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Title: Chemical oxidation as repairing technique to restore corrosion resistance on damaged anodized titanium

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Keywords: Titanium oxidation; chemical oxidation; anodizing; TiO<sub>2</sub>; surface treatment.

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Abstract: Anodized titanium shows an excellent resistance to pitting corrosion. However, it could be subject to failure in case of local removal of the oxide film due, for example, to incorrect handling during transport, installation, or use. Depending on part size and usage, an electrochemical anodizing treatment could be not feasible. In this case, localized chemical oxidation treatment could be used to recover damaged film and restore corrosion resistance. Chemical oxidation was performed on titanium by immersion in NaOH 10 M and H<sub>2</sub>O<sub>2</sub> 10 M at temperature from room to 90°C with duration ranging between 1h and 72h. Potentiodynamic tests in bromides 0.5 M were used to determine the effectiveness of the treatment in relation with the one obtained with anodic oxidation. Higher bath temperature led to faster growth of the film, however it has no effect on the final corrosion resistance. Breakdown potential in bromides increased with treatment duration. The establishment of a plateau occurs at earlier stage, as temperature is increased. Titanium samples anodized and then scratched, to simulate film mechanical removal, were recovered using chemical oxidation and initial corrosion resistance was restored. The suggested treatments for in-situ recovery are 72h of exposure to NaOH or 6h at H<sub>2</sub>O<sub>2</sub> at room temperature.

## Cover Letter

Dear Editor,

I am enclosing herewith a manuscript entitled: “Chemical oxidation as repairing technique to restore corrosion resistance on damaged anodized titanium”. The work has been presented at EuroCorr 2018 in the technical session Inorganic coating. The manuscript has been prepared according to the “Surface and Coatings Technology” guidelines.

The article evaluates the effect of chemical treatment on the enhancement of corrosion resistance of commercially pure titanium.  $\text{TiO}_2$  protective layer that is formed spontaneously on its surface giving titanium a strong passive electrochemical behavior. Commercially pure titanium may suffer localized corrosion in halides containing environment, above all fluoride and bromides, in hot salty water, in non-oxidizing solution, such as anhydrous methanol and red-fuming nitric acid. To cope these problems, anodic oxidation, consisting in applying an anodic polarization of several tens of volts to the metal, promoting the growth of an artificial oxide layer, has been proposed. Anodized titanium has a very high corrosion resistance. 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  $\text{H}_2\text{O}_2$  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.

All authors of this research paper have directly participated in the design, execution, or analysis of this study; all authors have read and approved the final version submitted. The authors declare no competing financial interest.

The paper is original and not considered for publication elsewhere.

Please consider it for publishing in your Journal.

Thank you for kind attention.

The corresponding author:

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## COMMENTS TO REVIEWER

Dear Reviewer, thank you again for the further suggestions and comments.

- As suggested we rename the paragraph
- We reduce the number of the figures, using scatter plots in place of histograms, also condensating some figures
- Conclusions were reviewed
- English has been improved

Changes in the manuscript are yellow highlighted.

## \*Highlights (for review)

- Commercially pure titanium was chemically oxidized in NaOH and H<sub>2</sub>O<sub>2</sub> baths
- The maximum of corrosion resistance in NaOH was achieved after 12h at 60°C
- H<sub>2</sub>O<sub>2</sub> kinetic is faster: the same resistance is achieved in 6h at room temperature
- Both treatments can restore corrosion resistance on damaged anodized titanium

## Chemical oxidation as repairing technique to restore corrosion resistance on damaged anodized titanium

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### Abstract

Anodized titanium shows an excellent resistance to pitting corrosion. However, it could be subject to failure in case of local removal of the oxide film due, for example, to incorrect handling during transport, installation, or use. Depending on part size and usage, an electrochemical anodizing treatment could be not feasible. In this case, localized chemical oxidation treatment could be used to recover damaged film and restore corrosion resistance. Chemical oxidation was performed on titanium by immersion in NaOH 10 M and H<sub>2</sub>O<sub>2</sub> 10 M at temperature from room to 90°C with duration ranging between 1h and 72h. Potentiodynamic tests in bromides 0.5 M were used to determine the effectiveness of the treatment in relation with the one obtained with anodic oxidation. Higher bath temperature led to faster growth of the film, however it has no effect on the final corrosion resistance. Breakdown potential in bromides increased with treatment duration. The establishment of a plateau occurs at earlier stage, as temperature is increased. Titanium samples anodized and then scratched, to simulate film mechanical removal, were recovered using chemical oxidation and initial corrosion resistance was restored. The suggested treatments for in-situ recovery are 72h of exposure to NaOH or 6h at H<sub>2</sub>O<sub>2</sub> at room temperature.

**Keywords:** Titanium oxidation; chemical oxidation; anodizing; TiO<sub>2</sub>; surface treatment

### 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 [8–14].

In such aggressive environments, commercially pure titanium may suffer different form of corrosion [15,16], as pitting promoted by the presence of concentrated halides, hot salty water or bromide salts [3,17].

To improve titanium corrosion resistance, Ti alloys with palladium were developed [18], together with alternative surface techniques, such as nitration, that consist in introducing nitrogen in the first  $\mu\text{m}$  of the surface to promote the formation of TiN. [19,20] 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. [21]

For this reason, treatments that act on the naturally formed passive layer are preferred. The easiest and cheapest treatment to adjust oxide layer is anodic oxidation. It consists in applying an anodic polarization of several tens of volts to the metal, promoting the growth of a compact, adherent and corrosion resistant oxide with thicknesses ranging from about 40 nm with anodizing potential 10 V, to about 250 nm at 100 V. [22–24]

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 would be suitable to provide the corrosion resistance enhancement needed. Moreover, chemical oxidation can be used to restore mechanically disrupted oxide continuity. Abrasions and scratches during parts transport or installation can lead to lack of protection where anodic oxide is locally removed. In-situ recovery prevents the need of part re-treatment.

Most common reagents used for chemical oxidation are alkoxides (e.g. NaOH, KOH) and hydrogen peroxide [25–27]. Sodium and potassium hydroxide dissociate in water releasing metal cation and hydroxide anion. The latter promotes titanium oxide growth [28]. Hydrogen peroxide treatment has been less investigated in literature; the proposed mechanism of oxide formation pass through numerous intermediates [26–29], with the formation of OH radicals responsible of Ti oxidation.

The purpose of this work was to find key parameters that influence the formation of chemically promoted oxide layer, to tune them in order to achieve the highest corrosion resistance and to use this treatment to spot recover oxide on previously anodized parts.

## **2 Materials and Methods**

### **2.1 Specimens**

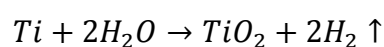
Samples with dimensions 20x20x1.6 mm were cold-cut from a titanium UNS R50400 (ASTM grade 2) sheet, and polished with 100 and 300 grit silicon carbide paper. To remove possible surface contaminations, the specimens were degreased with ethanol in ultrasonic bath for 4 minutes and then rinsed in distilled water in ultrasonic bath for 4 minutes.

