GD Day
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CHARACTERIZATION AND CORROSION BEHAVIOR OF PURE TITANIUM IN SULFURIC MEDIUM

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Although titanium is a chemically very reactive species, it is extremely oxidizable and, thanks to the formation on the surface of a protective oxide layer of a few nanometers thick, is deemed to have a high corrosion resistance. This very adherent natural oxide layer reforms spontaneously if scratching of the surface in the presence of air or water. However, very reductive conditions, as in sulfuric medium, decrease the protective nature of the layer and can cause corrosion. Therefore, in the case of the use of titanium in the design of electrolyzers for hydrogen production, the risk of degradation of parts is real. In addition, the presence of hydrogen in the system increases this risk and can exacerbate damage. Indeed, the production of hydrogen can be followed by adsorption with diffusion of hydrogen molecules in the phase of the material (phase α for pure titanium). However, if the solubility limit of hydrogen in titanium is reached, there may be hydrides precipitation causing metal embrittlement. These two phenomena, corrosion and hydrogenation, can cause a decrease in the lifetime and efficiency of electrolyzers, hence the need to determine the exact origin and to characterize the nature of the damage.

EXPERIMENTAL METHODOLOGY

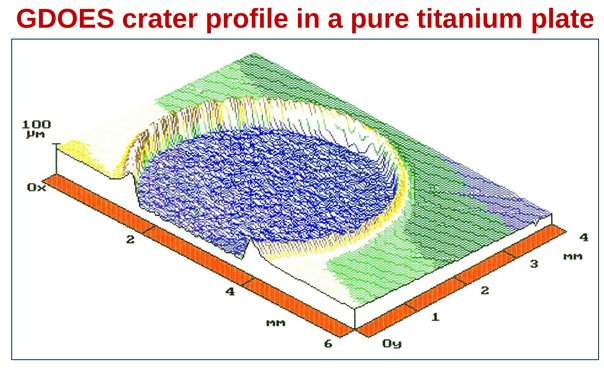
In this context, the work performed was to:

- **study the corrosion behavior of pure titanium** using **electrochemical methods**, in the closest possible conditions on the operating conditions of an electrolyser,
- **characterize morphology of damage** and **determine corrosion mechanisms** using **Scanning Electron Microscopy (SEM)**,
- **analyze**, by **Glow Discharge Optical Emission Spectrometry (GDOES)**, the **possible embrittlement of titanium by hydrogen**.

Parameters of Horiba JY 10000 RF spectrometer equipped with a 4 mm diameter anode used:

. constant pressure of 650 Pa
. moderate power of 35 W
. atomic emission lines: H: 121.574 nm, O: 130.223 nm, C: 156.149 nm, S: 180.738 nm, Ti: 365.355 nm

GDOES crater profile in a pure titanium plate

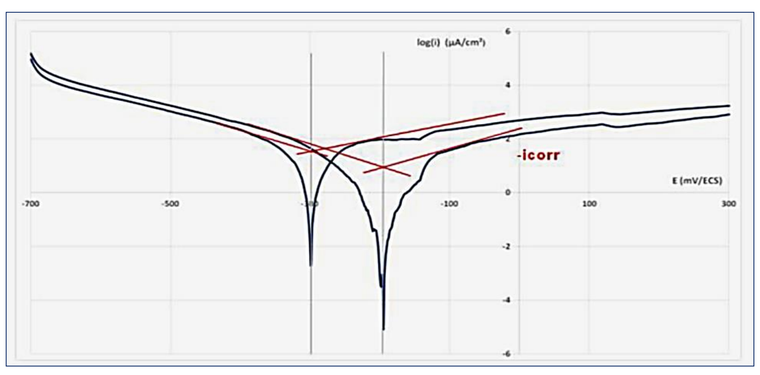


The crater shape sputtered with the chosen parameters is relatively clean: the crater bottom is sufficiently flat and, the bottom and the surface roughness similar.

