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Improvement of Corrosion Resistance of Tin Coated on Titanium Alloy for Biomedical Application

A Shah¹, Siti Nurul Fasehah², Mas Ayu Hassan³, R Daud⁴ and Che Ghani Che Kob⁵

^{1,5}Faculty of Technical and Vocational, Universiti Pendidikan Sultan Idris, 35900 Tanjung Malim, Perak, Malaysia

²Faculty of Agriculture, Universitas PGRI Yogyakarta, Jalan PGRI I, Sonosewu No. 117, Yogyakarta, 55182, Indonesia

³Faculty of Manufacturing & Mechatronics Engineering Technology, Universiti Malaysia Pahang, Pekan, Pahang, 26600, Malaysia

⁴Faculty of Mechanical and Automotive Engineering Technology, Universiti Malaysia Pahang, Pekan, Pahang, 26600, Malaysia

Email: armanshah@ftv.upsi.edu.my

Abstract. This work aims to study the effect of mechanical treatment technique on titanium coated with PVD for the enhancement of corrosion resistance for the biomedical implant. First, substrates were coated with TiN via PVD then applied the mechanical treatment through ultrasonic vibration. Results show that all coated samples treated with ultrasonic vibration improve the surface of the coated sample and produce a compact coating as compared with a substrate coated without mechanical treatment. The corrosion test evaluated by Potentiodynamic polarization and Electrochemical Impedance Spectroscopy indicated that all coated samples treated with mechanical treatment showed high corrosion resistance as compared with the untreated sample. It can be concluded that mechanical treatment which is a simple technic can be used as an alternative to improve the corrosion resistance thus reduce the implant and manufacturing cost for biomedical applications.

1. Introduction

In last several decades, titanium and its alloy have been widely used in biomaterial for application included plate, screw hip and elbow joint and knee replacement due to high strength to weight ratio, and good corrosion resistance [1, 2]. Nevertheless, these materials have problem related to corrosion resistance due to aggressive Cl⁻ ion attack the substrate lead to failure of material that cause revision surgery. Several researchers have attempt to solve this problem using coating technique [3-6]. One of the versatile coating is PVD due to low substrate temperature. However, this technique has drawbacks such as defect on the structure thus affected the substrate due to corrosion attack, especially in body fluids. Several researchers attempt to solve this problem via multilayer coating on the surface but it increases the production cost. Besides, some researchers applied mechanical treatment method to increase the performance of mechanical properties or corrosion resistance for the coated or untreated samples. For instance, Thirumavalavan et al., [7] studied the effect of Severe Surface Mechanical Treatments (SSMT) on aluminium alloy. They reported that surface mechanical treatment increases corrosion resistance due to the introduction of compressive residual stress and dislocation strengthening. This finding was inline with the result of Kumar et al., [8] who studied the effect of mechanical treatment on corrosion resistance of Cr-Cu Alloy. Similar behaviour can be observed in result of Dos Santos et



al., Alwan et al., [9] Rahimi and Marrow [10], Hafeez et al. [11] and Marković et al. [12]. In contrast, Toboła et al. [13] reported that the mechanical treatment introduces a large number of defects in the form of dislocations and grain boundaries. Result from literature show that many researchers have conducted study on mechanical treatment, however, the effect of other mechanical treatment especially on ultrasonic vibration treatment to improve corrosion resistance on coated sample are scarce. Therefore, the aim of this research is to evaluate the effect of mechanical treatment based ultrasonic treatment on titanium alloy for improvement corrosion resistance for biomedical application.

2. Research method

Titanium alloy with composition (Nb: 14; Zr: 13.5; Fe: 0.05; C: 0.04; N: 0.02; H: 0.002; O: 0.10; and Ti: Balance) have been employed as substrate. Prior to coating with PVD, Titanium alloy were cut with precision cutter into diameter size of 12mm X 2mm thickness. After that, these samples were ground and polishing with SiC #320 with final roughness about Ra 0.02mm. Then, the substrates were coated with PVD with parameter. the following fixed parameters were applied to the deposition process: 100 A for the cathodic current, 300 standard cubic centimetres per minute (SCCM) for the nitrogen gas flow rate, 300 °C for the temperature of the substrate, -125 V for the substrate bias, and 1 h for the deposited time. The ultrasonic milling machine in this study was set to 16 kHz with the exposure time from 5 to 11 minutes. The samples were attached to the fixture, followed by pouring the ball steel (about 200 µm) into the installation before the ultrasonic treatment. The fixture is placed on a magnetic table and aligned with the ultrasonic tool (electrode). The z-axis was secured to avoid excessive load and vibration that can destruct the sample.

