Investigation on plasma electrolytic oxidation duty cycle on Ti6Al7Nb titanium alloy performance for biomedical application

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Abstract. In the current investigation, surface modification of Ti6Al7Nb is done with the help of the plasma electrolytic oxidation process to understand the effect of duty cycle on its performance. Ti6Al7Nb is a better alternative as compared to Ti6Al4V and Ti6Al4V ELI titanium alloys for biomedical applications because vanadium is replaced with niobium, which does not have adverse effects on cells like vanadium does. This study investigates the influence of plasma electrolytic oxidation (PEO) duty cycle on the coating properties of Ti6Al7Nb titanium alloy, focusing on thickness, hardness, surface roughness, pore size, and corrosion resistance. Na_2SiO_3, $Na_3PO_4 \cdot 12H_2O$, and KOH was used as electrolyte for coating Ti-6Al-7Nb titanium alloy, PEO coating is done at constant voltage of 500 V. Five different duty cycle 20%, 30%, 40%, 50% and 60% are used to understand the effect of it on the performance of Ti-6Al-7Nb titanium alloy. For characterisation of coating SEM, EDS, XRD techniques are used. From current study it was noticed that coating thickness increases from 10.19 mm to 18.73mm as duty cycle increases from 20% to 60%, however hardness increases from 718.80 HV to 883.35 HV as duty cycle increases from 20% to 60%. It was observed that high duty cycle increases coating hardness and thickness due to intense discharge events. From EIS testing it was notice that coating is made-up of two-layer structure. Uniform distribution of electrolyte compositions was observed in PEO coated Ti-6Al-7Nb titanium alloy.

1 Introduction

Titanium and its alloys possess exceptional characteristics that make them desirable for different biomedical uses, such as orthopaedic and dental implants. These characteristics

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include elevated resistance against corrosion, great specific strength, low density, good biocompatibility and low elastic modulus [1]. Due to its reactive nature, titanium can withstand environmental deterioration by forming a persistent and densely adhering oxide layer on its surface when come in contact with air or moisture. Nevertheless, this oxide layer's thickness (<10 nm) makes it easily destroyed by friction and corrosion [2]. When such material is implanted in the body, the body may experience allergic responses and inflammation as a result of metallic implants' poor corrosion protection. Furthermore, due to its bioinert nature and lack of a surface bioactive chemical stimulus that might promote the production of apatite, uncoated titanium has poor osseointegration capabilities. A broad range of biomedical implants are produced from cpTi, which is frequently chosen as the material of choice. However, its application is restricted in scenarios that demand exceptional wear resistance, tensile strength, and fatigue durability [3]. Because titanium has relatively low hardness, it is prone to fatigue, particularly in smaller diameter implant that must maintain precise mechanical stability to avoid overloading and failure. Furthermore, its relatively high elastic modulus and the challenge of enhancing its mechanical characteristics without compromising biocompatibility are major factors that limit the wider adoption of cpTi for implant use [4].

The excellent mechanical characteristics of Ti6Al7Nb alloy have resulted into its widespread applications. However, presence of Al in titanium alloy results into negative effects on biocompatibility and cell viability [5]. From past literature it was observed that Al is linked with noteworthy neurotoxic effects, especially in investigation liking it to Alzheimer's disease, bone fragility and possible localised inflammation [6]. Also, vanadium has negative effects of human body cells. Due to these studies, there is discouragement from using Ti-6Al-7Nb titanium alloy, otherwise it was most used titanium alloy for biomedical applications, which promoted the development of alloy which has elements that are inert in the oral environment and human body. Ti-6Al-7Nb can be used as superior solution to the above problem. Ti6Al7Nb titanium alloy is mostly used in orthopaedic and dental applications. Ti-6Al-7Nb titanium alloy does not have cancer-causing vanadium (V), also has lower weight-to- strength ratio, and shows good corrosion resistance. Vanadium (V) has negative harmful effects on human tissues; V has been categorised as a hazardous element. As there are chances of vanadium ions release, it is important to design titanium alloys without vanadium for biomedical applications.

In past, to enhance the tribological characteristics of titanium alloy, various methods like physical vapour deposition, plasma nitriding, plasma electrolytic oxidation and electrodeposition have been utilised. Among the different surface modification techniques, PEO is best technique due to its excellent adhesion strength and ecofriendly nature [7]. Plasma electrolytic oxidation (PEO) is effective, cost efficient and environmentally friendly surface treatment technique most suitable for alloys and valve metals. Also, PEO is the most effective method for oxide coatings which improve the specimen's insulation, resistance to wear, thermal shock resistance and overall thermal stability [8]. The properties of PEO coating are depended on number of factors, such as treatment time, electrolyte [10], electrical parameters [9], and substrate. PEO coating properties are depended on chemical composition of electrolytes. Electrolyte composition can be changed by varying concentration or by adding additional elements.

Several studies [11] have documented how processing variables affect the properties and characteristics of the resulting coating. The mechanism of Plasma Electrolytic Oxidation (PEO) remains inadequately understood despite extensive investigation because of the difficulty in investigating the transient plasma discharges which happen on the surface of the workpiece throughout the method. To develop coatings with appropriate qualities for many innovative applications, it is essential to understand the PEO process.

