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Abstract

Titanium owes its astounding corrosion resistance to a thin, compact oxide layer that is formed spontaneously when the metal is exposed to the environment. However, even titanium can be subject to corrosion in very aggressive environments. To enhance its corrosion resistance, it is possible to exploit the same mechanism that leads to the formation of the protective oxide layer and force its growth with an external contribution. Oxidation can be easily stimulated with the use of an electrochemical cell. However, when part geometry or dimensions do not allow the immersion in an anodizing bath, chemical oxidation can be used. This study compares corrosion resistance enhancement after NaOH and H₂O₂ treatment. Treatment duration and temperature, solution concentration and quantity are optimized to achieve the best corrosion resistance with the least time and chemicals consumption, by maintaining the process easy to perform and safe for the operator.

Keywords: Anodization, Corrosion, Electrochemical characterization, Pitting, Titanium.

1   Introduction

Titanium and its alloys are widely appreciated for their high corrosion resistance in environments that are critical even for high-end stainless steel (duplex UNS S31803 and UNS S32750), such as concentrated chlorides [1, 2]. This resistance is due to a thin (1.5 nm - 10 nm) [3] but compact oxide layer that is naturally formed when the metal is

exposed to the air. For this property, together with high strength, high fracture toughness and low density, [4, 5] titanium is used where other metals would fail, such as offshore, acid environment, aerospace [6, 7], automotive, high temperature, chemical & food industry [8–10], marine hydrometallurgical application and nuclear fuel wastes containment [11–14].

In such aggressive environments, commercially pure titanium may suffer different form of corrosion. Generalized corrosion is caused by small quantity of fluorides ions (more than 0.002 M [15]) that combining with titanium forms a soluble complex (TiF_4), destroying passivity film. Hydrogen embrittlement happens on alpha and alpha plus beta titanium due to their low hydrogen solubility in α-Ti [16], stress corrosion cracking can also happen in very specific environments, e.g. nitrogen tetroxide (N_2O_4), red-fuming nitric acid or solid cadmium [17, 18]. However, the most critical forms of corrosion of titanium are due localized breaking of passive layer and this is favored by the presence of concentrated halides, such hot salty water (above 200°C) or bromide containing species [3, 19].
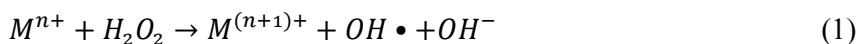
To further improve titanium corrosion resistance in these environments, specific treatments can be employed. It is the case of inclusion of elements that promote cathodic reaction, raising cathodic polarization curve above the critical active anodic curve at higher potentials in the passive region, such as palladium [20], or nitration, that consist in introducing nitrogen in the first μm of the surface to promote the formation of TiN and increase corrosion resistance [21, 22]. These methods, acting on titanium composition, are effective but complicated to perform and expensive as well other surface coating techniques, such as vacuum plasma spray coating, plasma spraying and chemical vapor deposition [23].

For this reason, treatments that act on the naturally formed passive layer are preferred. The easiest and cheapest treatment to tune oxide layer is anodic oxidation, that consists in applying an anodic polarization of several tens of volts to the metal, promoting the growth of the natural oxide layer with thicknesses from about 40 nm with anodizing potential 10 V, to about 250 nm at 100 V [24, 25].

Anodic oxidation produces a compact, adherent and corrosion resistant oxide and was studied in previous works [26, 27]. However, in case of already installed part, localized treatment, small part or complex geometry, anodic oxidation could be un-feasible. In these cases, chemical oxidation, not requiring any applied current and particular cell setup, would be suitable to provide the corrosion resistance enhancement needed.

Most common reagents used for chemical oxidation are alkoxides (e.g. NaOH, KOH) and hydrogen peroxide [28–30]. Sodium and potassium hydroxide dissociate in water releasing metal cation and hydroxide anion. Contrary of the amphoteric metals (Al, Zn, Sn, Pb), which in alkaline environment forms soluble metal hydroxide, titanium is favored by hydroxide, that promotes the formation of its passivity oxide [31]. Hydrogen peroxide treatment has been less investigated in literature compared to alkoxides, the proposed mechanism of oxide formation pass through numerous intermediates [29]:

$$M^{n+} + H_2O_2 \rightarrow M^{(n+1)+} + OH \bullet + OH^- \qquad (1)$$

$$M^{n+} + OH \bullet \rightarrow M^{(n+1)+} + OH^- \qquad (2)$$

$$OH \bullet + H_2O_2 \rightarrow H_2O + HO_2 \qquad (3)$$

$$M^{n+} + HO_2 \rightarrow M^{(n+1)+} + HO_2^- \qquad (4)$$

$$HO_2 \rightarrow H^+ + O_2^- \qquad (5)$$

$$M^{(n+1)+} + O_2^- \rightarrow M^{n+} + O_2 \qquad (6)$$

Which leads to the competing reactions of formation of titanium dioxide and evolution of oxygen [32]:

$$Ti + 2H_2O_2 \rightarrow TiO_2 + 2H_2O \qquad (7)$$

$$2H_2O_2 \rightarrow H_2O + O_2 \uparrow \qquad (8)$$

The purpose of this work was to find key parameters that influence chemically promoted oxide layer, and to tune them in order to achieve the highest corrosion resistance while maintaining industrial and in-situ applications feasible.