2.1. Characterization

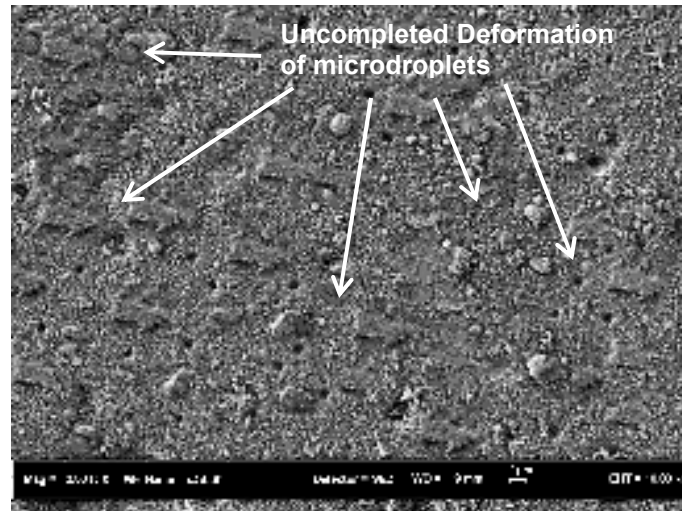
Field emission scanning electron microscopy (FESEM, Supra 35 VP, Carl Zeiss, Germany) were employed in this experiment to evaluate the surface morphology of coated and uncoated sample. The Kokubo solution at 37 ± 0.1 °C was used for the electrochemical tests with a conventional three-electrode cell that is run by a potentiostat/galvanostat (Princeton Applied Research Model VersaSTAT 3 - 300). The counter and reference electrodes were saturated calomel (SCE) and graphite electrodes, respectively. The samples were fixed at scan rate of 0.6667 mV/s. This study used an electrochemical impedance spectroscopy (EIS) to measure the corrosion process between the coatings and substrate. This study used three conventional electrodes, which were similar to the Tafel plot. The Kokubo solution (pH 7.4) was set at 37 °C for all the electrochemical procedure tests. This study used frequency response analyser (FRA) to analyse impedance measurements. The frequency range between 10 kHz and 1 Hz was used to record the spectrum.

3. Results and discussion

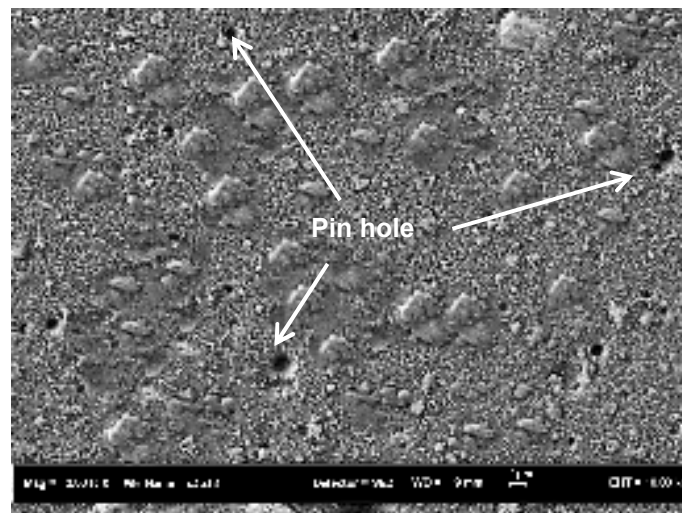
Figure 1 shows the result of SEM micrographs of TiN coated by PVD on titanium alloy after subjected with mechanical treatment at different parameters (5,8 and 11 min). It was found that at varied exposure time parameter, the significant result observed on surface morphology of coated sample. The results also revealed that the microdroplet and pin hole are still visible on coated surface regardless of exposure time. As exposure time increases, the more intense deformation can be shown especially on exposure time at 11 min. It was also found that the number of pin hole reduce when exposure time increases to 11 min. In contrast, uncompleted deformation can be shown on coated sample subjected with ultrasonic treatment at exposure time 5 and 8 min. In conclusion, this result show that the more intense deformation and least number of pin hole present when exposure time increase into 11 min.

