JPIChE 48 (2) 2020: 9-14

PAKISTAN INSTITUTE OF CHEMICAL ENGINEERS Since 1969

Journal of Pakistan Institute of Chemical Engineers

journal homepage: www.piche.org.pk/journal

Electrochemical Characterization of PVD Coated AlTiN Coating on Stainless Steel Substrate for Biomedical Implant

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Submitted: 23/07/2020, Accepted: 20/01/2021, Online: 29/01/2021

Abstract

Physical Vapor Deposition technology is an established technique to deposit metallic and ceramic coatings on different metallic substrates. Lateral Arc Rotating Cathode (LARC) technology has an added advantages of better mechanical uniform coating, consistent erosion of the electrodes and greater degree of ionization. LARC technology was used to deposit AlTiN coating on stainless steel SS 316L samples. The electrochemical behavior of the coating and the substrate was investigated using Electrochemical Impedance Spectroscopy (EIS) technique. Ringer Lectate solution was used as a simulated body fluid at 35 ± 2°C. The coating and substrate were characterized by Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDX) and Surface Profilometry. The Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy analysis revealed a consistent coating as a whole. The surface profilometry showed lower surface roughness after the coating. The Electrochemical Impedance Spectroscopy tests indicated that corrosion resistance of the coated sample was better, than the uncoated substrate in the electrolyte solution for short duration (one day) and behaved like cathodically protected coating and showed more resistivity. However, the Electrochemical Impedance Spectroscopy results varied because of the penetration of chlorite ions through the porosity in th coating and reaction with the coating material after the prolonged insertion.

Keywords: *Physical Vapor Deposition Coating, AlTiN Coating, Corrosion Resistance, Electrochemical Impedance Spectroscopy, Scanning Electron Microscopy*

1. Introduction:

Physical Vapor Deposition is a coating technique that is used to deposit thin hard coatings on a variety of substrates for numerous applications The basic principle of physical vapor deposition deals with the ionization of gas atoms in the vacuum chamber. The ionized gas particles strike the working cathode electrode and sputter out the metal ions which are to be deposited. In conventional PVD system the cathode is stationary and the erosion is uneven. In the latest LARC technology, the cathodes are rotating giving an advantage of uniform coating thickness, uniform erosion of the cathode and higher degree of ionization [1, 2]. The metal ions from the cathode accelerated towards the negatively biased substrate and deposited [3, 4].

Nitrides coatings are used as protective and functional coatings due to low co-efficient of friction, oxidation resistance, wear resistance, high hardness, thermal and chemical stability [5]. TiN coating is widely used on cutting and machining

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tools to improve their wear resistance and tool life. But the coating gets oxidized up to 500°C and limits its application. The introduction of Al in the TiN matrix improves its oxidation resistance to some higher temperature. Various deposition techniques have been used to deposit nitride coatings. Among them, Chemical Vapor Deposition (CVD) and Physical Vapor Deposition (PVD) are the two promising techniques. Rather, PVD has advantage over CVD in terms of lower deposition temperature [6].

Austenitic stainless steel 316L are the most suitable materials for biomedical applications as compared to Co-Cr alloys due to high density of the later materials. SS 316L is used as implants and prosthesis in the human body because of their high corrosion resistance and biocompatibility but their low wear resistance is making it less attractive for this particular application as an implant. Nitride based coatings are used as protective coating in order to increase the wear resistance, corrosion resistance and most importantly life expectancy of the implant materials.

AlTiN coatings are developed from more than two decades because of their superior properties like improved oxidation resistance and high temperature hardness for an industrial application in high speed cutting and machining. The coatings are produced from the variety of physical vapor deposition (PVD) techniques and have better tool life as compared to TiN coatings. It was observed by the researchers [7, 8] that high Aluminium content in the AlTiN coating emerges a soft wurtzite AlN phase [9, 10] that lowers the mechanical properties of the coating which is undesirable for the industrial applications subsequently this high aluminium content make it more oxidation resistant[11]. The protective nature of aluminium oxide [12] is very well known and this property make it suitable for biomedical application. The lamellar structure of Al rich AlTiN coating demonstrates significant increase in wear resistant properties up to 900°C and under dry conditions as well [13] [14].

The strength and toughness of the TiAlN coating is increased by the biomimetic self-assembly approach in which hard and tough sublayers were developed during the coating process and each sublayer having complex lamellar hierarchy nanostructure is responsible for the improved mechanical properties [15].

Researchers have worked on the adhesion, improved mechanical properties and compressive residual stress [16] of thin nano ceramic coating on different substrates for textile [17], biomedical implant [18] [19] among other various applications.

