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Surface Treatment to Improve Corrosion Resistance of Pure Titanium

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ABSTRACT

The corrosion behavior of pure titanium UNS R50250 and UNS R50400 were investigated and compared with electrochemical behavior of Ti-0.2Pd and Ti-0.3Mo-0.8Ni alloys (UNS R52400 and UNS R53400 respectively). Surface treatments, especially anodic oxidations, were conducted in order to enhance the corrosion resistance of pure titanium up to the corrosion resistance of titanium alloys one. Samples were then tested with potentiodynamic analyses in chloride and fluoride containing solutions, in order to find critical pitting potentials for each condition and treatment. The results show that, despite all anodization treatments increased titanium corrosion resistance to different extents, no treatment was able to increase it up to UNS R52400 level. A suggestion on the best anodization procedure to increase corrosion resistance while maintaining ease of treatment is given based on potentiodynamic test results.

Key words: Titanium, anodic oxide, corrosion, pitting.

INTRODUCTION

Titanium has an outstanding corrosion resistance due to the thin oxide protective layer (max 10 nm thick[1]) that is formed spontaneously on its surface when exposed to aerated environment. This protective layer allows using titanium in severe working condition, such as offshore (up to 260°C), acid environment, aerospace, automotive, high temperature, chemical & food industry[2–4], where no other metals can be used.

Nevertheless commercially pure titanium may suffer localized corrosion in hot salty water as well as acidic corrosion in fluoride containing solution or hydrogen embrittlement.[5] To overcome these potential issues, specific alloys containing palladium, nickel and molybdenum were introduced. These elements promote cathodic reaction, helping the system to reach passive condition. However, the inclusion of such elements is expensive.

To partially overcome this problem it is possible to increase the natural thickness of TiO_2 by surface treatments.[6-7] Oxidation treatments, specifically anodization, have been considered to tune the TiO_2 layer in order to increase its thickness and to obtain a mostly amorphous phase with the final aim to increase pure titanium corrosion resistance up to the level of more expensive alloys. Preliminary results were presented at NACE corrosion conference 2016.[8] A deeper laboratory investigation has been performed; the main results are presented in this paper.

EXPERIMENTAL PROCEDURE

Materials

During the study, four different titanium alloys were tested. Two commercially pure titanium with different amount of impurities and two alloys containing palladium, nickel and molybdenum. Table 1 reports the composition of each metal.

Table 1
Composition of used metals

Metal	C% max	H% max	O% max	N% max	Fe% max	Other
UNS R50250	0.10	0.015	0.18	0.03	0.20	
UNS R50400	0.10	0.015	0.25	0.03	0.30	
UNS R52400	0.10	0.015	0.25	0.03	0.30	0.12-0.25 Pd
UNS R53400	0.10	0.015	0.25	0.03	0.30	0.2-0.4 Mo 0.6-0.9 Ni

Samples were tubular in shape. In order to test external surface, tubes were cut longitudinally. Specimens were then covered with an epoxy-based electrical insulator resin, apart from a 2 cm² region used for test and a connection region to ensure electrical contact with testing instruments, as visible in Figure 1.
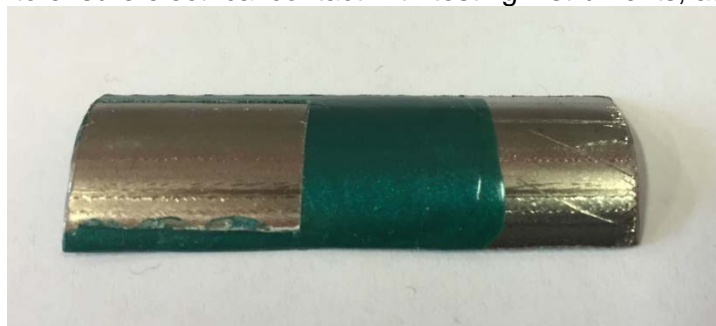

Figure 1: Example of used sample.

Due to high requirements of UNS R50400, flat specimens were also used. Samples were polished until grit 600 to ensure the same surface finish of tubular shaped samples. Dedicated tests demonstrated the independence of results from UNS R50400 source. In order to analyze surface finish effect, some samples were polished until 2400/4000 grit and then with 6 μm alumina particles until mirror finish. To overcome difficulties in obtaining reproducible mirror finish surface on titanium, tests were performed in triplicate, with good reproducibility.

Anodic and thermal oxidation treatments

Anodization treatments were conducted in fixed current density regime, with increasing voltage up to the desired one with zero maintenance time at final voltage. Currents were supplied by AimTTi PLH120 DC[*] power supply, able to operate up to 120 V and 0.75 A.
In order to optimize treatment, anodization in several electrolytes, at different final voltage and current density were conducted: Table 2 lists the anodizing treatments performed.

Table 2
Anodization treatment summary

Electrolyte	Anodization current density		
	5 mA/cm^2	20 mA/cm^2	50 mA/cm^2
H$_2$SO$_4$		10 V	
	20 V	20 V	20 V
		30 V	
		40 V	
		60V	
		80 V	
Na$_2$SO$_4$		20 V	
(NH$_4$)$_2$SO$_4$		20 V	
NH$_4$BF$_4$		20 V	

Thermal treatment was also considered to oxidize titanium, which is a well-known process to produce a thick and protective oxide.[9] Calcinations were conducted at 550°C for 1 hour, this temperature was selected to obtain oxide thickness similar to the one obtained with anodization at 20 V, accordingly to the interference color acquired by the sample after treatment.

Corrosion resistance test

Corrosion resistance was measured by potentiodynamic tests performed with EG&G Princeton Applied Research* potentiostat/galvanostat. Anodic current and potential difference between metal and reference electrode were registered with PowerCorr* software. Reference electrode used was Ag/AgCl.
Tests were conducted in 1 L cell, as the duration didn't exceed 6 hours, no sealing was necessary and neither chemical (ΔpH $\approx$ 0.05) nor physical (ΔT $\approx$ 2°C) deviations were detected. A silver/silver chloride in a KCL saturated solution was used as reference electrode. The cell is shown in Figure 2.

Anodic potentiodynamic tests were conducted in three different electrolytes at different concentrations:

- NaCl   10 – 35 – 100 g/L
- NaF   1 – 3.5 – 10 – 20 – 35 g/L
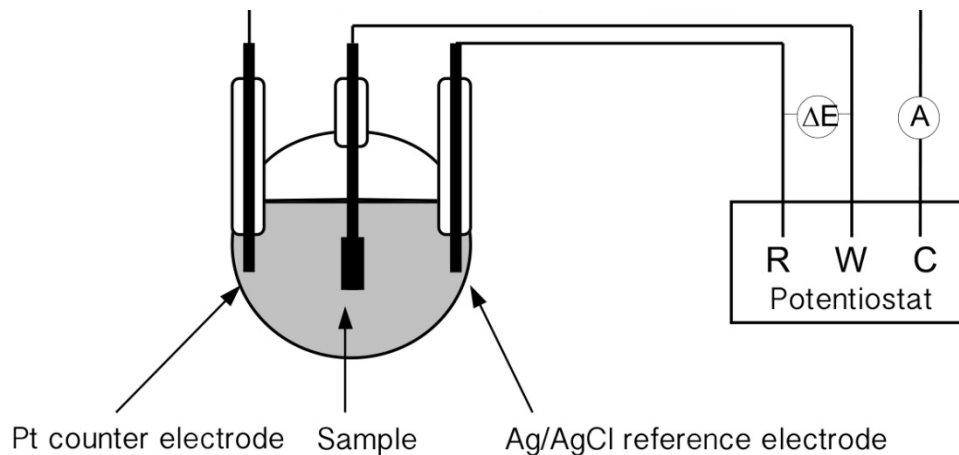- Na$_2$SO$_4$ 0.7 M

[*] Trade name

Figure 2: Scheme of an electrochemical cell.