Figure 2 shows the cress section views of TiN coated on titanium alloy after subjected with ultrasonic treatment with varied of exposure time between 8 to 11 min. Results show that the coated sample revealed uniform and no void found between coated sample and substrate which shown that good adhesion strength. The more intense result for coating thickness can be observed on Figure 3. It

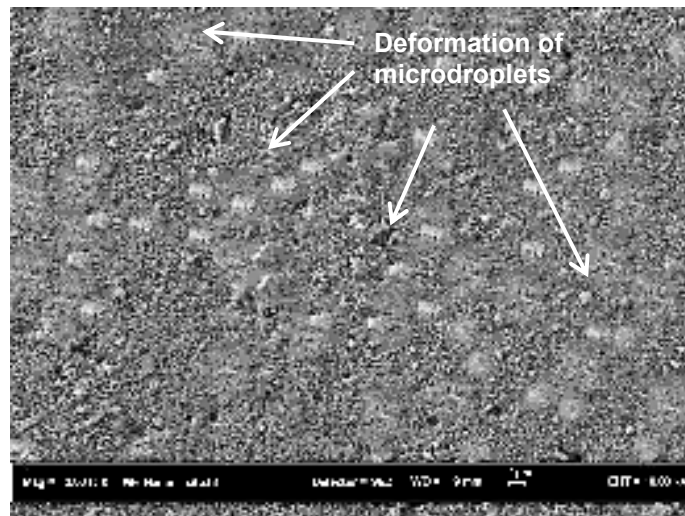
was observed that as the exposure time increases to 11 min, the coating thickness decline between 1.72 and 1.57 μm . These findings show that the coated sample had experience of compressing and compact. It was indicated that the ultrasonic treatment had improve the coated compactness and it improve the permeable defect that normally happened on PVD coating.



(a)

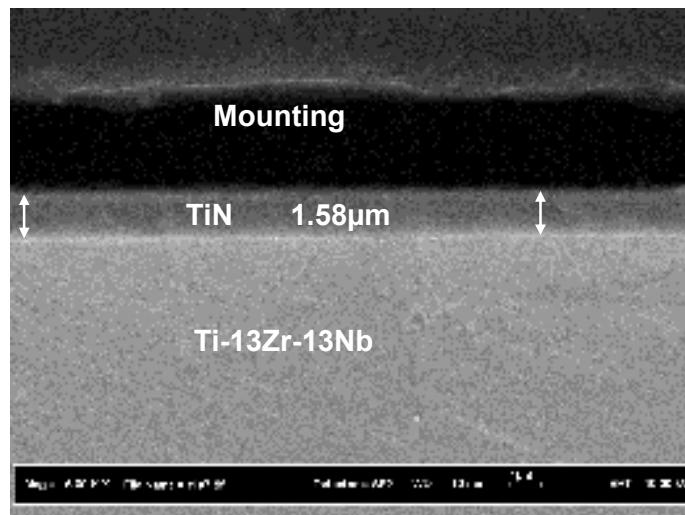


(b)