2 Materials and process

2.1 Materials

The elemental composition Ti6Al7Nb used in current research taken from Bhagyashali Metals, Mumbai has detailed in Table 1. The specimens, each having a radius of 6 mm and thickness of 2 mm, were prepared from a 12 mm diameter round bar using the wire-cut electro discharge machining process. The surfaces were then polished sequentially with abrasive papers of 400, 600, and 800 grit. Afterwards, the specimens were immersed for one minute in a solution containing HF (1 mol dm^{-3}) and H_2SO_4 (4 mol dm^{-3}) [14]. Subsequently, it is washed with distilled water and subjected to ultrasonic cleaning for fifteen minutes. To remove the fine particles, polishing debris, and organic contaminants from the surface of specimen it is necessary to clean the specimen by ultrasonic technique. These materials and residue may cause improper dielectric discharges during oxidation process. Specimen is clean at a microscopic level by ultrasonic technique due to its cavitation effect. Excellent adhesion and uniform oxide growth layer is developed on uniform and clean surface of specimens during PEO process. Ultrasonic cleaning helps to enhance corrosion resistance, coating quality and mechanical performance.

Table 1. Ti6Al7Nb composition by weight %.

Elements	N	H	Fe	C	O	Ta	Nb	Al	Ti
Weight %	0.01	0.003	0.08	0.04	0.11	0.35	7.01	6.06	Balance

2.2 Plasma electrolytic oxidation (PEO) method

Electrolytes (15 g/l Na_2SiO_3), (2.8 g/l KOH) and (10 g/l $Na_3PO_4 \cdot 12H_2O$) were used to create stable alkaline coatings at pH 12, with a conductivity of 7.1 mS/cm. During PEO technique, the temperature is regulated under 289 K using a chilling device and thermometer. The voltage was controlled to maintain the required current density once it had been elevated to it. Ti6Al7Nb titanium alloy was the anode and stainless steel (SS) the cathode in the experiment. The applied voltage was gradually raised until the target current density was achieved. Once this target current density was achieved, the voltage was maintained at that level through precise control measures. The treatment continued until noticeable arcing occurred; this was an intentional endpoint to prevent the coating from being adversely affected by excessive arcing. Figure 1 shows the experimental setup for the PEO technique. PEO is an electrochemical method which includes the electrolysis of an aqueous solution as well as several other electrode activities [13]. On the anodic surface, gaseous oxygen is released and metal is oxidised; on the cathodic surface, gaseous hydrogen forms. A critical stage in the process is to generate micro discharges at the working electrode's surface in the appropriate electrolyte using a high voltage.

In the preliminary phase of electrolysis, gaseous oxygen is generated at the anode until the breakdown voltage, which rises linearly over time. When the metallic surface seems devoid of visible sparks, the ionic current generated by the diffusion of electrolyte ions represents the overall current in that area. Faraday's law posits that ionic current is the principal determinant in oxide production. The system starts deviating from the previously recognised linearity in the second stage, and the slope of the V-t graphs decreases. The intense electric field causes dielectric breakdown, and during this phase, a greater number of tiny sparks are equally spread throughout the whole surface. The current density is determined by summing the ionic current and the electron current caused by sparking after their occurrence. To keep the similar current as in the previous stage, a substantially slower rate of voltage rise

is necessary since electron current density is predominantly produced by sparking and hence unaffected by coating resistance. When the anodic voltage reaches a relatively constant level in stage III, the film develops a constant resistance configuration, suggesting that maintaining the same current requires no appreciable increase in anodic voltage. This stage's slope change might be caused by the considerable rise in the proportion of electronic current in total current due to dielectric breakdown.

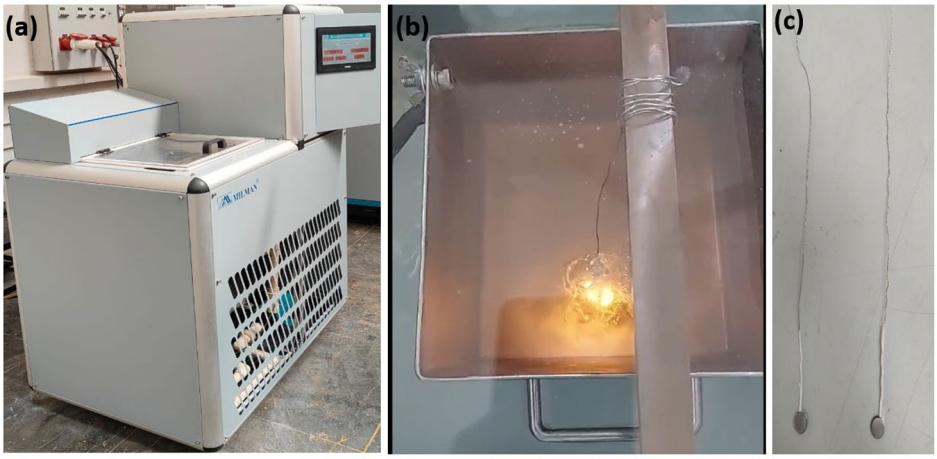

Fig. 1. PEO experimental setup (a) PEO machine, (b) PEO tank, and (c) Specimen.