## 2.2 Passivation

### 2.2.1 Hydroxides

NaOH was used for its ease of production and storage, and for its tendency to produce less porous and more compact oxide film. [25] Treatments were performed by soaking titanium samples in 100 ml beakers, with different quantity of electrolyte: 10 ml, 50 ml and 100 ml. Different soaking duration were tested: 3h - 6h - 12h - 24h - 72h. NaOH concentration was 10 M and 50 M. Temperature was kept at 25°C and 60°C.

Temperature was maintained below 60°C to avoid hydrogen embrittlement due to the formation of titanium hydrides with hydrogen generated by the secondary reaction: [28]



Post-treatment annealing was performed on some samples to convert sodium titanate hydrogel, formed on the surface during chemical oxidation, into amorphous titanate layer, in order to reduce protective layer porosity. [30,31] Annealing treatments were performed at 400°C, 500°C or 600°C for 1 hour in air.

### 2.2.2 Hydrogen Peroxide

Hydrogen peroxide treatments were performed in a 10 M H<sub>2</sub>O<sub>2</sub> solution, prepared few minutes before the treatment, from a H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub>, the minimum solution quantities tested was 50 ml. With lower solution quantity, the H<sub>2</sub>O<sub>2</sub> decomposition becomes relevant, then affecting the solution concentration during the test.

Annealing was performed at either 350°C, 400°C, 450°C 500°C, 600°C and 700°C for 1h. Annealing is 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.[27]

## 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 rupture. Scales detached in this way were gold sputtered, turned by 90° 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-K $\alpha$  radiation with a wavelength of 0.154 nm. This technique does not 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 test

Samples corrosion resistance were characterized with potentiodynamic tests performed with MetroOhm Autolab potentiostat M204. A standard 3-electrode 1 liter cell was used. An activated titanium counter electrode, a silver/silver chloride (SSC) reference electrode and a working electrode 1 cm<sup>2</sup> of exposed area were used. Tests were carried out in 0.5 M ammonium bromide [32]. Open circuit potential (OCP) was recorded for 1h of sample immersion in the testing solution. Then potential was scanned from -0.1 V vs OCP up to 8 V vs SSC with a scan rate of 20 mV/min. A current density of 10 A/m<sup>2</sup> was chosen as threshold to define localized oxide breakdown.

As the duration of each test did not exceed 8h, no sealing was considered. Previous works on titanium oxide tested in such conditions showed that nor chemical ( $\Delta\text{pH} \approx 0.05$ ) nor physical ( $\Delta\text{T} \approx 2^\circ\text{C}$ ) deviations were expected [24]. In order to ensure repeatability, a minimum of three measurements were made for each treatment.

## 2.5 Scratch test

To simulate and abrasion event occurred during part transportation, installation or usage, anodized samples were scratched, leading to a partial removal of protective oxide. Scratched samples were then vibrated in ethanol and rinsed in water to remove possible silicon carbide embedded particles.

For a reproducible scratching procedure, a rectangular strip of grit 300 emery paper (1 cm x 4 cm) was dragged over the titanium coupon for its whole length, being subject to a weight of 1 kg over its 4 cm<sup>2</sup> surface. A uniform pressure was guaranteed by placing supports of the same height of the sample (Fig. 1)

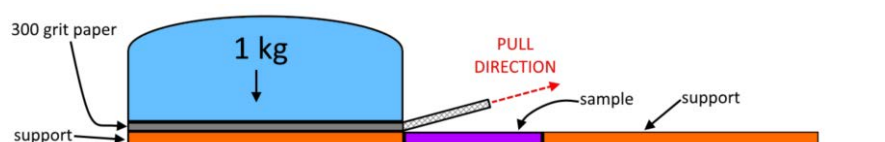


Figure 1 Scheme of scratching mechanism

Anodized and scratched samples were then subject to chemical oxidation to repair the oxide.



### 3 Results and Discussion

#### 3.1 Solution concentration and quantity

The effect of the volume of solution on titanium corrosion resistance is shown in Fig. 2. The five-plotted curves are a representative of all the repetitions performed. Blue curves describe the corrosion behavior observed on titanium anodized in 10 ml, 50 ml and 100 ml of NaOH. The effect on localized corrosion lays within the experimental error. The same phenomenon is observed on red curves, obtained on titanium anodized in different volumes of H<sub>2</sub>O<sub>2</sub>.

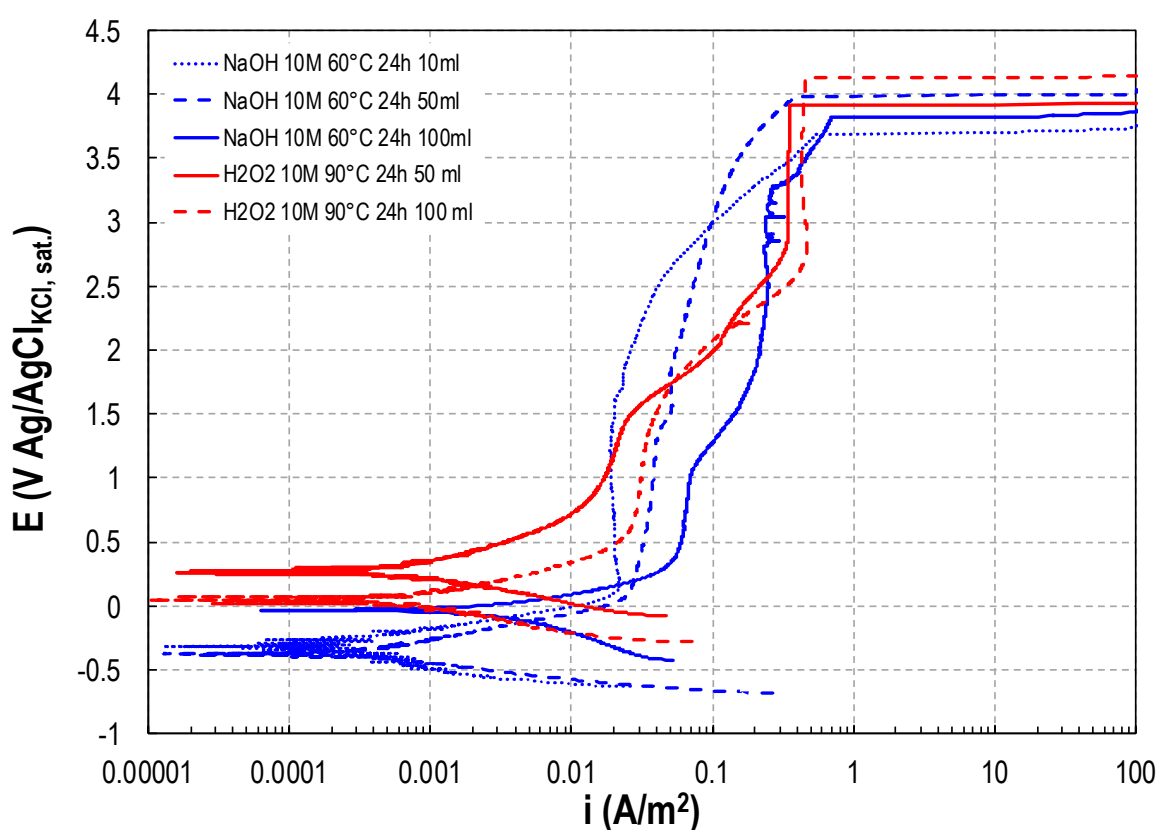


Figure 2 Effect of NaOH and H<sub>2</sub>O<sub>2</sub> treatment solution volume on samples corrosion resistance to NH<sub>4</sub>Br 0.5 M