Alkoxides and hydrogen peroxide treatments were performed by varying treatment temperature and duration, solution concentration, solution-to-sample surface ratio, solution agitation and annealing post treatment.

2 Materials and Methods

Square samples 20x20x1.6 mm were cold-cut from a titanium UNS R50400 (ASTM grade 2) sheet, and polished with 100 and 300 grit SiC paper. To remove possible surface contaminations, the specimens were degreased with EtOH in ultrasonic bath for 4 minutes and then rinsed in distilled water with the same ultrasound exposure.

2.1 Alkoxides

NaOH was used as representative of the alkoxide family for its ease of production and storage, and for its tendency to produce less porous and more compact oxide film [28]. Treatments were performed by submerging titanium samples in 100 ml beakers. Values of investigated parameters are:

- Duration: 3h - 6h - 12h - 24h - 72h

- Treatment temperature: 25°C - 60°C

- Quantity of solution: 10 ml - 50 ml - 100 ml

- Solution concentration: 10 M - 50 M

- Agitation: Yes - No

Temperature was maintained below 60°C to avoid excessive hydrogen embrittlement due to the formation of titanium hydrides with hydrogen generated by the secondary reaction [31]:

$$Ti + 2H_2O \xrightarrow{OH^-} TiO_2 + 2H_2 \uparrow \qquad (9)$$

Solution stirring during chemical oxidation of some samples was provided using a magnetic stirrer, regulated to obtain a vigorous agitation without the formation of vortex at the surface.

Post-treatment annealing was performed on some samples to convert sodium titanate hydrogel, formed on the surface during chemical oxidation, into amorphous titanate layer, to reduce protective layer porosity [33, 34]. Temperature was maintained to either 400°C, 500°C or 600°C for 1h in air.

2.2 Hydrogen Peroxide

Hydrogen peroxide treatments were performed in H_2O_2 solution 10 M, prepared just before the treatment from a master solution 35% wt. stored at 5°C to prevent thermal decomposition. Treatments were performed in 50 ml or 100 ml of solution, with duration ranging from 6h to 24h and temperatures from 25°C to 90°C. Due to the high decomposition rate of H_2O_2, solution quantities below 50 ml were not tested, to prevent excessive decrease in solution concentration during test. For the same reason, solution agitation was not applied. Annealing was performed at either 400°C, 500°C or 600°C for 1h as they are reported to be able to positively modify surface morphology by decomposing oxygen bubbles from the gel layer of the reaction products attached to the surface, causing the appearance of grooved structure on the surface during the heating process [30].

2.3 Microscopy

After chemical oxidation field emission SEM FEI Nova nanoSEM 450, and tungsten filament SEM Stereoscan 360 were used to characterize samples morphology and oxide thickness. Sacrificial samples were bent to a narrow curvature radius to promote film descaling. Scales detached in this way were gold sputtered and observed in cross-section.

The presence of crystalline structure in the oxides was detected using XRD technique with a diffractometer model Phillips PW 1830, able to generate a Cu-Kα radiation with a wavelength of 0.154 nm. This technique doesn't allow the measurement of absolute crystalline fraction, but was used to detect the presence of sodium titanate after NaOH treatments of different durations, comparing the amount by normalizing sodium titanate peaks height with the titanium principal one.

2.4 Corrosion resistance

Samples corrosion resistance were characterized with potentiodynamic tests performed with MetroOhm Autolab potentiostat M204. A standard 1 liter, 3-electrode cell was used, including an activated titanium counter electrode, a silver/silver chloride (SSC) counter electrode and the working electrode with 1 cm^2 of exposed area. Open circuit potential (OCP) was recorded after 1h of sample exposure to the testing solution. Then potential was scanned from 100 mV below the OCP up to 8 V SSC with a scan rate of 20 mV/min. Anodic current and potential difference between metal and reference electrode were registered with Nova® 2.1.1 software.

To assess titanium resistance to corrosion it is necessary to distinguish different forms of corrosion. By recognizing that for titanium the most dangerous and difficult to identify is localized corrosion, the effectiveness of different halides in promoting localized oxide

breakdown was studied [35]. As result, the corrosion tests were performed in 0.5 M ammonium bromide solution, that was proven to be the most effective in promoting localized corrosion. A current density of 10 A/m^2 was chosen as threshold to define localized oxide breakdown events.

As the duration of each test did not exceed 8h, no sealing was necessary. Previous works on titanium oxide tested in such conditions showed that nor chemical (ΔpH $\approx$ 0.05) nor physical (ΔT $\approx$ 2°C) deviations were to be expected [27]. In order to ensure repeatability, a minimum of three measurements were made for each treatment procedure.