The TiAlN coating deposited by reactive radiofrequency sputtering method as an intervening layer to improve the biocompatibility of substrate for dental application [20]. The improved corrosion resistant properties of the Ni-Cr dental alloy by immersing the samples in Ringer Lectate solution for 24 hours and then implanted in guinea pigs for 12 weeks was observed. Cheng et. al. [21] deposited TiAlN coating on austempered ductile iron by Cathodic arc deposition for the evaluation of erosion resistance and corrosion behavior in 3.5% NaCl solution. Improved corrosion resistance was observed again due to the formation of passive aluminium oxide passive film. A comparative study of different coatings like TiN, CrN and hydrogenated amorphous carbon coating a-C:H deposited on tungsten carbide (WC) discs by cathodic arc magnetron sputtering was studied [22]. The samples were immersed in Simulated Body Fluid for a period of three hours for corrosion resistance evaluation. In this study, different coatings were compared for electrochemical behavior using EIS technique, but the TiAlN coating did not reflect the required results out of a-C:H, CrN, TiN coating due to hydration effect.

Al_2O_3 and TiO_2 oxides are formed on the surface of AlTiN film which act as barrier for passage of oxygen atoms from environment to coating layer or substrate and make material oxidation/corrosion resistance. These oxides make thicker layer on the surface and give protection and better strength to substrate [23]. Besides this, these oxides give some other properties to coating like TiO_2 gives lubricating effect while Al_2O_3 provides wear resistance and hardness to AlTiN coating layer and protects it at high temperature and in load application.

Electrochemical behavior of thin hard Al rich AlTiN coating on austenitic stainless steel SS 316L substrate has not been explored by the researchers so far, for the purpose of biomedical implant application. In the current research, coating is immersed in the Ringer Lectate solution over a period of 40 days for the compatibility of the solution with the coating.

2. Materials & Methods:

The austenitic stainless steel SS 316L sheet with 5 mm thickness was purchased from the local market. For coating and characterization purposes, the test samples were cut through arc cutting in circular disc shape with one-inch diameter and some of the samples were cut into rectangular shape of area 1 cm2. The test samples were ground and polished using ASTM E 3 standard. Grinding was done as per FEPA grade on P100, P200, P400, P600, P800 and P1000 SiC grinding papers. Polishing was done on velvet and nylon clothes using a diamond paste with particle size of 6, 3, 1 and 0.25 mm on (*Ecomet 250 Grinder/Polisher USA*) automatic polisher.

AlTiN coating was deposited by Physical Vapor Deposition technique using LARC technology (PLATIT ð 80) on an austenitic stainless steel grade 316L substrate. The deposition parameters are given in table 1.

Table 1: Physical Vapor Deposition Coating Parameters

Parameters	**N_2 gas flow rate**	**Cooling water flow rate**	**Arc current cathode 1 biasing**	**Arc current cathode 2 biasing**
Range	25 ccm	25L/min	60 A, 120 V	50 A, 110 V

The coating thickness of the samples was measured on Scanning Electron Microscopy (Mira 3 TESCAN). The electrochemical impedance spectroscopy and open circuit potential (OCP) techniques are used to analyze the behavior of the coated as well as uncoated samples. GAMRY 3000 Potentiostat was used to carry out Electrochemical Impedance Spectroscopy (EIS) on coated and uncoated samples in Ringer Lectate solution to study the corrosion behavior. Ringer lectate solution contains comparatively high chloride environment. The active area for electrochemical testing was of 1 cm^2. A three-electrode system consisting of a reference (saturated calomel electrode (SCE)), a counter electrode (pure platinum sheet) and the working electrode (coated sample). Before the electrochemical measurements, samples were allowed to stabilize at their open-circuit potential (Eoc) for 500 seconds. The electrochemical impedance spectroscopy (EIS) measurement was taken using a scanning frequency ranging from 10^{-2} to 10^5 Hz, and the testing signal is 20 mV. All the measurements are taken at room temperature (22°C). Scanning Electron Microscopy analysis was carried out on rectangular shaped samples using Mira 3 TESCAN electron microscope. Roughness of uncoated and coated samples was taken by using stylus profilometer by Mitutoyo Japan.

3. Results & Discussion:

The AlTiN coating thickness and elemental composition were measured from SEM and EDX respectively. SEM image of nearly 2.58 microns coating thickness is shown in figure 1.

