



Article Alloying Element Depletion and Phase Transition in Stainless Steel 304 Induced by PEO Treatment in KOH- and TaOH-Rich Electrolyte

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Abstract: Due to their lower cost and good mechanical and corrosion properties, ferrous materials such as stainless steel (SS) are commonly used as bio-materials, mainly as surgical instruments and implants. Surface treatments such as plasma electrolytic oxidation (PEO) can be a valuable tool to increase corrosion resistance and enhance the bio-compatibility of metallic materials. In this scenario, the current study evaluated the effect of electrolyte composition on the surface of SS304 submitted to PEO treatment. The variation in the amount of KOH and Ta(OH)₅ promoted significant changes in the surface characteristics, forming Fe-rich oxide plates, Ta-rich agglomerate particles, and an exposed substrate. The PEO-treated substrates were depleted of some alloying elements (Cr, Ni, and Mn), which, allied to the Ta-enrichment, affected the roughness, wettability, phase stability, micro-hardness, and corrosion resistance. All the PEO treatments presented a phase composition of single γ -Fe instead of a dual $\alpha + \gamma$ phase from the untreated substrate, which was understood in terms of the Ni_{eq}-Cr_{eq} diagram. The corrosion tests indicated that the PEO treatment significantly affected the corrosion parameters, having the presence of a non-uniform oxide layer. The findings show that it is possible to control the chemical and phase composition of SS304 material employing PEO treatment.

Keywords: plasma electrolytic oxidation; stainless steel; tantalum oxide; corrosion

1. Introduction

Among austenitic stainless steel (SS) materials, SS304 has been constantly employed in medicine and dentistry, especially as surgical devices and medical instruments, due to the favored combination of mechanical and corrosion properties [1]. The amount of Ni, Cr, and Mn are alloyed to stabilize the austenitic phase (γ -Fe) and enhance its corrosion resistance [2]. However, as a bio-tolerated metal, further surface modification is required to fulfill the requirements for use in contact with the human body. This coating on stainless steel becomes attractive due to the cost-effectiveness of the material in comparison with other metals and alloys [3]. Some earlier attempts have been made using magnetron sputtering [4], electron beam [5], mechanical attrition [6], and cold spray [7], but they still require further research regarding their feasibility for industrial applications.

Ceramic oxide coatings have often been used to protect metallic surfaces against corrosion and wear. In this sense, plasma electrolytic oxidation (PEO) applied in valve metals (e.g., Ti, Al, and Mg) can produce porous and thick oxide coatings strongly bound to the surface [8–10]. Studies have shown that PEO coating protects against corrosion, especially against body fluids. Furthermore, incorporating chemical species such as Ta₂O₅ particles has added bio-compatibility and bio-activity abilities to the surface [11]. Earlier studies have demonstrated the applicability of the PEO technique to coat Ti and



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Copyright: © 2023 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/). Mg surfaces, including bio-active and osseointegrative properties useful for bio-medical applications [12,13]. However, as Fe is not a valve metal, its oxide layer is unstable, limiting its usage in PEO treatment [14,15].

Besides this, some recent reports have achieved interesting surface properties on Febased materials after applying PEO treatment. Heo et al. [15] investigated the corrosion resistance of SS316L samples after cathodic plasma electrolytic oxidation (CPEO) in phosphoric and sulfuric acids. The authors found a double-layer structure, an outer porous Fe-rich oxide layer, and an inner dense Cr-rich oxide layer, which significantly improved the corrosion behavior of the surface. Chellappandian et al. [16] used the CPEO technique to produce N-rich coatings with multi-functional properties on ferritic steel (2.25Cr-1Mo), obtaining interesting anti-corrosion and wear properties in a 3.5% NaCl solution and Al₂O₃ counter-body, respectively. Jin et al. [17] used CPEO in a borax-rich electrolyte to produce a hard coating on SS304 samples. The authors also found a double layer, composed of an outer Fe₃O₄ layer and a compact inner multi-component layer (Cr, Ni, FeCr₂O₄, NiCr₂O₄, Fe₃O₄, and FeO), which provided superior wear resistance in the pin-on-disk tests against a ZrO₂ ball. Ma et al. [18] used PEO in a SiO₂-rich electrolyte on Q235 low-carbon steel to form a uniform Fe₃O₄ coating, which guaranteed enhanced corrosion resistance for use as ship pipes when compared to bare steel. Gui et al. [1] tuned the surface properties of 304 SS samples by applying electrolytic plasma processing (EPP) in a ZnSO₄-rich electrolyte at distinct voltages and times. Domínguez-Jaimes et al. [19] used the same PEO configuration to produce anodic organic layers on 304 SS samples using an electrolyte composed of NaAlO₂, Na2SiO3, and glycerol. The authors obtained superior corrosion properties compared to the bare material, which could positively impact its applications. And finally, Marcuz et al. [20] applied the PEO technique under a Ta-rich electrolyte on the low-carbon steel Q235 at distinct voltages. They obtained a significant improvement in corrosion resistance against 0.9% NaCl solution, which mimics the physiological environment of the human body.

