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Sealing of porous titanium oxides produced by plasma electrolytic oxidation

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Abstract

Plasma electrolytic oxidation (PEO) is a powerful technique allowing the formation of ceramic coatings with high degree of functionalization. Plasma-chemical interactions, resulting from the application of a high voltage in a conductive electrolyte, like 0.5 M NaOH, favour the development of a porous surface which deserves to be sealed to obtain proper corrosion resistance. In the present work the effect of temperature, employed during sealing in calcium acetate, is investigated finding 85 °C an optimum temperature to allow pores closure. Furthermore, a comparison with sealing performed in hot water is presented, demonstrated similar sealing efficiency. Scanning electron microscope and electrochemical impedance spectroscopy are the tools selected to investigate sealing effects. Impedance spectra are fitted according to feasible electrochemical equivalent circuits finding two time constants when applied to sealed samples indicative of the presence of barrier and porous layer respectively.

Keywords: calcium acetate; hot water; PEO; sealing; sodium hydroxide

1 INTRODUCTION

Plasma electrolytic oxidation is a process which allows to form an oxide film on a metal surface with excellent corrosion resistance. [1–3] However, the surface morphology of the oxide layer is irregular and porous, and doesn't stop effectively the diffusion of aggressive substances towards the substrate, making the corrosion resistance properties highly dependent of only the barrier layer present above the metallic substrate. One solution to overcome this drawback is the employment of a sealing step, whose purpose is to fill the porosities and form a more compact oxide. Sealing has demonstrated its effectiveness on various metals and metal alloys, such as aluminum [4,5] and magnesium. [6,7] Sealing can be performed chemically or electrochemically, in the present paper the former will be investigated. Chemical sealing is widely applied with good results but it's often too much energetically expensive and time consuming, like HWS (Hot Water Sealing) on aluminum [8] requiring a huge amount of thermal power to be provided to the system. To overcome this limitation few exceptions were advanced, like cold nickel fluoride sealing. [9] However, the use of fluoride makes the process quite expensive as a proper selection of the materials composing the implant should be done, moreover the use of nickel salts is subject of intense regulation. [10]

In the present paper the effectiveness of some common chemical sealing techniques as hot water (HWS) and calcium acetate (CAS) is evaluated on titanium oxides produced by PEO carried out in 0.5 M NaOH. Surface improvements will be evaluated according to electrochemical impedance spectroscopy (EIS) where the parameters extracted according to the use of feasible electrochemical equivalent circuit will be validated according to scanning electron microscope images (SEM).

2 MATERIALS AND METHODS

Sample preparation

All experiments were performed using square coupons of commercially pure (CP) Ti Grade 2, with sizes of 10 mm x 10 mm x 1.6 mm and active exposed area 1 cm². Before anodization, all samples were accurately cleaned to remove any form of dirt present on the surface by ultrasonic washing in ethyl alcohol for 5 minutes followed by rinsing in distilled water. Subsequently, samples were mechanically polished with 100, 320 and 600 grit SiC emery papers, to remove the oxide layer and expose the metallic Ti followed by subsequent washing in ethanol and distilled water.

Anodization

Samples were anodized in a NaOH 0.5 M solution, using a power supply Asterion AST 751 in potentiostatic regime, considering a treatment duration of 320 s with an imposed potential value of 160 V. The applied waveform consists of a 60% in anodic regime, followed by 40% in cathodic regime; the intensity of the cathodic peak is 7% with respect the anodic one. The frequency is fixed at 1000 Hz. This duty cycle has been previously investigated [11] and it was considered to be particularly advantageous for corrosion resistance purposes. A magnetic stirrer with a 200 rpm rate was employed to ensure chemical and temperature uniformity of the anodizing bath.

Sealing procedure

Anodic titanium oxide samples were sealed using two different sealants: calcium acetate 10 g/L (CAS), and hot water sealing (HWS). CAS was performed at 25 °C, 50 °C and 85 °C to assess the temperature influence on the process; HWS was carried out at 100 °C. Magnetic stirring was employed to ensure homogeneity of the sealing solution during the processes accounting for a duration of 30 minutes.

