



Article Fabrication of a Protective Hybrid Coating Composed of TiO₂, MoO₂, and SiO₂ by Plasma Electrolytic Oxidation of Titanium

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Abstract: This work examined the influence of dual incorporation of MoO_2 and SiO_2 on the corrosion behavior of pure titanium treated via plasma electrolytic oxidation (PEO). To achieve this purpose, pure titanium substrate was treated via PEO in an alkaline-molybdate electrolyte without and with SiO_2 nanoparticles. The microstructural observation revealed that the addition of SiO_2 nanoparticles into the electrolyte during PEO helped to seal the structural defects in the PEO coating so that a rougher, thicker, and denser coating rich in SiO_2 was successfully obtained. From the electrochemical measurements in a 3.5 wt.% NaCl solution, the TiO_2 -MoO₂-SiO₂ hybrid coating exhibited a higher corrosion resistance than the TiO_2 -MoO₂ coating which was attributed to the sealing effect by stable SiO_2 nanoparticles.

Keywords: titanium; plasma electrolytic oxidation; hybrid coating; corrosion

1. Introduction

Owing to the compelling physical and chemical characteristics, such as high melting point, high corrosion resistance, and biocompatibility, Ti and its alloys have useful applications in aerospace, petrochemical, and biomedical industries [1–3]. As is well-known, corrosion resistance plays a vital role in the overall functionality of the metal and its alloys for industrial applications. Various active metals have been used in the past, however, titanium metal exhibits strong resistance to corrosion in both acidic and alkaline environments [4]. The electrochemical corrosion behavior of Ti metal is mainly due to the formation of a stable, protective, and strongly adherent oxide layer. Titanium can restore this film almost instantly in any environment that includes a trace of moisture or oxygen because of its strong affinity for oxygen [4]. Despite the excellent stability of titanium, like any other metal, it is susceptible to corrosion in some environments, specifically hydrofluoric acid. The types of corrosion of titanium can be classified as general corrosion, crevice corrosion, and stress corrosion cracking, anodic breakdown pitting, hydrating and galvanic corrosion [5]. Therefore, further improvements in the electrochemical stability of Ti and its alloys in corrosive environments would be needed to extend their industrial applications [6-9].

To enhance the electrochemical stability of metals and their alloys, the fabrication of inorganic layers has been done by a process called plasma electrolytic oxidation (PEO). PEO is a plasma-assisted oxidized coating used for a variety of metals such as Mg, Al, Ti, Zr, Nb, Hf, and Ta [6]. The structure and composition of the coatings produced via the PEO process are affected by various factors, which can be intrinsic or extrinsic. The intrinsic factors are related to the substrate and electrolyte composition while the extrinsic factors are connected to the oxidation time, electrolyte temperature, and electrical parameters [6,10–13]. Among them, the modification of the electrolyte composition during PEO by



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). including either metallic salts or metallic oxide particles would lead to the incorporation of stable metallic oxides into the coating layer, leading to significant improvement in the protective properties [6,14]. For example, a porous coating with high corrosion resistance was successfully deposited on Al alloy through the inclusion of ZrO₂ and MoO₂ particles into the alumina layer via PEO treatment conducted in alkaline-silicate-molybdate electrolyte [15]. Similarly, the protective properties of Mg alloy were improved by the inclusion of SiO₂ or ZrO₂ particles into the PEO coating [16].

Although the incorporation of metallic oxides into PEO coatings is often focused specifically on Al, Mg, and their alloys due to their low protective properties in comparison to Ti and Ti alloys, several research groups aimed to improve the corrosion resistance of Ti by the incorporation of several metallic oxides' particles into the TiO_2 layer made via PEO. For instance, Gowtham et al. [17] examined the influence of KOH concentration on the incorporation of ZrO_2 into the TiO₂ layer formed on pure Ti via PEO. They reported that the coating prepared with 4 g/dm^3 KOH had higher corrosion resistance than the counterpart coatings produced with 2 and 6 g/dm³ KOH. This result was attributed to the fact that the addition of 4 g/dm^3 KOH into the electrolyte would lead to the formation of the less porous coating due to the highly inert incorporation of zirconia nanoparticles. As such, Di et al. [18] demonstrated that the corrosion rate of the PEO-coated pure Ti can be reduced upon the incorporation of CeO_2 nanoparticles, which resulted in a significant reduction in the porosity of the coating. Yao et al. [19] reported that the corrosion resistance of the PEO coating made on Ti-6Al-4V alloy in a solution containing K₂ZrF₆ additive can be increased by the ZrO₂ incorporated into the coating. While Shokouhfar et al. [20] prepared a hybrid coating on pure Ti substrate via PEO utilizing electrolyte containing SiC and SiO₂ nanoparticles, the corrosion behavior of the prepared coatings was not studied.