3 Experimental work

3.1 Characterisation of coatings with FESEM and EDS

The morphological study of MAO-coated Ti6Al7Nb was done by FESEM, more especially the FEI Nova NanoSEM 450, which is available at Savitribai Phule Pune University (SPPU), Pune, India. This advanced FE-SEM system provides high-resolution imaging capabilities, with resolutions of 1.8 nm at 3 kV, 1.4 nm at 1 kV and 1.0 nm at 15 kV under a chamber pressure of 30 Pa. For elemental composition analysis, EDS, namely the Bruker XFlash 6I30, was employed. Additionally, the EDS system provides exceptional energy resolution, achieving 45 eV at C Kα and 123 eV at Mn Kα, ensuring precise elemental identification and analysis.

3.2 XRD investigation

A comprehensive XRD investigation was done to find out the crystalline phases existing in the MAO-coated Ti6Al7Nb alloy. In current study specimens are scanned at angles between 20° and 80° (in terms of 2θ) to obtained diffraction patterns. A copper (Cu) Kα radiation source generated the X-rays. For generation of reliable and clear diffraction data this is standard method. The scanning was done under strict conditions, current of 40 mA and voltage was 40 kV are used, to get best possible resolution and intensity. These setting was selected to get good quality the diffraction data and accurately find the distinct crystalline phases existing in the coating. XRD technique gave details phases present in coating, which was helpful for understanding its structure and how it will impact he coating performance.

3.3 Measurement of surface roughness

The Ra parameter was utilised to meticulously examine the surface roughness of each sample using the Mitutoyo Surftest SJ-301 profilometer located at MIT World Peace University (MITWPU), Pune. The measurements were conducted as per EN ISO 4287:1997 standard. The Ra parameter is important for evaluating performance and quality of the surface under investigation and also indicates the overall roughness of the surface.
Mathematically, it is expressed as:

$$Ra = \frac{1}{l}\int_0^l |Z\ (X)|dx \tag{1}$$

|Z(x)| represents the absolute ordinate value of the surface profile within the elementary measuring length and l denotes the elementary length along the x-axis (mean line).

3.4 Hardness test

The hardness of MAO-coated Ti6Al7Nb titanium alloy was checked as per the ASTM E92 standard by using a micro-Vickers hardness tester. The measurements were taken at the metallurgy laboratory at MIT World Peace University Pune. After the indentation was made, two separate diagonal lengths, called d_1 and d_2, were carefully measured. Hardness is calculated from the following equation 2.

$$\mathrm{HV} = \frac{1.854 \times \mathrm{P}}{\mathrm{d1} \times \mathrm{d2}} \tag{2}$$

In above equation, P signifies the load used in kgf, and d_1 and d_2 are the measured lengths of the indentation diagonals.

3.5 Coating thickness

Coating thickness was measured by light microscope at the ELCA Quality and Calibration Lab in Pune; a light microscope was used to measure the coating thickness. To ensure accurate measurement, the specimens underwent a meticulous preparation process. Initially, the specimens were cold mounted using a binder and resin, providing structural support and stability for subsequent processing. Following mounting, the specimens were mechanically polished using emery papers of varying grit sizes, starting with 400 grit and progressing to 800 grit to achieve a smooth and refined surface. At last polishing is done, which brings the mirror-like finish on the surface of the specimen and assures accurate coating thickness measurement. An optical microscope was utilised to test coating thickness at five separate locations. After that, the final coating thickness was calculated by averaging the measurements. With an optical microscope, coating thickness was measured accurately and consistently.

3.6 Corrosion behaviour of MAO coated Ti6Al7Nb

The EIS system is used to find out the corrosion resistance of MAO-modified Ti6Al7Nb titanium alloy. This technique does the complete analysis of material response with electrochemical reactions, which gives the insights into its corrosion resistance, capacitance, and overall efficacy of a coating layer under different conditions. In the current study a 0.9% sodium chloride (NaCl) solution was used as an electrolyte. This solution was prepared using premium analytical-grade chemicals and distilled water to minimise extraneous influences and provide a regulated, uniform testing environment. The electrochemical investigation was performed by a three-electrode configuration. A working electrode made of Ti-6Al-7Nb, a

counter electrode constructed from platinum, and a reference electrode using saturated calomel (SCE) were utilised. The electrochemical impedance spectrometry (EIS) gives repeatability and accuracy of electrochemical measurements. For precise control of electrochemical parameters, a Vertex potentiostat/galvanostat was used. The temperature was maintained at 30 ± 1°C during measurements for consistence results. For EIS testing Ti-6Al-7Nb specimens were prepared carefully. The operative area was exposed, while all other surfaces were protected with epoxy glue. This precaution was taken to avoid electrochemical reactions that may skew data. The working electrode was securely connected with a copper wire. For EIS testing frequencies are selected from 1 MHz to 0.1 Hz. This extensive frequency sweep examined the coating's electrochemical characteristics, including corrosion resistance and charge transfer. The statistics reveal the MAO coating's effectiveness and durability in various environments.

4 Result and discussion

Duty cycle is one of the most critical parameters in the MAO technique, significantly influencing surface roughness, coating thickness, hardness, and pore size. As shown in Figures 2(a) to 2(e), the scanning electron microscope (SEM) images provide insight into the morphological changes occurring at different duty cycles. Increasing the duty cycle provides a greater energy supply per cycle, which leads to more intense plasma discharges, molten oxide formation, and the expulsion of gas bubbles to the coating surface, ultimately generating a highly porous structure. This phenomenon occurs because, with an increase in energy input, the discharges penetrate deeper into the coating through pre-existing weak points with lower electrical resistance, leading to an expansion of the discharge channel. As a result, a higher duty cycle facilitates the production of large and numerous surface pores, along with the deposition of expelled oxide material on the surface of a coating.