Electrochemical test

Electrochemical tests were carried out in the form of EIS using a three-electrode system employing a silver-silver chloride reference electrode (SSC) and an Amel Pt counter electrode in an acidic solution H_2SO_4 0.5 M, which represents a mild corrosion environment for anodized titanium. The potentiostat was a MetroOhm Autolab Potentiostat M204 equipped with the software Nova® 2.1.4 for electrochemical circuit fitting. The corrosion potential, E_{corr} , was stabilized for 30 minutes for every electrochemical test. The sinusoid with amplitude of $10 \text{ mV}_{\text{rms}}$ was applied from 10 mHz up to 100 KHz. collecting 10 points per decade.

3 RESULTS AND DISCUSSION

Determination of CAS quality was assessed by EIS. As it is possible to observe in Figure 1, as the sealing temperature increases, a progressive increase of the phase angle around 10^2 - 10^3 Hz is experienced. Furthermore, the semicircle observed in the Nyquist plot increases its diameter, suggesting that a higher impedance to charge transfer was encountered with the use of higher temperature.

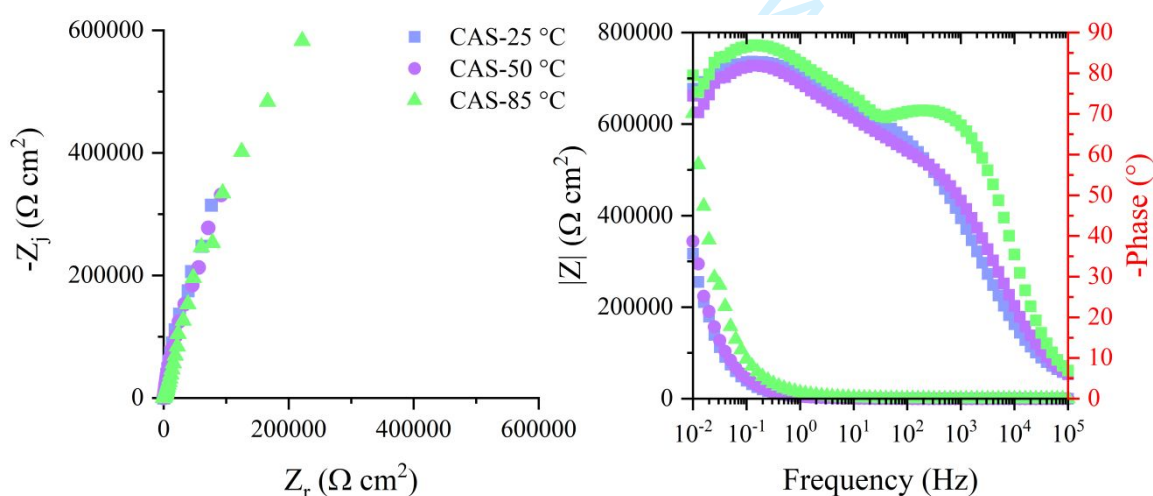
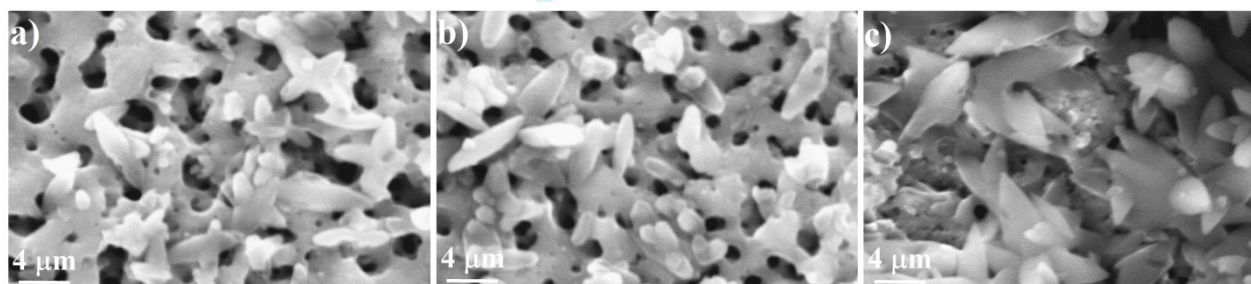


