Article

Improvement of Mechanical and Corrosion Properties of Commercially Pure Titanium Using Alumina PEO Coatings

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Abstract: In this study, the surface of commercially pure titanium (Cp-Ti) was covered by a 21–95 μm -thick aluminum oxide layer using plasma electrolytic oxidation. Coating characterization revealed the formation of nodular and granular α - and γ - Al_2O_3 phases with minor amounts of TiAl_2O_5 and $\text{Na}_2\text{Ti}_4\text{O}_9$ which yielded a maximum 49.0 GPa hardness and 50 N adhesive critical load. The corrosion resistance behavior in 3.5 wt.% NaCl solution of all plasma electrolytic oxidation (PEO) coatings was found to be two orders of magnitude higher compared to bare Ti substrate.

Keywords: aluminum oxide; Cp-Ti; PEO; corrosion resistance; hardness/adhesion; microstructure

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1. Introduction

Although titanium and its alloys have been extensively used in industry for a wide variety of applications (e.g., aerospace [1,2], automotive [1], medical [1], marine [2], chemical [3] and petrochemical [3] fields) due to their high strength [1], low density [3], corrosion resistance [1] and biological compatibility [3], research efforts have been devoted to enhancing the mechanical and corrosion-resistance properties of pure titanium and titanium alloys through various processing methods, including physical vapor deposition [4], plasma spraying [5], chemical vapor deposition [6], nitriding [7], laser surface engineering [8–10], atomic layer deposition [11] and plasma electrolytic oxidation (PEO) [12,13]. PEO involves the electrochemical oxidation of a metal substrate (usually Ti, Zr, Al or Mg) in an aqueous electrolyte in order to generate oxide coatings with improved wear and corrosion-resistance performance [14]. In this regard, aluminum and aluminum-titanium oxide layers have been successfully prepared on pure Ti when surface hardening and corrosion protection was required [15,16]. Similarly, another approach is to develop and maximize α - Al_2O_3 within the coatings with the aim of enhancing mechanical and corrosion properties of various alloys [17–20]. Ghafaripour [17] reported that an increase of corrosion and tribocorrosion resistance occurred after PEO processing the Al alloy substrate in an electrolyte containing α - Al_2O_3 particles. At the same time, plasma electrolysis of carbon steel with added α - Al_2O_3 in the electrolytic bath generated coatings with improved corrosion behavior [19]. Additionally, α - Al_2O_3 -based coatings on carbon steel substrate prepared by plasma electrolytic oxidation increased the protection against wear and corrosion conditions [20].

Therefore, the scope of this paper is to enhance the hardness and corrosion properties of Cp-Ti samples by increasing the α - Al_2O_3 content in the PEO layers starting from the

electrolyte composition and concentration. The novelty of the present approach is the strong influence of the electrolytic solution composition on the surface coatings with α - Al_2O_3 development on pure Ti when only sodium aluminate was employed in the PEO process, as opposed to using a mixture of sodium aluminate and sodium hydroxide solution, which led to a dominant aluminum titanate structure with lower mechanical and corrosion resistance properties of the coatings [15].

2. Materials and Methods

2.1. Coating Production

A detailed description of the oxidation process of grade 2 Cp-Ti substrates employing a unipolar, pulsed, direct-current power source at a frequency of 150 Hz was reported in our previous paper [15]. In this work, the electrolytic bath contained only NaAlO_2 at similar concentrations of 10 g/L (E1), 15 g/L (E2) and 20 g/L (E3), without additional NaOH. The new pH values were found to be 12.3, 12.8 and 13.0, those of electrical conductivity were 11.5, 18.0 and 22.5 mS/cm, respectively. During the galvanostatic mode of operation, the current density and duty cycle were fixed at 0.36 A/cm^2 and 32%, respectively. The actual value of electric voltage was increased slowly to 210, 200 and 190 V when spark discharges occurred in E1, E2 and E3 electrolyte, respectively, after which the electric current intensity was set and maintained at 2 A throughout the duration of the experiment. Three oxidation times of 10, 20 and 30 min were applied to the PEO process. The electrolyte temperature was kept at 20 °C.