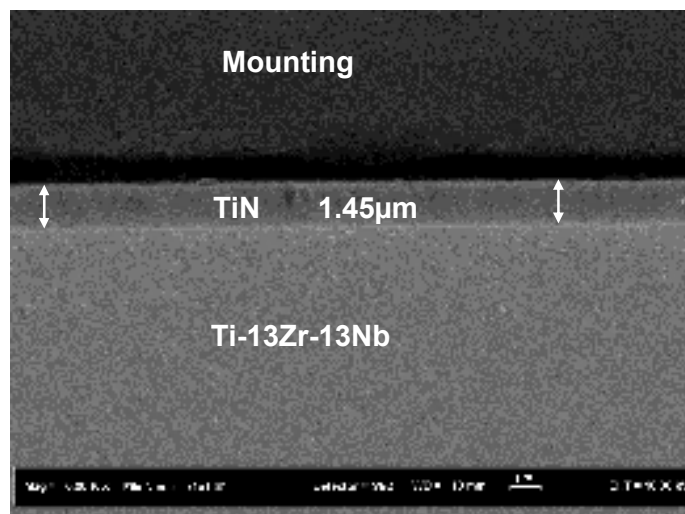


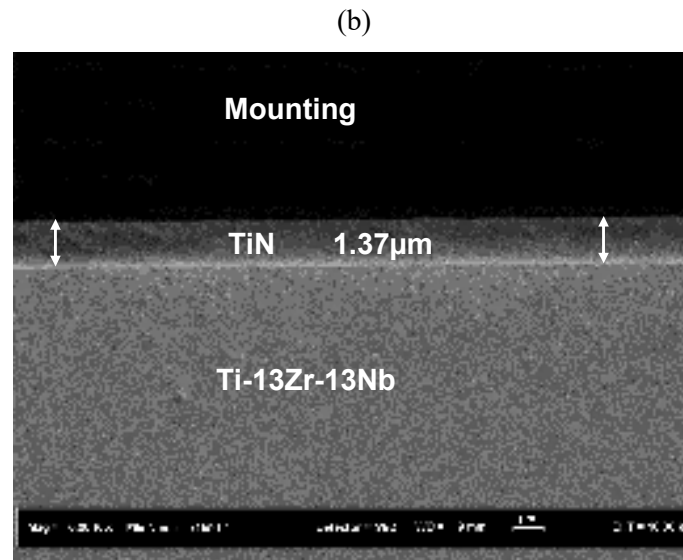
(c)

Figure 1. Surface morphology of coated samples after ultrasonic treated at 8 kHz for exposure time (a) 5 minute (b) 8 minute and (c) 11 minute



(a)





(c)

Figure 2. Coating thickness of TiN coated on titanium alloy after subjected with ultrasonic treated at 8 kHz for exposure times (a) 5 minute (b) 8 minute and (c) 11 minute

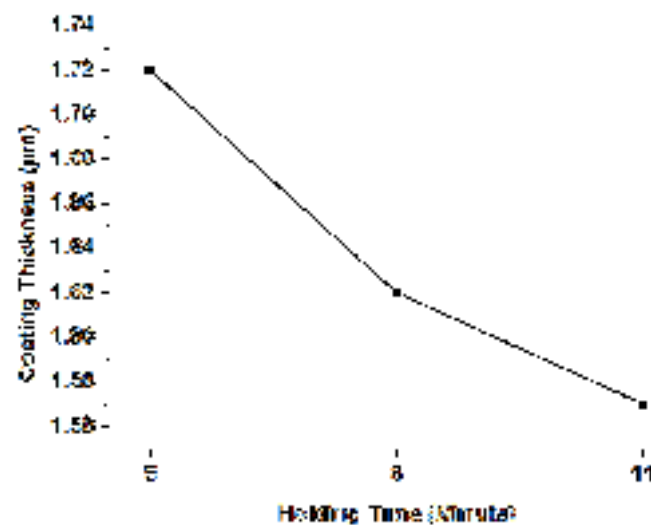


Figure 3. Coating thickness on TiN coated subjected with ultrasonic treatment at 8 kHz for different exposure times

Figure 4 depicts the result of corrosion resistance tested on coated sample illustrated in form of Tafel plot. In general, it was found that the coated sample subjected with ultrasonic treatment improve corrosion resistance regardless of exposure time. These results were proved in Figure 4 which indicated that the plots of coated samples more shifted to the left position of graph indicated lower corrosion current density. The lower current density indicates higher corrosion resistance as less electron movement and flow between coated sample and substrate. The Tafel plot output data are tabulated in Table 2. The result shows that as ultrasonic treatment increases in term of exposure time between 5 and 11 min, the current density decreases about 2.8 time. These findings revealed that the corrosion resistance increase at longer exposure time. This is because the higher deformation occurred and least number of microdroplet found at longer exposure time could be reason for the improvement of corrosion resistance. These results were found and prove in previous discussion in Figure 1.