NaCl solutions were tested both at ambient temperature and at higher temperature (80°C – 95°C) in order to study the effect of severe environmental conditions. High temperatures were avoided when NaF was tested in order to prevent damages to Pyrex cell due to high fluoride concentration. Tests were conducted starting 0.1 V below the free corrosion potential (OCP), measured after 30 minutes from immersion to reach potential stabilization, up to potentials between 1.5 V and 7 V depending on the electrolyte. In case of suspected pitting phenomenon, potentiodynamic scan direction was inverted after 10 A/m² anodic current density was reached, in order to find the repassivation potential. Potential scan rate was 1 V/h.

Cathodic potentiodynamic tests were conducted in HCl 10% solution, starting at OCP, decreasing the potential to -1 V Ag/AgCl. Potential scan rate was 1 V/h.

RESULTS AND DISCUSSION

Effect of anodization on anodic curves

NaCl 10 g/L tests.

In order to have a first screening of the four metals corrosion resistance, specimens were tested in NaCl 10 g/L, from 100 mV below OCP up to 1.5 V with 20 mV/min scan velocity. Tests were repeated twice to ensure reproducibility. Results are shown in Figure 3. No critical behavior was found in any sample, however UNS R52400 showed passive current density one order of magnitude lower than other samples at potential below 300 mV vs Ag/AgCl; at higher potential, behavior of the four metals is fairly uniform, with a slight worsening from UNS R53400 alloy.

NaCl 35 g/L tests

Tests in NaCl 35 g/L were performed in order to trigger localized corrosion at lower potential, and eventually observe pitting. Nevertheless, pitting did not initiate, despite the higher chloride concentration. Electrochemical behavior is similar for the four metals, apart from UNS R50250 that showed a lower corrosion current density at low potentials. In Figure 4 potentiodynamic test results are visible. After bare metal characterization, surface treatments were tested. The first group includes anodization at 20 V - 30 V in sulfuric acid and thermal oxidation at 550°C for 1 hour. Anodization parameters were chosen based on previous knowledge about formed oxide, balancing the need to obtain thick and protective oxide and the necessity not to reach potentials that may lead to oxide crystallization. [6, 10]
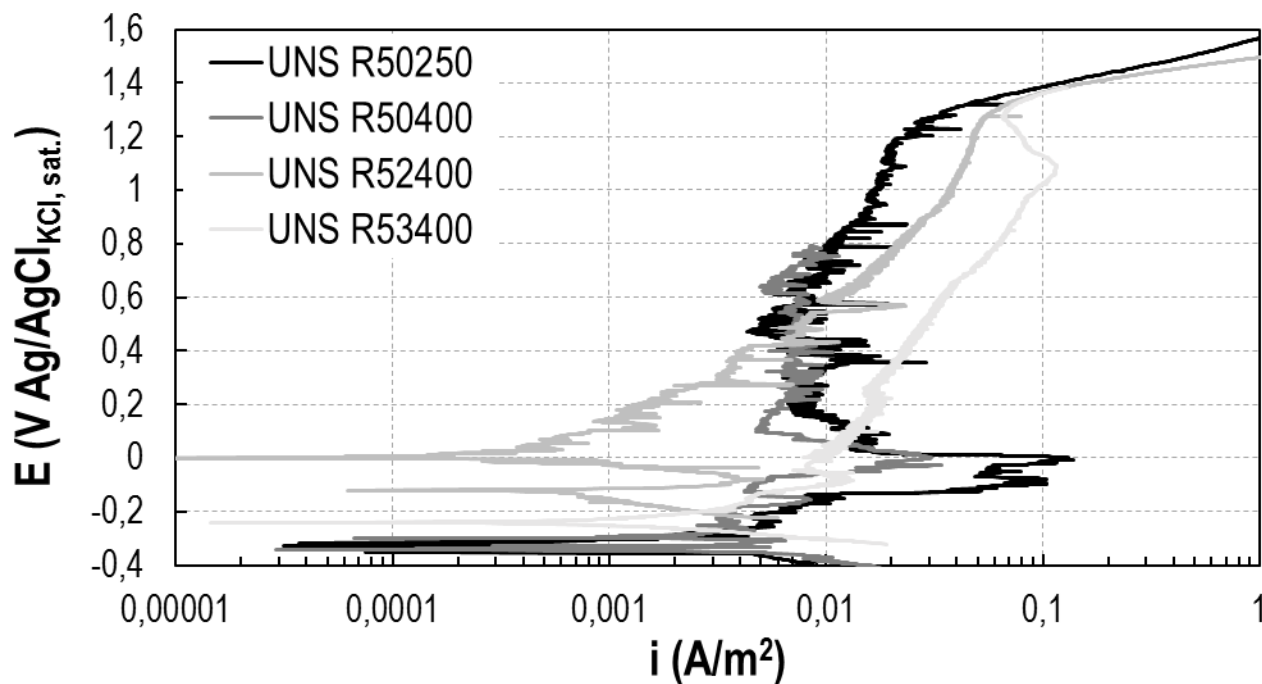Results are reported in Figure 5.