2.2. Coating Characterization

The surface composition of the PEO films was determined with an Escalab 250Xi electron spectrometer (Thermo Scientific, Leicestershire, UK) using monochromatic AlK_{α} radiation at 1486.6 eV. A base pressure of 10^{-8} Pa was maintained in the ultra-high vacuum chamber during the X-ray photoelectron spectroscopy (XPS) measurements. The acquired binding energies were referenced to the C1s line at 284.8 eV of the surface adventitious carbon.

The phase composition of the layers was investigated with a Rigaku Ultima IV X-ray diffractometer (Rigaku, Tokyo, Japan) in a θ - θ configuration using a CuK_{α} ($\lambda = 1.54 \text{ \AA}$) source. The X-ray diffraction (XRD) patterns were scanned in the 2θ range of 15° – 80° with 0.05° step size and $1^{\circ}/\text{min}$ scan speed. In order to evaluate the concentration ratio of α - Al_2O_3 and γ - Al_2O_3 polycrystalline phases in the PEO layers, high-resolution diffraction patterns were recorded in the 42.6° – 46.8° 2θ range using a 0.02° step size and a $0.5^{\circ}/\text{min}$ scan speed.

Qualitative phase analysis of the X-ray diffraction patterns was performed using PDXL: integrated X-ray powder diffraction software package (Rigaku, Version 2.4) and PDF-4+ (ICDD, 2020) database. Therefore, α - Al_2O_3 (DB card number 04-013-1687), γ - Al_2O_3 (DB card number 00-050-0741), titanium aluminum oxide (TiAl_2O_5 (DB card number 04-011-9497)) and sodium titanium oxide ($\text{Na}_2\text{Ti}_4\text{O}_9$ (DB card number 04-011-2997)) were the polycrystalline phases formed during PEO processing of all Cp-Ti samples.

The layers' thicknesses were measured using an Olympus B51M metallurgical microscope (Olympus, Tokyo, Japan) at proper magnitude. The microscope was initially calibrated using a standard objective micrometer of 2 μm .

Morphological and compositional investigations were based on scanning electron microscopy (SEM) and energy dispersive X-ray (EDS) measurements performed using a field-emission scanning electron microscope (HITACHI SU5000 Schottky, Tokyo, Japan) with a nominal resolution of 1.2 nm, integrating an energy-dispersive X-ray analyzer (Oxford Instruments, Oxford, UK) working at an electron accelerating voltage of 30 kV.

The adhesion of the deposited layers to the substrates was analyzed using a scratch tester (Teer ST-30, Teer Coatings Ltd, Hartlebury, UK) equipped with a 200 μm radius diamond tip. The applied load was linearly increased from 0–100 N across the sample surface with a loading rate of 10 N/min and a total scratch distance of 10 mm.

Vickers micro-hardness measurements were performed on a microhardness tester (FM-700 Future-tech Corp, Tokyo, Japan) using a diamond Knoop indenter, under an applied load of 1000 gf and a dwell time of 10 s (to minimize the creep effect), while mean values were reported.

The polarization curves were acquired with a PARSTAT-2273 electrochemical system (Princeton Applied Research, Ametek, Inc., Berwyn, IL, USA) over a voltage range of -0.3 to $+1.0$ V at 1.0 mV/s in a conventional three-electrode cell. The corrosion resistance of the samples was tested in 3.5 wt.% NaCl solution at room temperature.

3. Results

3.1. XPS

XPS investigations were carried out to assess the bonding state of atoms at the surface. The chemical interaction between the metal substrate and NaAlO₂ electrolyte solution, as well as the effects of plasma oxidation on Ti, were addressed by acquiring the high-resolution spectra of the detected elements.

