

THE BEHAVIOR OF Ti GRADE 2 IN DIFFERENT CORROSIVE ACIDIC MEDIA

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المخلص

عنصر التيتانيوم وسبائكه عبارة عن صفة من المواد التي تمتاز باستعمالات واسعة في مجالات الفضاء، الطب، والنفط والغاز. إلا أنه بجانب خواصها الممتازة فإن سبائك التيتانيوم قد تعاني من مشاكل تآكلية وهيدرجنة عند تعرضها لأوساط تحتوي على عنصر الهيدروجين. هذا البحث يدرس مدى تأثير الاحماض المركزة على المقاومة التآكلية والهيدرجنة لسبيكة التيتانيوم النقي ذو الرتبة الثانية. تم اختيار ثلاثة محاليل لهذا الغرض وهي: حمض النيتريك، حمض الكبريتيك، وحمض الهيدروكلوريك. تم اجراء سلسلة من الاختبارات الكهروكيميائية بطريقة جهد الدائرة الحر (Open Circuit Potential (OCP)) لدراسة تأثير الرقيقة الاكسيدية التي تتكون على سطح السبيكة على التصرف التآكلي والهيدرجنة عند الغمس في هذه المحاليل. تم أيضا استعمال طريقة حيود الاشعة السينية واختبار بنية السطح لدراسة التصرف التآكلي والهيدرجنة. دلت النتائج على أن الرقيقة الاكسيدية الغير فعالة التي تتكون على سطح سبيكة التيتانيوم يمكن اختراقها وذلك بتحليلها الكهروكيميائي في المحاليل الحمضية المركزة. البيانات المستخلصة من هذه الدراسة تعزز الدراسات السابقة، والتي تلمح إلى ان الرقيقة الاكسيدية الغير فعالة والتي تتكون على التيتانيوم هي أكسيد التيتانيوم (TiO₂) وهي المسؤولة على المقاومة التآكلية للتيتانيوم في عدد من الأوساط التآكلية

ABSTRACT

Titanium and its alloys are generic class of materials that have widespread applications in aerospace, medical, and oil and gas industries. Besides their excellent properties, corrosion and hydriding problems may arise when titanium base alloys are exposed to environments containing hydrogen. This work concentrates on understanding the effect of strong mineral acids on the corrosion resistance and hydriding of commercially pure titanium grade 2. Three solutions were chosen for this purpose, namely nitric acid, sulfuric acid, and hydrochloric acid. A range of electrochemical open circuit potential (OCP) measurements were used to study the influence of oxide film formed on titanium grade 2 on the corrosion and hydriding behavior in the above mentioned acids. X-ray diffraction and surface morphology examinations were used to study the corrosion and hydriding characteristics. It is found that the passive oxide film formed on titanium can be penetrated by electrochemical dissolution in strongly acidic solutions. The data generated from the lab experiments support published papers, which suggest that the passive film formed on titanium is composed of TiO₂, and is responsible for its electrochemical corrosion resistance in many aggressive corrosion media.

KEYWORDS: Titanium; Corrosion; Hydriding; Galvanostatic Measurement; OCP.

INTRODUCTION

This work is intended to explore the electrochemical corrosion and hydriding behavior of titanium (Grade 2) in HCl, HNO₃, and H₂SO₄ acidic solution corrosive media. The element titanium (Ti) is a unique metal. It is the fourth-most abundant structural metal in the Earth's crust (~0.5%). It has a desirable combination of physical, chemical

(corrosion resistance, low bioreactivity), and good mechanical properties that makes it attractive for many industrial applications [1,2]. Ti Grade 2 has an excellent biocompatibility, especially when direct contact with tissues or bones is required. However, problems may arise when hydrogen comes in contact with Ti and its base alloys. These alloys can pick up a large amount of hydrogen, especially at elevated temperatures. At a critical hydrogen concentration, titanium hydrides will precipitate.