Considering the great usage of metallic bio-materials and the necessity to improve their surface properties, this paper evaluated the effect of the proportion of KOH and Ta(OH)₅ on the surface of SS304 after PEO treatment. Then, the surface topography, chemical and phase composition, roughness, wettability, micro-hardness, and corrosion resistance were evaluated in terms of the chemical composition of the electrolyte.

2. Materials and Methods

Round-shaped samples (Ø19.05 mm) of SS304 (Chemical composition (wt%): 0.00–0.03 S; 0.00–0.05 P; 0.00–0.07 C; 0.00–0.11 N; 0.00–0.10 Si; 0.00–2.00 Mn; 8.00–10.50 Ni; 17.50–19.50 Cr; Fe balance) were previously ground with SiC waterproof paper and ultrasonically cleaned in water and acetone for 5 min each. PEO treatments were performed in a pulsed power source (MAO-30, Plasma Technology Ltd., Hong Kong, China), at 200 V, 1 kHz, 60%, for 10 min. The electrolyte comprised two groups: (2.0, 2.5, and 3.0) g·L⁻¹ KOH + 10 g·L⁻¹ Ta(OH)₅, and 2.0 g·L⁻¹ KOH + (10, 30, and 50) g·L⁻¹ Ta(OH)₅. The samples' terminology and the respective electrolyte composition are described in Table 1. The KOH and Ta(OH)₅ powders were purchased from Dinâmica Química Contemporânea Ltd. (Indaiatuba, SP, Brazil) and AMG Brazil Ltd. (São João del Rei, MG, Brazil), respectively, with a purity of 99.0% and a powder size of around a dozen micrometers.

Table 1. Samples' nomenclature.

Sample	Electrolyte				
2.0 KOH	$2.0 \text{ g} \cdot \text{L}^{-1} \text{ KOH} + 10 \text{ g} \cdot \text{L}^{-1} \text{ Ta}(\text{OH})_5$				
2.5 KOH	$2.5 \text{ g} \cdot \text{L}^{-1} \text{ KOH} + 10 \text{ g} \cdot \text{L}^{-1} \text{ Ta}(\text{OH})_5$				
3.0 KOH	$3.0 \text{ g} \cdot \text{L}^{-1} \text{ KOH} + 10 \text{ g} \cdot \text{L}^{-1} \text{ Ta}(\text{OH})_5$				
10 TaOH	$2.0 \text{ g} \cdot \text{L}^{-1} \text{ KOH} + 10 \text{ g} \cdot \text{L}^{-1} \text{ Ta}(\text{OH})_5$				
30 TaOH	$2.0 \text{ g} \cdot \text{L}^{-1} \text{ KOH} + 30 \text{ g} \cdot \text{L}^{-1} \text{ Ta}(\text{OH})_5$				
50 TaOH	$2.0 \text{ g} \cdot \text{L}^{-1} \text{ KOH} + 50 \text{ g} \cdot \text{L}^{-1} \text{ Ta}(\text{OH})_5$				

Surface topography was evaluated using scanning electron microscopy (SEM; JSM-6010LA, Jeol Ltd., Peabody, MA, USA) in secondary electron beam mode (SE). Chemical analysis was carried out using energy dispersive X-ray spectroscopy (EDS; Oxford Instruments Inc., Peabody, MA, USA) at 15 kV. Further chemical details were acquired using Fourier transform infrared spectroscopy (FTIR; Jasco Corp., Tokyo, Japan), in transmittance mode, with 120 scans, and a resolution of 2 cm^{-1} , and also using X-ray photoelectron spectroscopy (XPS; K-alpha instrument, Thermo Scientific Inc., Waltham, MA, USA), using AlK_{α} radiation source (1486.6 eV), a spot size of 400 μ m, step size of 200 eV and 50 eV, with resolution of 1 eV and 0.01 eV, for the survey and high-resolution scans, respectively. The quantitative results of the XPS data were collected from CasaXPS® software (version 2.3.24) from three distinct points of the sample. Structural analysis was performed using X-ray diffraction measurements (XRD; Panalytical X'Pert PRO, Westborough, MA, USA) using monochromatic CuK_{α} radiation (λ = 0.1544 nm), in the Bragg–Brentano configuration, fixed-time mode, step size of 0.02° , and collecting time of 1.6 sec. The phase composition and cell parameters were determined using the Rietveld method using GSAS/EXPGUI® software (version I) [21,22], Y₂O₃ sample for instrumental contribution, and ICSD crystallographic datasheets from metallic Fe and Fe oxide phases. Wettability was evaluated using water contact angle measurements (Ramé-Hart Instrument Corp., Succasunna, NJ, USA) using 30 µL droplets at room temperature, while average roughness (Ra) was collected using optical profilometry (Veeco Metrology, Tucson, AZ, USA) operating with a stylus radius of 12.5 µm, scan length of 2000 µm, resolution of 0.16 µm, for 20 s, and applied a load of 3 mg.