Therefore, Figure 1a–c shows the superimposed spectra of Al2p, Ti2p and Na1s for the three sample groups, indicating a similar chemical behavior. As seen below, the chemical environment of the constituent elements was unchanged during the PEO treatment.

Figure 1. XPS spectra of the three sets of samples: (a) Al2p; (b) Ti2p; (c) Na1s. Peak-fitted XPS spectra of the third set of samples prepared in E3 electrolyte: (d) Al2p; (e) Ti2p; (f) Na1s.

After curve-fitting the Al2p core-level (Figure 1d), the peak at 74.3 ± 0.2 eV was assigned to $\text{Al}_2\text{O}_3/\text{Al}(\text{OH})_3$ [21,22], which was grown on the surface of Ti samples. This is in excellent agreement with the bulk $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ composition determined by XRD analysis, discussed and illustrated in the next section. Quantitatively, each oxidation step led to an enrichment of aluminum at the surface (Table 1). Further, the Ti2p photoelectron line (Figure 1e) at 458.7 ± 0.2 eV can be attributed to Ti^{4+} in TiO_2 [21–23]. It is important to note that the low amount of Ti (Table 1) found oxidized at the surface suggests the formation of an alumina coating layer on top of the substrate surface. The Na1s core-level peak (Figure 1f) was fitted with two components located at 1071.8 ± 0.2 eV and 1073.0 ± 0.2 eV corresponding to $\text{Na}_2\text{Ti}_3\text{O}_7$ [24] and $\text{Na}_2\text{O}/\text{Na}_2\text{O}_2$ [21,25], respectively. In the absence of NaOH addition to the electrolytic solution, the oxidation process was different, as it maximized the appearance of aluminum and titanium oxides to the detriment of titanium aluminate, both on the surface and in the bulk of the PEO samples, in contrast to our previous study [15]. Therefore, the relevant changes in the PEO coatings produced only with sodium aluminate electrolyte showed an enhancement of aluminum oxide on pure Ti samples.

Table 1. Element relative concentrations (at.%).

Sample	O1s	Na1s	Al2p	Ti2p
Ti10M/E1	74.1	2.3	22.3	1.3
Ti20M/E1	71.5	5.1	22.4	1.0
Ti30M/E1	71.5	4.1	24.1	0.3
Ti10M/E2	73.5	3.8	21.9	0.8
Ti20M/E2	71.4	4.3	23.7	0.6
Ti30M/E2	69.0	3.9	26.2	0.9
Ti10M/E3	72.3	3.2	23.2	1.3
Ti20M/E3	75.0	3.5	21.0	0.5
Ti30M/E3	71.5	5.4	22.5	0.6

3.2. XRD Analysis

Figure 2a–c shows the XRD patterns of the PEO coatings obtained in E1, E2 and E3 electrolyte solutions.

The main phases present in the coatings were similar for the same duration of the PEO process, regardless of the electrolyte concentration involved. Consequently, aluminum oxide and aluminum titanate were the principal phases for a process time of 10 min while aluminum oxide dominated the growing oxide layer when a 30 min interval was applied.

Additionally, for any concentration of sodium aluminate in the electrolyte, aluminum titanate decreased with increasing aluminum oxide as a result of increased oxidation time. A comparison of the XRD lines of $\alpha\text{-Al}_2\text{O}_3$ ($2\theta = 25.6^\circ$; 62.4%) and TiAl_2O_5 ($2\theta = 26.4^\circ$; 100%) phases indicates there was a significant increase in the intensity of $\alpha\text{-Al}_2\text{O}_3$ accompanied by a decrease of TiAl_2O_5 , when an increased PEO process time was applied for samples prepared under E1, E2 and E3 electrolytes, respectively. Mass concentrations of the phases identified in the coating layers were estimated with PDXL Rietveld analysis package for pattern decomposition using the Pawley method [26]. Thus, the concentration of aluminum titanate decreased from ~65% to ~5% while the content of aluminum oxide increased from ~40% to 90% for 10 and 30 min treatment times, respectively, under E1 electrolyte solution. In the case of the E3 electrolyte, the amount of aluminum titanate decreased from ~24% to ~5%, accompanied by an increase of aluminum oxide from ~70% to ~93%, after 10 and 30 min process times, respectively.