Titanium corrosion resistance is due to a stable, protective, strongly adherent oxide film. This film forms instantly when a Ti fresh surface is exposed to air or moisture. A study of the corrosion resistance of Ti is basically a study of the properties of the oxide film. The oxide film on Ti is only attacked by a few substances, most notably hydrofluoric acid. Ti is capable of healing its oxide film almost instantly in any environment where a trace of moisture or oxygen is present because of its strong affinity for oxygen [3,4]. It is reported that in the active state, Ti may oxidize to form Ti^{2+} ions in solution. The metal readily passivates in aerated aqueous solutions, including dilute acids and alkalis. In the passive state, Ti is covered with a nonstoichiometric oxide film, the average composition of which is TiO_2 .

Table (1) shows typical compositions of Ti grade 2 [5,6]. The table indicates that Ti grade 2 is of high purity with only about 0.26 wt.% impurities, which is less than that demanded by medical applications. Other good physical and chemical characteristics of Ti are its low density (4.54 gm/cm^3 at 20°C) and high melting point (1668°C) making it a good candidate for high temperature applications. Ti also possesses mechanical properties that are comparable to wrought annealed materials and are better than cast materials. Its ultimate tensile strength of 570 MPa results in its high specific strength to weight ratio of $570 \text{ MPa}/4.54 \sim 110$. Hence in many engineering and medical applications titanium has replaced heavier, less serviceable or more expensive materials [6].

Table 1: Comparison of the chemical composition (in Wt.%) of typical grade 2 Ti alloy with that required by ASTM specification [5].

Impurities	Ti Grade 2, Typical	Ti Grade 2, Required*
Carbon, C	0.005%	<0.08%
Iron, Fe	0.05%	<0.3%
Oxygen, O	0.19%	<0.25%
Nitrogen, N	0.004%	<0.03%
Hydrogen, H	0.0009%	<0.015%
Titanium, Ti	Balance	Balance

*ASTM F67 (unalloyed titanium for surgical implant applications)

Hydriding of Ti can be predicted from its potential - pH diagram (see Figure (1), and Table (2) [5]) which shows that titanium oxide is stable over a wide range of pH and potentials, with the exception of a small region on the highly acidic (i.e. low pH) side of the diagram. It is also important to note that this region falls below the hydrogen evolution line. This means that environments with limited oxidizing power (those with limited ability to remove electrons from the metal) can lead to poor oxide stability. Because titanium relies on its oxide for corrosion resistance, these environments can lead to undesirable attack. At the high pH - moderate-potential region where Ti_2O_3 is stable, excessive hydrogen pickup can lead to embrittlement instead of the normal thinning caused by uniform corrosion. This condition occurs occasionally at elevated temperatures.

It was determined by the method of saturation that it is possible to attain a content of hydrogen in metal corresponding to the composition of TiH_2 . However, doubt is expressed concerning the existence of a chemical compound of this composition [3,6]. As for other bibliography, assumptions are expressed on the existence of a gasiform hydride of the composition TiH_4 [7]. Studies of diffusion rate of hydrogen in titanium indicated that absorption of hydrogen by titanium occurs after formation of hydride phase on surface of metal. This is due to the fact that the hydride will form a porous layer on the metal surface. Yan et. al. [8] studied the absorption of hydrogen into commercially pure Ti Grade-2 on oxide-free ($pH \leq 3$) surfaces at $25^\circ C$ under both potentiostatic and galvanostatic conditions. The rate of hydrogen absorption was found to be extremely rapid on oxide-free Ti. Complete hydride coverage of the surface was found to significantly suppress the rate of hydrogen absorption, which is consistent with the known decrease in diffusivity of hydrogen in the hydride phase. Y Zeng et. al. [9] found that a thin film of TiO_2 deposited uniformly on Ti resulted in hydrogen absorption at potential $E < -0.37$ V versus SCE. It is found that most of corrosion processes that limit the longevity of Ti and Ti alloy structures are associated with hydrogen absorption into the bulk metal. Anodizing protection is a method to thicken the Ti oxide film, increase the corrosion resistance, and limit hydriding.