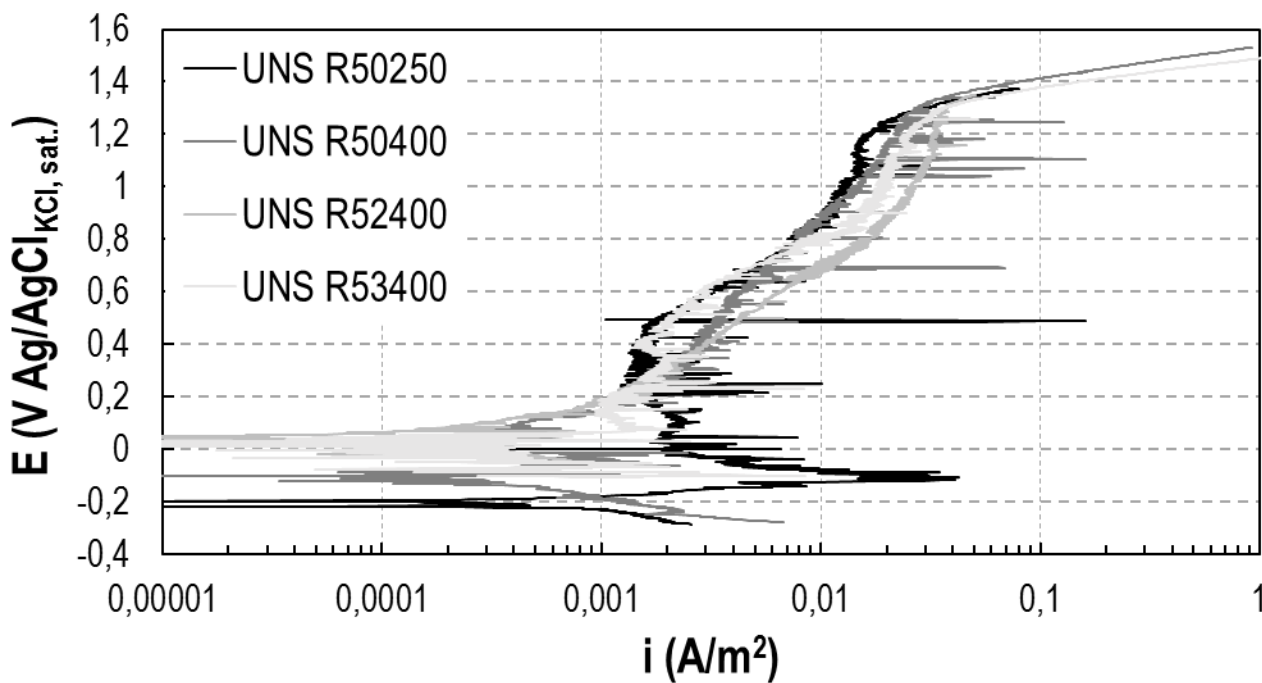**Figure 3: Potentiodynamic results in NaCl 10 g/L 25°C.**

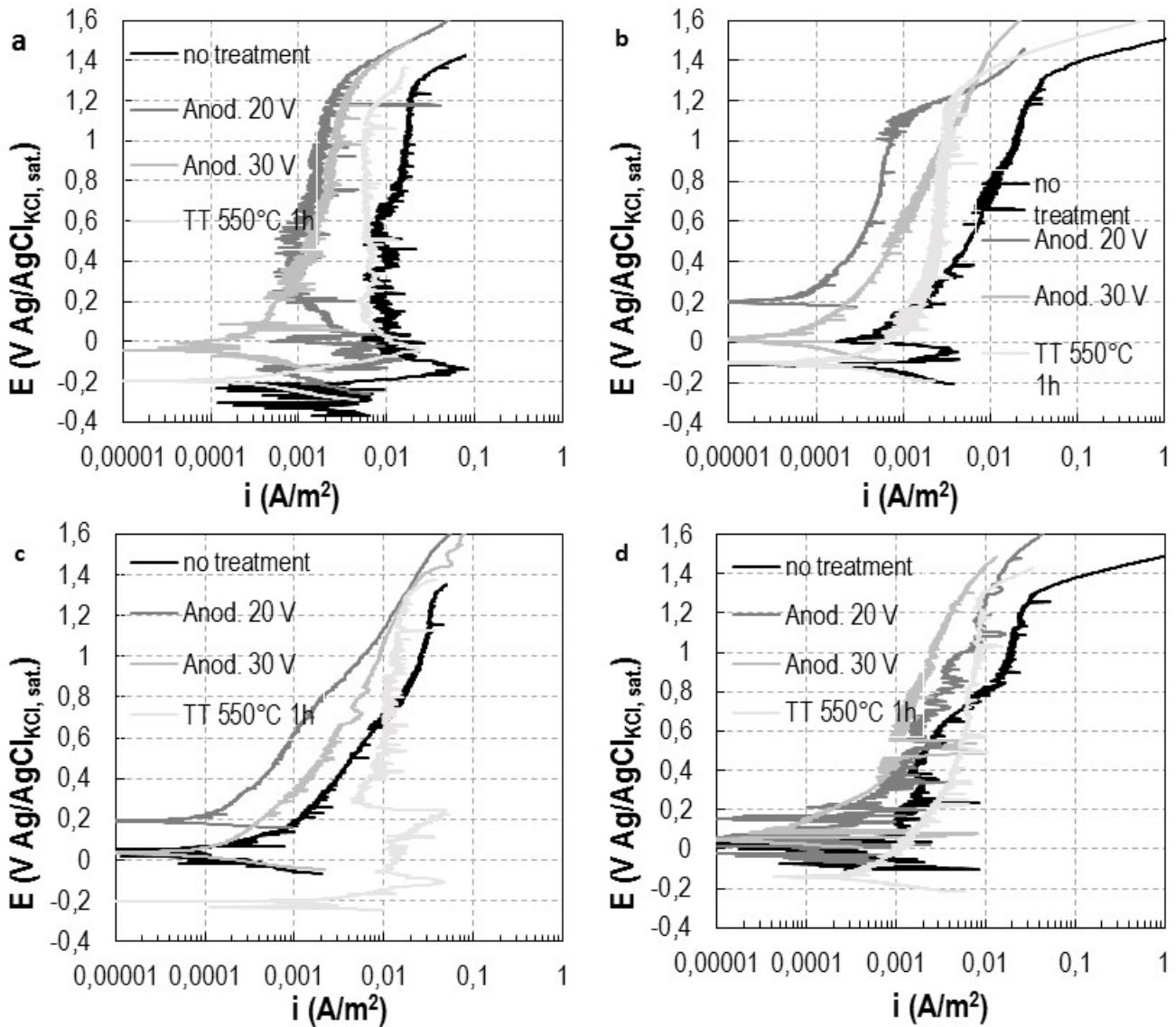**Figure 4: Potentiodynamic results in NaCl 35 g/L 25°C.**

Figure 5: Potentiodynamic tests in NaCl 35 g/L at 25°C on non-treated titanium, on titanium anodized at 20 V and 30 V, and on titanium thermally treated.
a) UNS R50250, b) UNS R50400, c) UNS R52400, d) UNS R53400

Results vary with the analyzed metal; for the two commercially pure titanium (UNS R50250 and UNS R50400), anodization treatment up to 20 V showed the lowest anodic current density for almost all the potential range scanned, followed by 30 V anodization, thermal oxidation and non-treated samples. The corrosion current density of the best treatment is one order of magnitude lower than the one obtained on pure metal.
The most important difference in results obtained on alloys is the inversion of thermally oxidized samples behavior with respect to a non-treated one, in these cases calcination gives worsening of corrosion resistance at potentials below 0.7 V, however, the behavior get better above this value.

