Sealing of porous titanium oxides produced by plasma electrolytic oxidation

Luca Casanova | Nicola Belotti | MariaPia Pedeferri | Marco Ormellese

Department of Chemistry, Materials and Chemical Engineering “G. Natta”, Politecnico di Milano, Milano, Italy

Correspondence
Marco Ormellese, Department of Chemistry, Materials and Chemical Engineering “G. Natta”, Politecnico di Milano, 20131 Milan, Italy.
Email: marco.ormellese@polimi.it

Abstract
Plasma electrolytic oxidation is a powerful technique allowing the formation of ceramic coatings with a high degree of functionalization. Plasma–chemical interactions, resulting from the application of a high voltage in a conductive electrolyte, like 0.5 M NaOH, favor 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 as an optimum temperature to allow pores closure. Furthermore, a comparison with sealing performed in hot water is presented, which 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 (PEO) is a process that allows the formation of 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 does not stop effectively the diffusion of aggressive substances toward the substrate, making the corrosion resistance properties highly dependent on 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 is often too energetically expensive and time-consuming, such as hot water sealing (HWS) 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 to intense regulation.[10]

In the present paper, the effectiveness of some common chemical sealing techniques as 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 circuits will be validated according to scanning electron microscope (SEM) images.

2 MATERIALS AND METHODS

2.1 Sample preparation

All experiments were performed using square coupons of commercially pure Ti Grade 2, with sizes of 10 mm × 10 mm × 1.6 mm and an active exposed area of 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 min, 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.

2.2 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 the anodic regime, followed by 40% in cathodic regime; the intensity of the cathodic peak is 7% with respect to 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.

2.3 Sealing procedure

Anodic titanium oxide samples were sealed using two different sealants: CAS 10 g/L and 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 min.

2.4 Electrochemical test

Electrochemical tests were carried out in the form of EIS using a three-electrode system employing a silver–silver chloride reference electrode and an Amel Pt counter electrode in an acidic solution H₂SO₄ 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, Ecorr, was stabilized for 30 min for every electrochemical test. The sinusoid with an amplitude of 10 mVrms 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. Figure 1 shows that 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 a higher temperature.

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

$$\text{TiO}_2(s) + 2\text{H}_2\text{O}(l) \rightarrow \text{Ti(OH)}_4(s) \quad \text{and} \quad \text{Ca}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow \text{Ca(OH)}_2(s). \quad (1)$$

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

Being the solubility of calcium hydroxide in water an exothermic process, its stability can be enhanced in service conditions, exploiting relatively high temperatures, thereby making the sealing procedure more efficient. In particular, knowing the high aggressivity of hot concentrated sulfuric acid on grade 2 titanium$^{[11,12]}$ inducing corrosion rates of several mm/year even in presence of anodic coatings$^{[13]}$ the reaction between Ca(OH)$_2$ and H$_2$SO$_4$ can favor the formation of a calcium sulfates skin. Depending on its uniformity and formation kinetics the reaction between the Ca(OH)$_2$ deposits and the acidic environment can be eventually stopped.

Knowing the benefits obtained using higher temperatures in CAS, the 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

![Figure 2](image-url) SEM images of samples undergoing CAS at (a) 25°C, (b) 50°C, and (c) 85°C. CAS, calcium acetate; SEM, scanning electron microscope

![Figure 3](image-url) Impedance spectra of sample sealed in (a) hot water (HWS), (b) CAS. CAS, calcium acetate; HWS, hot water sealing

[Color figure can be viewed at wileyonlinelibrary.com]
at 85°C is employed, the phase angle at high frequency reaches typical values shown in the low-frequency region of the spectrum.

Electrochemical equivalent circuits were used to fit Nyquist and Bode spectra for samples tested in both HWS and CAS at 85°C. Unsealed (Un.) 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. As a consequence, the circuit highlighted in Figure 4a was used, where the addition of a finite space Warburg element (T) had the aim of describing finite diffusive phenomena of electroactive species approaching the porous electrode. Constant phase elements (CPEs) were sometimes used in the substitution of capacitors to account for surface inhomogeneity related to roughness and porosity. 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 3a becoming a peak in the spectrum.

Table 1 lists all the parameters extracted from the fitting procedure of the spectra related to Un. and sealed samples in CAS at 85°C and HWS at 100°C. For sake of brevity, solution resistance \( R_s \) is avoided in 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 \( \times \) 10\(^{-3} \) for Un. samples (both CAS and HWS), to 3.6 \( \times \) 10\(^{-2} \) for sample CAS-85 and 7.3 \( \times \) 10\(^{-2} \) for sample HWS-100.

For Un. samples (Un.-CAS and Un.-HWS), the Brug's equation was used to convert CPE parameters to an effective capacitance \( C_{eff} \) (see Equation 2):

\[
C_{eff} = \frac{Y_0}{A} \left( \frac{1}{R_s} + \frac{1}{R_b} \right)^\frac{1}{\alpha},
\]

(2)

\[
C_{eff} = \frac{\varepsilon_r \varepsilon_0 A}{d},
\]

(3)

A value of 89.2 and 61.8 \( \mu F/cm^2 \) were extracted for samples denoted Un.-CAS and Un.-HWS, respectively. Using Equation (3), the thickness of the dielectrics, \( d \), was extracted, obtaining 198 and 286 nm for Un.-CAS and Un.-HWS (the dielectric constant for TiO\(_2\) was fixed equal to 100\(^1\)) indicative of the barrier layer thickness of PEO oxides produced at such a forming voltage. Application of Equation (3) to capacitances \( C_b \) related to barrier layer properties of sealed coatings determined a rather thicker barrier layer, 2.72 and 2.37 \( \mu m \) for CAS-85 and HWS-100, respectively. These values suggest that hydration products during the 30 min sealing treatment penetrated through the bottom of the coating forming a dense thick dielectric region.

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

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

Abbreviations: CAS, calcium acetate; HWS, hot water sealing; Un., unsealed.
According to electrochemical parameters previously extracted, a sealing efficiency can be obtained according to the equation given below:

$$\eta = \frac{R_{\text{tot}} - R_0}{R_{\text{tot}}} \times 100,$$

(4)

where $R_{\text{tot}}$ refers to the sum of barrier and porous layer resistances, while $R_0$ is the barrier layer resistance of the Un. 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 a sealant.

### 4 | CONCLUSIONS

PEO favors titanium surface conversion generating porous oxides requiring an appropriate sealing treatment to obtain desirable corrosion resistance properties in harsh environments. Hot water and CAS were the two sealants tested in the present research, finding improved properties if higher temperatures are employed. In particular, using CAS at 85°C resulted in the formation of Ca(OH)$_2$ filling almost all the oxide porosity as it was demonstrated, thanks to SEM observations. EIS 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 CAS performed at 85°C and hot water at 100°C.

### CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

### DATA AVAILABILITY STATEMENT

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

### ORCID

Luca Casanova [http://orcid.org/0000-0001-7656-0280](http://orcid.org/0000-0001-7656-0280)
Marco Ormellese [http://orcid.org/0000-0003-1546-1072](http://orcid.org/0000-0003-1546-1072)

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