In order to evaluate the variation of phase concentrations within the PEO coatings, the calculated ratio of $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ relative concentrations (C_α/C_γ) was performed using Equation (1) [27]:

$$I_\alpha/I_\gamma = (A_\alpha/A_\gamma)(C_\alpha/C_\gamma) \quad (1)$$

where, I_α and I_γ represent the integral intensities of $(113)_\alpha$ and $(004)_\gamma$ diffraction lines calculated from the high-resolution diffraction patterns. A_α and A_γ are the integral theoretical intensities of $(113)_\alpha$ and $(004)_\gamma$ diffraction lines.

Figure 2d–f displays the high-resolution diffractograms acquired in the angular range of 42.6° – 46.8° from which the integral intensity ratio (I_α/I_γ) of 100% intensity diffraction peaks was estimated according to (113) and (004) for α - Al_2O_3 ($2\theta = 43.35^\circ$) and γ - Al_2O_3 ($2\theta = 45.66^\circ$) phases, respectively.

Figure 2. X-ray diffraction patterns of the PEO coatings formed after 10 and 30 min process time in: (a) E1; (b) E2; (c) E3 electrolytes. High-resolution diffraction patterns of the PEO coatings formed after 10, 20 and 30 min process time in: (d) E1; (e) E2; (f) E3 electrolytes. 1: α - Al_2O_3 (DB card number 04-013-1687); 2: γ - Al_2O_3 (DB card number 00-050-0741); 3: TiAl_2O_5 (DB card number 04-011-9497); 4: $\text{Na}_2\text{Ti}_4\text{O}_9$ (DB card number 04-011-2997); S: Cp-Ti grade 2 (DB card number 04-007-9313).

The calculated value of the C_α/C_γ ratio from Equation (1) increased significantly, from ~1 to ~6 for samples treated for 10 and 30 min, respectively. It was found that for the

same period of the PEO process, there were no significant differences in the intensity ratios under increasing electrolyte concentration. Thus, the ratio values obtained at 10, 20 and 30 min electrolytic oxidation were in the ranges of 0.9–1.4, 3.4–4.4 and 5–6.5, respectively.

Qualitative phase analysis of the diffraction patterns of the PEO layers deposited on Cp-Ti substrates in electrolytes containing the same amount of sodium aluminate (10, 15 and 20 g/L) but with 2 g/L of NaOH (as performed in [15]) highlighted the existence of aluminum titanate as a dominant phase for all samples. In these layers, a depleted content of aluminum oxide was found. The experimental conditions under which the PEO treatment was performed corresponded to those used for processing the samples analyzed in this study.

The presence of aluminum oxide as a major component in the coatings prepared in E1, E2 and E3 electrolytes could be explained by the low electrical conductivity of these solutions (11.5, 18.0, 22.5 mS/cm) compared to the values obtained from the same electrolytes when 2 g/L NaOH was added (22.4, 26.0, 29.8 mS/cm) in our previous work [15]. This is why for an identical current density of 0.36 A/cm², the actual values of the working voltages applied on the samples during the process were considerably higher for the above electrolytes (E1, E2 and E3). Thus, we observed a variation of the effective voltage from 220 to 270 V when a NaOH-based electrolyte was employed [15]. In contrast, the actual voltage changed from 240 to 330 V in the absence of NaOH in the electrolytic bath. Because of this, in the outer layer, the higher working voltages reached during the PEO experiment produced a considerable temperature increase in the microarc electric discharge region, favoring the partial decomposition of TiAl₂O₅ (which is metastable) to TiO₂ and Al₂O₃ [28]. At the same time, aluminum oxide was subjected to phase transformation, leading to the formation of α - and γ -Al₂O₃ phases, while TiO₂ combined with Na₂O to form Na₂Ti₄O₉ (Na₂O·4TiO₂).