NaCl 35 g/L tests at high temperature

High temperature tests were conducted at 80°C, then increasing to 95°C to favor localized corrosion. At this stage, roughness effect was also studied by polishing samples until mirror-like finishing. Results of UNS R50400 tested at 80°C and 95°C with anodizing or polishing treatments are shown in Figure 6.
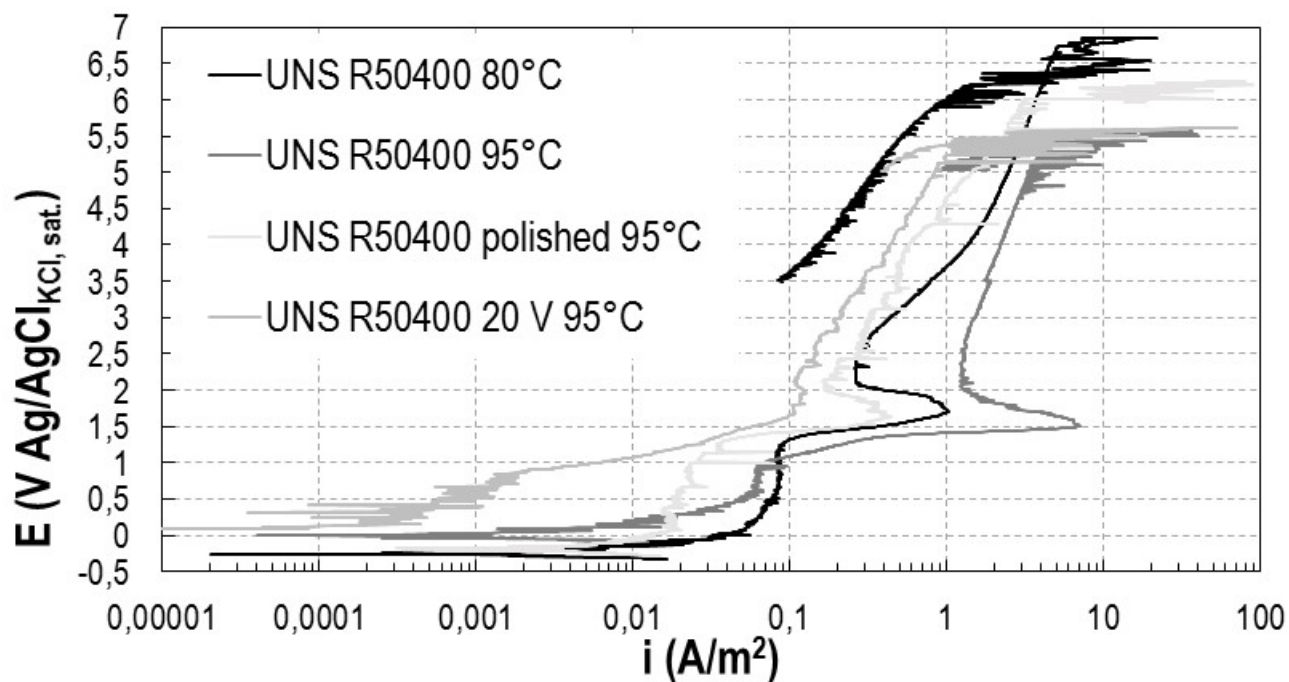
Figure 6: Potentiodynamic tests on UNS R50400 at high temperature, with anodization and polishing treatments

A corrosion resistance enhancement can be noticed both with anodic oxidation treatment and with mirror polishing treatment, especially at high potential. Anodization showed better behavior at low potential, which is more interesting for practical application, while polishing increases potential at which corrosion current density of 10 A/m² is reached, that is pitting corrosion resistance. Notice that the curves become very disturbed at potentials close to the one at which current reaches 10 A/m² that is the threshold chosen to distinguish pitting potential. This phenomenon is explained by the existence of "meta-pit", in which the material is subject to local failure and successive repassivation. Titanium UNS R52400 was tested in the same condition, as it is known as the most corrosion resistance titanium alloy, as visible in Figure 7. Its behavior is similar to non-treated UNS 50400, with corrosion current slightly lower at potential below 1 V and slightly higher above this value.

NaCl 100 g/L tests

NaCl concentration was raised up to 100 g/L, attempting to lower the potential at which metapits cause corrosion current to reach the threshold value of 10 mA/cm². Figure 8 shows that the potential at which current suddenly increases is similar to the one obtained at lower NaCl concentration, which is between 5.5 V and 6 V vs Ag/AgCl.