Figure 1. Nyquist **a)** and Bode **b)** plots of PEO treated oxides sealed in calcium acetate (CAS) at 25, 50 and 85 °C

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4 Going back to current voltage offset, pore closure provided by CAS enhances capacitive
5 effects responsible to raise the phase angle according to charge separation. SEM images were
6 acquired and collected in Figure 2 for samples sealed at different temperatures, corroborating
7 the previous hypothesis. Substantial modifications of the spectrum highlighted in Figure 1 b)
8 were observed only for chemical sealing performed at 85 °C, a sample presenting a rather
9 dens distribution of deposits filling oxide pores (Figure 2 c)). This evidence can find
10 justification in terms of the thermal energy required for the hydration reactions to occur
11 within pores according to:



12 Hydration products are voluminous, so they are able to fill the porosities. Moreover, as
13 $\text{Ca}(\text{OH})_2$ has a low solubility product in water ($K_{ps} = 5.5 \cdot 10^{-6}$), it precipitates into the pores
14 very quickly.



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42 **Figure 2.** SEM images of samples undergoing CAS at a) 25 °C, b) 50 °C and c) 85 °C

43 Being the solubility of calcium hydroxide in water an exothermic process, its stability can be
44 enhanced in service conditions exploiting relatively high temperatures, making the sealing
45 procedure more efficient. In particular, knowing the high aggressivity of hot concentrated
46 sulfuric acid on grade 2 titanium [11,12] inducing corrosion rates of several mm/year even in
47 presence of anodic coatings [13] the reaction between $\text{Ca}(\text{OH})_2$ and H_2SO_4 can favor the
48 formation of a calcium sulfates skin. Depending on its uniformity and formation kinetics the
49 reaction between the $\text{Ca}(\text{OH})_2$ deposits and the acidic environment can be eventually stopped.

Knowing the benefits obtained using higher temperatures in CAS, performance of the latter sealing treatment, carried out at 85 °C, were compared with the one of HWS through impedance spectra plotted in Figure 3. As it is possible to observe, even the use of HWS seems to be effective in promoting the rise of a shoulder in the high frequency region of the Bode spectrum, however showing a capacitive behavior limited to a thinner frequency range. On the other hand, when CAS at 85°C is employed, the phase angle at high frequency reaches typical values shown in the low frequency region of the spectrum.

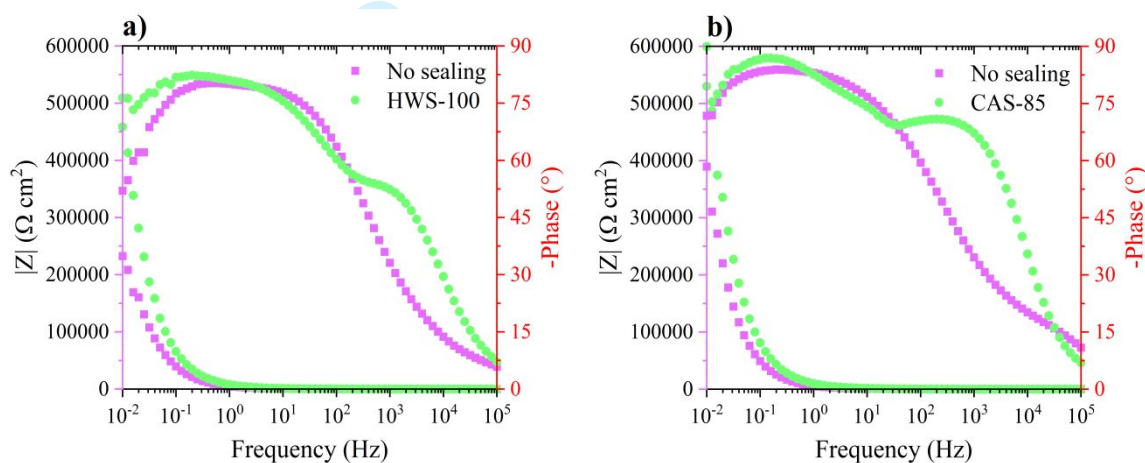


Figure 3. Impedance spectra of sample sealed in **a)** hot water (HWS), **b)** calcium acetate (CA)