Although several metallic oxide particles that were incorporated into the PEO layer of Ti and Ti alloys helped to improve their electrochemical, tribological, and bioactive properties to some extent [17–23], the effect made by dual incorporation of MoO₂ and SiO₂ into a TiO₂ layer on pure titanium substrate via PEO has not been reported yet. Here, the existence of Na₂MoO₄ salt and SiO₂ nanoparticles in the electrolyte during PEO treatment would lead to the incorporation of MoO₂ and SiO₂ into the TiO₂ layer under plasma conditions through a series of thermal decomposition and electrophoretic reactions. Due to the high chemical stability of MoO₂ and SiO₂, it is expected, therefore, that incorporation of MoO₂ and SiO₂ into the TiO₂ layer via PEO of pure Ti would provide a novel way to protect these materials from corrosion for longer periods. The main goal of the present work, therefore, is to fabricate a hybrid film, composed of TiO₂, MoO₂, and SiO₂, on pure titanium alloy, via PEO in a solution containing Na₂MoO₄ metallic salt and SiO₂ nanoparticles. The properties of the hybrid oxide films will be explored with regard to morphology, composition, and electrochemical behavior.

2. Experimental Procedures

Pure titanium plates with dimensions of 30 mm (L) × 20 mm (W) × 2 mm (T) were used as a substrate in the present work. Before PEO treatment, the titanium samples were polished with #1200 grit papers and cleaned in acetone. The polished samples were treated via PEO, in Baths A and B, under DC conditions at a voltage of 360 V for 20 min. Bath A consisted of 8 g/dm³ KOH and 4 g/dm³ Na₂MoO₄ while Bath B comprised 8 g/dm³ KOH, 4 g/dm³ Na₂MoO₄, and 3 g/dm³ SiO₂ nanoparticles (particle size ~20 nm). The concentration of SiO₂ nanoparticles was optimized to 3 g/dm³ to avoid the agglomeration of particles that can be happened at the higher concentrations. The morphologies of the coatings were examined by utilizing a field-emission scanning electron microscope (FE-SEM, HITACHI S-4800) connected with an EDS spectrometer. Atomic force microscopy (AFM, ToscaTM Analysis, Anton Paar, Austria) was employed to calculate the arithmetic mean roughness (R_a) and root mean square roughness (R_q). Potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) tests in a 3.5 wt% NaCl solution were used to evaluate the corrosion behavior of the PEO-coated samples. A three-electrode system consisting of a platinum sheet as a counter electrode, Ag/AgCl/sat KCl as a reference, and the coated sample as a working electrode was used. Before PDP and EIS measurements, the PEO-coated sample was left stabilizing at open circuit potential (OCP) for 5 h. The potential range during PDP tests was -0.25 to +0.4 V vs. OCP at a scan rate of 1 mV/s while frequency during EIS tests ranged from 0.1 Hz to 10^{6} Hz at 10 points per decade using 10 V rms AC signal. All tests were repeated at least three times to ensure data accuracy.

3. Results and Discussion

Figure 1 displays the surface images of the samples treated via the PEO in Baths A and B for 20 min. The coatings obtained in both baths exhibited a conventional microstructure containing well-developed microspores with a uniform distribution, which was the general morphology of the coatings formed via PEO [6,24–26]. Some white particles were found on the surface of the coating obtained in Bath B as indicated by white circles in Figure 1d–f. A spot analysis by EDS was carried out on the white area in Figure 1f (spot 'A'). The element compositions were 28.01 Si, and 56.04 O (at.%). Thus, the white area would be SiO₂ because the atomic ratio of Si to O was ~0.5. Interestingly, the incorporation of white particles into the coating obtained in Bath B helped to clog the structural defects (cracks and micropores) found in the coating obtained in Bath A. Indeed, the size of micropores decreased and the cracks disappeared upon the incorporation of SiO₂ nanoparticles. EDS area analysis on the surface of the coatings, obtained in Baths A and B, shown in Figure 2 revealed the presence of Ti, O, Mo elements in both samples coated in Baths A and B while Si element was only detected in Bath B as a result of the inclusion of SiO₂ into the electrolyte during PEO.



