Enhancement of pure titanium localized corrosion resistance by chemical oxidation

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ABSTRACT

The corrosion behavior of commercially pure titanium (UNS R50400, ASTM GRADE 2) was investigated in presence of aggressive, bromides containing solution reported to cause more severe localized corrosion compared to chlorides. To enhance localized corrosion resistance of the metal, chemical oxidation treatments were performed using NaOH and H_2O_2 10 M solutions. The effects of treatment duration (1 h to 72 h), temperature (25°C to 90°C), solution concentration and quantity on pitting potential were investigated. Treatments were optimized to achieve corrosion resistance comparable to the one obtained after anodization at low potentials (20-40 V).

Keywords: titanium, chemical oxidation, corrosion, oxidation, TiO_2

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, titanium is used where other metals would fail [4, 5].

In such aggressive environments, commercially pure titanium may suffer different form of corrosion. Generalized corrosion happens in small quantity of fluorides ions. Hydrogen embrittlement on alpha and alpha plus beta titanium due to low hydrogen solubility in α-Ti. Stress corrosion cracking in very specific environments, e.g. nitrogen tetroxide (N_2O_4), red-fuming nitric acid or solid cadmium [6, 7]. 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, 8].

To further improve titanium corrosion resistance in these environments, specific treatments can be employed. Among them, the ones that act on the naturally formed passive layer are generally easier and cheaper. It is the case of 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 [9, 10].

Anodic oxidation produces a compact, adherent and corrosion resistant oxide and was studied in previous works [11, 12]. However, in case of already installed part, localized treatment, small part or difficult 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 required corrosion resistance enhancement.

Most common reagents used for chemical oxidation are alkoxides (e.g. NaOH, KOH) and hydrogen peroxide [13, 14]. 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 [15]. Hydrogen peroxide treatment has been less investigated in literature compared to alkoxides. It is more prone to degradation and difficult to store but it leads to faster oxidation kinetic.

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. [13] Treatments were performed by submerging titanium samples in 100 ml beakers. Values of parameters investigated are shown in Table 1.

Table 1 Parameters used for NaOH treatments.

Duration [h]	1	3	6	12	24	72
Temperature [°C]	25	60				
Qt. of solution [ml]	10	50	100			
Concentration [M]	10	50				

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 [15]:

$$Ti + 2H_2O \rightarrow TiO_2 + 2H_2\uparrow \qquad (1)$$

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 6 h to 24 h 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.

2.3 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 then 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 0.5 M ammonium bromide solution was used. As it 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. In order to ensure repeatability, a minimum of three measurements were made for each treatment procedure.

3 RESULTS

The effect of the volume of solution used to treat samples in NaOH is shown in Figure 1.
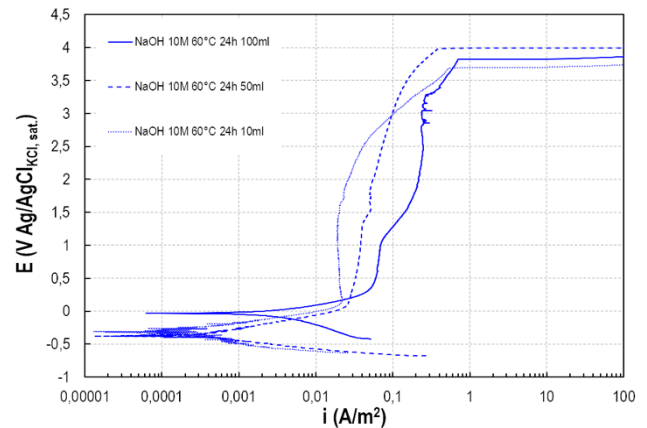

Figure 1: Effect of NaOH treatment solution volume on samples corrosion resistance to bromides 0.5 M

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_2O_2 treatment (Figure 2) passing from 50 ml to 100 ml.
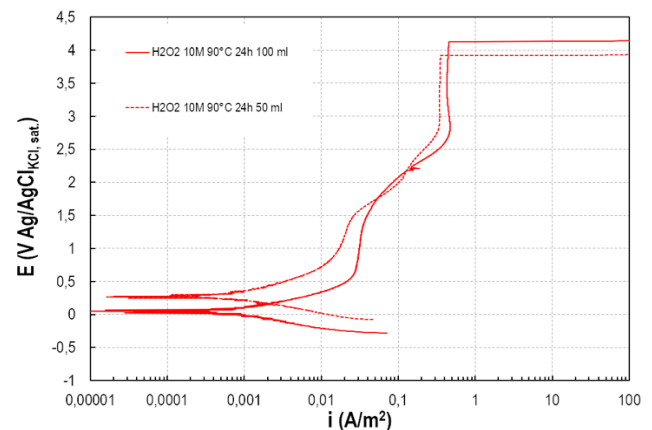

Figure 2: Effect of H_2O_2 treatment solution volume on samples corrosion resistance to bromides 0.5 M

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 wouldn't lead to higher corrosion resistance.