To confirm this hypothesis, diffraction data were acquired for the PEO films deposited on Ti10M/E1 and Ti30M/E1 samples, after mechanical polishing with sandpaper and removal of an approximately 10 μ m-thick surface layer. Figure 3a,b shows the results of the qualitative phase analysis for the superimposed diffraction patterns of the PEO layers before and after removing a portion of the surface. Therefore, for the Ti10M/E1 sample, we observed an enrichment of aluminum titanate accompanied with a depletion of aluminum oxide (the remaining PEO layer had a thickness of ~10 μ m) while an even higher concentration of aluminum titanate was found for the Ti30M/E1 sample. In this case, the remaining PEO layer had a thickness of ~70 μ m.

Figure 3. Qualitative phase analysis of the diffraction patterns of the Ti10M/E1 (a) and Ti30M/E1 (b) samples, before (1) and after (2) removing a 10 μ m-thick surface layer. 1: α -Al₂O₃; 2: γ -Al₂O₃; 3: TiAl₂O₅; 4: Na₂Ti₄O₉; S: Cp-Ti grade 2.

3.3. Layer Thickness

Cross-sectional optical metallography was used to observe and determine the coating layer thickness from an overall view perspective. Therefore, a direct proportionality

between the film thickness, treatment time and electrolyte concentration was observed, as expected (Figure 4). The thickness of the PEO layers varied from approximately 21.4 to 95.5 μm depending on the employed processing conditions. Moreover, it is worth mentioning that the oxide coating thickness was roughly similar for each oxidation step, confirming the uniform growth of the PEO films on Ti substrate (Figure 4, Table 2), in agreement with cross-sectional SEM results.

Figure 4. Cross-sectional metallographic images of the PEO layers for the three sets of experiments.

3.4. SEM/EDS Surface Morphology of the PEO Coatings

The surface morphology and the chemical composition of the PEO coated samples were investigated by SEM and EDS at different stages of the layer growth process. Figures 5 and 6 shows the SEM micrographs of the films obtained in E1 and E2 electrolytes after 10, 20 and 30 min treatment periods. From the low-magnification images in Figure 5a,c,e, it can be clearly seen that by increasing the oxidation time, the nodular structures on the surface increased dramatically, covering the micropores with aluminum oxide nodules, which led to a uniform and dense microstructure of the coating layer. As a consequence, being composed of Al_2O_3 , the abundance of these nodules on the surface

reduced the porosity and improved the hardness of the layers (Table 2). No cracks or fractures were visible in the investigated samples.

Table 2. Obtained thickness, microhardness and critical load values for the PEO layers after three sets of experiments.

Sample	Thickness of the Layers (μm)	HV1000 (GPa)	L _{c2} (N)
Cp-Ti	–	180, (1.8)	–
Ti10M/E1	21.4–27.2	1600, (15.7)	15
Ti20M/E1	45.9–47.9	2700, (26.5)	38
Ti30M/E1	84.1–85.5	4000, (39.2)	42
Ti10M/E2	33.4–34.8	2500, (24.5)	22
Ti20M/E2	47.9–50.0	3500, (34.3)	35
Ti30M/E2	76.2–81.0	5000, (49.0)	38
Ti10M/E3	51.7–57.2	1500, (14.7)	11
Ti20M/E3	66.9–76.9	2000, (19.6)	38
Ti30M/E3	91.4–95.5	3800, (37.3)	50

Likewise, high-magnification images (Figure 5b,d,f) showed a densification effect of aluminum oxide around the pores, resulting in a pore density decrease when longer process times were applied. A similar effect of pore reduction in the presence of $\alpha\text{-Al}_2\text{O}_3$ was reported [18,19]. The pore sizes were up to 20 μm . EDS analysis was performed in different regions of the samples to determine the chemical composition of the coatings, as shown in Figure 5b,d,f. As already stated, the highest concentration of aluminum and oxygen was in the region near the pore walls corresponding to the nodule structures. The pores and their walls contained larger amounts of titanium, coming from the substrate through the pore holes.