In case of corrosion of Ti, two oxidation reactions occur, depending on the potential of the metal environment. In weak oxidizing environments, the oxidation reaction is $Ti \rightarrow Ti^{3+} + 3e^-$, while in oxidizing environments; the reaction is $Ti \rightarrow Ti^{4+} + 4e^-$. In weak oxidizing (or reducing) environments, the primary reactions are $H^+ + e^- \rightarrow H_{ads}$, $2H_{ads} \rightarrow H_2$, and $H_{ads} \rightarrow H_{abs}$, where H_{ads} is an adsorbed (i.e. surface) hydrogen atom, and H_{abs} is an absorbed hydrogen atom.

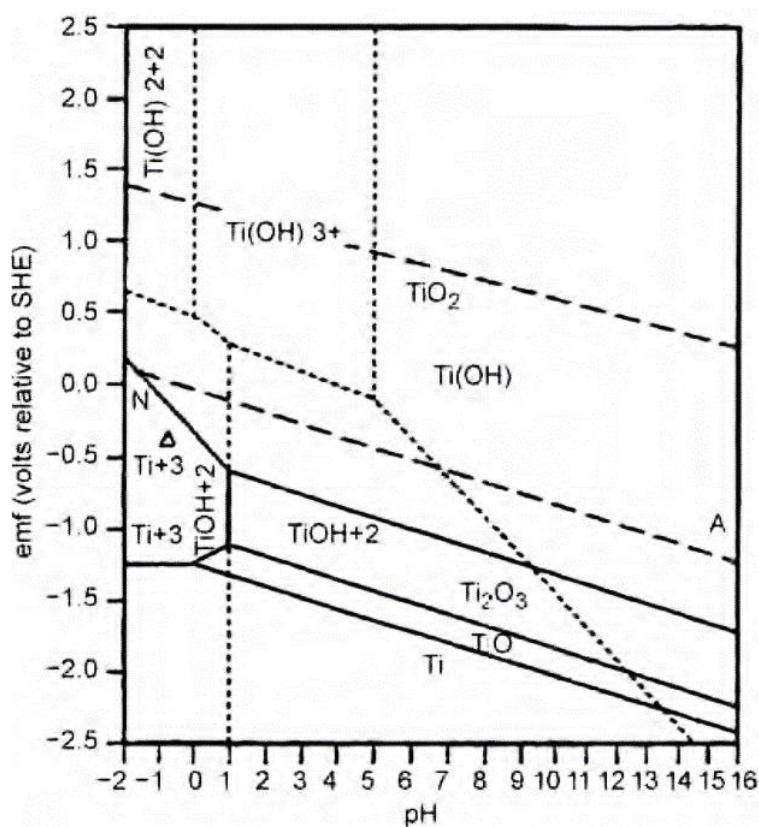


Figure 1: Potential (V) vs. pH phase stability diagram of Ti-H₂O system at 85°C [3].

Table 2: Corrosion standard reduction potentials of Ti.

$Ti^{2+} + 2e^- \leftrightarrow Ti$	- 1.36 V vs. SHE
$Ti^{3+} + e^- \leftrightarrow Ti^{2+}$	- 2.00 V vs. SHE
$TiO_2 + 4H^+ + 4e^- \leftrightarrow Ti + 2H_2O$	- 0.86 V vs. SHE
$Ti(OH)^{3+} + H^+ + e^- \leftrightarrow Ti^{3+} + H_2O$	+ 0.06 V vs. SHE

MATERIALS AND METHODS

Material Analysis

The as-received material used in this study was commercially pure Ti grade 2. The chemical composition of the material is shown in Table (3).

Table 3: Chemical composition of Ti Grade 2 material (in Wt. %).