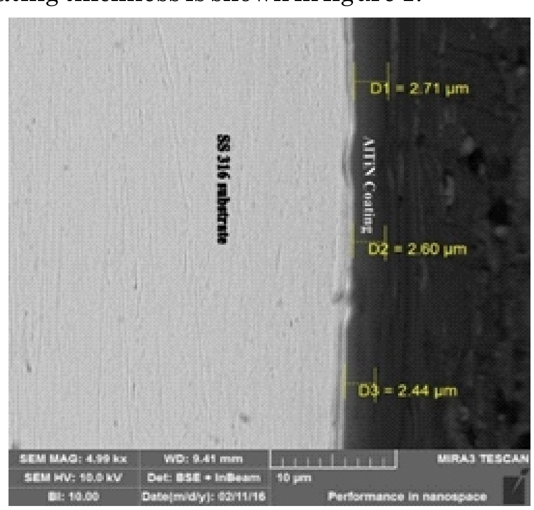


Figure 1: SEM analysis of coated interface

The average EDX elemental Al, Ti composition of the flat surface with standard deviation is shown in the figure 2. Figure shows the 50% composition of Aluminum in the matrix.

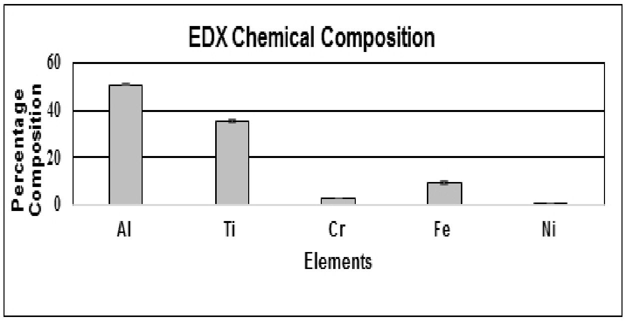


Figure 2: EDX composition of coating interface.

An average Surface roughness (R_a) and root mean square roughness (R_q) values of the coated and uncoated samples are shown in figure 3. There is an improved roughness values of the AlTiN coated sample as compare to the uncoated sample.

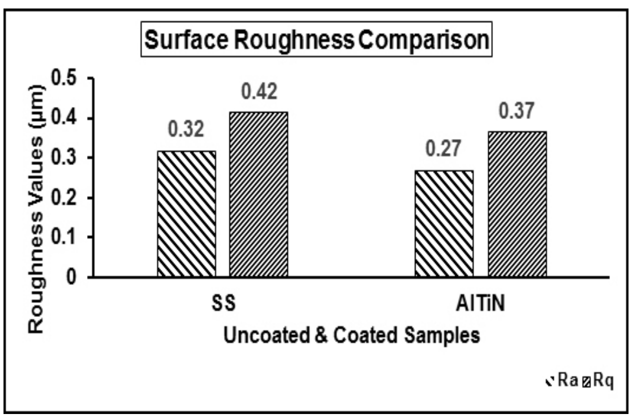


Figure 3: Average Roughness (Ra) and Root Mean Square Roughness (Rq) of coated and uncoated samples.

Electrochemical Impedance Spectroscopy (EIS) of bare SS316L and AlTiN coated SS316L was carried out in ringer lactate solution to understand the corrosion mechanism and coating's electrochemical behavior. Impedance is defined as complex resistance in the form of resistance, capacitance, inductor or combination of circuit elements measured when alternating current flows at a wide range of frequency[24]. Usually, the larger the diameter of the capacitive loop, the better the corrosion resistance of the sample. The total impedance is given in the equation (1) [25].

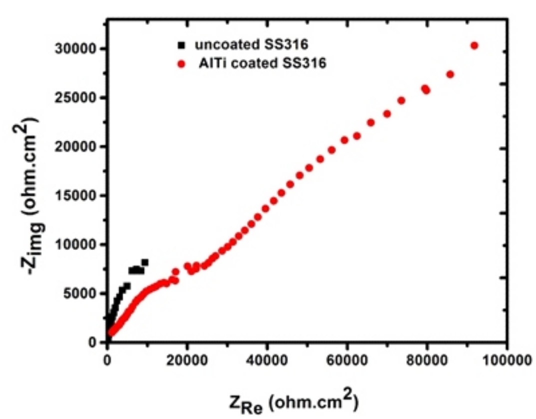
$$|Z| = \sqrt{Z_{real^2} + Z_{img^2}} \qquad (1)$$

Nyquist plot is plotted between the negative imaginary impedance Z at y-axis versus the real part of the impedance Z at axis at different frequencies on a linear scale is shown in figure 4a. The AlTiN coating possesses a larger capacitive resistance than the substrate, indicating that the AlTiN coating has better corrosion resistance.