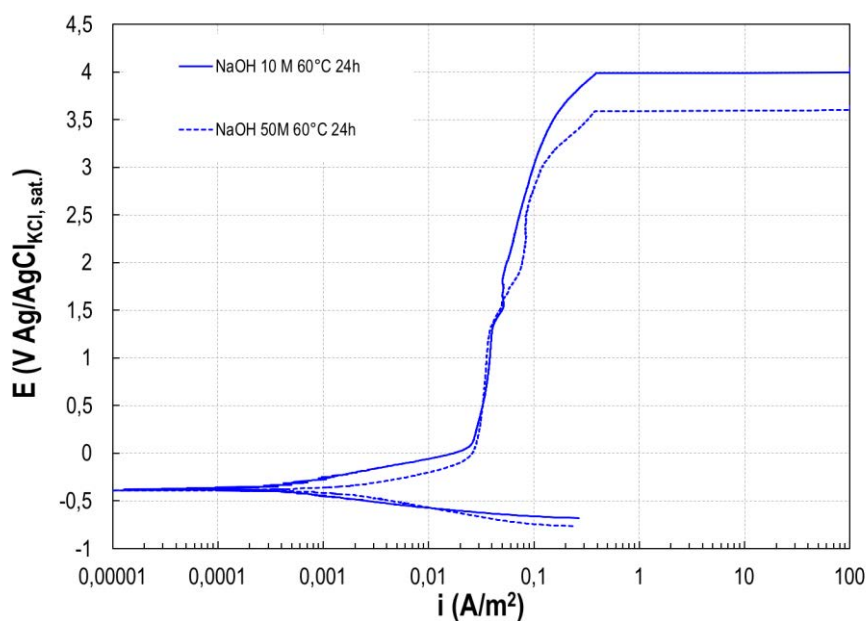
From this observation, two contrasting hypothesis were made.

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 second hypothesis is that 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 only marginally to the oxide growth and the effect are not visible on the breakdown potential.

To discern the correct hypothesis, the treatment was repeated by considering 50 M NaOH. 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 rate progressively slow down to negligible values, the higher concentration would not lead to higher corrosion resistance.

The effect of NaOH concentration increase from 10 M to 50 M is shown in **Fig. 3**.



**Figure 3** Effect of NaOH concentration on samples corrosion resistance to bromides 0.5 M

No differences in corrosion resistance were observed with NaOH concentration increase.

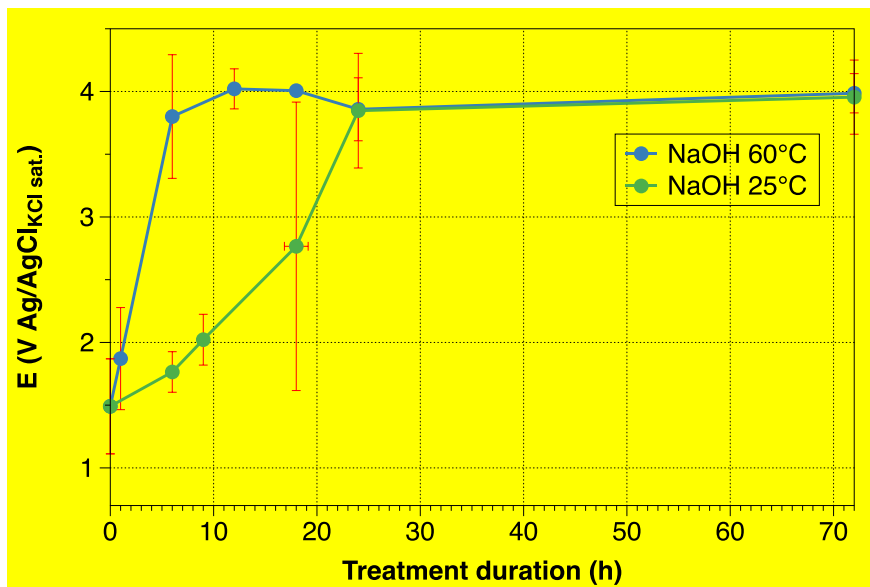
It is important to notice that, even if it does not affect the final corrosion resistance, the increase in concentration modifies oxide growth kinetic enough to produce different aesthetic appearance of the oxide. Titanium oxide interference color is strongly dependent on oxide thickness, its variation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



**Figure 4** Sample aesthetic appearance changing passing from 10 M NaOH (left) to 50 M NaOH (right) treatment conducted for 24h at 60°C

### 3.2 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. 5 shows the results of at least three potentiodynamic tests performed on samples treated for 1h, 6h, 12h, 18h, 24h and 72h at 60°C in NaOH.



**Figure 5** Effect of treatment temperature and duration on NaOH chemical oxidized samples breakdown potentials in  $\text{NH}_4\text{Br}$  0.5 M

After 12h of treatment the increase of corrosion resistance become negligible and the only effect is a narrowing of results distribution due to a stronger and more reliable oxide film.

The existence of a similar plateau was investigated also at room temperature, in order to simplify a possible in-situ treatment, without the requirement of a local heat at 60°C for many hours. Results are shown in Fig. 5. Lowering the temperature has the effect to increase the time necessary to get the maximum corrosion resistance plateau. In both the cases, the final corrosion resistance is not influenced by treatment temperature.

To validate oxide growth kinetic hypothesis, SEM observations of oxide cross-section were performed to measure the oxide thickness. Fig. 6 shows the cross-section of an oxide obtained by soaking titanium for 12 hours in NaOH 10 M. Oxide thickness is about 1  $\mu\text{m}$ . Fig. 7 reports the thickness of the oxide obtained at different soaking duration in NaOH 10 M at 60°C.

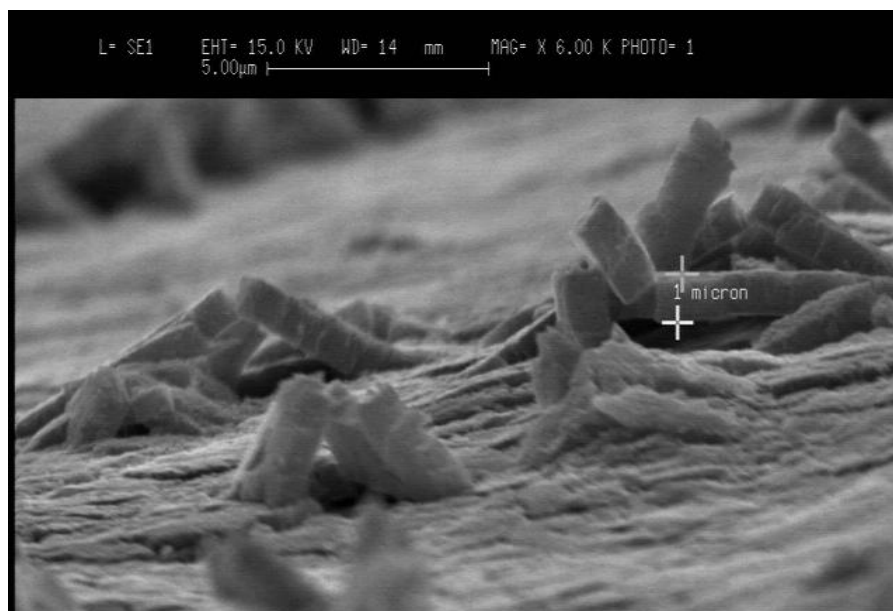


Figure 6 SEM observed cross section of the oxide produced by 12 hours of treatment in NaOH 10 M