Figure 1. Surface morphologies of the titanium samples treated by PEO in different electrolytes (a-c) Bath A and (d-f) Bath B.



Figure 2. EDS analysis on the surface of the coatings obtained in (a) Bath A and (b) Bath B.

The AFM results shown in Figure 3 indicated that the values of R_a and R_q in the coatings obtained by PEO coatings in Baths A and B were measured to be ~0.382 and ~0.469 µm and ~0.417 and ~0.543 µm, respectively. This implies that the surface roughness of the oxide layer formed in Bath B was somewhat higher than that in Bath A. Here, it is believed that the incorporation of SiO₂ nanoparticles was responsible for such a difference in the surface roughness of the coatings obtained in Baths A and B. The micropores of the coatings are formed due to the implosion of gas bubbles during the PEO process [6]. The pore structures are related to roughness and correspond to electrical transport behavior [27,28]. When SiO₂ was incorporated into the oxide layer, the electric resistivity of the oxide layer became higher than the case of the oxide layer in Bath A [29]. Thus, the high energy of plasma discharges would be consumed, causing the formation of a porous surface with high roughness.



Figure 3. 2D and 3D micrographs obtained via AFM analysis of the titanium samples treated by PEO in different electrolytes (**a**) Bath A and (**b**) Bath B.

Figure 4 displays the cross-sectional images of the coatings obtained in Baths A and B. As shown in Figure 4, an outer porous layer and a compact inner layer were identified in both coatings. The average thickness of the coating was measured to be $9.01 \pm 0.2 \mu m$ and $11.21 \pm 0.5 \mu m$. Interestingly, the coating obtained in Bath B was denser than that of Bath A, which was attributed to the incorporation of SiO₂ nanoparticles acting as micropore blockers. This result suggested that the SiO₂ nanoparticles could help the densification of molten TiO₂ during the PEO process by reducing the structural defects.



Figure 4. Cross-sectional morphologies of the titanium samples treated by PEO in different electrolytes (**a**) Bath A and (**b**) Bath B.

Figure 5a presents the XRD patterns of the coatings obtained in Baths A and B for 20 min. Anatase, rutile, and MoO_2 were found in both coatings while SiO₂ was identified only in Bath B. The titanium peaks from the substrate also appeared. Anatase and rutile phases were formed due to the formation of TiO₂ through oxidation of the Ti substrate during PEO.



Figure 5. (a) XRD patterns of the coatings obtained in Baths A and B. (b–d) XPS spectra of Ti2p, Mo3d, and Si2p, respectively, for the coating obtained in Bath B.

To shed more light on the chemical state of the hybrid layers compounds, XPS analysis was conducted on the surface of the sample coated in Bath B. Figure 5b–d shows the high-resolution Ti 2p, Mo3d, and Si2p spectra, which were deconvoluted to identify the various components. The Ti 2p1/2 peak at 464.1 eV and Ti 2p3/2 peak at 458.2 eV are attributed to TiO₂ [30]. The deconvolution of the Mo3d peak shown in Figure 5c led to four peaks located at binding energies of ~228.9, ~229.11, ~232.2, and ~232.7 eV corresponding to the oxidation state of Mo⁴⁺ MoO₂ [31,32]. This result suggested that MoO₂ has been incorporated into the porous TiO₂ coating. The high-resolution Si2p spectrum revealed only one peak at ~103.2 eV that corresponded to SiO₂ added to the electrolyte in Bath B [33], which suggests that SiO₂ nanoparticles have been incorporated successfully into the porous TiO₂ coating.

The formation mechanism of MoO_2 and SiO_2 by PEO treatment of pure titanium in Bath B is schematically illustrated in Figure 6. Due to the strong electric field during the PEO process, MoO_4^{2-} ions produced from the ionization of Na_2MoO_4 additive in the electrolyte tended to diffuse toward the anode surface (Equation (1)). MoO_4^{2-} ions would decompose under the plasma conditions, leading to the formation of MoO_2 according to Equation (2). SiO_2 nanoparticles in the electrolyte were apt to move toward the titanium sample due to electrophoresis associated with zeta potential disparity, and they adhered firmly to the coating surface because localized evaporation of the electrolyte containing SiO_2 particles would be concentrated by high temperature during the PEO process [6,29]. Thus, the structure of oxide nodules became more complicated, leading to high surface roughness.

$$Na_2MoO_4 \rightarrow 2Na^+ + MoO_4^{2-} \tag{1}$$

$$MoO_4^{2-} \xrightarrow{\Delta} MoO_2 + O_2 + 2e^-$$
 (2)



Figure 6. Schematic illustration underlying the incorporation mechanism of MoO₂ and SiO₂ phases into the TiO₂ layer.