3   Results and Discussion

3.1   Solution concentration and quantity

The effect of the volume of solution used to treat samples in NaOH on titanium corrosion resistance is shown in Fig. 1. The three plotted curves are good representation of all the repeatability performed, they show that passing from 10 ml to 100 ml, keeping constant the sample dimension (20x20x1.6 mm), the effect on localized corrosion is within the experimental error. The same phenomenon is observed with H$_2$O$_2$ treatment (Fig. 2) passing from 50 ml to 100 ml.

<< Figure 1 >>

<< Figure 2 >>

From this observation, two contrasting hypothesis were made:

- The chemically developed oxide growth has linear kinetic and the amount of reagent consumed in 24h at 60°C is lower than the one contained in 10 ml of solution 10 M. So it is not entirely consumed by the oxidation and an increased amount of available reagent does not contribute to oxide growth.

- The growth kinetic decreases exponentially so the film formed in the first stage leads to the shown increase in corrosion resistance, any further exposure to the solute contributes marginally to the oxide growth and the effect are not visible on the pitting potential.

To discern the correct hypothesis, the treatment was repeated with five time the initial concentration of NaOH (50 M). In case of linear growth, the exposure to a more concentrated reagent would lead to an appreciably thicker oxide. On the other side, if after the initial oxidation the oxide growth velocity progressively slow down to negligible values, the higher concentration would not lead to higher corrosion resistance.

In Fig. 3 the effect of NaOH concentration increase from 10 M to 50 M is shown. As no difference in corrosion resistance are observed with NaOH concentration increase, the existence of a plateau after which the treatment has no more effect is proven.

It is important to notice that, even if it does not affect final corrosion resistance, the increase in concentration modifies oxide growth kinetic enough to produce different aesthetic appearance of the oxide. Titanium oxide interference color is strongly dependent on oxide thickness, its variation (visible in Fig. 4) indicates a difference in oxide thickness on samples produced with 10 M and 50 M NaOH.

<< Figure 3 >>

<< Figure 4 >>

3.2   Solution agitation

Stirring the solution during treatments is an effective way to remove H_2 as soon as it is formed at sample surface. Reducing the amount of H_2 bubble on the surface not only reduces the risk of hydrogen embrittlement, but also uniforms the contact between the solution and the surface, leading to more homogeneous coating. In Fig. 5 the effect of solution agitation on NaOH 10 M treated samples is visible. The difference between the pitting potential of samples produced in agitated and non-agitated solution is within the experimental error typical of these tests. Thus, no effect is reported on halides promoted localized corrosion. The effect of gas bubble permanence on the surface is believed to be mitigated by the long duration of the treatment. Further studies will determine the effect on hydrogen embrittlement and on faster treatment.

<< Figure 5 >>

3.3   Treatment duration and temperature

Under the hypothesis, confirmed by Fig. 3, that a plateau exists after which the oxide growth become too slow to affect corrosion resistance, the time of establishment of this plateau at a temperature of 60°C was searched. Fig. 6 shows the results of at least three potentiodynamic test performed on samples treated for 1h, 6h, 12h, 18h, 24h and 72h at 60°C in NaOH. After 12h of treatment the increase of corrosion resistance become negligible and the only effect is a narrowing of results distribution.

The existence of a similar plateau was researched at room temperature, to simplify a possible in-situ treatment, without the requirement of local heat at 60°C for several hours. The results are shown in Fig. 6. Lowering the temperature has the effect to delay the reaching of the maximum corrosion resistance plateau. Note its final value is not influenced by treatment temperature.

To validate oxide growth kinetic hypothesis, SEM observations of oxide cross-section were performed. Results are shown in Fig. 7. Oxide growth rate is about 117 nm/h in the first 6h, then 50 nm/h passing from 6h to 9h and 83 nm/h from 9h to 12h, but drop down to 4 nm/h from 12h to 24h of treatment. These data correlate the stabilization of corrosion resistance given by increasing treatment duration with oxide growth kinetic.

<< Figure 6 >>

<< Figure 7 >>

The same trend was found on H_2O_2 treatments, as reported in Fig. 8. Increasing temperature from 25°C to 90°C and duration from 6h to 24h does not lead to any significant variation in corrosion resistance. The establishment of the plateau on H_2O_2 happens before 6h at 25°C, suggesting a faster kinetic compared to NaOH oxidation.

<< Figure 8 >>

3.4 Post treatment annealing

To achieve better corrosion resistance in bromides, passing the 4 V pitting potential plateau observed in both NaOH and H_2O_2 treatments, annealing for 1h at 400°C and 600°C was performed. Results and comparison between the effect of calcination on samples chemically oxidized in both the solution and sample of non-treated titanium are shown in Fig. 9. Thermal treatment has a moderate effect on corrosion resistance of non-pre-oxidized titanium. This is due to the thickening of titanium dioxide layer due to thermal oxidation.