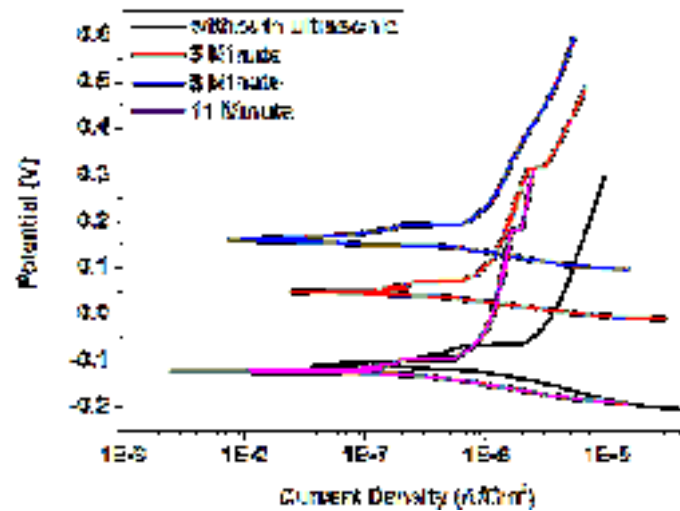


Figure 4. Tafel plots of coated sample after subjected with ultrasonic treated at 8 kHz for exposure times a) 5 min (b) 8 min, and (c) 11 min,

Corrosion resistance represented in Nyquist plot for ultrasonic treatment on TiN coated sample are shown in Figure 5. A single time constant found in this studied which indicated that the corrosion process is controlled by charge transfer. The result shows that coated samples subjected with ultrasonic treatment improves in term of corrosion resistance as compared with sample without ultrasonic treatment. It was also observed that as exposure time increases between 5 and 11 min, the resistance of coated sample to the corrosion decreases. It can be noted that at longer exposure time, the more compact coating can be found thus improve the corrosion resistance.

Figure 6 (a) and (b) present the result of corrosion resistance in term of Bode Plots for treated coated sample and uncoated samples. It was observed that as exposure time increases, the value of $|z|$ was increased. These results were confirmed the finding from previous discussion which indicated that the corrosion resistance improves as exposure time increases. There result also revealed that two-time constant appears in Figure 6 (b) indicating that this finding having two interface a) solution and substrate and b) substrate and coated samples. These results are tabulated in Table 1. It shows that about 25 % increases in term of R_{ct} when exposure time increase between 5 to 8 min. Similar behaviour can be observed when exposure time increase between 8 and 11 min which increase about 28 % of R_{ct} . In contrast the values of double layer capacitance (C_{dl}) decreases at longer exposure time of ultrasonic treatment indicating the formation of a surface film. It can be concluded that Increasing the R_{ct} values and decreases in C_{dl} values of coated sample after ultrasonic treatment is related to the increased degree of protection of TiN in Kokubo's solution.