Electrochemical equivalent circuits were used to fit Nyquist and Bode spectra for samples tested in both HWS and CAS at 85 °C. Unsealed samples always demonstrated a single time constant according to their passive behavior in the testing solution, where circuit elements highlighted by the letter “b” are indicative of the description of the barrier layer properties. [11,14] As a consequence, the circuit highlighted in Figure 4 a) was used, where the addition of a finite space Warburg element (T) had the aim in describing finite diffusive phenomena of electroactive species approaching the porous electrode. [15] Constant phase elements (CPE) where sometimes used in substitution of capacitors to account for surface inhomogeneity related to roughness and porosity. [16] When a sealing treatment was applied the two time

constants generally encountered were fitted selecting a “ladder” circuit instead of a simple Randles one. This choice was a direct consequence of the shoulder highlighted in Figure 3 a) becoming a peak in case of CAS at 85 °C (Figure 3 b)). In fact, as the resistance of the porous layer increases, the time constant describing the process manifests (as the product RC is no more negligible) requiring the addition of a CPE_p and a R_p for porous layer description. Moreover, as even barrier layer properties were improved by the sealants, charge separation resulted in a higher phase angle at low frequency requiring the use a capacitor (C_b) instead of a CPE.

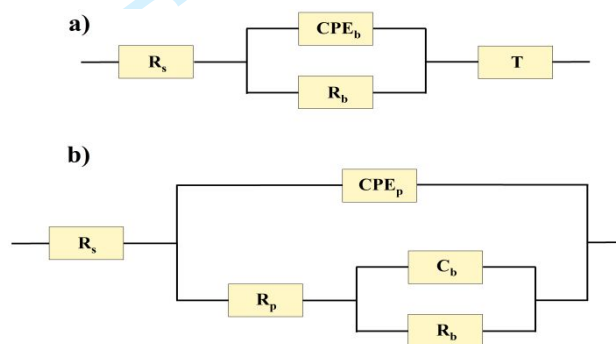


Figure 4. Electrochemical equivalent circuits used to fit the unsealed **a)** and sealed sample **b)**

Table 1 collects all the parameters extracted from fitting procedure of the spectra related to unsealed and samples sealed in CAS at 85 °C and HWS at 100 °C. For sake of brevity, solution resistance R_s was avoided from the Table, however its values were always constant at about 12 Ω . Fitting quality was evaluated according to R^2 values, corresponding respectively to $4.2 \cdot 10^{-3}$ for unsealed samples (both CAS and HWS), to $3.6 \cdot 10^{-2}$ for sample CAS-85 and $7.3 \cdot 10^{-2}$ for sample HWS-100.

Table 1. Parameters extracted from fitting of experimental spectra collected in Figure 3 according to circuits in Figure 4.

Sample	R_b ($\Omega \text{ cm}^2$)	C_b (F cm^{-2})	Y_0^b ($\text{S}\cdot\text{s}^n/\text{cm}^2$)	n_b	R_D ($\Omega \text{ cm}^2$)	R_p ($\Omega \text{ cm}^2$)	Y_0^p ($\text{S}\cdot\text{s}^n/\text{cm}^2$)	n_p
Un.-CAS	$2.9 \cdot 10^5$	/	$59.7 \cdot 10^{-6}$	0.887	1703	/	/	/
CAS-85	$8.3 \cdot 10^6$	$6.51 \cdot 10^{-6}$	/	/	/	$2.7 \cdot 10^4$	$13.1 \cdot 10^{-6}$	0.815
Un.-HWS	$2.6 \cdot 10^5$	/	$44.5 \cdot 10^{-6}$	0.907	787	/	/	/
HWS-100	$5.4 \cdot 10^6$	$7.45 \cdot 10^{-6}$	/	/	/	$2.4 \cdot 10^3$	$15.9 \cdot 10^{-6}$	0.836