A preliminary mechanical test was carried out using Vickers micro-hardness (Shimadzu Ltd., model HMV-G, Carlsbad, CA, USA) using a load of 0.100 kgf (9.807 N) and a dwell time of 15 s. Average values were taken from ten measurements collected along the surface. Corrosion tests were performed in an Autolab PGSTAT128N potentiostat/galvanostat (Metrohm Ltd., Riverview, FL, USA) using the three-electrode configuration at room temperature with the sample set up as a working electrode, a Pt wire as a counter electrode, and an Ag/AgCl wire as a reference electrode. The electrodes were immersed in physiological 0.9% NaCl solution with a contact area limited by an O-ring $(\emptyset 1.0 \text{ cm})$. The open-circuit potential (OCP) was previously measured for 1 h. Then, the potentiodynamic polarization (PDP) test was performed from -1 to 2 V vs. OCP, with a scan rate of $1 \text{ mV} \cdot \text{s}^{-1}$ and step size of 1 mV. The obtained results were analyzed using NOVA $2.0^{\text{\tiny (B)}}$ software (version 2.1.5), which evaluated the corrosion potential (E_{corr}), corrosion current density (icorr), and polarization resistance (Rp) using Tafel's extrapolation method and the Butler–Volmer equation [20]. Finally, the electrochemical impedance spectroscopy (EIS) test was performed in the frequency range of 100 kHz to 100 mHz with ten points per decade and a signal amplitude of $V_{rms} = 10 \text{ mV}$. The corresponding Bode and Nyquist plots were fitted in the corresponding electrochemical equivalent circuit (EEC) using Zview[®] software (version 3.3).

3. Results

The current vs. time plot collected during the PEO treatment of the samples is shown in Figure 1, where a typical step decay caused by the oxidative reactions and micro-arc discharges can be noted [8]. This phenomenon originates from the formation of a dense oxide film together with water hydrolysis that generates gas bubbles containing ions arising from the aqueous solution used in the PEO treatment, and the base material, which loses metal ions in according to the following reactions [8,23]: $H_2O \leftrightarrow 2H + O^{2-}$ and $xMe + yH_2O \rightarrow Me_xO_y + yH_2$. As a result, the applied voltage along the oxide coating and the ionic environment promotes dielectric breakdown and the generation of plasma micro-discharges along the oxide layer and substrate interface, with local high temperature and pressure [24,25]. In Figure 1, it is also possible to note the maximum current values possessed a direct dependence on the electrolyte's composition, resulting from the distinct electrical conductivity provided by the number of dissolved OH⁻ ions [26]. Figure 2a displays the topography of a representative PEO-treated sample, where three distinct regions can be seen: oxide plates (red), agglomerated oxide particles (green), and exposed substrate (blue). The punctual EDS analysis (Figure 2b) and elemental EDS mapping (Figure 2c) indicated that the agglomerates were mainly composed of Ta-enriched oxides originating from the electrolyte, while the oxide plates were Fe-enriched. Similar results were obtained for the other samples of each PEO treatment condition (see Figures S1–S5 in Supplementary Material). Marcuz et al. [20] found similar curves during PEO treatment on low-carbon steel, which was related to the oxidative reaction and plasma discharges that occurred on the surface.



Figure 1. Current vs. time plot during PEO treatments as a function of KOH (a) and Ta(OH)₅ (b).