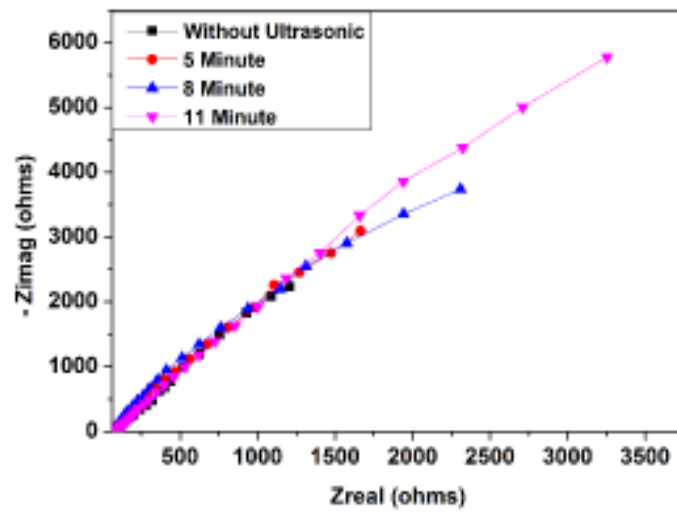
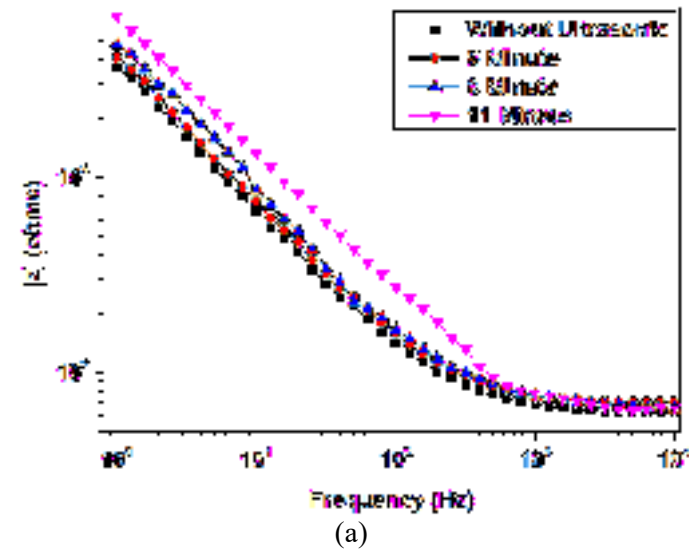
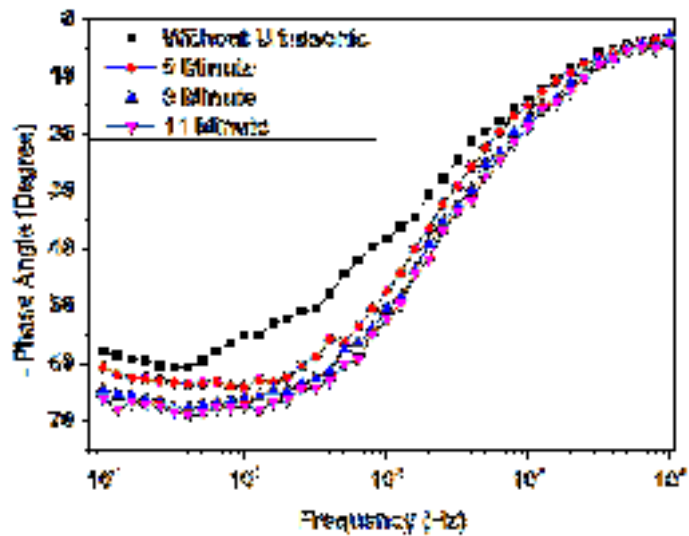


Figure 5. Nyquist plots for of TiN coated after ultrasonic treated at 8 kHz for various exposure times



(a)



(b)

Figure 6. Bode Plots (a) $\log |z|$ vs $\log f$ and (b) Phase angle vs $\log f$ for ultrasonic treated on TiN coating at 8 kHz for various exposure times

Table 1. Corrosion resistance of coated sample in term of Tafel and EIS for ultrasonic treated on TiN coating at 8 kHz for different exposure times

Samples	E_{corr} (mv)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion Rate (mm/Year)	R_{ct}	C_{dl}
Without Ultrasonic	-110.11	0.971	18.6323E-3	1883	2.7E-5
5 min, 8KHz	49.07	0.261	4.9241E-3	2816	1.73E-5
8 min, 8KHz	38.64	0.1950	3.9185E-3	3507	9.96E-6
11 min, 8KHz	-59.19	0.1363	2.7554E-3	4510	7.11E-6

4. Conclusion

The following conclusion can be drawn from the experimental result:

- Mechanical treatment found improve the surface morphology of coated sample regardless of parameters.
- It was found that coating thickness reduce after mechanical treatment due to compression tress.
- Corrosion resistance result showed that the mechanical treatment increases the corrosion resistance due to improving of surface morphology and compression stress.

Acknowledgement

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