By comparing the coated and uncoated SS 316L samples, it shows that coated sample is far more corrosion resistant than the uncoated one. Also the real impedance (Z) of coated sample is 105170.90 .cm2 and that of uncoated is 22962.19 .cm2 Hence, the coated sample is 64.15 % more resistant than uncoated one.

It is also indicated that the equilibrium state is not achieved in the cell completely as both coated and uncoated samples show non-ideal capacitive behavior because the Nyquist plot is not in complete semi-circle form. After 20 days of intimate contact of electrolyte and electrodes, EIS is performed again on electrodes keeping the delay time of 500 sec.

40 days of intimate contact of electrodes with ringer lactate is shown in figure 4b. the figure reveals that the corrosion resistance of the coated sample is decreased as compared to uncoated sample. The values of Z real for coated sample is 1260.536 .cm2 and that of uncoated sample is 16173.13 .cm2. The uncoated substrate shows 85.53% more resistance than the coated substrate. It can also be proved that uncoated sample has shown capacitive behavior by approaching za semi-circle showing more resistance than the coated one.



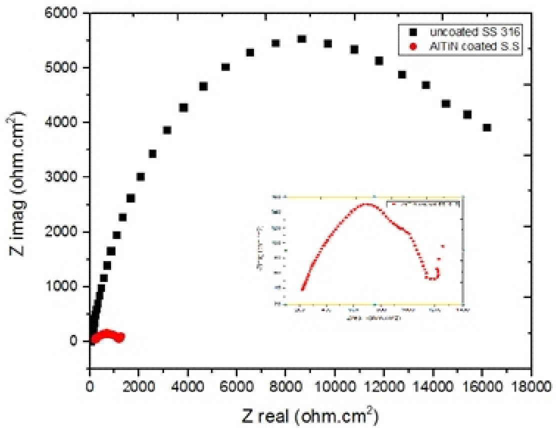


Figure 4: Graph between Z_{Re} and Z_{img} (a: 1 day, b: 40 day) Inste showing Coating behavior up to 2000 $ohm.cm^2$

After characterizing the samples with electrochemical impedance spectroscopy over a prolonged period of 40-day time, figure 5a shows visible white layers. These white layers can be due to salt formation during the contact of surface with ringer lactate. These salts are deposited on SS 316L which might be cause of decreasing the resistance of substrate. The coating morphology is showing non-uniformity of the coating as shown in figure 5b with pits and holes in it. this porosity in layer is the reason of the decrease in resistance of the coated substrate.

AlTiN coatings have added advantages over TiN coating in terms of Oxidation and corrosion resistance as Al_2O_3 and TiO_2 act as barrier for corrosion elements to reach inside the coating and deteriorate the substrate [26-28]. The coatings deposited by PVD possess high density and strong adhesion. However, the macro defects such as inclusion and voids formed due to the micro-metal droplets emitted from the cathodes reduce the corrosion resistance of the coatings. In many application, the coated parts are frequently exposed to an aggressive working environment, for instance, a Chloride containing corrosive medium, particularly in a marine region, due to the strong effect of Cl- in promoting localized corrosion [29].

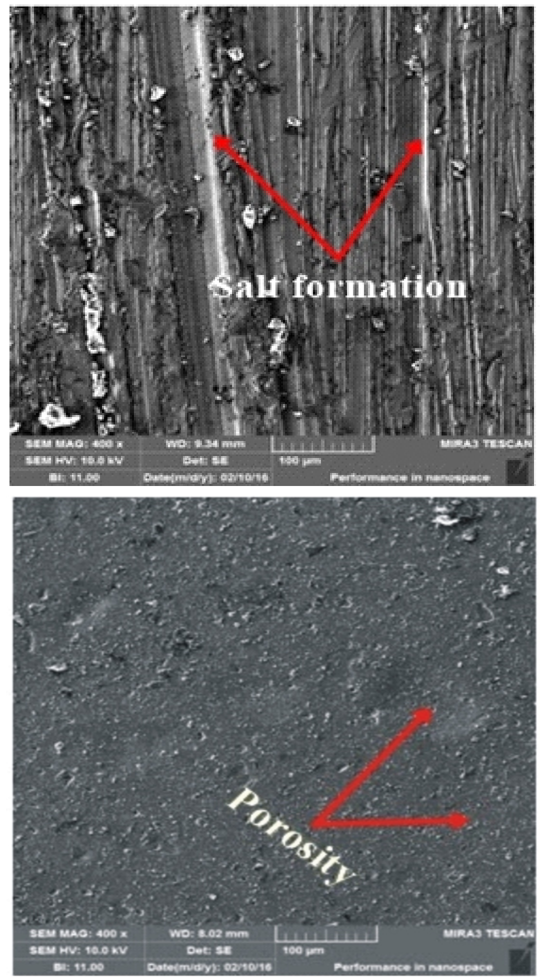


Figure 5: SEM images of 40 days of immersion (a) uncoated SS 316L and (b) AlTiN coated SS 316L (400x)