As expected, the tendency of aluminum oxide to conglomerate on the surface was also found when the aluminate electrolyte concentration was increased. However, the shape of Al_2O_3 surface formations changed from nodular to grain-like structures (Figure 7b,d,f).

In terms of mechanical characteristics, the surface morphology could be associated with variations in hardness and adhesion strength values, possibly caused by changes in the microstructure from nodules to grains. In this regard, the results presented in Table 2 indicate a slight decrease of microhardness values as well as an increase of scratch resistance after an increased electrolyte concentration. On the other hand, the corrosion resistance was clearly improved after PEO oxidation, regardless of the morphology of the coatings (Table 3).

Table 3. Results of potentiodynamic polarization tests in 3.5 wt.% NaCl solution at room temperature.

Sample	E _{corr} (mV)	i _{corr} (A/cm ²)	V _{corr} (mmpy)
Cp-Ti	−518	0.8×10^{-6}	102.4×10^{-4}
Ti10M/E1	−142	4.5×10^{-8}	10.0×10^{-4}
Ti20M/E1	−8.5	1.0×10^{-8}	4.5×10^{-4}
Ti30M/E1	134	0.3×10^{-8}	1.8×10^{-4}
Ti10M/E2	−247	3.0×10^{-8}	8.8×10^{-4}
Ti20M/E2	193	1.0×10^{-8}	3.5×10^{-4}
Ti30M/E2	225	0.2×10^{-8}	1.0×10^{-4}
Ti10M/E3	−253	2.0×10^{-8}	5.9×10^{-4}
Ti20M/E3	155	0.8×10^{-8}	2.6×10^{-4}
Ti30M/E3	314	0.1×10^{-8}	0.6×10^{-4}

(a) Ti10M/E1

(c) Ti20M/E1

(e) Ti30M/E1

(b) Ti10M/E1

Point scan no.	Ti (wt.%)	Al (wt.%)	O (wt.%)	Na (wt.%)
1	39.7	19.5	40.4	0.4
2	8.2	31.7	59.7	0.4
3	31.5	28.0	40.2	0.3
4	4.3	39.7	53.6	2.4
5	17.4	35.0	46.6	1.0

(d) Ti20M/E1

Point scan no.	Ti (wt.%)	Al (wt.%)	O (wt.%)	Na (wt.%)
1	9.2	39.4	50.1	1.3
2	7.1	41.8	49.8	1.3
3	29.9	24.6	44.7	0.8
4	0.5	45.8	53.2	0.5
5	2.5	46.9	49.1	1.5

(f) Ti30M/E1

Point scan no.	Ti (wt.%)	Al (wt.%)	O (wt.%)	Na (wt.%)
1	7.2	41.1	50.5	1.2
2	4.8	42.9	51.2	1.1
3	0.2	45.8	53.3	0.7
4	0.7	49.4	48.3	1.6
5	1.2	47.5	50.2	1.1

Figure 5. SEM images of the layers grown in E1 electrolyte after 10, 20 and 30 min treatment period: low magnification (a,c,e); high magnification and EDS analysis points (b,d,f); point element mass concentrations (wt.%).