Behavior around 1.3 V

At 1.3 V vs Ag/AgCl an increase in corrosion current was detected in all the potentiodynamic tests. Even if some literature assign this behavior to a possible pitting phenomenon, potentiodynamic performed by reverting scan direction after 1.3 V showed that no localized corrosion was happening on the sample (Figure 9). To determine if this phenomenon is caused by anodic reaction of chlorine evolution, tests in Na_2SO_4 0.7 M were performed to avoid Cl^- ions. The same behavior is observed even in absence of chlorine, as visible in Figure 10, then confirming the nose at 1.3 V cannot be attributed to a localized corrosion. More possibly it is a sort of titanium passivation.
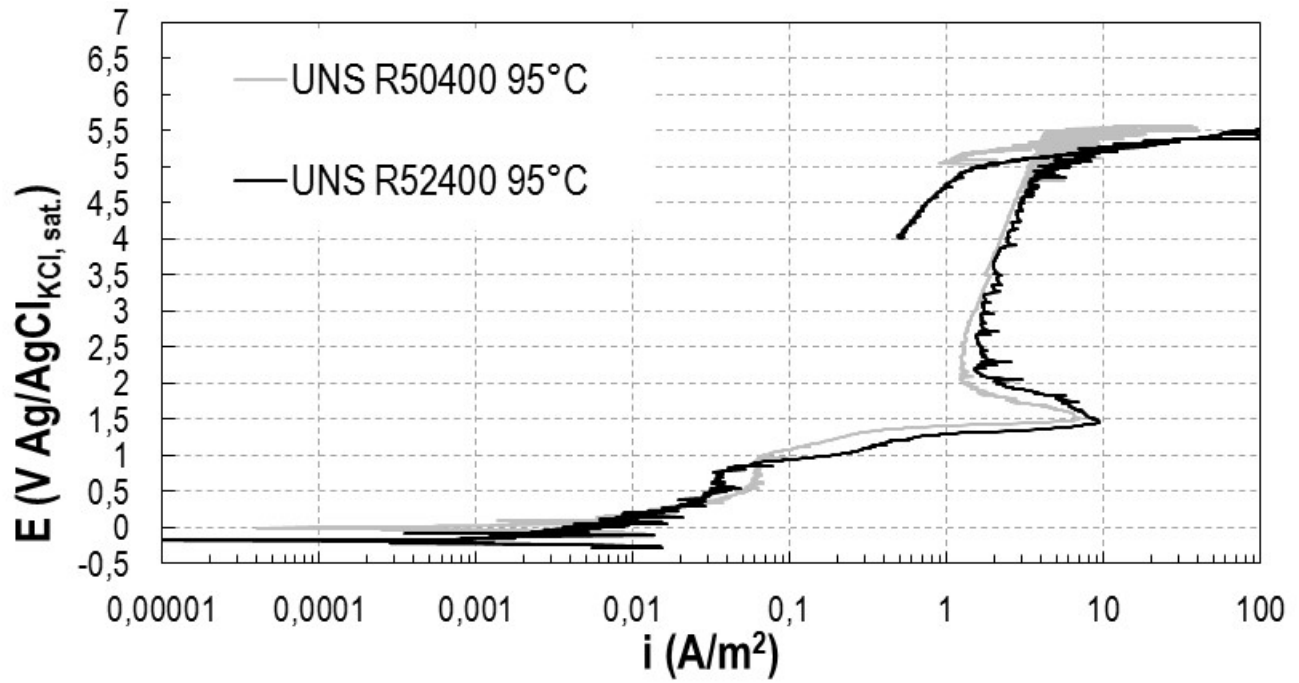
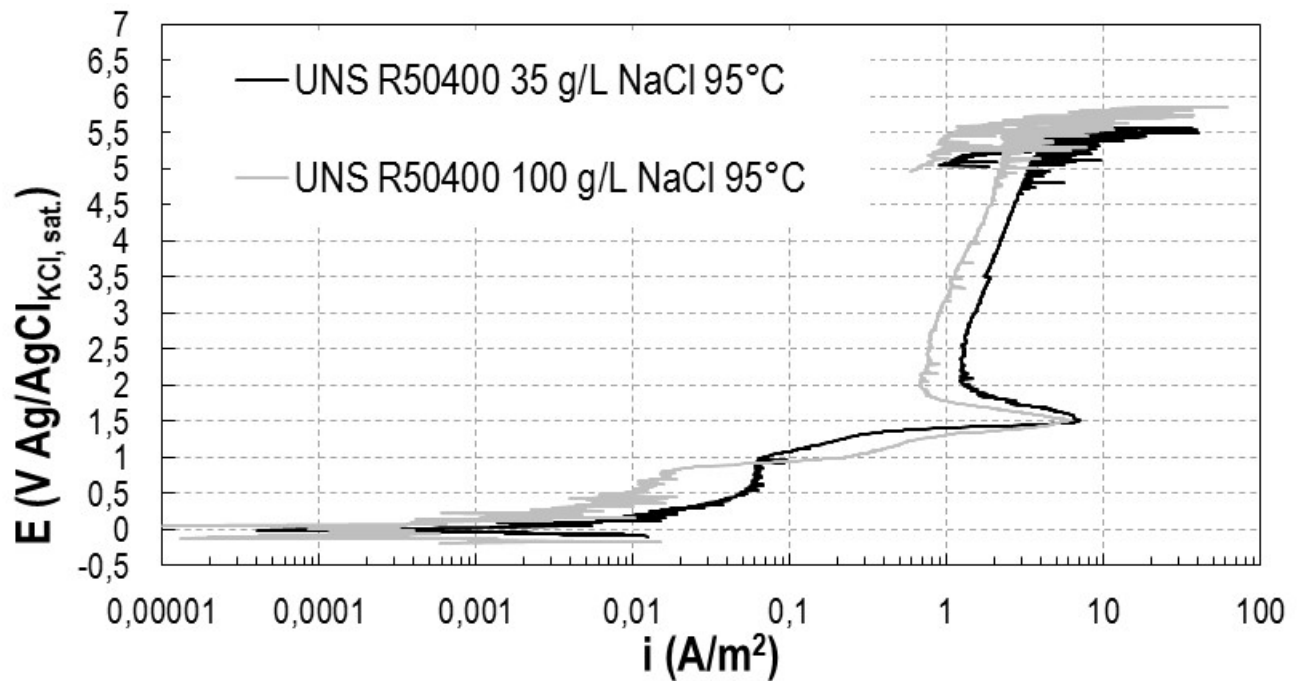**Figure 7: Potentiodynamic tests results in NaCl 35 g/L at 95°C on UNS R50400 and UNS R52400.**

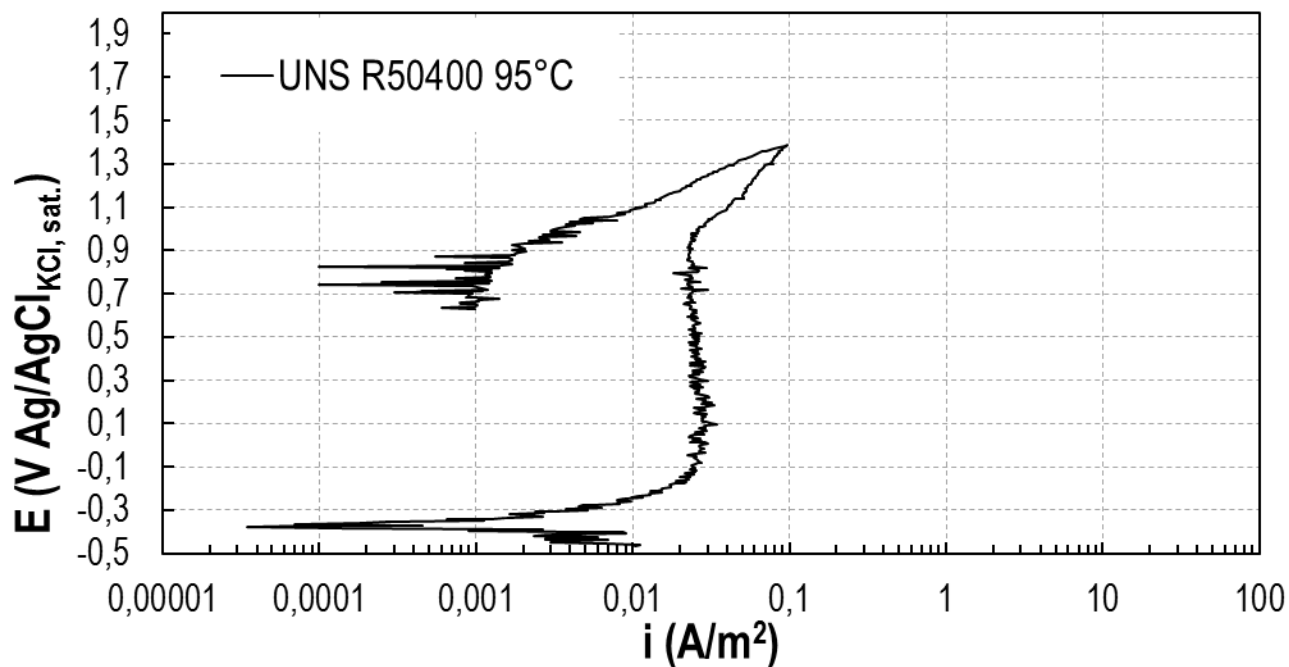**Figure 8: Potentiodynamic results of UNS R50400 in NaCl 35 g/L and 100 g/L at 95°C.**