<< Figure 9 >>

Annealing shows no effect at both temperatures on samples treated in NaOH. As a positive effect is reported in literature [36], the reason of stationary corrosion resistance was searched on thermal treatment duration. Fig. 10 shows the effect of doubling the annealing duration. As no effect is observed by doubling calcination time the effective presence of sodium titanate gel available to be transformed was checked with XRD analyses. Fig. 11 shows the relative intensity of XRD peak associated with sodium titanate on the main titanium peak.

<< Figure 10 >>

<< Figure 11 >>

After 1h of treatment in NaOH at 60°C, titanate formation is too low to be revealed by XRD analyses, after 12h a small peak became visible. The minor peak increase between 12h and 24h shows the very slow kinetic of sodium titanate formation. Such a small quantity, although detectable, is not enough to produce a visible increase in corrosion resistance after thermal treatment.

Fig. 9 shows a remarkable effect of annealing on corrosion resistance of samples oxidized with H_2O_2, that exceeds 6.5 V of pitting potential after 600°C treatment. A positive effect is also observable on anodic current density at 1 V and 2 V of each curve, as shown in Fig. 12.

<< Figure 12 >>

H_2O_2 treatment performed for 6h at 25°C forms oxide with disordered lamellar structure at the μm scale (Fig. 13). This structure is maintained with annealing up to 550°C while is recovered when calcination is performed above 600°C as shown in Fig. 14 This behavior is responsible to the enhanced corrosion resistance of samples treated at higher temperatures.

<< Figure 13 >>

<< Figure 14 >>

4   Conclusion

Commercially pure titanium ASTM grade 2 was chemically oxidized using NaOH and H_2O_2. The effects of solution concentration, quantity and stirring on corrosion resistance

to NH$_4$Br 0.5 M environment were studied, together with the influence of treatment temperature, duration and the presence of post-treatment annealing.

A plateau of corrosion resistance was identified in both the oxidizing solution. After the establishment of that plateau, any further increase of treatment duration, temperature, solution concentration and solution quantity leads to a marginal increase of oxide thickness, without any noticeable effect on corrosion resistance. SEM oxide thickness measurement were performed to confirm the relation between corrosion resistance plateau and oxide thickness growth kinetic.

The maximum of corrosion resistance in NaOH is achieved after 12h at 60°C and after 24h at room temperature. H$_2$O$_2$ kinetic is faster and the same resistance is achieved before 6h at room temperature.

The effect of annealing at 400°C and 600°C was studied on samples treated in both the solutions. The independency of corrosion resistance of NaOH treated samples to calcination temperature was justified by the small amount of sodium titanate gel developed after 24h at 60°C reveled with XRD analyses.

Annealing was found to have a strong effect on pitting potential in bromides environment when applied to samples oxidized in H$_2$O$_2$. This is believed to be cause by the deep morphology changes happening at samples surface during thermal treatment.

way to spot recover anodizing treatment locally removed by mechanical abrasion.

Acknowledgements

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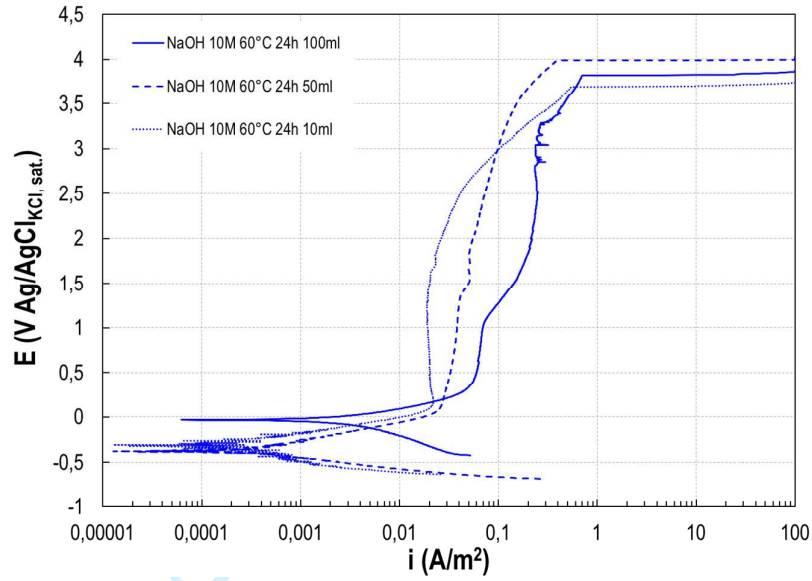
Figure 1 Effect of NaOH treatment solution volume on samples corrosion resistance to
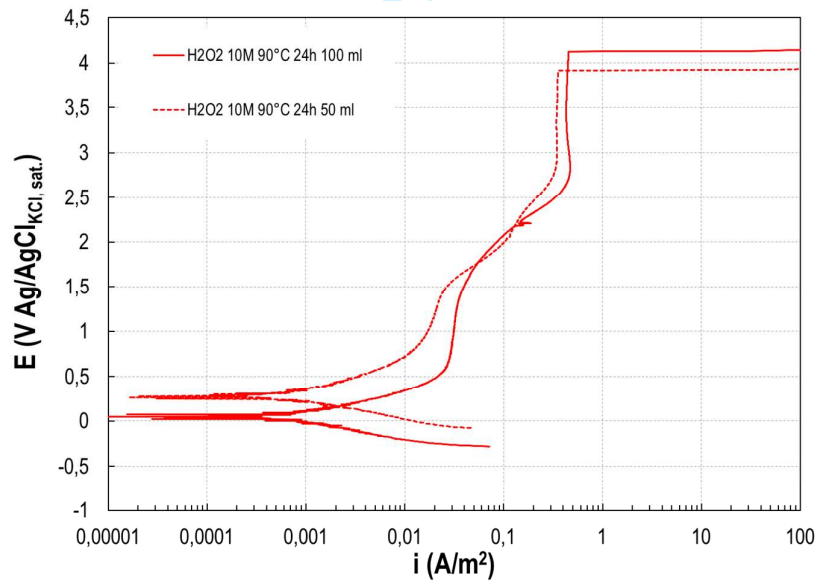
bromides 0.5M