Details about the chemical composition of the oxide coating in a selected PEO-treated sample compared with the non-treated substrate are depicted in Figure 3. The 30 TaOH sample was selected due to its high amount of incorporated Ta on the surface. The XPS survey spectrum (Figure 3a) indicated a pronounced O1s peak with prominent peaks from the alloying elements of the substrate (Fe, Cr, Ni, and Mn) and the reagents from the electrolyte (Ta and K). The corresponding semi-quantitative chemical analysis (Figure 3b) indicated an extensive incorporation of C and O atoms and an atypical enrichment of the outer region of the oxide coating with some alloying elements (Cr, Ni, and Mn). The high-resolution XPS spectrum for Fe2p (Figure 3c) indicated the presence of Fe^{3+} peaks located at around 712 and 726 eV (Fe₂O₃; 66%), Fe²⁺ peaks located at around 710 and 724 eV (FeO; 32%), and Fe^0 peak located at around 707 eV (metal; 2%), while for Ta4f (Figure 3d), the depicted Ta^{5+} peaks were located at around 26 and 28 eV (Ta_2O_5 ; 45%) and the Ta⁰ peaks were located at around 22 and 23 eV (metal; 55%). The results indicated that the micro-arc discharges that occurred during the PEO treatment possibly promoted a depletion of alloying elements from the substrate in the interface with the oxide coating, while the applied voltage induced metal oxidation and Ta enrichment [27]. FTIR results (Figure 4) also showed that some organic molecules, such as water and carbon-based ones, were also absorbed into the surfaces, which naturally originated from the electrolyte.



Figure 2. Surface topography and chemical aspects of a PEO-treated sample: (**a**) SE-SEM imaging, (**b**) punctual EDS analysis, and (**c**) elemental EDS mapping.



Figure 3. XPS chemical results: (**a**) spectrum survey, (**b**) semi-quantitative chemical composition, (**c**) Fe2p high-resolution spectra, and (**d**) Ta4f high-resolution spectra.



Figure 4. FTIR profiles for each PEO-treated sample as a function of KOH (a) and Ta(OH)₅ (b).

The XRD profiles of the PEO-treated samples are depicted in Figure 5a,b, which indicate that the non-treated substrate exhibits a biphasic composition (α -Fe and γ -Fe). In contrast, the PEO-treated samples displayed a single γ -Fe phase, without evident peaks from Ta- or Fe-based oxide phases. Thus, it can be concluded that the micro-arc discharges in fact promoted some phase transition on the substrate and produced a thin oxide layer, which is undetectable in the XRD experiment. The phase transformation can be directly linked to the Cr, Ni, and Mn depletion of the substrate once they play a role in phase stabilization, as depicted in Figure 5c, corroborating the EDS and XPS chemical results. The Rietveld method successfully refined the XRD profiles (see Figure S6 and Table S1) and confirmed the presence of a single γ -Fe phase in the PEO-treated samples. The respective a_{γ} cell parameter (Figure 5d) changed randomly due to the depletion of alloying elements that have distinct atomic radius. It is well known that the $\alpha \rightarrow \gamma$ phase transition in SS304 can be induced by chemical composition [2], temperature [28], and pressure [29]; thus, the micro-arc discharges generated during the PEO treatment can provide an aggressive local environment and induce proper phase transition along the surface.

The PEO-treated samples exhibited micro-roughened surfaces (see Figure S9) with Ra values in the order of 0.2–0.6 μ m, and highly hydrophilic behavior (see Table S2) with contact angles far below 90° due to the irregular topography formed after micro-arc discharges and the incorporation of Ta, respectively [20]. The Vickers micro-hardness values (Figure 6) exhibited some dependence on the electrolyte's composition, besides the similar values indicated by the standard deviation. The tendency for decay of the micro-hardness in the PEO-treated samples with high amounts of KOH and Ta(OH)₅ can be indicative of the $\alpha \rightarrow \gamma$ phase transition once the α phase possesses greater hardness than the γ phase [30].

The OCP values (Figure S8) depicted a step decay, most likely due to the non-uniform oxide coating and the alloying elements depletion. The PDP results (Figure 7a,b) exhibited that the PEO treatment also affected the Tafel's curves, with the increase in KOH provoking a weakening of the corrosion potential. At the same time, the amount of $Ta(OH)_5$ enhanced it compared to the non-treated substrate. The E_{corr} , i_{corr} , and R_p values plot (Figure 7c) showed that low amounts of KOH and intermediary $Ta(OH)_5$ quantities provided the best chemical proportion for promoting the corrosion resistance of SS304 in saline 0.9% NaCl solution. Marcuz et al. [20] found similar results on the surface of PEO-treated low-carbon steels enriched by Ta oxide.