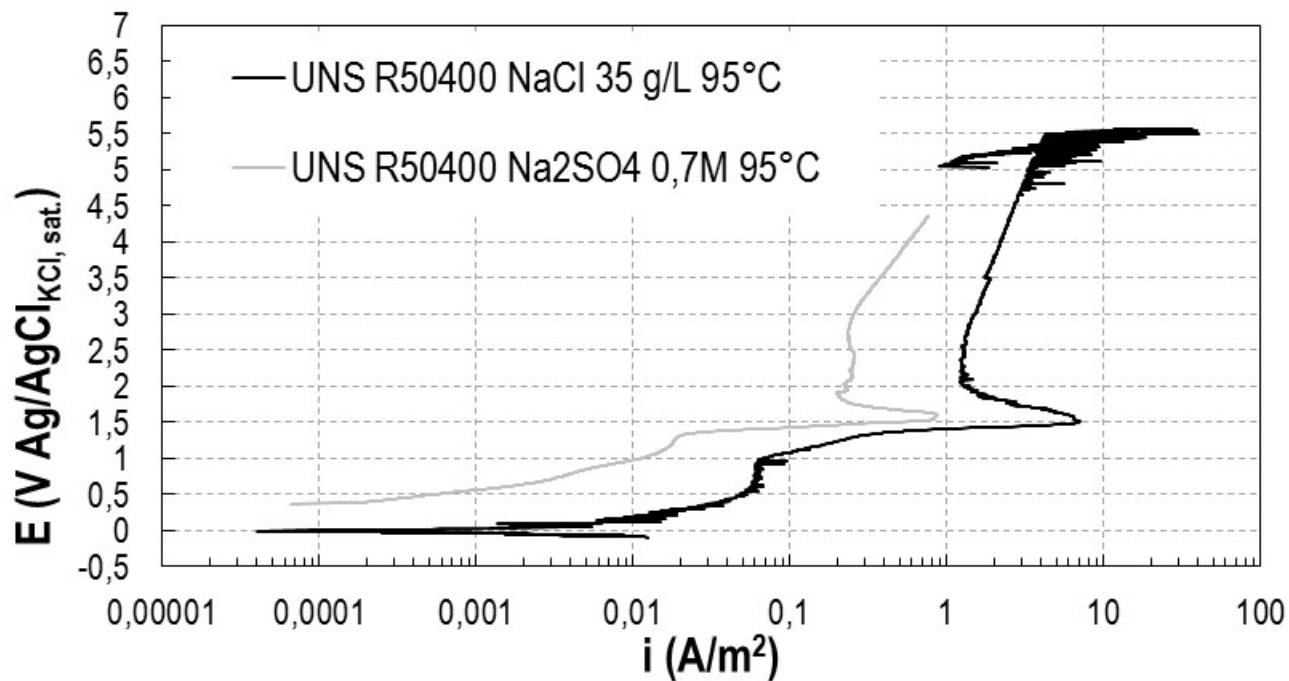**Figure 9: Potentiodynamic scan reversed at 1.3 V.**

Figure 10: Potentiodynamics on UNS R50400 in NaCl 35 g/L and Na₂SO₄ 0.7M at 95°C.

<u>NaF tests</u>

Preliminary tests were performed on UNS R50400 with different NaF concentrations in order to determine the proper content to obtain a measurable corrosion without reaching excessive severity of the environment that may lead to complete metal dissolution. NaF solution from 1 g/L to 35 g/L were tested. Comparisons between non-treated titanium and anodized one were conducted at low NaF concentrations.

Results are reported in Figure 11. At NaF content higher than 3.5 g/L, passivity of non-treated titanium is completely destroyed: specimens show the typical behavior of an active metal with an increasing current at increasing potential. At lower NaF concentration, non-treated titanium showed a passive behavior, with a lower passive current density at lower NaF concentration.

Tests on treated titanium were conducted in solution with NaF content 1 g/L, 3.5 g/L and 10 g/L. It is clearly visible (Figure 11) that the anodizing treatment improved corrosion resistance of commercially pure titanium, in fact:
- at the same fluoride content, passive current density of anodized titanium is lower than passive current density of non-treated one
- the critical NaF content to activate passive titanium increased from 3.5 g/L in the case of non-treated titanium, to 10 g/L in the case of anodized one.

Tests in 3.5 g/L NaF solution were performed to evaluate the effect of anodizing voltage (voltage ranged from 10 V to 80 V). Each test was repeated at least twice to ensure reproducibility. Potentiodynamic curves are visible in Figure 12. A slight correlation between electrochemical behavior and anodizing potential is visible: specimens anodized below 40 V appear more corrosion resistant than specimens anodized at higher voltages. However, the behavior of all the anodic oxidized samples is similar and corrosion current density is one order of magnitude lower with respect to the one obtained on non-treated sample. From these results it appears that titanium oxide thickness – that increases proportionally with anodizing potential [6] - is not directly correlated to the corrosion resistance. Conversely, the better corrosion behavior obtained at lower anodizing voltages suggest a possible effect of oxide crystallinity.
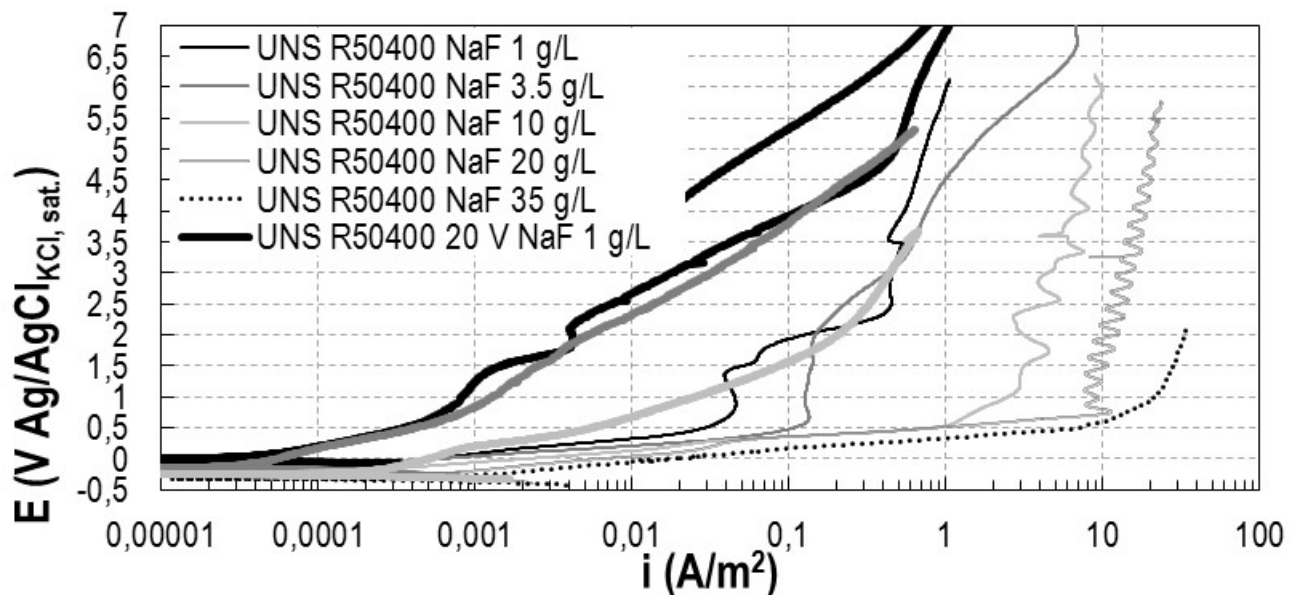