Figure 2 Effect of H₂O₂ treatment solution volume on samples corrosion resistance to
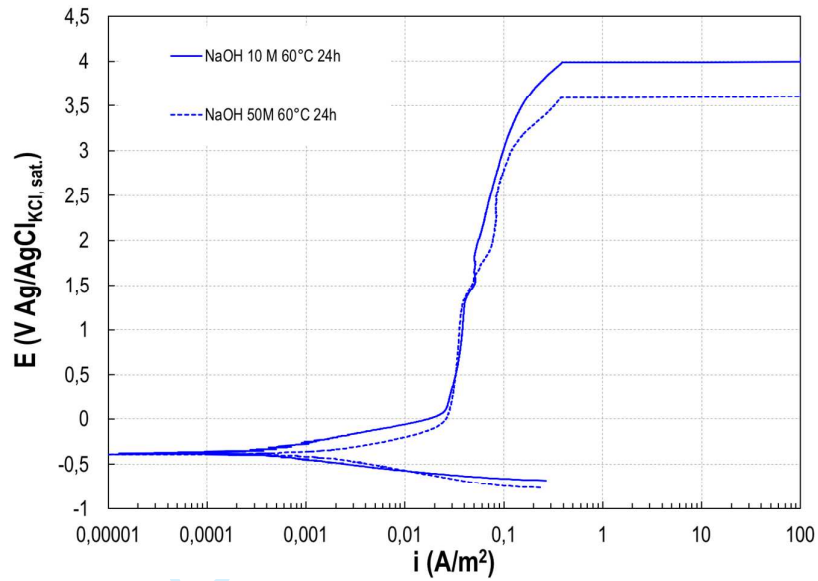
bromides 0.5M

Figure 3 Effect of NaOH concentration on samples corrosion resistance to

bromides 0.5 M

Figure 4 Sample aesthetic appearance changing passing from 10 M NaOH (left) to

50 M NaOH (right) treatment conducted for 24h at 60°C
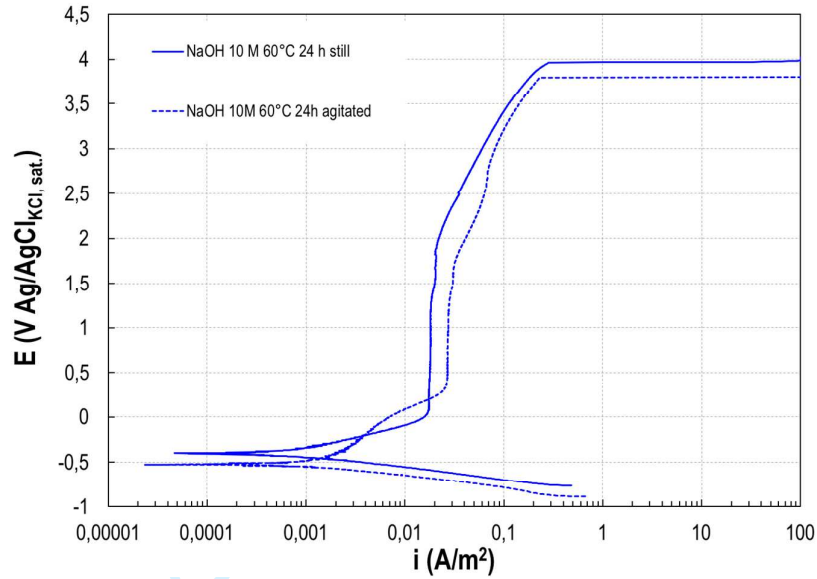
Figure 5 Effect of solution agitation on corrosion resistance of samples oxidized in