Figure 5. Phase composition and crystalline structure: (a) XRD profiles as function of KOH, (b) XRD profiles as function of Ta(OH)₅, (c) Ni_{eq}-Cr_{eq} diagram (Ni_{eq} = Ni + 30 C + 0.5 Mn; Cr_{eq} = Cr + Mo + 1.5 Si + 0.5 Nb + 2 Ti; wt%) [2], and (d) cell parameter variation.



Figure 6. Vickers micro-hardness values as a function of KOH and Ta(OH)₅.



Figure 7. Electrochemical results: (**a**,**b**) PDP curves as function of KOH and Ta(OH)₅, (**c**) Tafel's parameters, and (**d**) schematic diagram of micro-arc discharges during PEO treatment.

The obtained results can be understood considering the mechanism of micro-arc discharges during the PEO treatment, as illustrated in Figure 7d. The applied voltage promotes the formation of the Fe oxide layer through oxidative reactions. However, contrary to the valve metals (e.g., Ti, Al, and Mg), the Fe oxide is not firmly adhered to the surface and can be removed during the discharges. In addition, the alloying elements (Cr, Ni, and Mn) could also be depleted in the substrate by the eruption of molten metal particles, as discussed by Nie et al. [14]. This assumption could explain the non-uniform coating and the phase transition noted in the PEO-treated samples. The amount of KOH raises the electrolyte's conductivity, facilitating the appearance of micro-arc discharges and reinforcing the alloying elements depletion, while the Ta(OH)₅ increases the Ta enrichment into the coatings, contributing to the enhancement of corrosion resistance [20].

The OCP and PDP electrochemical results can be corroborated by the EIS results shown in Figure 8. To further evaluate the influence of the distinct oxide layers in the surface, the EIS results for the 10 TaOH sample condition compared to the untreated substrate are depicted. The Bode diagrams (Figure 8a,b) present an initial high impedance modulus and phase angles at low frequencies, which decreased gradually with the frequency increase. The initial impedance modulus of the PEO-treated sample remained higher than the substrate, indicating that the oxide layer successfully protected the samples against the corrosion mechanism [31]. As a result, the phase angle of the PEO-treated sample remained below the substrate, indicating a successful blocking of charged species from the electrolyte and also assuring it better corrosion resistance. The Nyquist plot (Figure 8c) indicated a large semi-circle curve for the PEO-treated sample compared to the substrate, indicating the presence of a constant phase element (CPE) in the surfaces. The zoomed plot also indicated the presence of a small semi-circle in the PEO-treated sample, which is related to the nonuniform and porous coating of the surface, as indicated by the SEM images. These results match with the EECs shown in Figure 8d, which indicated a double layer on the surface of the samples, composed of a double CPE and corrosion resistance (R) for the non-uniform

PEO-treated sample, and a CPE and R linked with a pure capacitor (C) related to the dense oxide layer for the substrate. As already seen in other studies involving similar materials with porous coatings [15], the Nyquist diagrams had an imperfect capacitor response with phase constants smaller than 1, different from the untreated substrate, which had purely capacitive responses at the interface between metal and passive film. Table 2 shows the quantitative results for the EEC fitting of all samples, where the successful adjustment of the curves in the low χ^2 value can be seen. The R values of the PEO-treated samples remained in the same order for R2 and superior in R1 when compared to the untreated substrate, indicating a superior corrosion resistance. The CPE values of the PEO-treated sample were below the substrate, expressing a minor tendency to accumulate charges, polarize the surface, and start possible degradation processes. Thus, it can be concluded that the PEO treatment promoted the formation of a double layer on the metallic surface, probably related to the Fe-rich plate and Ta-rich agglomerates as indicated in the SEM images. This double layer favored the corrosion resistance of the sample against saline 0.9% NaCl solution. This result follows some earlier studies involving the PEO treatment of non-valve metals [14,32].



Figure 8. EIS results of the 10 TaOH sample compared to the substrate: Bode diagrams (**a**,**b**), Nyquist plot (**c**), and (**d**) corresponding EECs.

