \cdot 10^3$

After determination of b and β constant, grain size was calculated as 3.4 nm.

B. Potentiodynamic polarization test

Fig.4 presents potential vs. current density of uncoated and coated samples. Results reveal a downward shift on the polarization curve to the substrate. In addition, applying this coating increased failure potential (pitting) drastically in comparison to substrate. This downward shift indicates a more active behavior of Titanium coating rather than stainless steel substrate. However, corrosion current density kept constant. The reason is probably due to low thickness and existence of defects in the coating. Nevertheless, it is observed that no failure occurred on the anodic branch of the coated sample. This shows that failure of Titanium passive layer is independent of immersion time in the solution. Although titanium coating had less corrosion resistant than the substrate but it can be useful because of no failure of the passive layer.

Table 3-2 shows the extrapolation results from polarization test (corrosion current density, corrosion potential, and breakdown potential, slope of anodic and cathode branches for coated and uncoated samples. Anodic slope reveals that for each constant potential, coated sample has more current density (solubility).

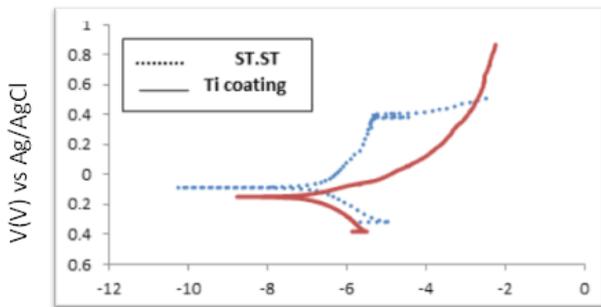


Figure 2-potentiodynamic polarization curves for 316L stainless steel coated and uncoated in Ringer's Solution with 37 degrees Celsius

Table 1- Corrosion parameters obtained from potentiodynamic polarization curves

E_b (V)	β_a (V/dec)	β_c (V/dec)	I_{corr} (A/cm ²)	E_{corr} (V)	sample
0.383	0.55	0.25	1×10^{-7}	-0.104	316L stainless steel
1	0.22	0.24	1×10^{-7}	-0.107	Pure Titanium coating

C. Tribocorrosion tests

Fig.5 shows potential changes with time in open circuit and anodic circumstance, during and after friction for uncoated and pure Titanium coated stainless steel inside Ringer's solution at 37 °C. Recorded potential for coated sample before friction was more than uncoated sample, and in anodic conditions,

recorded current density is approximately the same for both samples. This fact is in coincident with its corrosion behavior. Results show drastic potential decrease in starting point of both samples in open circuit. This sudden decrease for uncoated stainless steel is 280 mA and 550 mA for coated sample. Also in anodic conditions, sudden increase of current after starting the friction is about 27 μ A.cm² for uncoated sample and 15 μ A.cm² for pure Titanium coated sample. This sudden potential decrease and current increase is due to destruction and breakdown of passive film. Passive film that was formed in contact with Ringer's solution, is removed by initial contact of Alumina ball. Meanwhile, coating onto the surface is subjected to active corrosion in this area. Therefore, groove surface is encountered with extreme solution and reactivates after stopping friction.

By continuing friction, both samples show a constant behavior. During friction, current fluctuations are because of competition between mechanical reactivation and electrochemical passivation. At the end of friction, retrieval stage started by formation of passive film on the surface. Passive film is formed without any barrier from friction process inside the groove.

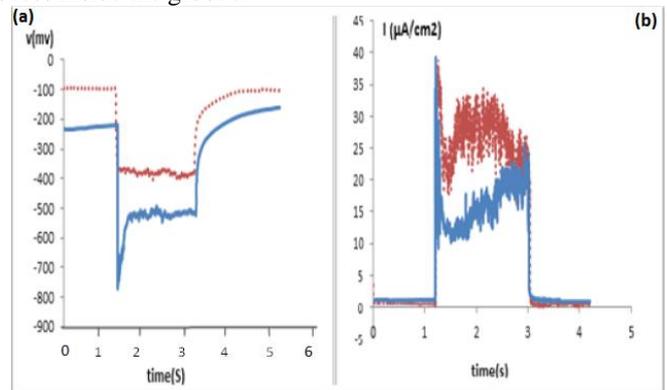


Figure 3-diagram of tribocorrosion test under a) open circuit b) anodic conditions for uncoated and coated 316L stainless steel in Ringer's solution.