NaOH 10M
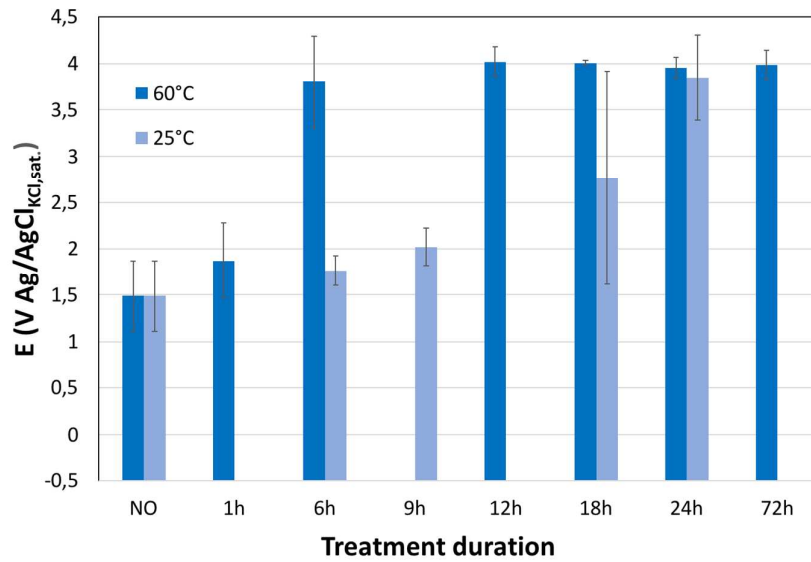
Figure 6 Effect of treatment temperature and duration on NaOH chemical oxidized
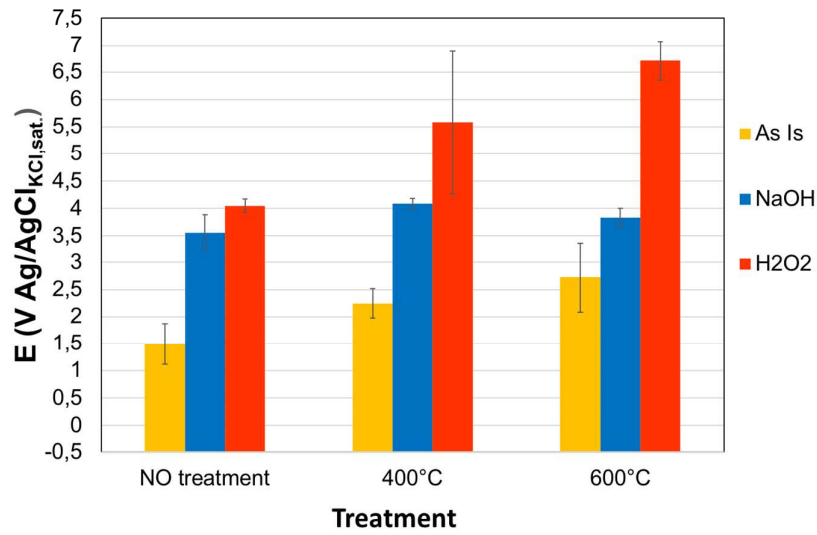
samples pitting potentials in NH$_4$Br 0.5M
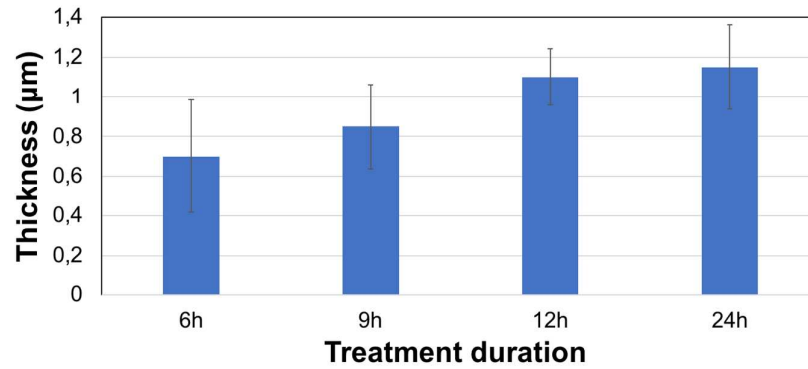
Figure 7 Effect of NaOH treatment duration on titanium oxide thickness
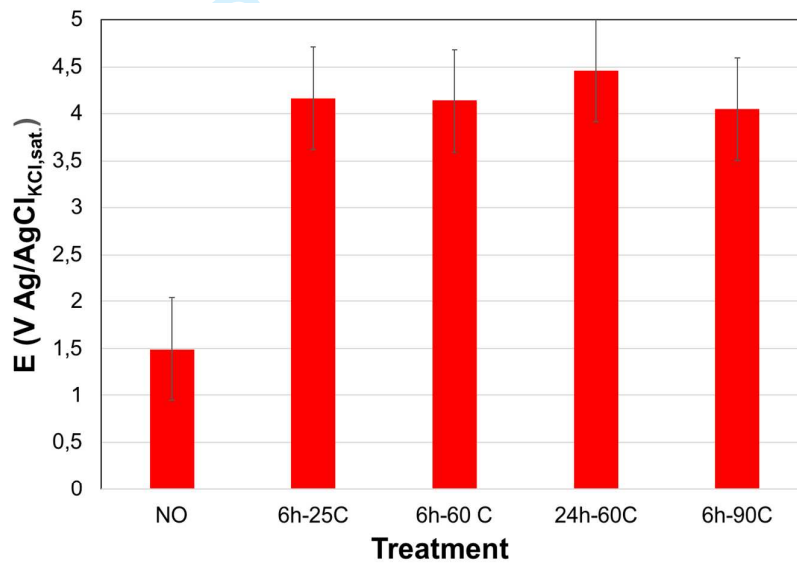
Figure 8 Effect of treatment temperature and duration on H_2O_2 chemical oxidized