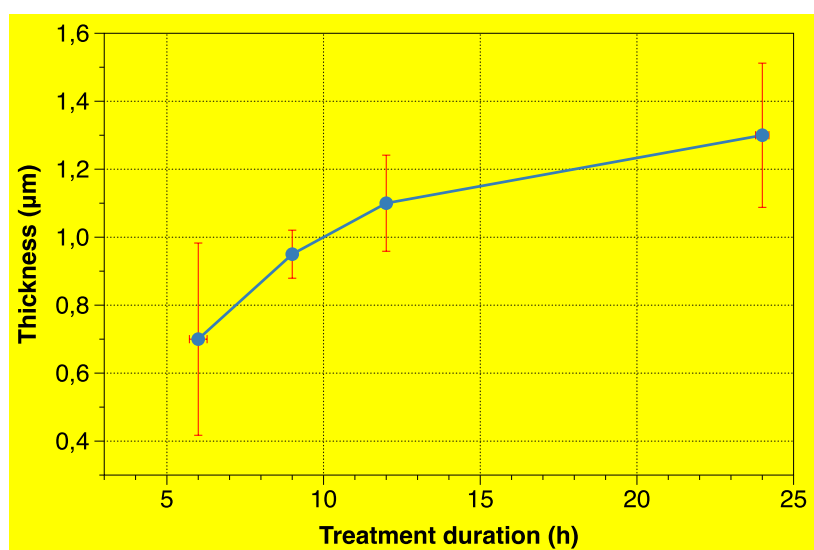
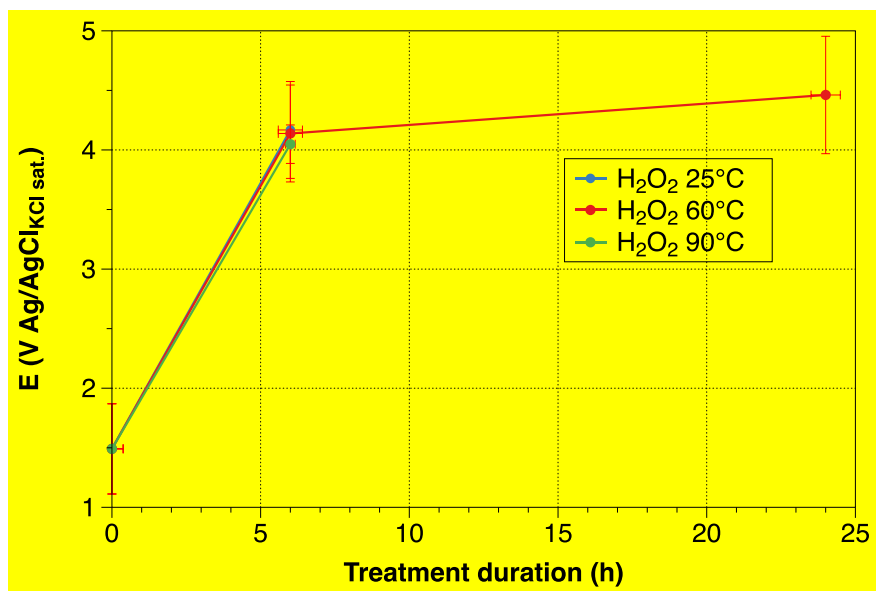


Figure 7 Effect of NaOH treatment duration on titanium oxide thickness at 60°C

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 passing from 12h to 24h of treatment. These data correlate the stabilization of corrosion resistance given by increasing treatment duration with oxide growth kinetic.

The low conductivity of TiO<sub>2</sub> film, in the order of 10<sup>-11</sup> S/m [33], hinders current flow from the electrolyte to the sample, increasing ohmic drop at the interface. Thus, thicker oxides provide higher corrosion protection if their composition and phase remains constant. It was proved that, if the oxide grow in thickness but increase in crystallinity, no advantage on corrosion resistance is provided. [24]

The same trend was found on H<sub>2</sub>O<sub>2</sub> treatments, as reported in Fig. 8.



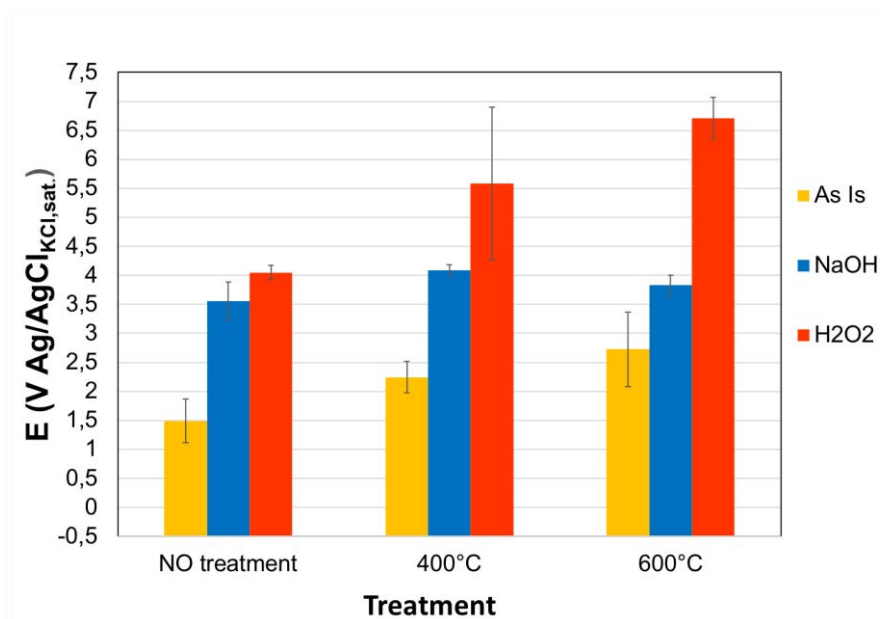
**Figure 8** Effect of treatment temperature and duration on H<sub>2</sub>O<sub>2</sub> chemical oxidized samples breakdown potentials in NH<sub>4</sub>Br 0.5 M

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<sub>2</sub>O<sub>2</sub> occurs before 6h at 25°C, suggesting a faster kinetic compared to NaOH.