To explore the corrosion behavior of the coatings obtained in Baths A and B, PDP curves for the substrate and PEO coatings obtained in Baths A and B are presented in Figure 7. The obtained electrochemical parameters, such as corrosion potential (E_{corr}),

corrosion current density (i_{corr}), and cathodic Tafel slopes (β_c) are listed in Table 1. The anodic branches did not exhibit enough Tafel kinetics due to several reasons, such as surface roughness, film form, a complex composition of the coating. Therefore, the anodic region was not considered during the calculation i_{corr} due to the abnormal behavior (negative difference effect) exhibited by the metallic alloys during anodic dissolution [34,35]. In general, the high corrosion resistance can be reflected by low i_{corr} and/or high E_{corr} [6,36]. As expected, the titanium substrate exhibited the highest value of icorr and the most negative value of E_{corr} which implied a higher corrosion susceptibility for the titanium substrate in comparison to the PEO coatings. It could also be seen from Figure 7 that PDP curves for the sample coated in Bath B are shifted to a more positive region of E_{corr} compared to that in Bath A, while the *i*_{corr} for the sample formed in bath B was lower than that of Bath A. Thus, it can be stated that the coating obtained in Bath B had superior corrosion resistance to the counterpart obtained in Bath A. This result was attributed to the fact that SiO₂ nanoparticles have higher stability in the corrosive environment, the effect of small pore size and high-density coatings created by SiO₂ nanoparticles towards the corrosion properties were more predominant. Mashtalyar et al. [37] presumed that the highly chemically stable SiO₂ nanoparticles incorporated into the coating during PEO were the main reason for the improved corrosion resistance of the Mg alloy. The larger thickness of the coating obtained in Bath B in comparison to that of Bath A would also delay the movement of the corrosive ions towards the titanium substrate.



Figure 7. Potentiodynamic polarization curves of the substrate and the coatings obtained in Baths A and B after immersion in a 3.5 wt.% NaCl solution for 5 h.

Sample	E_{corr} (V)	i_{corr} (Acm ⁻²)	$ \beta_c $ (V/Decade)
substrate	-1.092	$1.12 imes 10^{-5}$	0.815
Bath A	-0.933	$2.85 imes 10^{-6}$	0.188
Bath B	-0.472	$6.35 imes10^{-10}$	0.660

Table 1. Results of PDP tests of the substrate and PEO-coated samples immersed in 3.5 wt.% NaCl solution.

To provide deep insight into the corrosion behavior of the titanium substrate and PEO coatings, the results of the EIS tests, conducted in 3.5 wt.% NaCl solution, are presented in the form of Nyquist plots (Figure 8a) and Bode plots (Figure 8b). As shown in Figure 8a, the impedance response (resistive-capacitive arc) of the titanium substrate was smaller than the coating obtained in Baths A and B, which agrees well with PDP tests, indicating that the PEO coating provided higher reliable protection against corrosion. Moreover, it can be noted that the coating obtained in Bath B had the largest arc, suggesting the best improvements in the corrosion resistance were obtained when the titanium substrate was treated via PEO utilizing a solution containing SiO₂ nanoparticles. The difference in the electrochemical response of the substrate and the coatings obtained in Baths A and B would suggest differences in their electrochemical properties. As shown in Figure 8b, the low-frequency impedance of the coating obtained in Bath B was higher than that obtained in Bath A and that of titanium substrate, indicating better corrosion resistance was successfully achieved via the inclusion of SiO_2 nanoparticles into the electrolyte during PEO. Analysis of the Bode plots shown in Figure 8b allows distinguishing of two bends on phase angle plots. Thus, EIS spectra were fitted using the equivalent electric circuit (EEC) shown in Figure 9. The ECC model shown in Figure 9a was used for fitting the EIS spectra of titanium substrate while the EEC model shown in Figure 9b was employed for fitting the EIS spectra of PEO coatings. In Figure 9b, the presence of two-time constants of resistor and capacitor were associated with properties of the inner barrier layer and the outer porous layer of PEO coatings. Here, Rs is the solution resistance between the working electrode and the reference electrode, whereas R_0 is the resistance of the outer layer in parallel with CPEo, and Ri is the resistance of the inner layer in parallel with CPEi. The Warburg element (W) was added to describe the corrosion mechanism controlled by the diffusion process [6]. The CPE_{dl} shown in Figure 9a represents the double layer capacitance between the electrolyte and the substrate while R_{ct} indicates the charge transfer resistance. The values of Rs and Rct obtained from the fitting of EIS results for titanium substrate were found to be 97.4 $\Omega \cdot \text{cm}^2$ and 2.61 \times 10⁴ $\Omega \cdot \text{cm}^2$, respectively, while the values of the CPE_{dl} parameters (*n* and *Y*) were found to be 0.79 and 4.25×10^{-7} S·Sⁿ cm²⁻, respectively. For better understanding of the EIS results for PEP coatings, the fitting results for PEO coatings are listed in Table 2. As shown in Table 2, the values of R_0 and R_i for coating obtained in Bath A were lower than those obtained in Bath B, implying that the capabilities of the coating to suppress corrosion were improved upon the incorporation of SiO₂ nanoparticles into the coatings. Furthermore, the R_i values in both coatings were higher than values of R_0 , which would be attributed to the compact structure of the inner layer [38]. The high value of R_i in the coating obtained in Bath B as compared to that obtained in Bath A would be attributed to the role of SiO_2 nanoparticles in changing the growth behavior of the inner layer during PE which resulted in the formation of a barrier inner layer with a denser structure. On the other hand, it is notable that the coating obtained in Bath B had a lower value of n_0 compared to the coating obtained in Bath A, implying a porous coating with a higher surface roughness could be deposited on the surface of pure titanium via PEO treatment in a solution with SiO_2 nanoparticles [39]. This result agreed well with the AFM results displayed in Figure 3. Similarly, the lower value of n_i for the coating obtained in Bath B would suggest that the uniformity of the inner layer of PEO coating was improved with the incorporation of SiO_2 nanoparticles into the coating. Moreover, the lower values (Y_0 and Y_i) of the coating obtained in Bath B in comparison to that in Bath A