RESULTS AND DISCUSSION

Corrosion behavior

The open-circuit potential (OCP) and linear polarization resistance (LPR) measurements, **the potentiodynamic polarization curves to determine the corrosion current (i_{corr}) by Tafel slopes were performed at room temperature in a cell corrosion in sulfuric acid medium (1 M).**



Polarization curves of pure titanium plates in H_2SO_4 medium

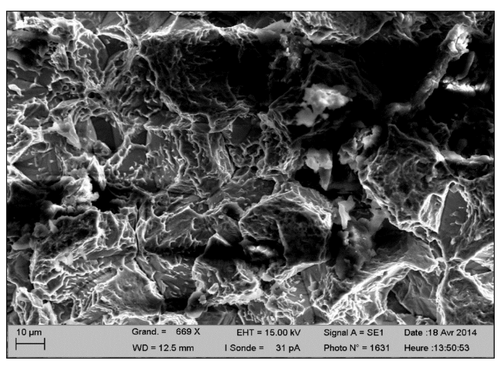
After several hours of immersion, the pure titanium becomes less noble*: its potential decreases because its surface is attacked by sulfuric acid. Titanium goes into solution in ionic form Ti^{3+}. Then E_{OCP} stabilizes again following the formation of corrosion products on the surface, which slows degradation.*

In a second step, the evolution of current versus potential was analyzed using polarization curves (see curves below). And there again, the behavior of pure titanium is well reproducible. It is possible to observe that the current intensity after switching to E_{OCP} (- 250 mV / ECS) continues to increase. Indeed, ***titanium corrodes relatively slowly without ever passivate****. It should be noted that the value of E_{OCP} may vary depending on the initial state of the surface.*

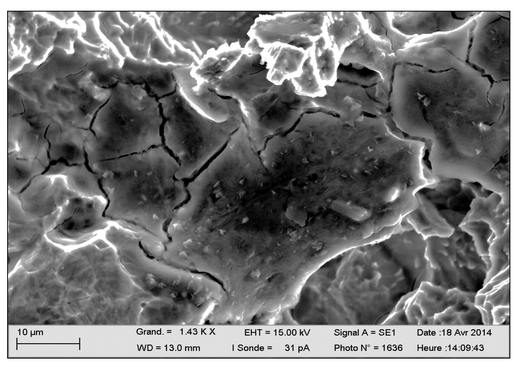
The corrosion current of pure titanium, in sulfuric medium (H_2O_4 1 M), is therefore of the order of 1.7 µA / cm² (average of all tests performed). And its average corrosion rate, under the same conditions, may therefore, by applying Faraday law, estimated to be 20 µm / year.

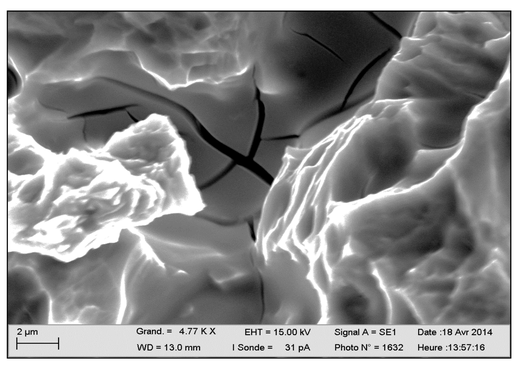
SEM characterization

SEM observations of a degraded area of a pure titanium plate after 5000 hours in sulfuric acid medium (1 M), at a temperature between 30 and 50 °C, under hydrogen bubbling environment were performed.