Figure 11: Potentiodynamic tests of UNS R50400 in different concentration of NaF with and without 20 V anodization treatment at 25°C.
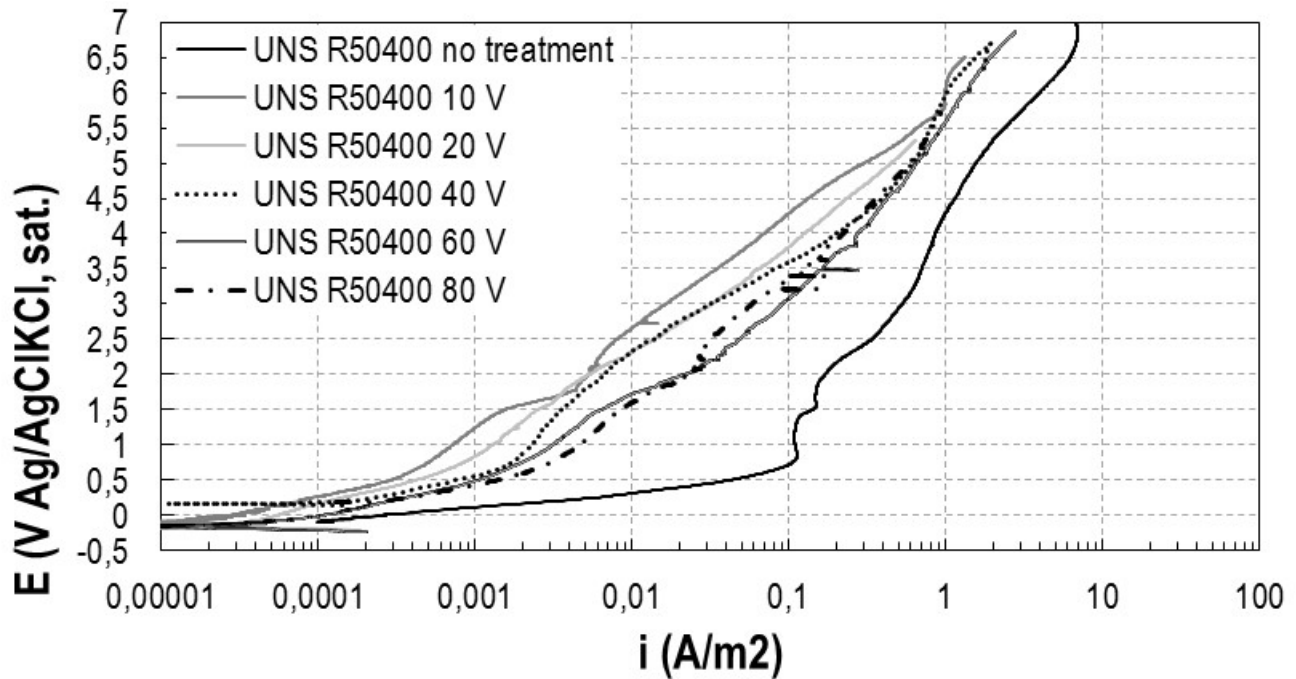
Figure 12: Potentiodynamic tests in NaF 3.5 g/L on UNS R50400 anodized at different voltages at 25°C.

Figure 13 shows the effect on corrosion resistance of the anodizing current density applied to reach the 20 V voltage. Current densities ranged from 5 mA/cm² to 50 mA/cm². The higher the current density, the quicker the oxide formation rate. Even if a possible effect on the crystalline structure of the oxide was expected due to the different oxide growth rate, only a marginal effect on electrochemical behavior was observed. Anodization carried out at 5 mA/cm² shows slightly lower corrosion current density.
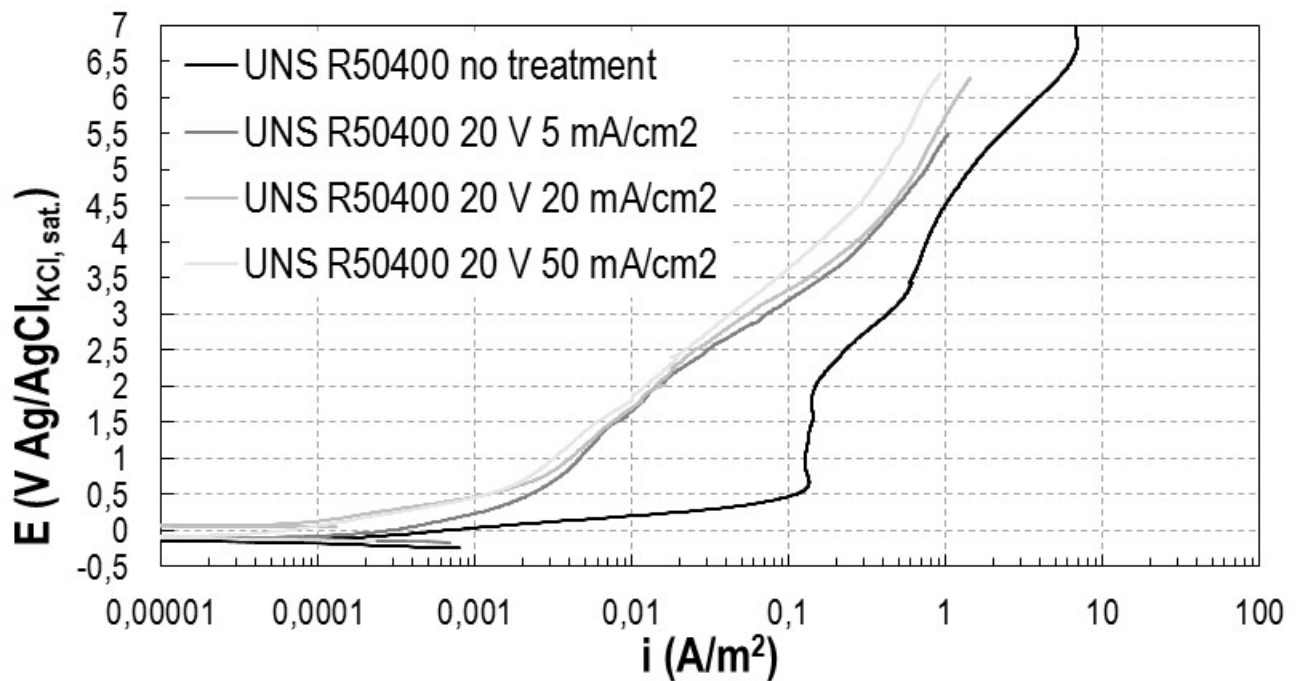

Figure 13: Potentiodynamic tests in NaF 3.5 g/L on UNS R50400 anodized at different current density at 25°C.

To investigate the effect of anodization bath, three solutions were tested apart from sulfuric acid: $(NH_4)_2SO_4$, Na_2SO_4 and NH_4BF_4. These solutions were chosen in order to find a treatment suitable for industrial applications; in fact the use of sulfuric acid solution would have some drawbacks in handling the cell and in the disposal of the used acid. UNS R50400 was anodized at 20 mA/cm^2 up to 20 V in every considered bath and then tested twice in NaF 3.5 g/L. Results are visible in Figure 14: the electrolyte does not affect the corrosion behavior.