### 3.3 Post annealing treatment

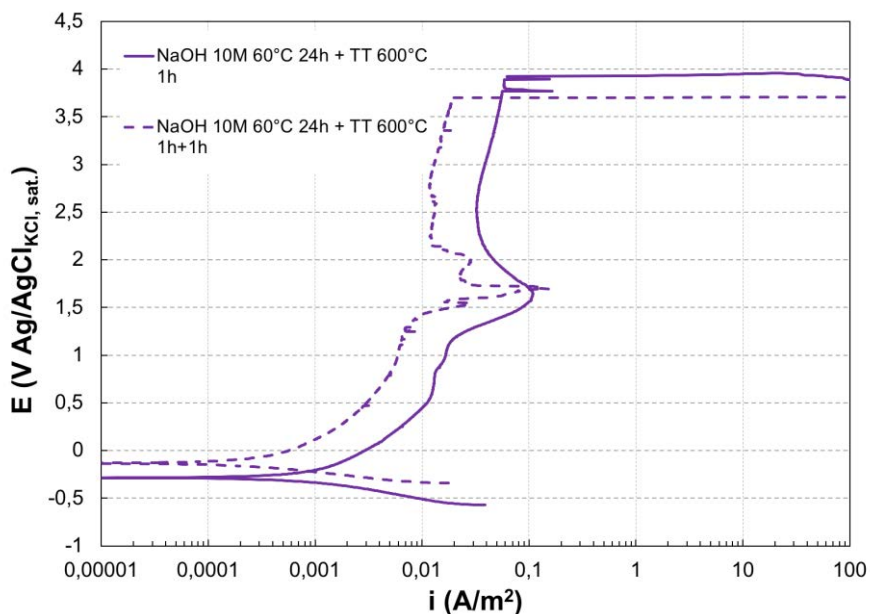
To achieve better corrosion resistance in bromides, overcoming the 4 V breakdown potential plateau observed in both NaOH and H<sub>2</sub>O<sub>2</sub> treatments, annealing for 1h at 400°C and 600°C was performed. Fig. 9 compares between the effect of calcination. Thermal treatment has a moderate effect on corrosion resistance of non-pre-oxidized titanium, due to the thickening of titanium dioxide during the thermal oxidation. Annealing has no effect at both

temperatures on samples treated in NaOH, while it has an interesting effect on titanium oxidized in NaOH promoting an increase of the breakdown potential up to 6.5 V SSC.



**Figure 9** Effect on breakdown potential in  $\text{NH}_4\text{Br}$  0.5 M of thermal treatments at 400°C and 600°C for 1h on non-treated titanium, NaOH oxidized titanium and  $\text{H}_2\text{O}_2$  oxidized titanium

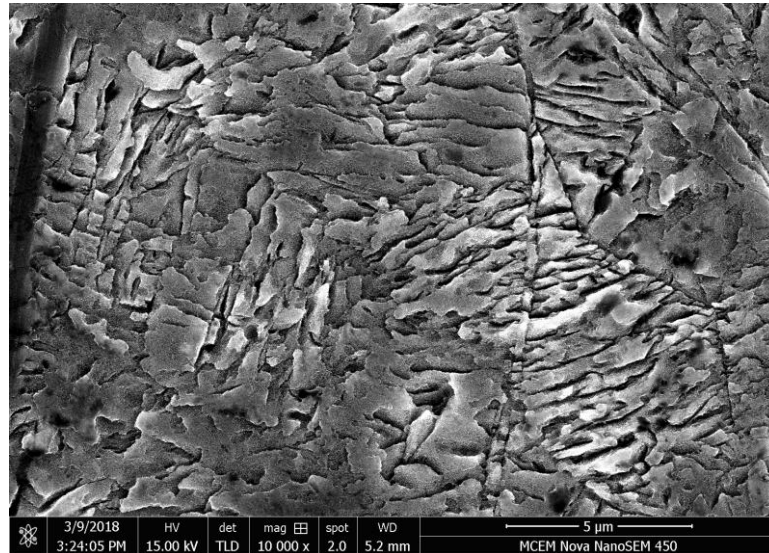
As a positive effect of annealing on  $\text{H}_2\text{O}_2$  treated titanium is reported in literature [34], the duration of the treatment was doubled. No effect on corrosion resistance was observed (Fig. 10).



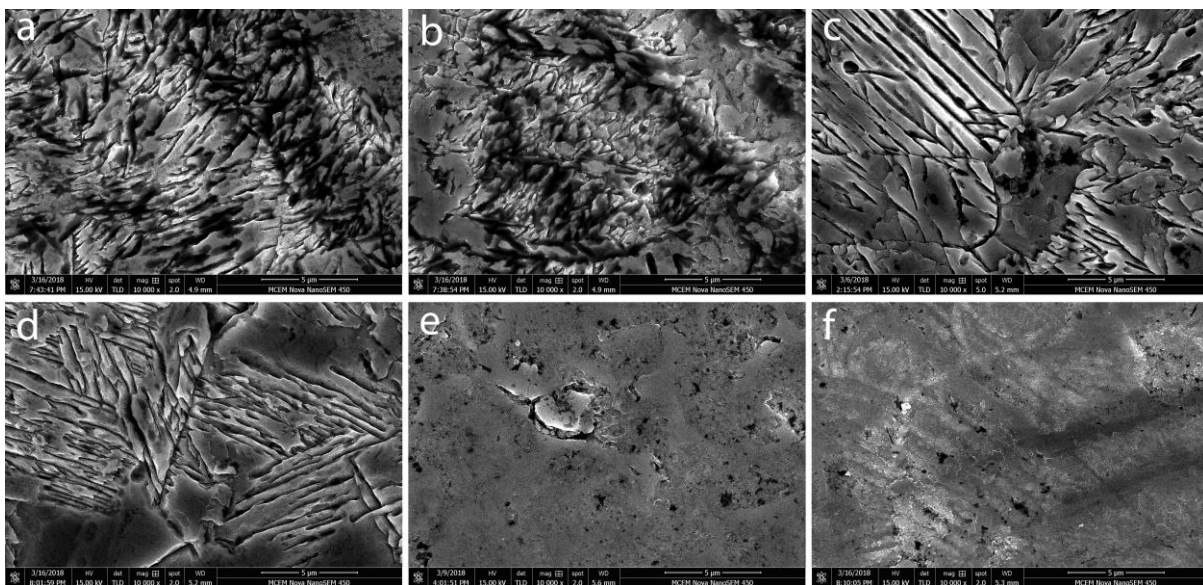
**Figure 10** Effect of thermal treatments duration on breakdown potential in  $\text{NH}_4\text{Br}$  of samples oxidized in NaOH at 60°C for 24h



The positive effect of annealing on titanium treated with  $H_2O_2$  was further investigated, by performing SEM analysis on the treated surface. The oxide obtained at room temperature has a disordered lamellar structure with cracks 0.1-0.2  $\mu m$  wide (Fig. 11). This structure does not change up to 500°C (Fig. 12). At higher temperature, cracks are recovered, mainly due to the thermal film growth. This has been assume the reason of the enhanced corrosion resistance of samples treated at higher temperatures (Fig. 9).