Similar type of results is obtained in past literature. One of the researchers [12] found that pore size and coating thickness increases with increase in duty cycle during investigation of TiO_2/P coating developed by PEO process. Specifically, coating thickness values of 10.19 µm, 10.48 µm, 16.49 µm, 18.49 µm, and 18.73 µm were recorded at duty cycles of 20%, 30%, 40%, 50%, and 60% (Table 2 and Figure 4), respectively. At higher energy input there is improved plasma-chemical reactions which help for more oxide growth, resulting into higher coating thickness. Also, it was observed that pore size increases from 0.92 µm to 3.77 µm, and surface roughness increases from 1.52 µm to 4.09 µm as duty cycle varied from 20% to 60%. At higher duty cycle resulting into higher melting and re-solidification of the materials, leading to generation of more porous structure because of more molten materials.

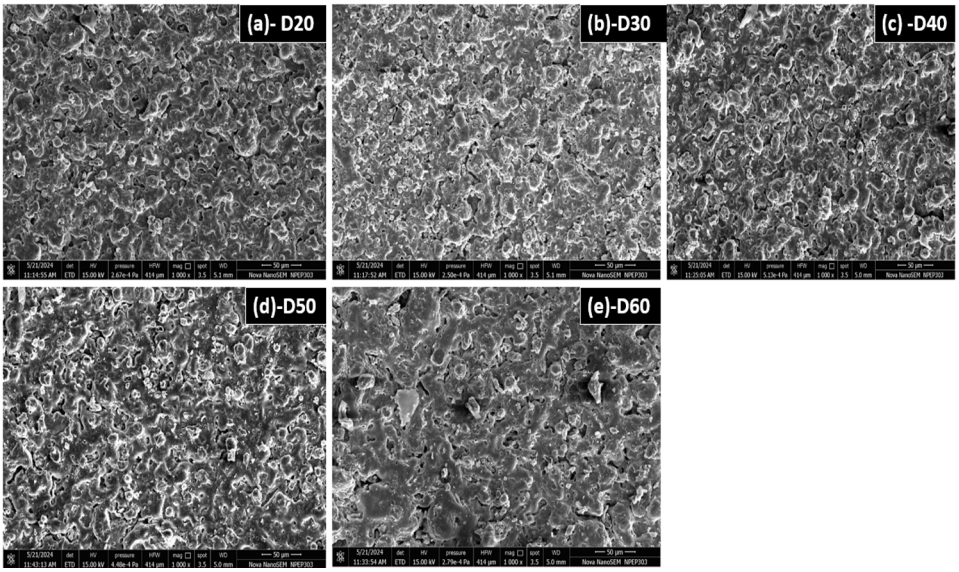

Fig. 2. Surface morphology (SEM images) of specimens at various duty cycles.

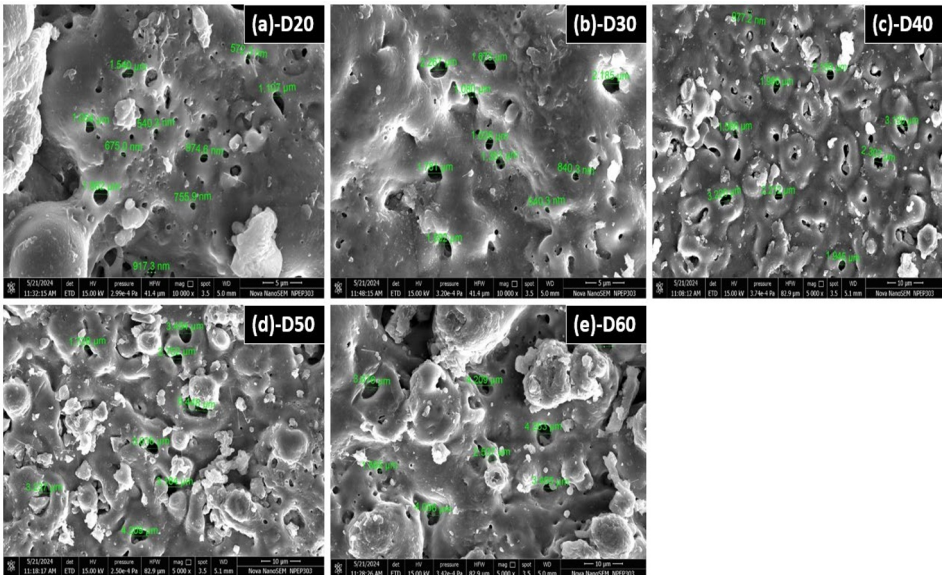

Fig. 3. SEM images of Ti6Al7Nb samples at various duty cycles.

Refer Figure 3, SEM pictures show the morphology of PEO coated Ti6Al7Nb alloy at various duty cycle: 20%, 30%, 40%, 50%, and 60%. SEM images show how changes in duty cycles impact he coating characteristics such as pore size, surface roughness and coating porosity, which are important for biomedical applications. During PEO lower duty cycle such as 20% there in low energy input and weaker micro discharges, which results into relatively small, smooth, uniform and widely distributed pores having 574 nm to 1.5 µm pore size. Higer and slightly larger pores (400 nm – 2.1 µm) are produced as duty cycle increases to 30% due to higher plasma interaction and good surface oxidation which are helpful for promoting early osseointegration for biomedical applications.