Element	Oxygen	Carbon	Nitrogen	Iron	Titanium
Wt. %	0.14	0.02	0.008	0.08	Balance

Specimen Preparation

Titanium specimens of dimensions 2cm x 1cm x 1mm were cut from as-received commercially pure titanium grade 2 rod of 5 cm diameter using a Discotom-2 cut-off machine. The specimens were wet ground on silicon carbide (SiC) paper from grade 400 to 1000 grit. Subsequently, the specimens were oxide polished using 1 μ m, then 0.3 γ alumina-distilled water suspension. After polishing, the specimens were cleaned in acetone, rinsed in de-ionized water and dried in a cool air stream. Specimens in as polished condition is denoted as AP.

Electrochemical Measurements

The electrochemical measurements on titanium were performed using a Gamry Series G300 Potentiostat/Galvanostat instrument. For Galvanostatic measurement each Ti sample was made as a working electrode using a connecting Al wire at backside and insulating the Ti sample/Al wire assembly using Epoxy coat so that about 1 cm² of sample surface is exposed to the electrolyte solution, as seen in Figure (2). The Electrochemical measurements were performed at room temperature in aerated electrolyte solutions of H₂SO₄, HCl and HNO₃ with different concentrations. The tests were done for as-polished (AP) condition sample (Hence it should have a passive titanium oxide removed), and for same sample after exposing the as polished surface to air for one day (24 hours to reform surface oxide film, labelled as PO).

Open Circuit Potential (OCP) Measurements

In aqueous solutions the naturally developed Ti oxide film on polished surface may grow, dissolve or both. This depends on solution composition. The OCP, for AP and PO Ti samples were followed with time over a period of 90 minutes at room temperature in H₂SO₄, HCl and HNO₃ of 10%, 20%, and 30% acid concentrations in de-ionized water. The corrosion tests were repeated at least 3 times for each specimen until all repeated runs exhibited similar OCP curves.

Figure (3) shows the electrochemical cell used for Galvanostatic measurement. The Ti sample is the working electrode (WE), the reference electrode is a standard calomel electrode (SCE). A salt bridge is used to connect the oxidation and reduction half-cells of the galvanic cell. A Graphite rod is used as anode. The Open circuit potential (OCP) refers to the potential in WE relative to SCE electrodes, when there is no current or potential existing in the cell. Once a potential relative to the OCP is made present, the

entire system gauges the potential of the open circuit prior to turning on the cell. This is followed by the application of potential relative to the existing measurement.

Hydride Crystal Structure Determination

X-ray diffraction (XRD), Model APD 2000 was used to determine crystal structure of hydrides that form on the surface of individual samples after the charging procedure is completed. In all of the x-ray scans, Cu-K α radiation (40kV, 35mA, $\lambda=1.5405 \text{ \AA}$) was used and the diffraction scans were made between $2\theta = 0$ to 100° . This range of angles included peaks from both the sigma- and delta-hydrides, the two most likely to occur under the conditions that was used. In addition, x-ray diffraction can tell us about the type of the oxide layer formed on the Ti Grade 2 alloy.

Microstructural Investigation

Metallographic examination of as received was determined using a bench top optical microscope. Scanning electron microscopy (Model LEO 1430VP) was used for microstructural determination of treated Ti sample.



Figure 2: Sample preparation for OCP experiment.

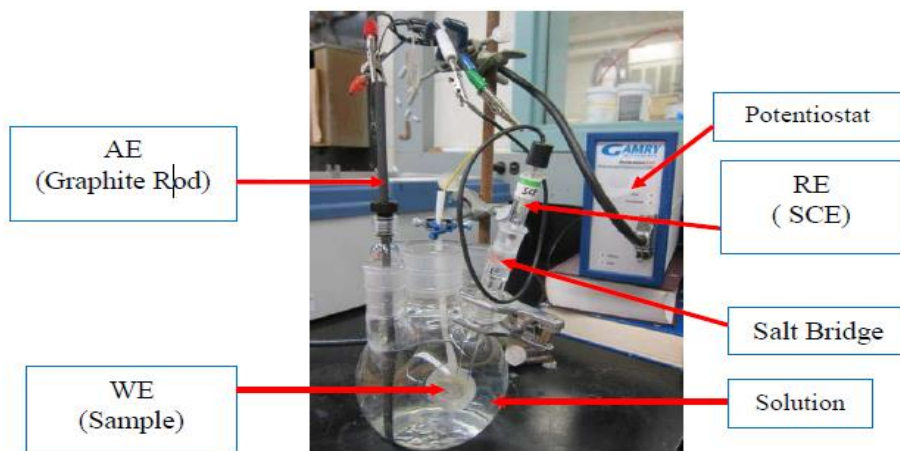


Figure 3: Electrochemical cell used for Galvanostatic measurement.