Sample	Rs (Ω)	R1 (Ω)	CPE1 $(\Omega^{-1} \text{ cm}^{-2} \text{ s}^{-\alpha})$	α_1	R2 (Ω)	C1 (C)	$\frac{\text{CPE2}}{(\Omega^{-1} \text{ cm}^{-2} \text{ s}^{-\alpha})}$	α2	x ²
Substrate	171	$1.7 imes 10^5$	$1.9 imes 10^{-5}$	0.9	$13.5 imes 10^5$	$2.8 imes10^{-5}$	-	-	$2.0 imes 10^{-4}$
2.0 KOH	$2 imes 10^3$	$6 imes 10^6$	$4.1 imes10^{-6}$	0.8	$3.1 imes 10^5$	-	$1.9 imes10^{-6}$	0.5	$3.4 imes10^{-4}$
2.5 KOH	$8.3 imes10^4$	$6.7 imes 10^7$	$2.8 imes10^{-7}$	0.4	$5.2 imes 10^5$	$1.2 imes 10^{-6}$	-	-	$9.1 imes10^{-5}$
3 KOH	160	$6.7 imes 10^5$	$2 imes 10^{-5}$	0.8	$2.4 imes10^4$	-	$4.3 imes10^{-5}$	0.8	$1.8 imes10^{-4}$
10 TaOH	$2 imes 10^3$	$6 imes 10^6$	$4.1 imes10^{-6}$	0.8	$3.1 imes 10^5$	-	$1.9 imes10^{-6}$	0.5	$3.4 imes10^{-4}$
30 TaOH	$5 imes 10^3$	$2 imes 10^5$	$1.4 imes10^{-6}$	0.7	$1 imes 10^{20}$	-	$1.8 imes10^{-6}$	0.4	$5.8 imes10^{-5}$
50 TaOH	$4.4 imes10^4$	$2 imes 10^7$	$2.9 imes10^{-7}$	0.5	$6.2 imes10^4$	-	$5.2 imes10^{-7}$	0.5	$7.6 imes10^{-5}$

Table 2. EIS quantitative results of the samples.

4. Conclusions

SS304 samples were submitted to PEO treatments employing several KOH and Ta(OH)₅ concentrations. Subsequent analysis revealed that PEO-treated specimens displayed a heterogeneous coating comprising Ta-rich agglomerates, iron oxide plates, and an exposed substrate. Chemical analyses confirmed successful Ta enrichment within the iron oxide coatings, resulting in the depletion of certain alloying elements (Cr, Ni, and Mn) from the substrate. Consequently, the phase composition of the samples changed from a biphasic ($\alpha + \gamma$) structure to a single γ -iron phase. The quantity of KOH and Ta(OH)₅ had impacts on surface roughness, wettability, micro-hardness, and induced varied corrosion behaviors in a saline environment. EIS results revealed the presence of a double layer associated with Ta- and Fe-rich regions within the oxide layer, effectively enhancing the corrosion resistance of the samples. Thus, this study demonstrates the feasibility of inducing chemical and phase composition alterations in SS304 by precisely controlling the electrolyte's composition during PEO treatment, offering potential applications across a broad spectrum of industries.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/cryst13101480/s1, Figure S1: SEM imaging of the PEO-treated samples as function of KOH; Figure S2: SEM imaging of the PEO-treated samples as function of TaOH; Figure S3: Elemental EDS mapping of the PEO-treated samples as function of KOH; Figure S4: Elemental EDS mapping of the PEO-treated samples as function of TaOH; Figure S5: Semi-quantitative EDS chemical composition acquired in area mode from the region illustrated in Figures S3 and S4; Figure S6: Refined XRD profiles; Figure S7: Roughness values of the PEO-treated samples; Figure S8: OCP curves of the PEO-treated samples; Table S1: Merit parameters of the Rietveld refinements; Table S2: Wettability of the PEO-treated samples.

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Data Availability Statement: The data can be shared under request to the e-mail address: diego.correa@unesp.br.