**Figure 11** Surface morphology of samples treated in  $H_2O_2$  for 6h at 25°C without any further treatment

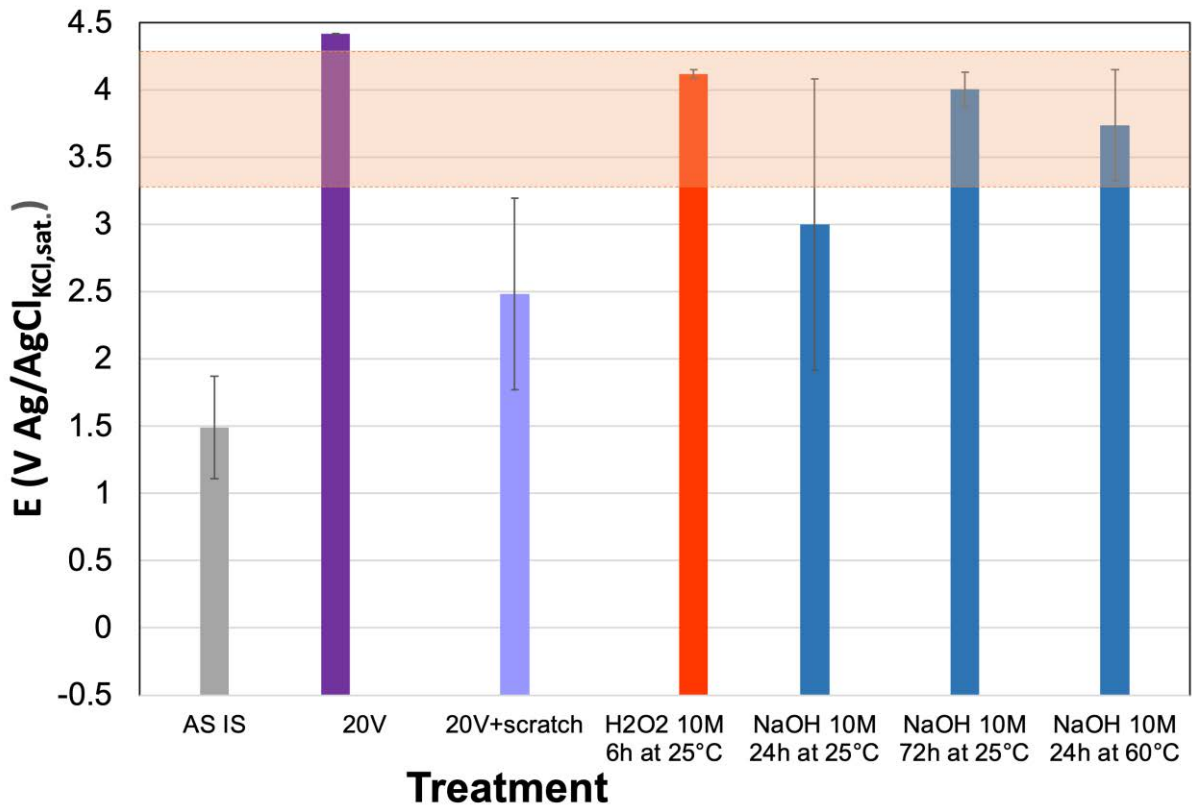


**Figure 12** Surface morphology of samples treated in  $H_2O_2$  for 6h at 25°C and subject annealing at: a) 350°C, b) 400°C, c) 450°C, d) 500°C, e) 600°C, f) 700°C

### 3.4 Recovery

In order to test the recovery capability of the chemical oxidation treatments, electrochemical anodized samples were abraded and then treated by chemical oxidation. An anodizing voltage of 20 V was selected to simulate a possible industrial treatment. Scratches were carried out according to procedure described in par. 2.5.

In Fig. 13 breakdown potentials in  $\text{NH}_4\text{Br}$  0.5 M solution of non-treated sample, anodized sample, scratched sample and recovered sample are shown.



**Figure 13** Comparison of breakdown potential in  $\text{NH}_4\text{Br}$  0.5 M solution of samples subject to anodization or/and chemical oxidation treatment

Anodization process increases breakdown potential of about 3 V, even at low anodizing voltage (20 V). After scratch, corrosion resistance abruptly decreases to values close to the non-treated one, and the variability of measurements increases significantly.

Although NaOH 10 M treatment was theoretically able to increase breakdown potential to 4 V in 24h at 25°C, to repair scratched samples 72h at 25°C or 24h at 60°C are necessary.

$\text{H}_2\text{O}_2$  10 M treatment was able to recover corrosion resistance in 6h at 25°C. This solution it is more difficult to handle and more prone to self-decomposition, so, even if it requires lower treatment time, its usage is deprecated in favor of NaOH.



## 4 Conclusion

Commercially pure titanium ASTM grade 2 was chemically oxidized using NaOH and H<sub>2</sub>O<sub>2</sub>. The effects of solution concentration and quantity on corrosion resistance to NH<sub>4</sub>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 volume 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 establishment of a plateau after which no further oxide growth occurs at appreciable velocity was proved.

This plateau, and the associated maximum of corrosion resistance is achieved after 12h at 60°C and after 24h at room temperature in NaOH. In H<sub>2</sub>O<sub>2</sub>, kinetic is faster and the same corrosion resistance is achieved in 6h at room temperature.

The effect of annealing at 400°C and 600°C on chemically oxidizes titanium was studied. Samples treated in NaOH do not show any improvement in corrosion resistance. Annealing has a strong effect on breakdown potential in bromides environment when applied to samples oxidized in H<sub>2</sub>O<sub>2</sub>. This is caused by the deep morphology changes occurring on samples surface during thermal treatment, as observed through the observation of samples annealed at temperatures ranging from 350° to 700°C.

The best chemical oxidation procedures were applied as repairing treatment to recover the corrosion resistance on damaged electrochemical anodized titanium. Results showed that NaOH treatment 24h long at 60°C or 72h long at 25°C can restore the original corrosion resistance of a 20 V anodized sample. H<sub>2</sub>O<sub>2</sub> treatments requires only 6h at 25°C. For this reason, H<sub>2</sub>O<sub>2</sub> treatment is suggested in case a short treatment time is required, while NaOH, being more stable and easier to store, is preferred when fast treatment is not required.