Uniform and well-distributed pore are form at intermediate duty cycle such as 40%, pore sizes are ranging from 600 nm to 2.4 μm. There is improved bioactivity and coating stability due to balance between porosity and mechanical properties, which make it ideal biomaterials. More irregular and larger pores (~1.1–4.2 μm) are formed as duty cycle increases further to 50%, results into higher surface roughness because of intensified micro-discharges and molten oxide generations. Higher porosity is beneficial for bioactivity but higher surface roughness can affect the mechanical stability of an implant. Larger discharge craters (up to ~4.9 μm) and highly porous coating formed at duty cycle of 60% because of higher energy supply at higher duty cycle. Porosity was highest at 60% duty cycle but it produces other defects which may affect the coating properties and life.

So, it was observed that lower duty cycle such as 20%, 30% generate uniform and small pores, which will improve corrosion resistance of coating but limits the bioactivity. Intermediate duty cycle like 40% gives balance between porosity and mechanical strength, which make it ideal coating for biomedical applications. However, higher duty cycle such as 50% and 60% gives higher surface roughness, greater discharge craters and higher coating defects, which will affect coating properties and life. Hence, 40 % duty cycle can be optimal value of duty cycle, which will give bioactivity, better coating life, and corrosion resistance in PEO-coated Ti-6Al-7Nb alloys.

Table 2. Coating properties at various duty cycles.

Experiment No	Current (mA)	Frequency (HZ)	Time (Min)	Duty Cycle (%)	Surface roughness (μm)	Coating thickness (μm)	Hardness (HV)	Pore Size (μm)
1	300	500	15	20	1.52	10.19	718.8	0.92
2				30	2.72	10.48	765.46	1.63
3				40	3.66	16.49	795.81	2.19
4				50	3.84	18.49	826.64	3.18
5				60	4.09	18.73	883.35	3.77

Figure 4 illustrates how the duty cycle affects various properties of the coating. Coating hardness increases with increase in duty cycle as shown in Table 2 and Figure 5. At higher duty cycle dense and thick oxide layer is formed due to higher energy available, which help to enhance the mechanical properties of coating such as hardness similar observation was reported by Torres-Ceron et al. [12]. It was observed that coating hardness increases from 718.80 HV to 883.35 HV as duty cycle increases from 20% to 60%. This increase in hardness is linked with higher ceramic phase content and dense coating at higher energy input. The varication in coating thickness, surface roughness, pore size and coating hardness shows the important role of duty cycle in tailoring PEO coatings for biomedical applications. For better mechanical properties, corrosion resistance, and desirable tribological properties, it is important to know the crucial role of duty cycle for optimising the PEO process.

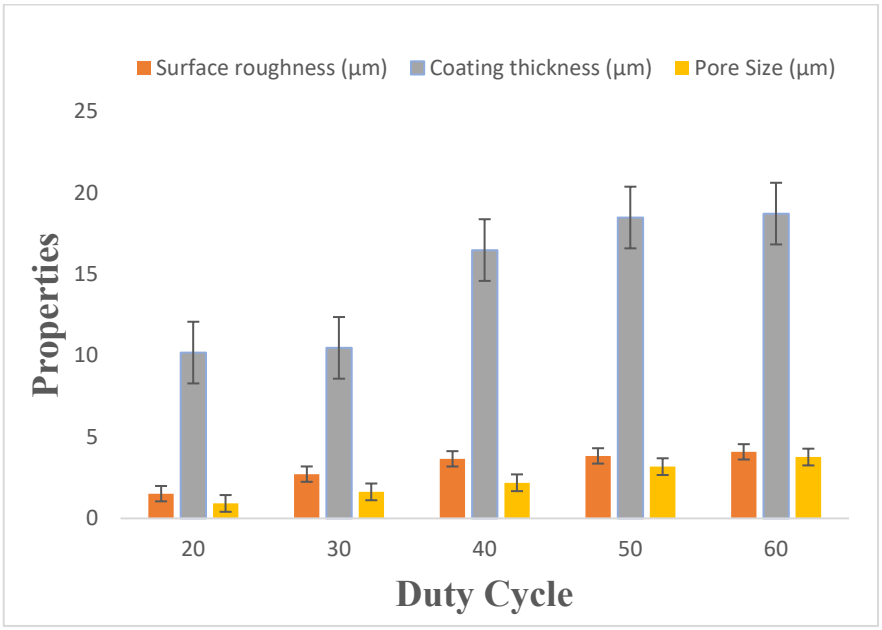

Fig. 4. Surface roughness, coating thickness and pore size at different duty cycles.