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References

- 1. Gui, W.; Lin, J.; Hao, G.; Qu, Y.; Liang, Y.; Zhang, H. Electrolytic Plasma Processing-an Innovative Treatment for Surface Modification of 304 Stainless Steel. *Sci. Rep.* **2017**, *7*, 308. [CrossRef] [PubMed]
- Zhang, S.; Wang, Q.; Yang, R.; Dong, C. Composition Equivalents of Stainless Steels Understood via Gamma Stabilizing Efficiency. Sci. Rep. 2021, 11, 5423. [CrossRef] [PubMed]
- Peng, C.; Izawa, T.; Zhu, L.; Kuroda, K.; Okido, M. Tailoring Surface Hydrophilicity Property for Biomedical 316L and 304 Stainless Steels: A Special Perspective on Studying Osteoconductivity and Biocompatibility. ACS Appl. Mater. Interfaces 2019, 11, 45489–45497. [CrossRef] [PubMed]
- Chabanon, A.; Michau, A.; Schlegel, M.L.; Gündüz, D.C.; Puga, B.; Miserque, F.; Schuster, F.; Maskrot, H.; Pareige, C.; Cadel, E.; et al. Surface Modification of 304L Stainless Steel and Interface Engineering by HiPIMS Pre-Treatment. *Coatings* 2022, 12, 727. [CrossRef]
- Rabadzhiyska, S.; Kotlarski, G.; Shipochka, M.; Rafailov, P.; Ormanova, M.; Strijkova, V.; Dimcheva, N.; Valkov, S. Duplex Surface Modification of 304-L SS Substrates by an Electron-Beam Treatment and Subsequent Deposition of Diamond-like Carbon Coatings. *Coatings* 2022, 12, 401. [CrossRef]
- 6. Thangaraj, B.; TS Nellaiappan, S.N.; Kulandaivelu, R.; Lee, M.H.; Nishimura, T. A Facile Method to Modify the Characteristics and Corrosion Behavior of 304 Stainless Steel by Surface Nanostructuring toward Biomedical Applications. *ACS Appl. Mater. Interfaces* **2015**, *7*, 17731–17747. [CrossRef]
- 7. Fahad, N.D.; Radhi, N.S.; Al-Khafaji, Z.S.; Diwan, A.A. Surface Modification of Hybrid Composite Multilayers Spin Cold Spraying for Biomedical Duplex Stainless Steel. *Heliyon* **2023**, *9*, e14103. [CrossRef]
- 8. Simchen, F.; Sieber, M.; Kopp, A.; Lampke, T. Introduction to Plasma Electrolytic Oxidation—An Overview of the Process and Applications. *Coatings* **2020**, *10*, 628. [CrossRef]
- Torrento, J.E.; Grandini, C.R.; Sousa, T.S.P.; Rocha, L.A.; Gonçalves, T.M.; Sottovia, L.; Rangel, E.C.; Cruz, N.C.; Correa, D.R.N. Bulk and Surface Design of MAO-Treated Ti-15Zr-15Mo-Ag Alloys for Potential Use as Biofunctional Implants. *Mater. Lett.* 2020, 269, 127661. [CrossRef]
- 10. Moga, S.; Malinovschi, V.; Marin, A.; Coaca, E.; Negrea, D.; Craciun, V.; Lungu, M. Mechanical and Corrosion-Resistant Coatings Prepared on AZ63 Mg Alloy by Plasma Electrolytic Oxidation. *Surf. Coat. Technol.* **2023**, *462*, 129464. [CrossRef]
- 11. Wang, Y.; Yu, H.; Chen, C.; Zhao, Z. Review of the Biocompatibility of Micro-Arc Oxidation Coated Titanium Alloys. *Mater. Des.* **2015**, *85*, 640–652. [CrossRef]
- 12. Kuroda, P.A.B.; Rafael, F.M.; Rossi, M.C.; Correa, D.R.N.; Grandini, C.R.; Afonso, C.R.M. Influence of Zr Addition in β Ti-25Ta-XZr Alloys on Oxide Formation By. *Vacuum* **2023**, *217*, 112541. [CrossRef]
- 13. Chaharmahali, R.; Fattah-alhosseini, A.; Esfahani, H. Increasing the In-Vitro Corrosion Resistance of AZ31B-Mg Alloy via Coating with Hydroxyapatite Using Plasma Electrolytic Oxidation. *J. Asian Ceram. Soc.* **2020**, *8*, 39–49. [CrossRef]
- 14. Nie, X.; Cai, R.; Zhao, C.; Sun, J.; Zhang, J.; Matthews, D.T.A. Advancement of Plasma Electrolytic Oxidation towards Non-Valve Metals. *Surf. Coat. Technol.* **2022**, 442, 128403. [CrossRef]
- 15. Heo, J.; Lee, J.; Kim, S.; Alfantazi, A.; Cho, S.O. Corrosion Resistance of Austenitic Stainless Steel Using Cathodic Plasma Electrolytic Oxidation. *Surf. Coat. Technol.* **2023**, *462*, 129448. [CrossRef]
- 16. Chellappandian, R.; Jena, G.; Neelakantan, L.; Adlakha, I. Development of Multi-Functional Coating for Ferritic Steels Using Cathodic Plasma Electrolytic Nitriding. *JOM* **2023**, *7*, 9–13. [CrossRef]
- 17. Jin, X.; Wang, B.; Xue, W.; Du, J.; Wu, X.; Wu, J. Characterization of Wear-Resistant Coatings on 304 Stainless Steel Fabricated by Cathodic Plasma Electrolytic Oxidation. *Surf. Coat. Technol.* **2013**, 236, 22–28. [CrossRef]
- 18. Ma, C.; Liu, J.; Zhu, X.; Xue, W.; Yan, Z.; Cheng, D.; Fu, J.; Ma, S. Anticorrosive Non-Crystalline Coating Prepared by Plasma Electrolytic Oxidation for Ship Low Carbon Steel Pipes. *Sci. Rep.* **2020**, *10*, 15675. [CrossRef]
- Domínguez-Jaimes, L.P.; Arenas, M.A.; Conde, A.; Escobar-Morales, B.; Álvarez-Méndez, A.; Hernández-López, J.M. Growth of Anodic Layers on 304L Stainless Steel Using Fluoride Free Electrolytes and Their Electrochemical Behavior in Chloride Solution. *Materials* 2022, 15, 1892. [CrossRef]
- Marcuz, N.; Ribeiro, R.P.; Rangel, E.C.; Cristino, N.; Rafael, D.; Correa, N. The Effect of PEO Treatment in a Ta-Rich Electrolyte on the Surface and Corrosion Properties of Low-Carbon Steel for Potential Use as a Biomedical Material. *Metals* 2023, 13, 520. [CrossRef]
- 21. Toby, B.H. EXPGUI, a Graphical User Interface for GSAS. J. Appl. Crystallogr. 2001, 34, 210–213. [CrossRef]
- Larson, A.C.; Von Dreele, R.B. General Structure Analysis System (GSAS); Los Alamos National Laboratory Report LAUR; Los Alamos National Laboratory: Los Alamos, NM, USA, 2004; pp. 86–748.
- 23. Hutsaylyuk, V.; Student, M.; Posuvailo, V.; Student, O.; Sirak, Y.; Hvozdets'kyi, V.; Maruschak, P.; Veselivska, H. The Properties of Oxide-Ceramic Layers with Cu and Ni Inclusions Synthesizing by PEO Method on Top of the Gas-Spraying Coatings on Aluminium Alloys. *Vacuum* **2020**, *179*, 109514. [CrossRef]
- 24. Schwartz, A.; Kossenko, A.; Zinigrad, M.; Danchuk, V.; Sobolev, A. Cleaning Strategies of Synthesized Bioactive Coatings by PEO on Ti-6Al-4V Alloys of Organic Contaminations. *Materials* **2023**, *16*, 4624. [CrossRef] [PubMed]