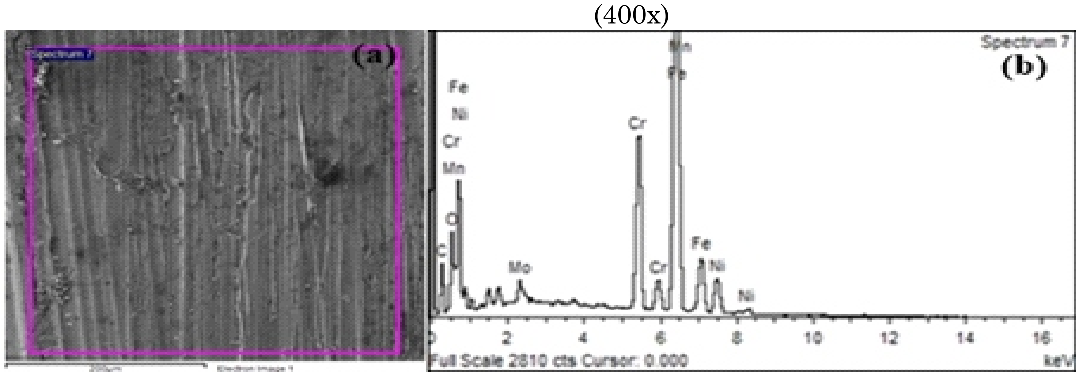


Figure 6: EDX analysis of SS 316L specimen after 40 days of immersion

These porosity defects in the AlTiN coating, originating from the deposition of the coatings, acted as pathways for Chloride ions to penetrate through the coatings and attack the steel substrate [30]. By increasing the immersion time, pitting was observed to expand, moving downward and further corroding the steel substrate.

The results of EIS show that after first test when the exposure, of both the coated and uncoated samples, was about 10-20 minutes, the coating behave like a hard corrosion resistant coating than the uncoated sample. After 20-day interval, when the exposure of the electrolyte with the electrode is further prolonged, there is a chemical reaction between the coating and the ringer lectate solution. The ringer lectate solution has a tendency to react with Al_2O_3 layer which might be formed on coated sample when the exposure is not so prolonged. As given by the following reaction:

$$Al_2O_3 + 6HCl \quad 2AlCl_3 + 3H_2O$$

But in case of uncoated sample which is SS 316L, the corrosion resistance has increased because of the presence of Cr and Mo as an alloying elements in stainless steel 3016L to resist the pitting corrosion of the substrate more than that of the coating.

After the interval of 40 days, the coated sample has shown further decrease in the impedance. The electron microscope image and EDX analysis in figure 6 are showing salt formation image and chemical composition of coating after a prolonged time. No Aluminium peak is showing in the EDX analysis and it has proved that Aluminium content has decreased when the interaction with the ringer lectate was prolonged [30,31]. The removal of Aluminium from the coating, has left porosity in the coating as shown in figure 6 and ultimately its corrosion resistance was decreased.

4. Conclusions:

AlTiN coating was developed on stainless steel grade SS 316L substrate by Physical Vapor Deposition Sputtering process using LARC technology to evaluate its usefulness for biomedical application. Coating thickness was measured using the Scanning Electron Microscope and was reported nearly 2.58 microns. The Scanning Electron Microscopy images with EDX elemental composition of uncoated and coated samples revealed the behavior of electrolyte solution. Electrochemical characterization was done to evaluate its resistance in artificial body fluids. EIS was performed at regular intervals which reveal that AlTiN coating is more corrosion resistant when the interaction with the solution is for limited period of time (1 day). But it was not last long in the ringer lectate solution because of the reaction of AlTiN coating material with the chloride ions of the electrolyte solution and $AlCl_3$ salt formation on the coated surface and also confirm the removal of Al from the coating

Acknowledgement:

The authors would like to thank the PITMAEM, PCSIR Labs Complex, Lahore for providing the necessary arrangement for coating and also to The University of the Punjab Lahore for providing necessary financial supports in completing this research.

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