(a) Ti10M/E2

(b) Ti10M/E2

Point scan	Ti	Al	O	Na
no.	(wt.%)	(wt.%)	(wt.%)	(wt.%)
1	53.3	12.5	33.8	0.3
2	20.9	30.6	48.3	0.2
3	32.8	22.1	44.4	0.6
4	4.9	58.9	35.7	0.5
5	27.7	32.2	39.5	0.6

(c) Ti20M/E2

(d) Ti20M/E2

Point scan	Ti	Al	O	Na
no.	(wt.%)	(wt.%)	(wt.%)	(wt.%)
1	12.1	36.6	50.3	1.0
2	11.2	37.2	50.6	1.1
3	31.0	26.2	42.2	0.6
4	16.2	34.3	48.8	0.7
5	0.9	51.5	47.1	0.5

(e) Ti30M/E2

(f) Ti30M/E2

Point scan	Ti	Al	O	Na
no.	(wt.%)	(wt.%)	(wt.%)	(wt.%)
1	6.3	42.4	50.0	1.3
2	19.4	28.9	51.0	0.7
3	5.3	44.6	49.3	0.9
4	1.0	49.0	48.4	1.7
5	29.7	30.4	39.4	0.6

Figure 6. SEM images of the layers grown in E2 electrolyte after 10, 20 and 30 min treatment period: low magnification (a,c,e); high magnification and EDS analysis points (b,d,f); point element mass concentrations (wt.%).

(a) Ti10M/E3

(c) Ti20M/E3

(e) Ti30M/E3

(b) Ti10M/E3

Point scan no.	Ti (wt.%)	Al (wt.%)	O (wt.%)	Na (wt.%)
1	47.4	14.5	37.6	0.5
2	27.7	21.8	49.8	0.7
3	4.6	45.1	49.5	0.8
4	1.3	45.6	51.6	1.6
5	17.5	42.5	39.4	0.6

(d) Ti20M/E3

Point scan no.	Ti (wt.%)	Al (wt.%)	O (wt.%)	Na (wt.%)
1	7.8	40.6	50.6	0.2
2	26.1	24.6	48.6	0.7
3	6.8	40.7	52.3	0.3
4	0.5	50.4	48.6	0.5
5	1.2	50.1	47.8	1.0

(f) Ti30M/E3

Point scan no.	Ti (wt.%)	Al (wt.%)	O (wt.%)	Na (wt.%)
1	7.4	41.1	50.4	1.1
2	7.7	40.5	50.7	1.1
3	15.2	32.5	51.5	0.8
4	12.5	35.4	52.0	0.2
5	5.0	47.4	46.8	0.8

Figure 7. SEM images of the layers grown in E3 electrolyte after 10, 20 and 30 min treatment period: low magnification (a,c,e); high magnification and EDS analysis points (b,d,f); point element mass concentrations (wt.%).

3.5. Cross-Sectional SEM/EDS Analysis of the Layers

The cross-sectional measurements of the coating thickness showed a strong agreement with the metallographic results given in Figure 4, both indicating a layer thickness increase from the initial $\sim 21 \mu\text{m}$ to $\sim 95 \mu\text{m}$ (Figure 8) which is an improvement by a factor of five in the oxide films generated under enhanced oxidation conditions (i.e., increased electrolyte concentration and time periods). As Figure 4 shows, the coatings were rather uniform in terms of thickness and varied up to approximately $10 \mu\text{m}$.

Figure 8. Cross-sectional images and EDS line profiles of the PEO coatings formed in E3 electrolyte after 10, 20 and 30 min treatment period. (a) Ti10M/E3; (b) Ti20M/E3; (c) Ti30M/E3.

The EDS line profiles illustrated in Figure 8 indicate the distribution of each element across the PEO layer and the metal substrate as well as all the elements of the coating. As the oxidation time increased, the substrate interface varied depending on the layer thickness, which is normal considering the increase of oxygen and aluminum content. This can be interpreted as supplementary evidence for alumina occurrence at the surface and in the bulk, as demonstrated by XPS and XRD results (Figures 1–3).

3.6. Microhardness

For the microhardness measurements of the coatings, three different points were tested for each sample with the resulting mean values given in Table 2. The standard deviation was found to be in the range of 5–10%.