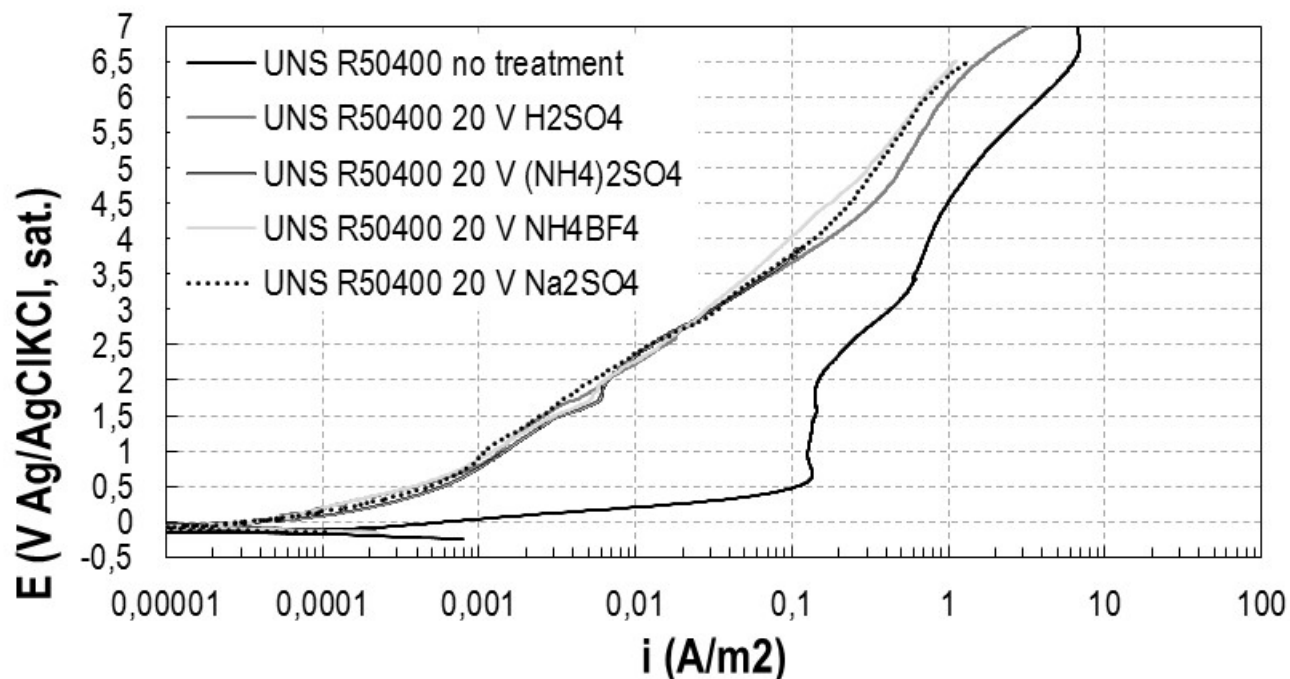**Figure 14: Potentiodynamic tests in NaF 3.5 g/L on UNS R50400 anodized in different electrolytes at 25°C.**

Effect of anodization on cathodic curves

Cathodic potentiodynamic curves were performed to investigate the effect of anodized titanium on the slope of the hydrogen evolution reaction. It is well-know that the enhanced corrosion resistance of UNS R52400 is related to the decrease of hydrogen overvoltage given by palladium addition into the alloy.[11] Tests were performed in HCl 10%. Results are shown in Figure 15. Cathodic Tafel slopes in the order of 130 mV/decade, 150 mV/decade and 170 mV/decade were measured on UNS R52400, UNS R50400 anodized and UNS R50400, respectively. Anodized UNS R50400 has an effect on the cathodic behavior in between the non-anodized titanium and the Ti-Pd alloy; however, the difference in Tafel slopes is minimum to deduce affordable conclusions.

CONCLUSIONS

Anodization treatment can be used to improve the corrosion behavior of commercially pure titanium. Treated titanium has an higher resistance both to chloride and fluoride containing solutions. The better improvement is achieved at anodizing voltages lower than 40 V, due to the formation of an almost amorphous oxide layer. This enhanced corrosion resistance is independent from anodization current density and anodization bath. Anodization at low current density is preferable because of the lower energy required. However, while lower current requires less power, higher current accelerates the process, reducing required time.
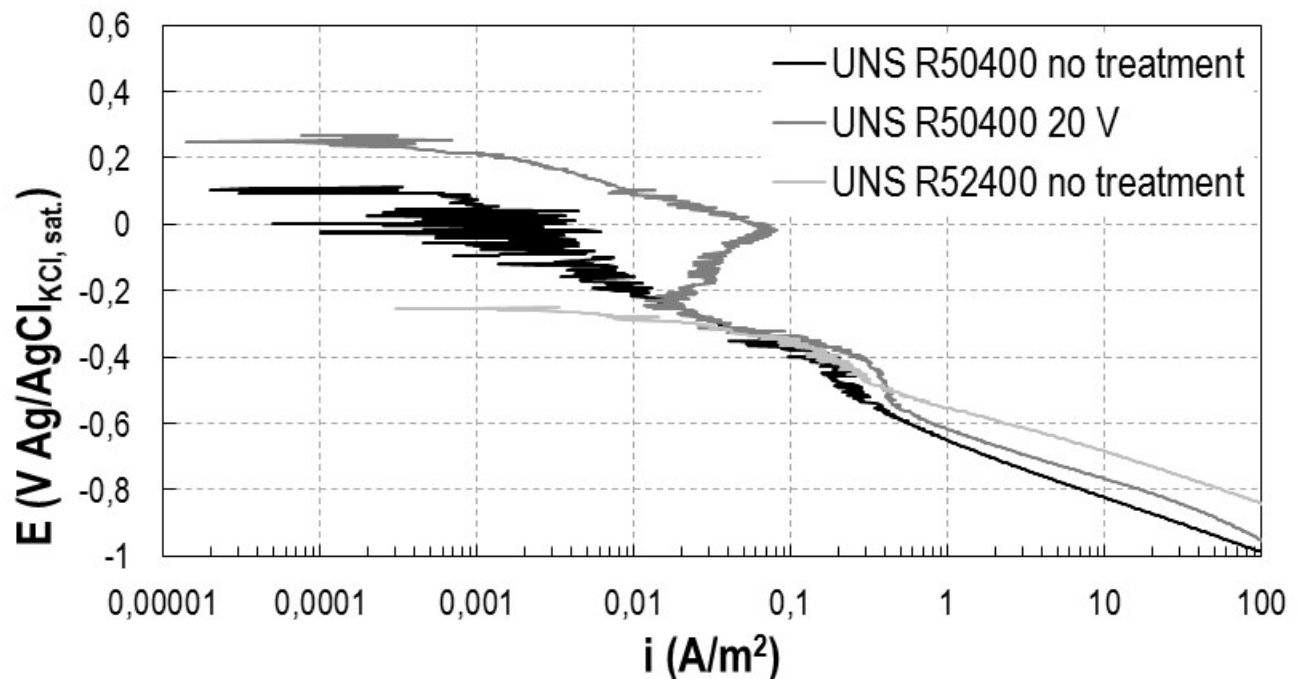
Figure 15: Cathodic curves in HCl 10% at 25°C.

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