## 5 Acknowledgements

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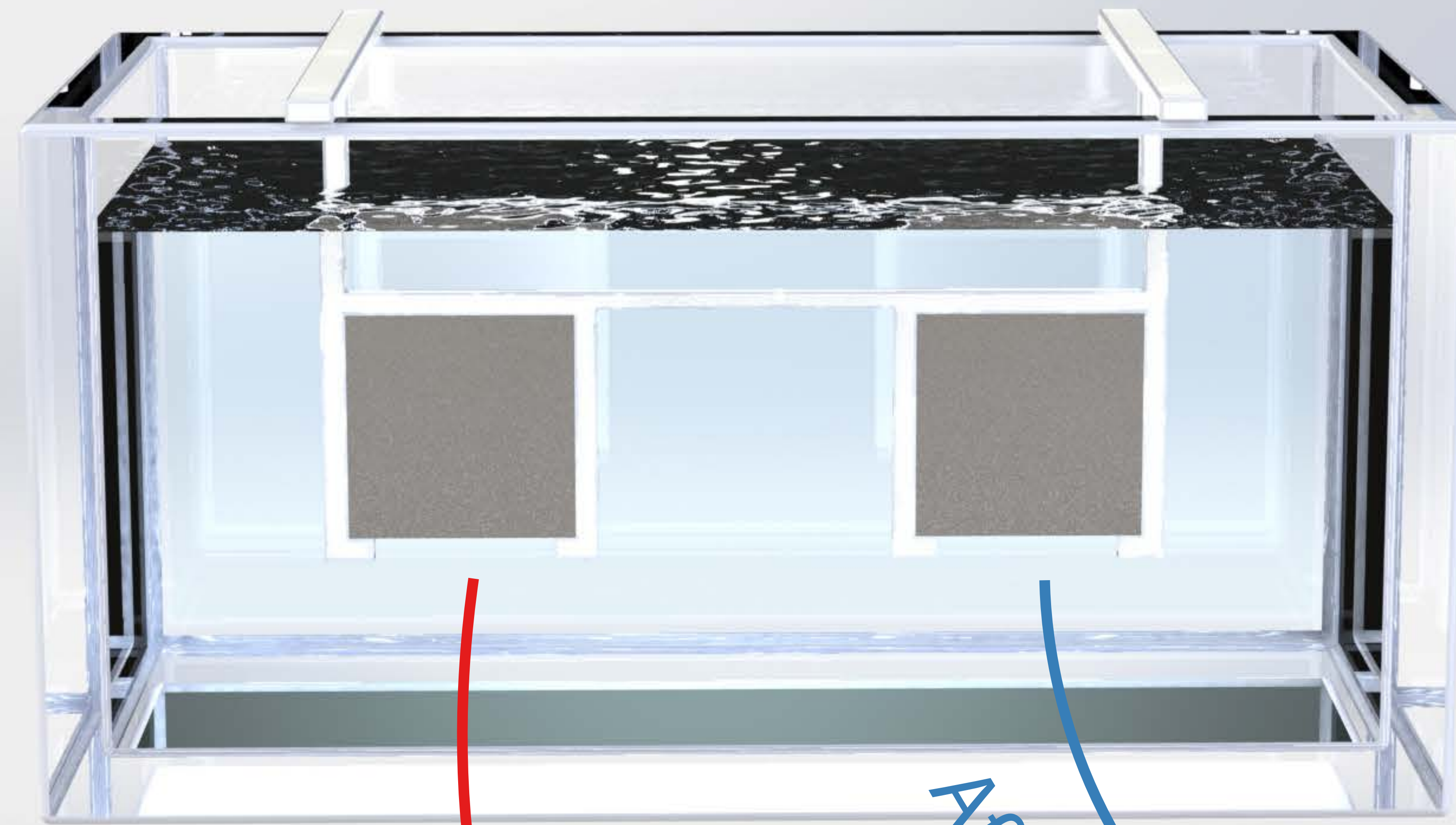
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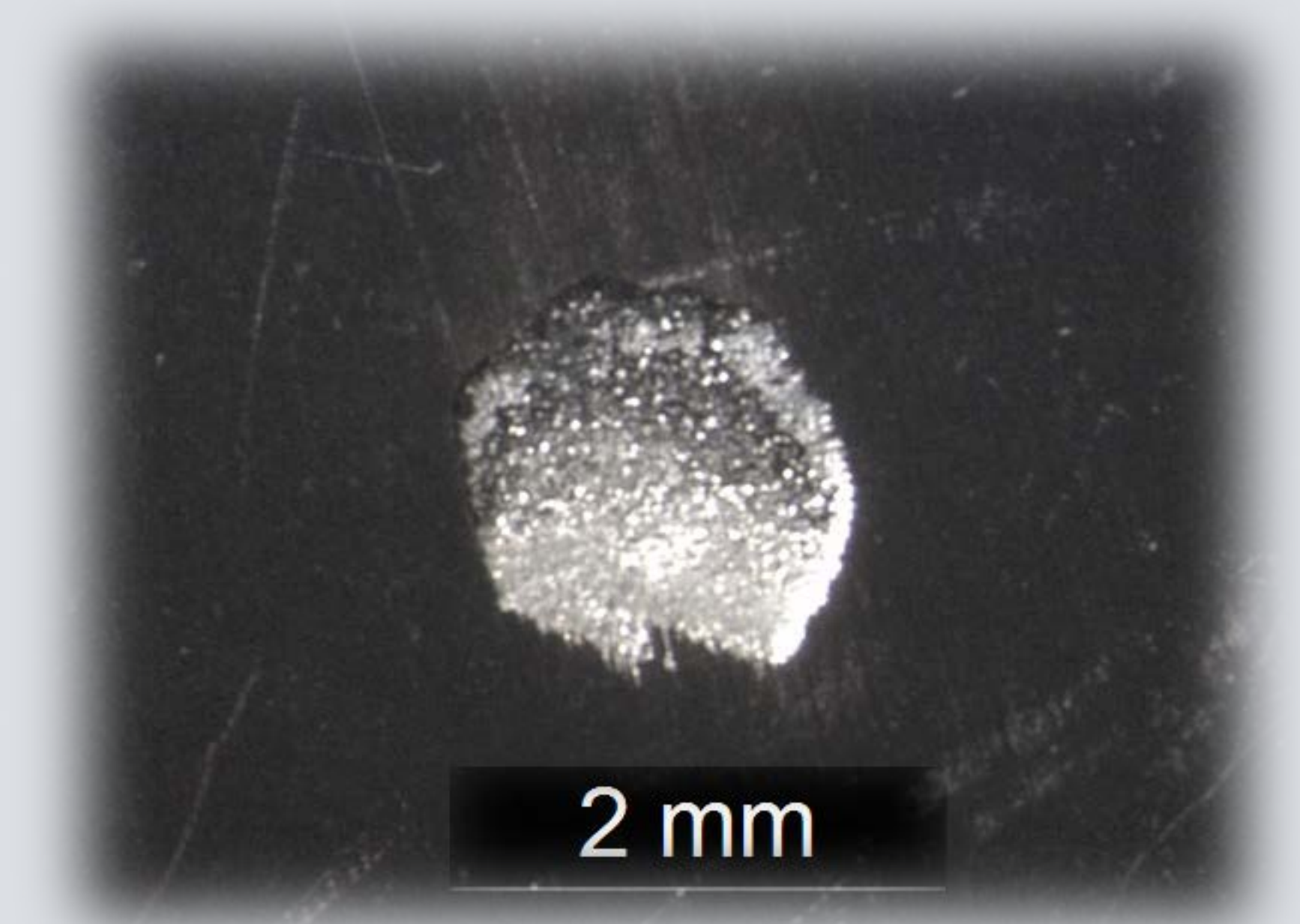
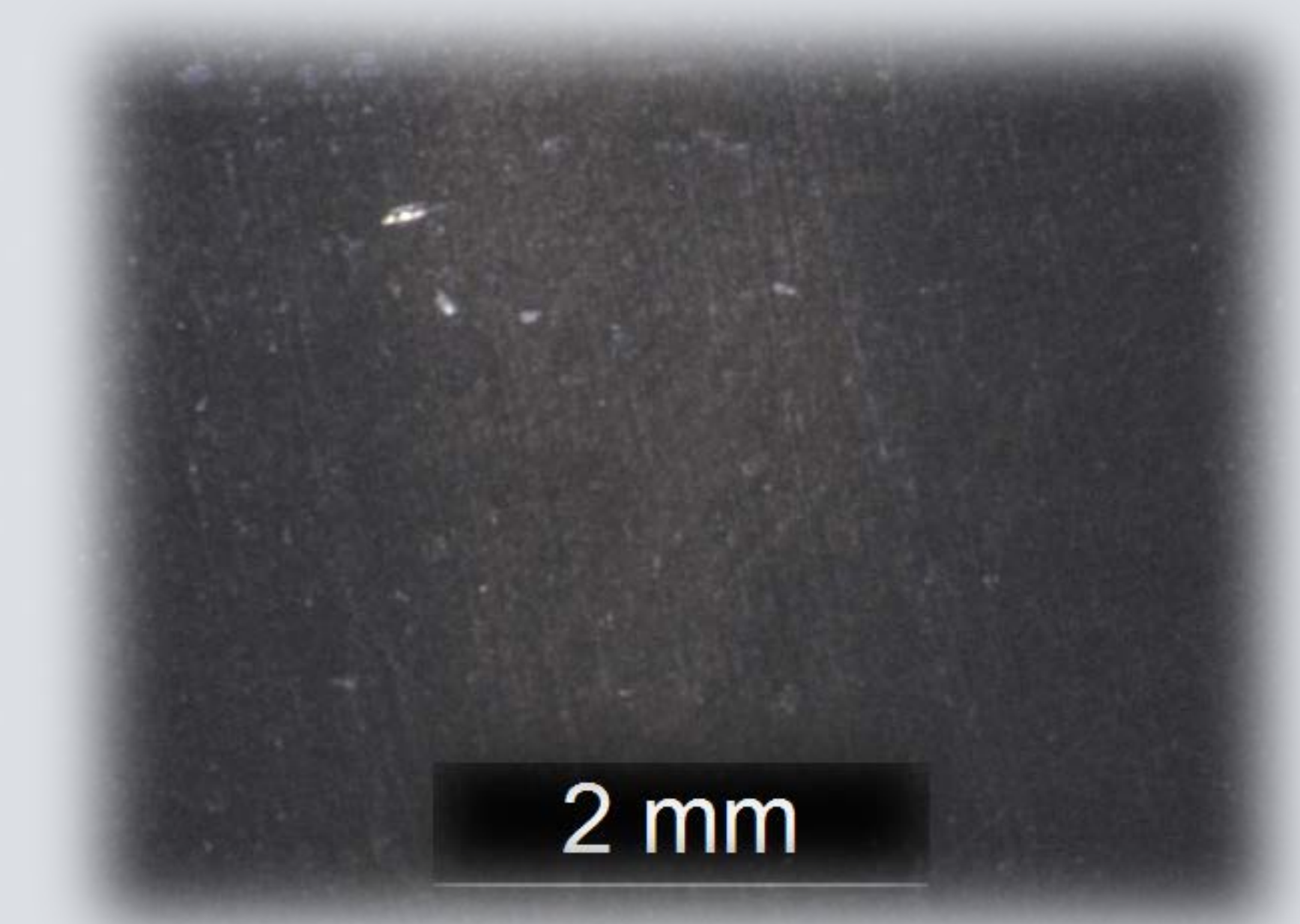