Thus, it is very easy to notice the increasing tendency of hardness with the PEO process duration for every sample set. Additionally, compared to the uncoated substrate, the coatings exhibited hardness values 9 to 28 times higher than those of pure Ti. However, a peculiar behavior of microhardness with decreased values was observed when the electrolyte concentration reached its maximum. As discussed in the previous section, this mechanical response of the PEO surface layers could be attributed to the morphological changes occurring at higher concentration of aluminate and associated with grain-like surface structures (Figure 7). Nevertheless, the current hardness values are much higher than those reported in our previous work [15] in which the PEO coatings were grown without additional NaOH; this can be linked to the higher alumina content and lower aluminum titanate inside the films.

3.7. Adhesion Strength

Similar to the microhardness measurements, three values of the critical loads at which detachment of the film from the substrate (Lc2) occurred were recorded, and the average values are reported in Table 2. The standard deviation was estimated at 5–10%.

Regarding the scratch resistance of the studied samples, the coated surfaces exhibited a significant improvement after each growth cycle of the PEO process with respect to the process duration and electrolyte concentration. The critical loads ranged from 11 to 50 N, and the best scratch resistance was found for the thickest coatings at higher oxidation periods and aluminate concentrations, as presented in Table 2. When compared to the samples oxidized in NaOH conditions [15], the layers in the present study exhibited a better adhesion strength due to the high presence of alumina in the PEO films.

3.8. Potentiodynamic Polarization Tests

The corrosion resistance was assessed by means of potentiodynamic polarization measurements with a 3.5 wt.% sodium chloride solution at room temperature. By comparing the uncoated and coated surfaces of Ti substrate, one can notice decrease of corrosion current densities by two orders of magnitude compared to the bare Ti substrate (Figure 9, Table 3). Additionally, a close inspection of Table 3 reveals the correlations between process time and electrolyte concentration regarding the corrosion behavior of the coatings; hence, the corrosion resistance was enhanced by increasing the PEO duration and NaAlO₂ concentration. The best corrosion performance was achieved for the sample treated for 30 min in E3 electrolyte, which was associated with the thickest PEO film obtained (Figure 4, Table 2). A comparison of the layers prepared with [15] and without NaOH addition indicates that there was a clear improvement in the corrosion behavior of samples obtained in the absence of NaOH in the electrolytic solution (Table 3), which can also be correlated with higher α - and γ - alumina and lower aluminum titanate concentrations in the coating layers.

Figure 9. Potentiodynamic polarization curves of Cp-Ti substrate and PEO coatings formed after 10, 20 and 30 min PEO process time in: (a) E1; (b) E2; (c) E3 electrolyte.

4. Conclusions

Grade 2 commercially pure titanium was successfully processed by plasma electrolytic oxidation method using a galvanostatic regime operated at a constant current density of 0.36 A/cm² in a NaAlO₂ electrolyte solution at concentrations of 10, 15 and 20 g/L to

produce coatings with enhanced hardness and corrosion resistance as compared to bare titanium substrate.

The coating layers were mainly composed of aluminum oxide crystallized as α -Al₂O₃ and γ -Al₂O₃, with a minor contribution from TiAl₂O₅ and Na₂Ti₄O₉ phases. In the outer layers, the temperature increase in the microarc electric discharge region due to the high working voltages applied in the PEO process favored the partial decomposition of the metastable TiAl₂O₅ to TiO₂ and Al₂O₃.

The highest amount of aluminum oxide inside the coatings was higher than 90% after 30 min PEO treatment.

The obtained layer thicknesses were in the range of 21–95 μ m and increased with increasing electrolyte concentration and oxidation time.

The surface morphology of the coatings showed a conglomeration of aluminum oxide as nodules and grains, both of which reduced the pore density when increased aluminate concentration and process duration were applied.

The best scratch resistance was found for the thickest coatings at higher oxidation periods and aluminate concentrations.

All PEO coatings exhibited excellent hardness and corrosion resistance performance, far exceeding the values of pure titanium samples.

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