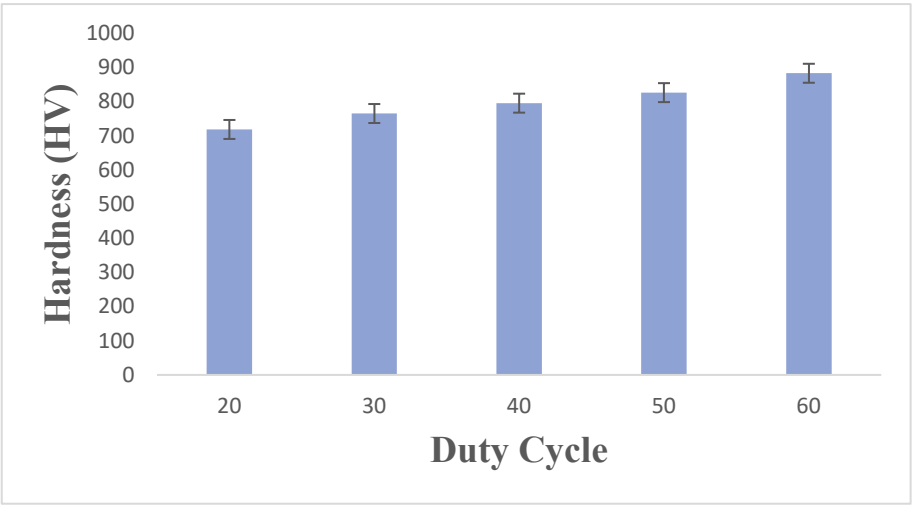

Fig. 5. Graph of frequency Vs Hardness of coating.

4.1 XRD investigation

Figure 6 show the phases of PEO-coated Ti-6Al-7Nb titanium alloy processed at different duty cycles 20%, 30%, 40%, 50%, and 60% obtained from XRD analysis. Variation in peak sharpness and intensity of crystalline structure of the PEO-coated Ti-6Al-7Nb is observed as duty cycle varied from 20% to 60%. Lower duty cycles (20% and 30%) show peaks primarily related to anatase and some rutile phase, indicating the early stages of oxide layer formation. The transformation of anatase to rutile phase happen because of higher thermal energy and longer pulse duration at higher duty cycles such as 40%, 50%, and 60%. The presence of

titanium peaks throughout all samples suggests that the oxide layer is relatively thin, allowing X-rays to penetrate and detect the substrate beneath.

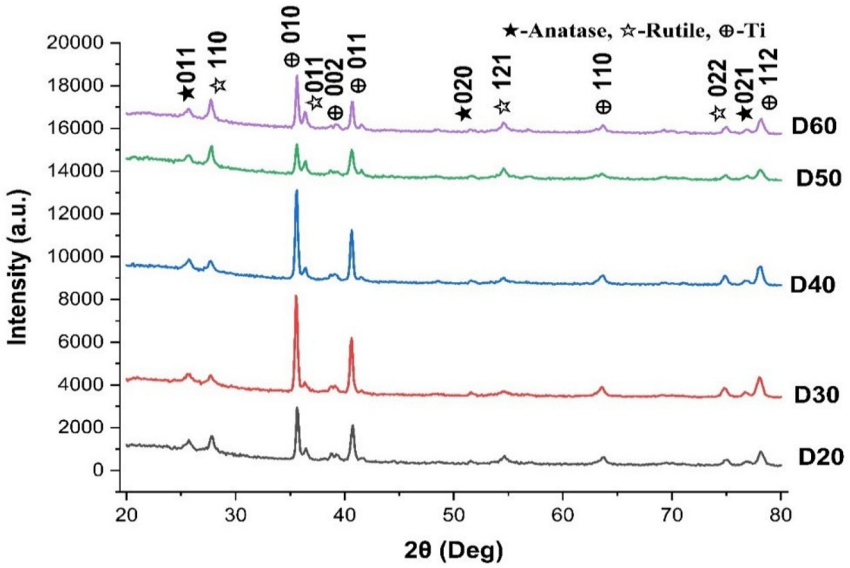

Fig. 6. Different duty cycle coating XRD patterns.

It was observed that phase composition of coating changes as duty cycle increases, leading to growth of TiO2 based ceramic layer. Rutile phase formation takes place at higher duty cycle, which is linked with higher thermal stability and improved mechanical properties, however, anatase phase formation take place at lower duty cycle. Anatase phase is important for biocompatibility point of view. XRD pattern analysis show the different crystalline phases linked with titanium oxide (TiO_2). Rutile (TiO_2) peaks are found out at 2θ angles of 27.06° and 54.63°. These peaks are attributed to the (110) and (121) crystallographic planes, respectively, with measured lattice spacings of 3.228 Å and 1.678 Å. Along with rutile, anatase phase of TiO_2 is also detected at 2θ angles of 25.322° and 76.62°, which can be linked with the (011) and (021) crystallographic planes. The associated lattice spacings for these planes are determined to be 3.514 Å and 1.203 Å, respectively. Titanium substrate diffraction peaks are also observed in XRD pattern. From XRD pattern it was concluded that PEO coated Ti-6Al-7Nb have both anatase and polymorphs of TiO_2, alongside unreacted titanium. The coexistence of these phases suggests a complex structural composition influenced by the oxidation process, which has an important role in influencing the coating's final properties.

The phase composition of the TiO_2 coatings during PEO process is influences by the percentage of electronic current. It was observed that anatase to rutile phase transformation is gradual at lower current densities due to more frequent and less intense microcharges. The increase in micro-discharges supplies localised high temperatures and energy that facilitate the nucleation and growth of the rutile phase. Additionally, the presence of sufficient time during the process allows for the diffusion of oxygen anions, promoting the rearrangement of TiO_2 into its thermodynamically stable rutile structure. This change takes place because the rutile phase has lower surface energy and greater density than the metastable anatase phase. Conversely, at higher current densities, the increased energy input leads to a rapid oxidation process, forming predominantly the anatase phase with minimal rutile transformation. The high-energy micro-discharges create localised melting and rapid cooling cycles, inhibiting the anatase-to-rutile transformation by limiting the necessary diffusion

processes. As a result, the development of the rutile phase is suppressed, and the material remains in the anatase state, which has a lower density and higher surface energy compared to rutile.