D. Investigating friction surface

Fig.6 and 7 show optical images from groove surface for coated and uncoated 316L stainless steel under cathode and open circuit. Comparing these pictures shows that groove width for coated 316L stainless steel samples rather than uncoated one. Thus, destruction was more severe. This groove width for coated under open circuit condition was 415 μ m and 521 μ m for uncoated and 302 μ m for uncoated under anodic conditions and 649 μ m for coated ones. It shows that penetration of friction ball inside 316L stainless steel was more than that of a uncoated 316L stainless steel due to low hardness of pure Titanium.

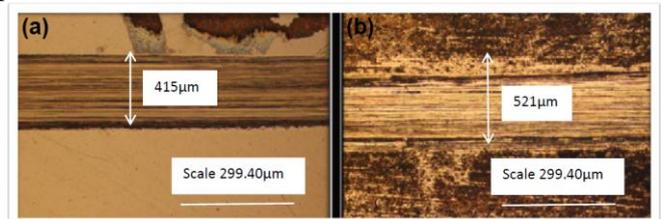


Figure 4- Optical image of groove width for, a) uncoated 316L stainless steel under open circuit conditions b) coated 316L stainless steel

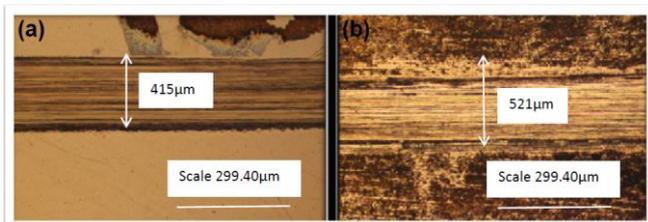


Figure 5-Optical image of groove width for a) uncoated 316L stainless steel, b) coated 316L stainless steel under anodic conditions

Fig.8 and 9 show roughness profiles of coated and uncoated 316L stainless steel under open circuit and anodic conditions respectively. Investigation on roughness profiles shows the least abraded surface for uncoated 316L stainless steel and the most abraded surface for coated 316L stainless steel. One of the reasons of having more mass loss of coated sample rather than uncoated 316L stainless steel is less hardness of the coating. low thickness and defects of PVD test can be counted as reasons too.

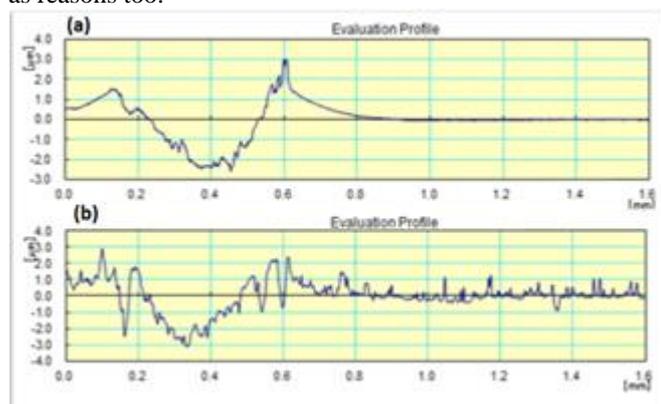


Figure 6-Roughness profile from a) uncoated 316L stainless steel and b) coated 316L stainless steel under open circuit conditions.

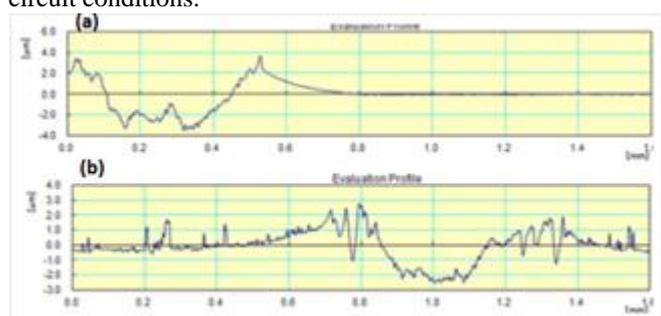


Figure 7-Roughness profile from a) uncoated 316L stainless steel and b) coated 316L stainless steel under anodic conditions.

IV. CONCLUSION

Applying pure Titanium coating on 316L stainless steel by means of PVD was conducted in this research. According to the obtained results, applying pure Titanium on stainless steel 316L increased breakdown potential. However, this coating did not increase corrosion resistance. Moreover, potential drop off of the coated sample during friction in open circuit condition was more for substrate and verified its more active electrochemical behavior. Under anodic conditions highest increasing in current, anodic breakup and fluctuations were belonging to the coated sample. Increasing active areas which leads to destruction of grooves, low hardness of coating and tendency of the coating for anodic breakup can be counted as the reasons of such behaviors here. Finally, lower thickness and hardness of the coating comparing to substrate caused groove width and mass loss under open circuit and anodic conditions.

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