In Figure 3 the effect of NaOH concentration increase from 10 M to 50 M is shown.
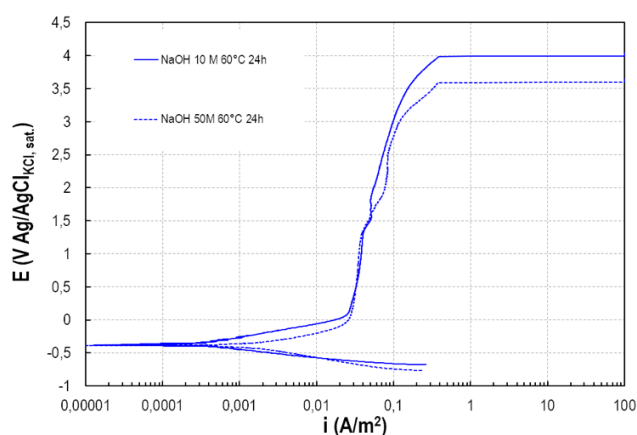
Figure 3: Effect of NaOH concentration on samples corrosion resistance to bromides 0.5 M

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 doesn't 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 indicates a difference in oxide thickness on samples produced with 10 M and 50 M NaOH.

Under the hypothesis, confirmed by Fig. 3, that a plateau exist 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. 4 shows the results of at least three potentiodynamic test performed on samples treated for 1 h, 6 h, 12 h, 18 h, 24 h and 72 h at 60°C in NaOH.
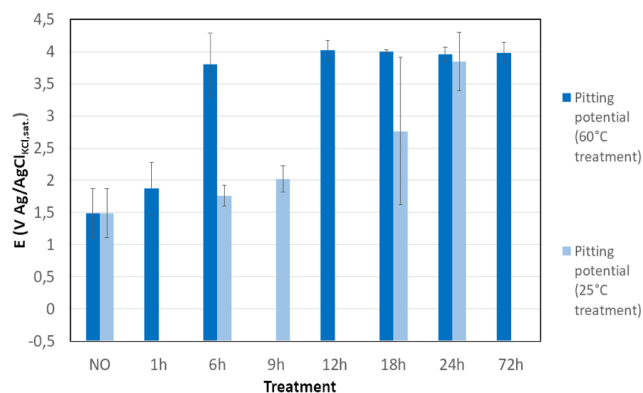
Figure 4: Effect of treatment temperature and duration on NaOH chemical oxidized samples corrosion resistance

After 12 h of treatment the increase of corrosion resistance become negligible and the only effect is a narrowing of results distribution.

The same 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 Figure 4. 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 Figure 5.
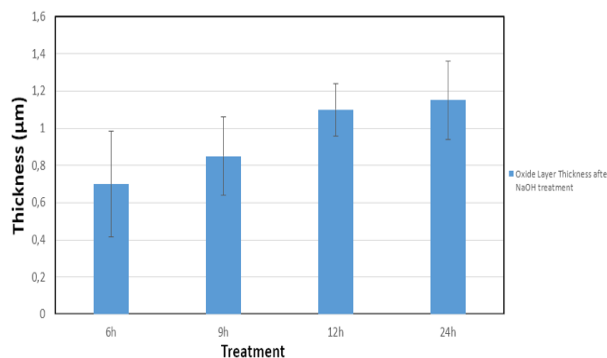
Figure 5: Effect of NaOH treatment duration on titanium oxide thickness

Oxide growth rate is about 117 nm/h in the first 6h, then 50 nm/h passing from 6 h to 9 h and 83 nm/h from 9 h to 12 h, but drop down to 4 nm/h from 12 h to 24 h of treatment. These data correlate the stabilization of corrosion resistance gain with increasing treatment duration with oxide growth kinetic. The same trend was found on H_2O_2 treatments, as reported in Figure .6
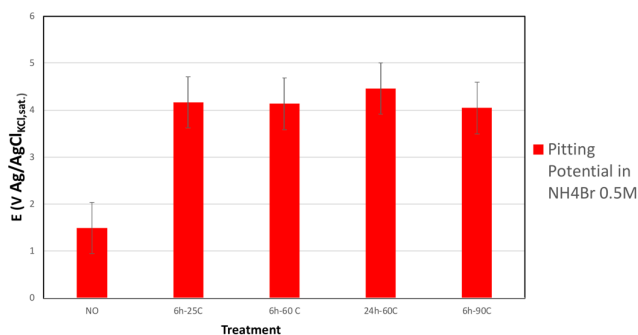
Figure 6: Effect of treatment temperature and duration on H_2O_2 chemical oxidized samples corrosion resistance

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

4   CONCLUSIONS

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 NH4Br 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 12 h at 60°C and after 24 h at room temperature. H_2O_2 kinetic is faster and the same resistance is achieved before 6h at room temperature.

5   ACKNOWLEDGEMENTS

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