The findings of this study align with the anatase-to-rutile transformation (ART) process, which has been extensively studied in the context of TiO_2 phase transitions. Past researchers observed comparable outcomes during their study on the PEO of titanium alloys. Their studies confirm that the stable rutile phase can be achieved permanently through the transformation of metastable anatase, which is governed by two critical factors: temperature and time. The transition typically occurs within the temperature range of 600 to 1000°C, though variations in this range depend on multiple factors like the surrounding environment, heating rate, impurity levels, dopant concentration, and type. Impurities and dopants have an important role in modifying the activation energy required for the anatase-to-rutile transition, thereby either accelerating or delaying the phase transformation. Additionally, the presence of an oxidative atmosphere can enhance the rutile formation by providing ample oxygen for diffusion and lattice restructuring. In conclusion, the XRD analysis of the PEO coatings demonstrates that the phase composition is impacted by the applied current. While lower current densities promote the formation of thermodynamically stable rutile through gradual phase transformation mechanisms, higher current densities predominantly lead to the retention of anatase due to rapid cooling effects. The findings support existing research on the ART process, emphasising the significance of thermal treatment conditions, processing parameters, and material-specific characteristics in determining the final phase structure of TiO_2 coatings.

4.2 EDS analysis

Figure 7 represents the EDS spectra of a PEO coating produced on Ti6Al7Nb. The elemental composition of different PEO coatings was identified by EDS analysis results. A more profound look reveals that each coating contains the following elements: O, Si, Ti, Nb, K, P, Na, and Al. The higher proportion of oxygen detected in the coatings indicates that they are primarily made up of oxides of elements like P, Si, Al and Ti. Ti, Na, and Al present in the coatings come from the base substrate, whereas the P, Si, Na and K are introduced from the phosphate or silicate electrolytes. Therefore, the development of PEO coatings is driven by both the incorporation of compounds originating from the electrolyte and the oxidation of the specimen materials. Thus, it can be said that the deposition of electrolyte-borne chemicals (for example, silicate oxides) in silicate electrolyte is the primary process that forms the PEO coating on Ti6Al7Nb. Additionally, as the PEO method progresses, the oxidation of the Ti6Al7Nb samples appears less evident, whereas the deposition of silicate oxides increases. Titanium concentration in the coating is much greater than phosphorus, indicating that the PEO coating is largely formed by oxidation of the titanium alloy specimen in the phosphate-based electrolyte. The levels of Ti, Si, and P imply that the coating's formation is largely governed by the incorporation of compounds derived from the electrolyte, even though the titanium alloy substrate undergoes considerably greater oxidation compared to the coating itself.

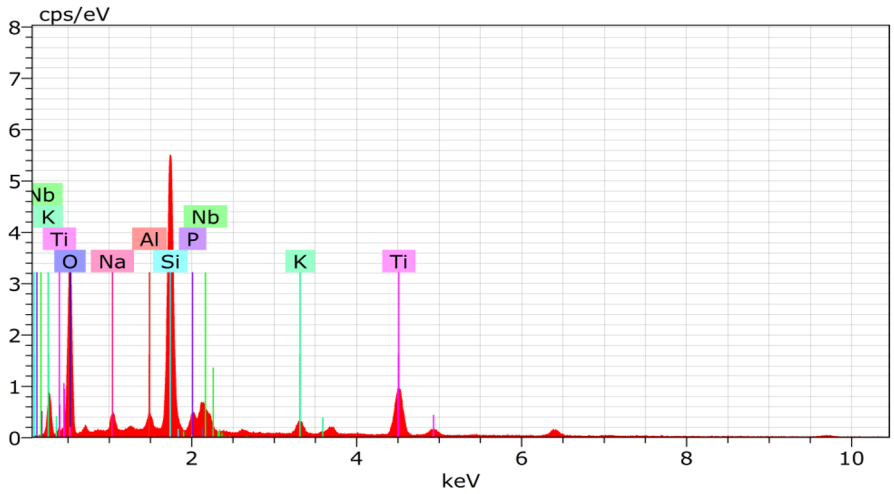

Fig. 7. EDS spectra of PEO coated Ti6Al7Nb.

4.3 Electrochemical analysis

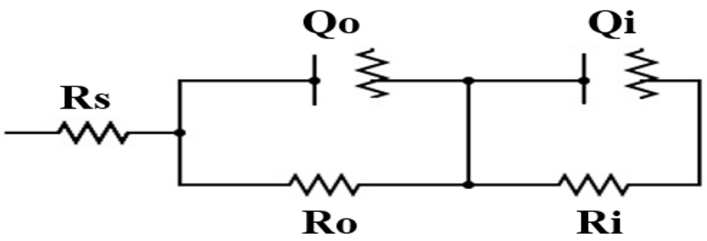

Fig. 8. EIS analogous circuit schematic of coated specimen.