This SEM image of the surface of the titanium plate reveals an ***intergranular fracture****. This type of fracture is* ***characteristic of embrittlement at grain boundaries of a metallic material after hydrogen absorption****.*





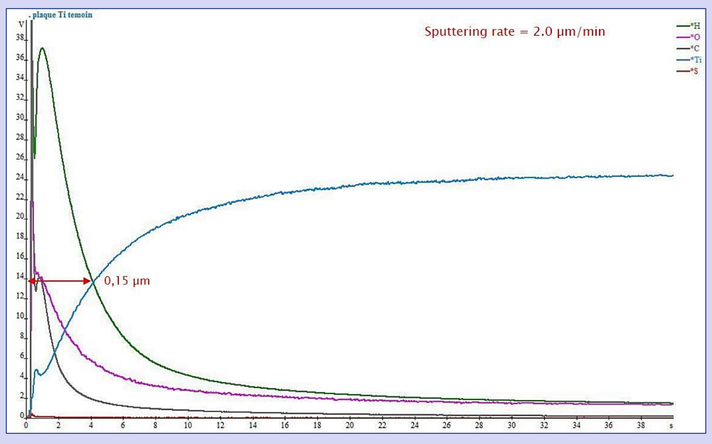
This other images allow to highlight the ***presence of a very strongly degraded deposit (cracks) to the titanium surface****.*

This deposit probably corresponds to a titanium oxide layer, covering itself, following the absorption of hydrogen, a hydride layer*.*

GDOES analysis

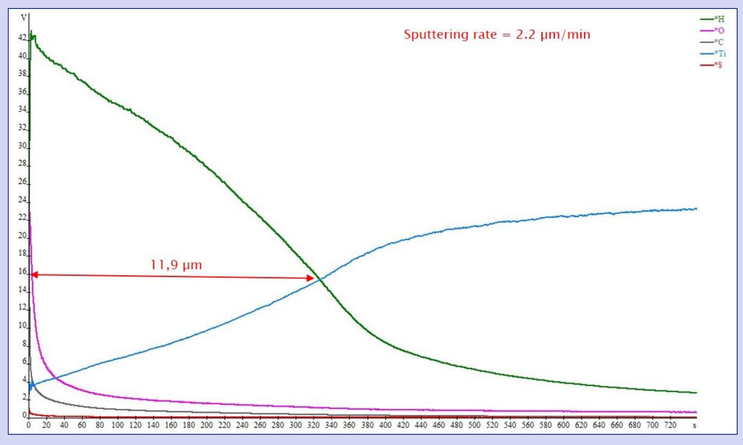
GDOES was used to analyze the possible embrittlement of titanium by hydrogen and to determine the depth of penetration of hydrogen in a pure titanium plate after 5000 hours in sulfuric acid medium (1 M), at a temperature between 30 and 50 °C, under hydrogen bubbling environment.

This profile indicates the ***presence of carbon****,* ***hydrogen*** *and* ***oxygen to the surface of a pure titanium uncorroded plate,*** *due to pollution, oxidation and hydration.*
For this plate, ***only a thin hydrated layer (0.15 µm) in extreme surface contains hydrogen.***



Qualitative profile of a pure titanium uncorroded plate

This profile indicates the ***significant presence of hydrogen to a great depth (greater than 11.9 µm), which tends to confirm the absorption of hydrogen*** *resulting in the degradation observed by SEM:* ***intergranular fracture due to embrittlement at grain boundaries of the pure titanium surface.***



Qualitative profile of a pure titanium corroded plate

CONCLUSION AND PERSPECTIVES

This study was first allowed, after characterization by Scanning Electron Microscopy (SEM) and Glow Discharge Optical Emission Spectrometry (GDOES) of the damage observed on the pure titanium plates after 5000 hours immersion in sulfuric acid under hydrogen bubbling, **to determine the corrosion mechanisms** that have driven these degradations. **The GDOES profiles in particular revealed significant diffusion of hydrogen in titanium (to a depth greater than 11.9 micrometers)**. Moreover **the SEM images have led to observe a fracture of intergranular type on the surface of the plates**, all this results clearly showing **a phenomenon of embrittlement of the titanium by hydrogen**.

Therefore, **in the context of use in the manufacture of electrolyzers for hydrogen production, it would be interesting to test resistance to corrosion of certain grades of stainless steels** in the same conditions.

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