samples pitting potentials in NH_4Br 0.5M

Figure 9 Effect on pitting potential in NH$_4$Br 0.5M of thermal treatments at 400°C and

600°C for 1h on non-treated titanium, NaOH oxidized titanium and H$_2$O$_2$ oxidized

titanium
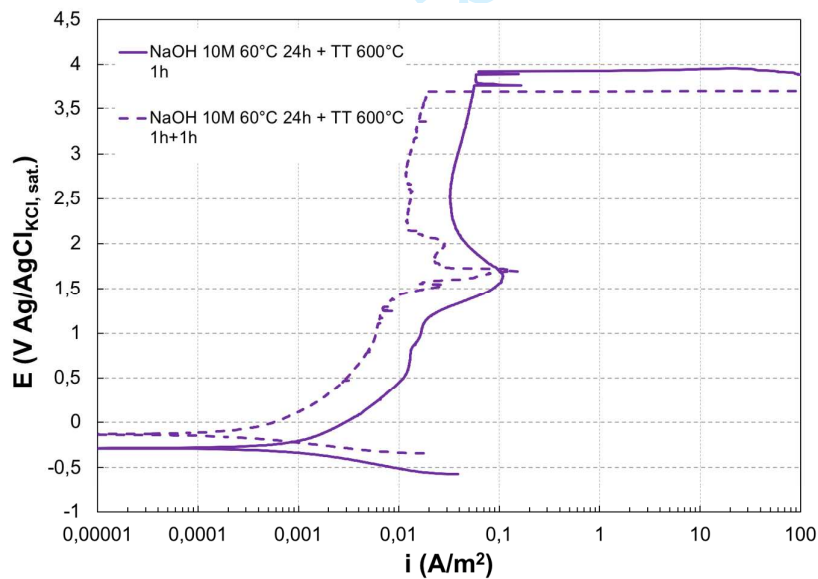
Figure 10 Effect of thermal treatments duration on pitting potential in NH$_4$Br of