Figure 9 displays the Nyquist plot that shows the real component of the impedance vs. the imaginary part at each frequency. Data from Nyquist plots of coated samples were obtained using Figure 8's electrical circuits. It was found that two layers of coating developed on Ti-6Al-7Nb: a porous outer layer and a dense inner layer. In Figure 8, Ro and Qo were associated with the outer layer, whereas Qi and Ri were the corrosion resistance and constant phase components of the inner layer of coating. Table 3 presents the acquired fitting data from the respective electrical circuits. In all coated samples, the interior layers were more corrosion resistant than the outer layers. It was found that the inner layers of the PEO coatings played a key role in providing corrosion resistance, while the outer layers had little to no significant effect on protecting the titanium substrate from corrosion [15]. As inner layer of coating is dense as compared to outer layer which is porous in nature, inner layer offers more corrosion resistance.

Denser and thicker oxide layers were obtained at higher duty cycles. The thickest and fewest flaws were found in coatings created at a 60% duty cycle. Higher impedance values were displayed by coatings with more duty cycles, suggesting better corrosion resistance. In EIS testing, the coating with a 60% duty cycle showed the highest performance. Nyquist plots shown in Figure 9.

Table 3. The values of corrosion resistance derived from Nyquist plot electrical equivalent circuits.

Expt No	Duty Cycle (%)	(Ro) (kΩ) Outer Layer	(Ri) (kΩ) Inner Layer
1	20	89300	10100000
2	30	116000	10300000
3	40	127000	10400000
4	50	131000	10600000
5	60	135000	12600000

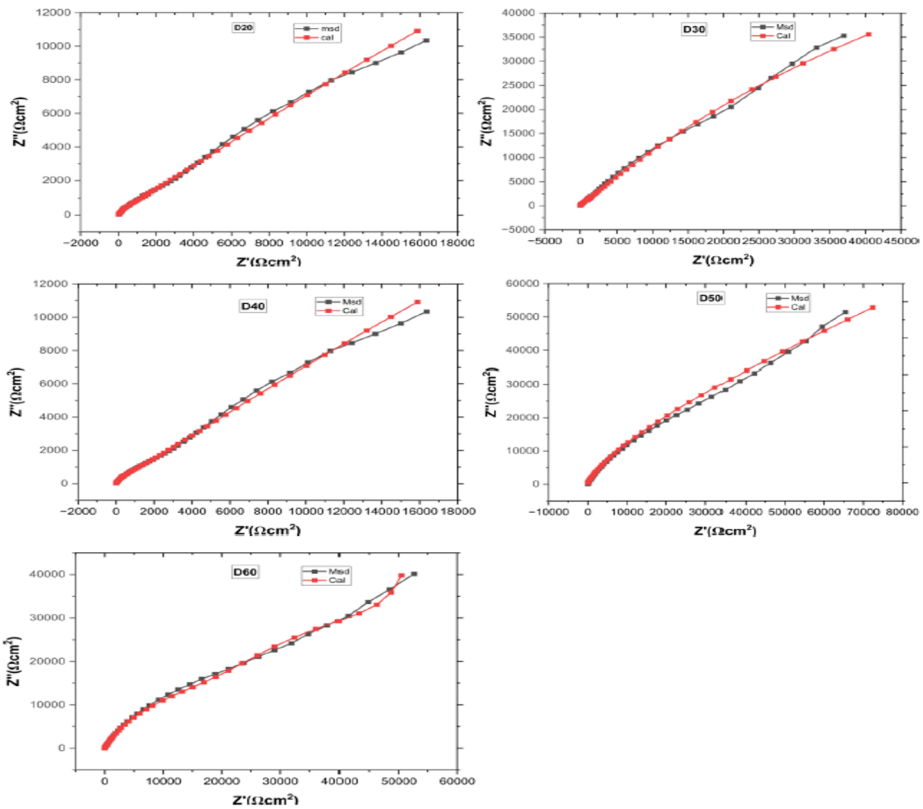

Fig. 9. Fitting Nyquist plots of MAO coated Ti6Al7Nb samples at different duty cycle.

5 Conclusion

This research investigates how the duty cycle influences the properties of PEO-coated Ti6Al7Nb. The experiments were performed at a voltage of 500 V and electrolyte solution having KOH, $Na_3PO_4 \cdot 12H_2O$, and Na_2SiO_3 mixture. The study led to the following conclusions:

From the investigation it was noted that with increase in duty cycle, coating hardness, surface roughness, pore size and coating thickness increase due to the significant quantity of energy that will be supplied to the oxidation process as the duty cycle rises, producing more vigorous discharge channels, molten oxides, and gas bubbles expelled to the surface, and

ultimately the formation of a thicker coating. Coating thicknesses of 10.19 µm and 18.73 µm were recorded at duty cycles of 20% and 60%, respectively. Surface roughness increases from 1.52 µm to 4.09 µm as duty cycle rises from 20% to 60%. Pore size also increases from 0.92 µm to 3.77 µm as duty cycle rises from 20% to 60%. 718.80 HV and 883.35 HV coating hardness were recorded at duty cycles of 20% and 60%, respectively.

Electrolyte components integrated into the PEO coating were discovered by the use of EDS spectra. Electrolyte components are evenly distributed throughout the coating.

From XRD analysis it was demonstrates that metastable anatase transition, which is dependent on temperature and time, may permanently produce the stable rutile phase. Although differences in this range depend on a number of parameters, including the surrounding environment, heating rate, impurity levels, dopant concentration, and type, the transition usually takes place within the temperature range of 600 to 1000°C.

EIS testing findings and equivalent circuits indicate that the coating consists of two layers. It was found that the inner layers of the PEO coatings played a key role in providing corrosion resistance, while the outer layer had little to no significant impact on protecting the titanium substrate from corrosion.

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