NaOH 10M 25°C Bath

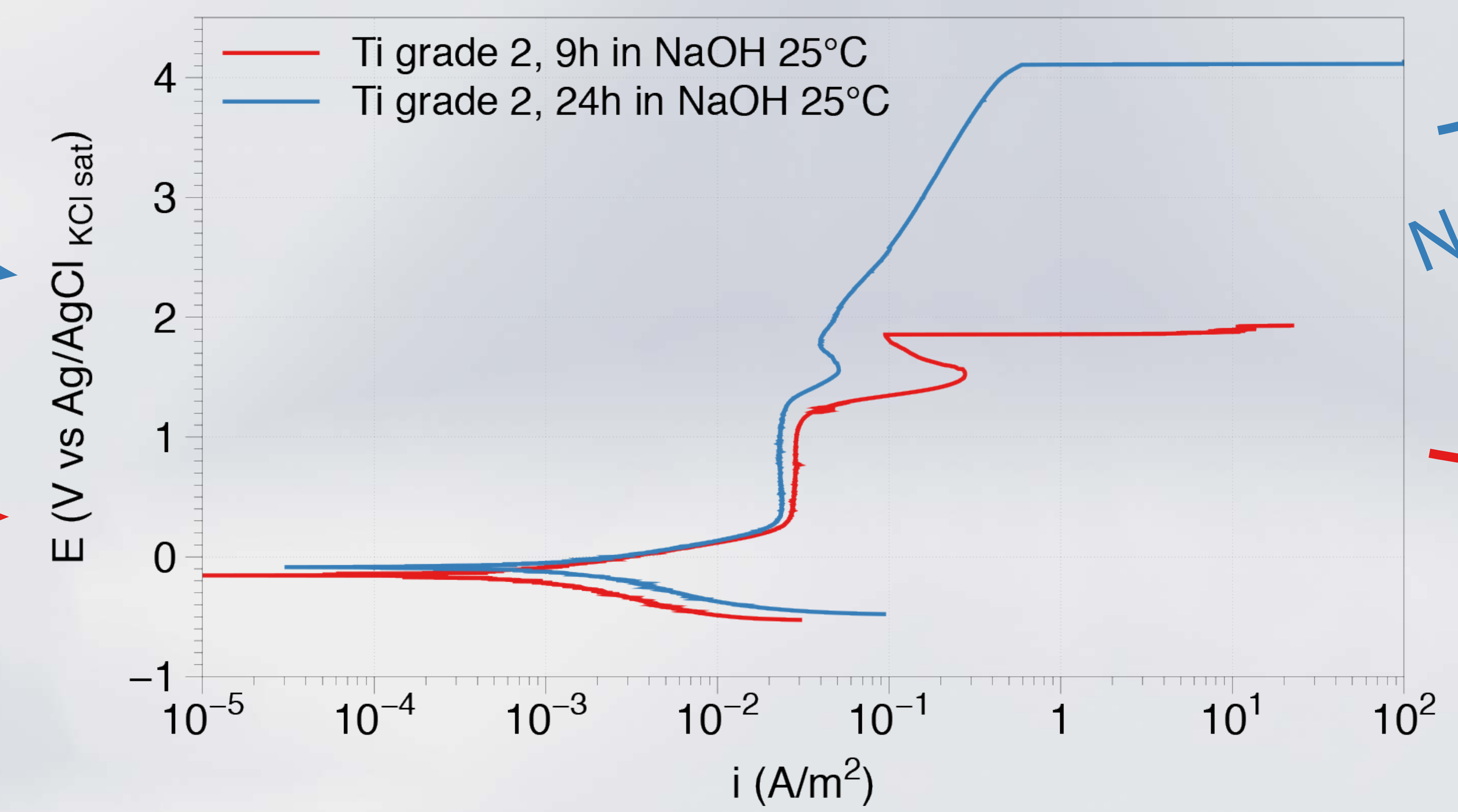


After 9h treatment

After 24h treatment



Potentiodynamic test in NH<sub>4</sub>Br 0.5 M



No oxide breakdown up to 4 V

Oxide breakdown below 2 V