- Orsetti, F.R.; Bukman, L.; Santos, J.S.; Nagay, B.E.; Rangel, E.C.; Cruz, N.C. Methylene Blue and Metformin Photocatalytic Activity of CeO2-Nb2O5 Coatings Is Dependent on the Treatment Time of Plasma Electrolytic Oxidation on Titanium. *Appl. Surf. Sci. Adv.* 2021, *6*, 100143. [CrossRef]
- Molaei, M.; Nouri, M.; Babaei, K.; Fattah-Alhosseini, A. Improving Surface Features of PEO Coatings on Titanium and Titanium Alloys with Zirconia Particles: A Review. *Surf. Interfaces* 2021, 22, 100888. [CrossRef]
- Sikdar, S.; Menezes, P.V.; Maccione, R.; Jacob, T.; Menezes, P.L. Plasma Electrolytic Oxidation (PEO) Process—Processing, Properties, and Applications. *Nanomaterials* 2021, 11, 1375. [CrossRef]
- Carvalho, C.E.R.D.; Costa, G.M.D.; Cota, A.B.; Rossi, E.H. High Temperature Oxidation Behavior of AISI 304 and AISI 430 Stainless Steels. *Mater. Res.* 2006, *9*, 393–397. [CrossRef]
- 29. Nataraj, M.V.; Swaroop, S. Deformation-Induced Phase Transition and Nanotwins in SS 304 Steel during Cryogenic Laser Shock Peening without Coating. J. Mater. Res. Technol. 2022, 19, 2611–2622. [CrossRef]
- Dewangan, S.; Mishra, S. Analysing Microstructure and Hardness of SS-304 under Annealed, Normalized, Quenched and Step Cooled Conditions. J. Inst. Eng. Ser. D 2023, 104, 1–14. [CrossRef]
- Revilla, R.I.; Wouters, B.; Andreatta, F.; Lanzutti, A.; Fedrizzi, L.; De Graeve, I. EIS Comparative Study and Critical Equivalent Electrical Circuit (EEC) Analysis of the Native Oxide Layer of Additive Manufactured and Wrought 316L Stainless Steel. *Corros. Sci.* 2020, 167, 108480. [CrossRef]
- Fattah-alhosseini, A.; Molaei, M.; Babaei, K. The Effects of Nano- and Micro-Particles on Properties of Plasma Electrolytic Oxidation (PEO) Coatings Applied on Titanium Substrates: A Review. Surf. Interfaces 2020, 21, 100659. [CrossRef]

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