For unsealed samples (Un.-CAS and Un.-HWS), the Brug's equation was used to convert

CPE parameters to an effective capacitance C_{eff} (see Equation 1):

$$C_{eff} = Y_0^n \left(\frac{1}{R_s} + \frac{1}{R_b} \right)^{\frac{n-1}{n}} \quad (1)$$

$$C_{eff} = \frac{\epsilon_r \epsilon_0 A}{d} \quad (2)$$

A value of 89.2 and 61.8 $\mu\text{F}\cdot\text{cm}^{-2}$ were extracted for sample denoted Un.-CAS and Un.-HWS, respectively. Using Equation 2, thickness of the dielectrics, d , was extracted, obtaining 198 nm and 286 nm for Unsealed-CAS and Unsealed-HWS (the dielectric constant for TiO_2 was fixed equal to 100 [17]) indicative of the barrier layer thickness of PEO oxides produced at such a forming voltage. Application of Equation 2 to capacitances C_b related to barrier layer properties of sealed coatings determined a rather thicker barrier layer, 2.72 μm and 2.37 μm for CAS-85 and HWS-100, respectively. These values suggest that hydration products during the 30 minutes sealing treatment penetrated through the bottom of the coating forming a dense thick dielectric region.

Finally, application of above equations to the porous region determined a thickness of 694 nm and 619 nm for CAS-85 and HWS-100, respectively.

Considering the sum of the barrier layer and porous layer thicknesses extracted from EIS parameters it is possible to determine a total thickness of the coatings around 3 μm , perfectly in agreement with the oxide cross section image highlighted in Figure 5.

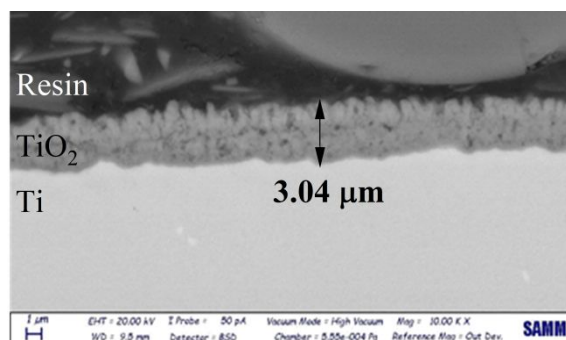


Figure 5. SEM image of oxide cross section undergoing CAS-85

According to electrochemical parameters previously extracted, a sealing efficiency can be obtained according to Equation 3:

$$\eta = \frac{R_{tot} - R_0}{R_{tot}} \cdot 100 \quad (3)$$

where R_{tot} refers to the sum of barrier and porous layer resistances, while R_0 is the barrier layer resistance of the unsealed coating. An efficiency of 96.5 and 95.1 % was verified on CAS-85 and HWS-100 indicative of the fact that both treatments were effective as sealant.

4 CONCLUSIONS

Plasma electrolytic oxidation favours titanium surface conversion generating porous oxides requiring an appropriate sealing treatment to obtain desirable corrosion resistance properties in harsh environments. Hot water and calcium acetate were the two sealants tested in the present research, finding improved properties if higher temperatures are employed. In particular, using calcium acetate at 85 °C resulted in the formation of $\text{Ca}(\text{OH})_2$ filling almost all the oxide porosity as it was demonstrated thanks to SEM observations. Electrochemical impedance spectroscopy was used to evaluate surface modifications, verifying the rise of a shoulder in the high frequency region of the phase angle, indicative of charge separation according to pores closure. According to resistances extracted from the use of electrochemical equivalent circuits it was possible to define an efficiency parameter reaching values close to 95 % for both calcium acetate performed at 85 °C and hot water at 100 °C.

CONFLICT OF INTEREST

The authors declare no financial or commercial conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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