would suggest that the area exposed to the corrosive solution was smaller in the case of the coating obtained in Bath B due to the clogging of micropores by SiO_2 nanoparticles [38–40]. Thus, it is concluded that the formation of a hybrid coating composed of TiO_2 , MoO_2 , and SiO_2 via PEO would be an efficient method to improve the protective properties of pure titanium for industrial applications. The higher surface roughness together with high corrosion resistance could be exploited to develop a new implant material for biomedical applications. However, more investigations in vitro and in vivo would be needed before usage in the biomedical field.



Figure 8. (**a**,**b**) Nyquist and Bode plots (impedance and phase angle) of the coatings obtained in Baths A and B after immersion in a 3.5 wt.% NaCl solution for 5 h where (**a**) Nyquist plots and (**b**) Bode plots.



Figure 9. The equivalent circuit models, which are used to interpret the impedance responses of the (a) titanium substrate and (b) the coatings obtained in Baths A and B.

Sample	$R_s (\Omega \cdot \mathrm{cm}^2)$	$R_{\rm o}$ ($\Omega \cdot {\rm cm}^2$)	CPE-n _o	$CPE-Y_{o}$ $(S \cdot s^{n} \cdot cm^{-2})$	$R_i \ (\Omega \cdot \mathrm{cm}^2)$	CPE-n _i	$CPE-Y_i$ $(S \cdot s^n \cdot cm^{-2})$	$W\left(S \cdot S^{1/2}\right)$
Bath A	117.2	$7.70 imes10^5$	1.00	1.65×10^{-11}	$5.18 imes10^6$	0.58	$4.92 imes 10^{-8}$	$1.20 imes 10^{-7}$
Bath B	118.4	$1.89 imes10^7$	0.92	$1.33 imes 10^{-12}$	$1.33 imes 10^8$	0.67	$4.97 imes10^{-9}$	$1.90 imes 10^{-5}$

Table 2. Results of the EIS tests of PEO-coated samples immersed in 3.5 wt.% NaCl solution.

4. Conclusions

In the present study, a hybrid coating composed of TiO₂, MoO₂, and SiO₂ was successfully deposited on the surface of pure titanium via PEO treatment in an alkaline solution containing Na₂MoO₄ and SiO₂ additives. Microstructural results showed that a less porous coating containing stable metal oxides could be obtained upon the incorporation of SiO₂ nanoparticles that act as a sealing agent of the micropores in the coating. Accordingly, although the surface of the coating became slightly rougher with the incorporation of SiO₂, the corrosion resistance of this coating was significantly improved as compared to the coating obtained in the electrolyte without SiO₂ nanoparticles.

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