samples oxidized in NaOH at 60°C for 24h
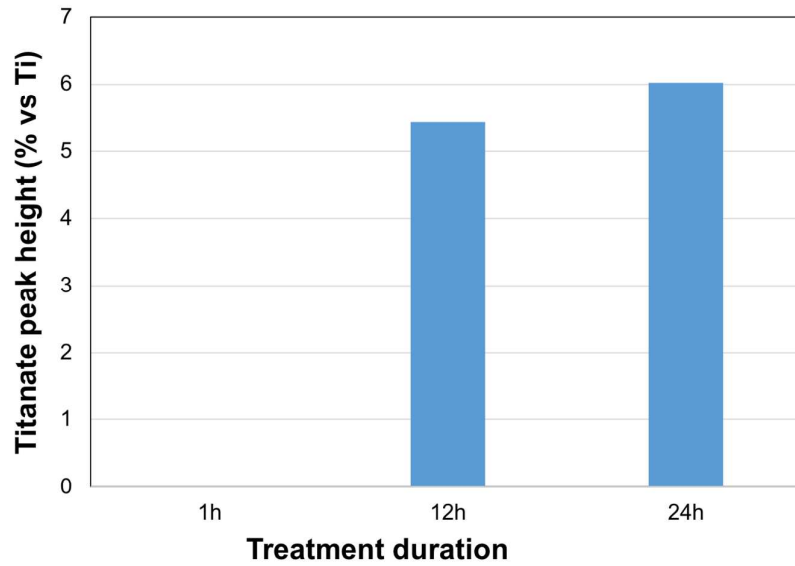
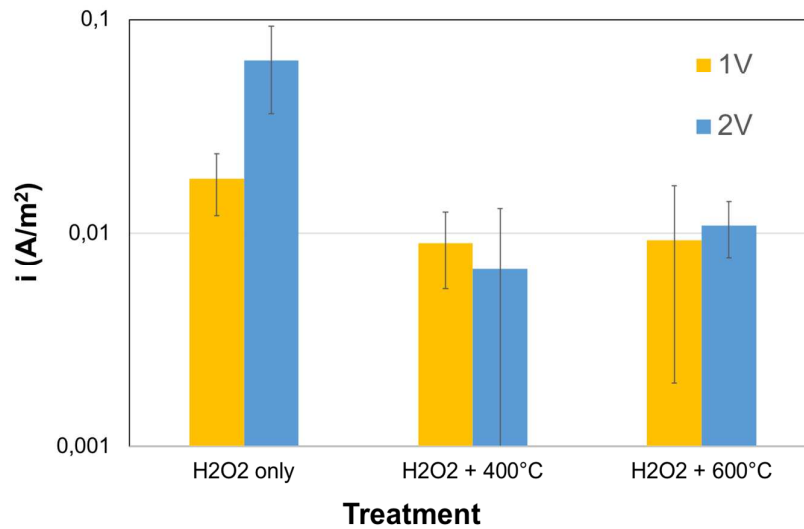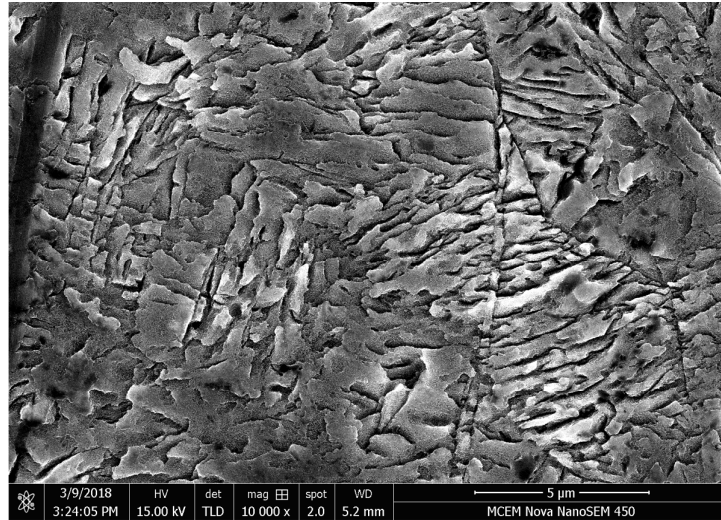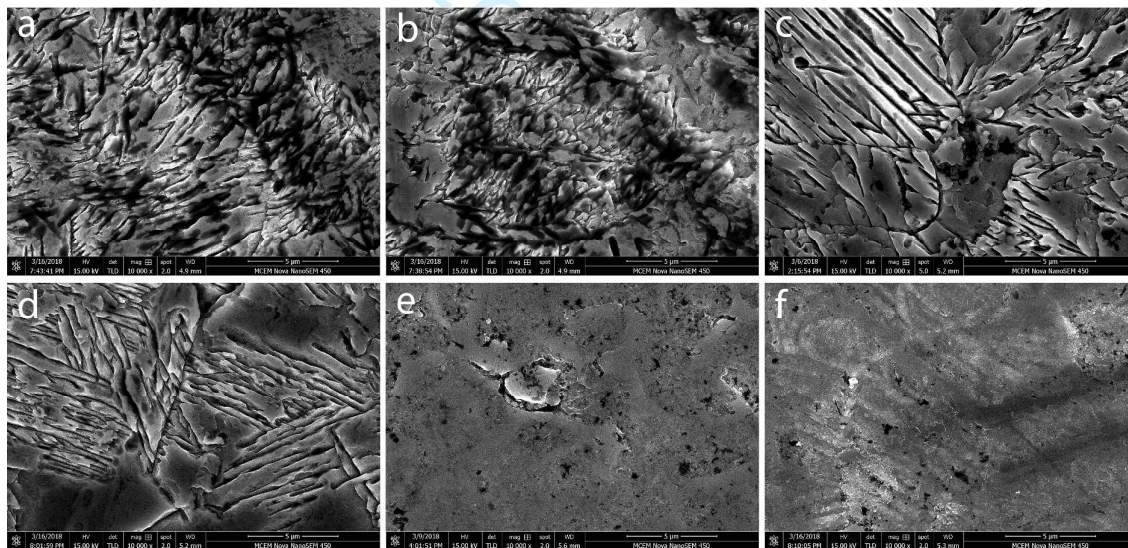*Figure 11 XRD analyses on samples treated in NaOH for 1h, 9h and 12h at 60°C*

Figure 12 Effect on anodic current density at 1V and 2V of thermal treatments

performed at 400°C and 600°C on H_2O_2 oxidized titanium

Figure 13 Surface morphology of samples treated in H_2O_2 for 6h at 25°C without any

further treatment

Figure 14 Surface morphology of samples treated in H_2O_2 for 6h at 25°C and subject

annealing at: a) 350°C, b) 400°C, c) 450°C, d) 500°C, e) 600°C, f) 700°C