RESULTS AND DISCUSSION

Microstructural Investigation

It is found that Ti Grade 2 microstructure consists of fine α -grains as illustrated in Figure (4).



Figure 4: Micrograph of as-received Ti Grade 2 material, 100X.

X-ray Diffraction Results

The crystal structure of as-received Ti material was determined by x-ray diffraction. Figure (5) shows the x-ray spectrum obtained. A computer search identified the peaks as α Ti (reference code 03-065-3362) which has an hcp crystal structure. The hkil (omitting index $i=-(h+k)$ for simplicity) of identified peaks of as-received Ti are shown in Figure (5). For titanium samples immersed in acid solutions, a typical x-ray diffraction pattern obtained is that of AP Ti immersed in 30% HCl shown in Figure (6).

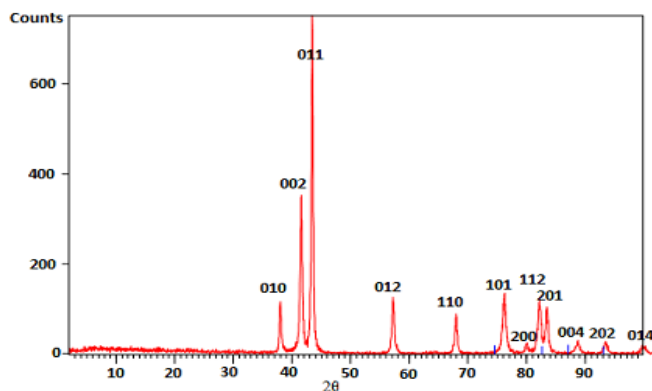


Figure 5: XRD pattern of as-received Ti.

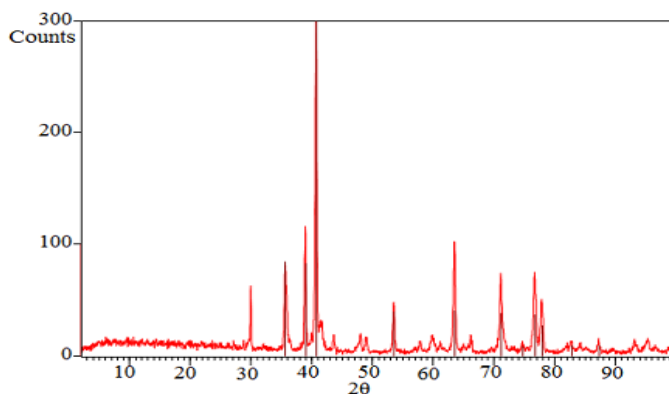


Figure 6: XRD pattern of AP Ti sample immersed in 30% HCl.

The intensity vs. 2θ of Figure (6), when compared with the x-ray diffraction spectrum of as-received Ti specimen (Figure 5) reveals the existence of additional peaks besides the original Ti peaks (Notice that peak at 40.65° is strongest peak of α Ti). The visible peaks in Figure (6) at $2\theta = 35.74, 40.65, 59.79,$ and 71.08° match well with typical

peaks of cubic titanium hydride (TiH_2) [10], and their broadening indicates that these surface hydrides are of small crystallite size. The somewhat large background under peaks (as compared to α Ti spectrum of Figure 5) might indicate that these hydrides have some amorphous characteristics.

Metallographic Examination

Scanning electron microscopy (SEM) is employed to observe the effects of the acid corrosion environments on the sample surface morphology. Figure (7) shows a secondary electron SEM image of as-received titanium sample before immersion in the acid solutions.

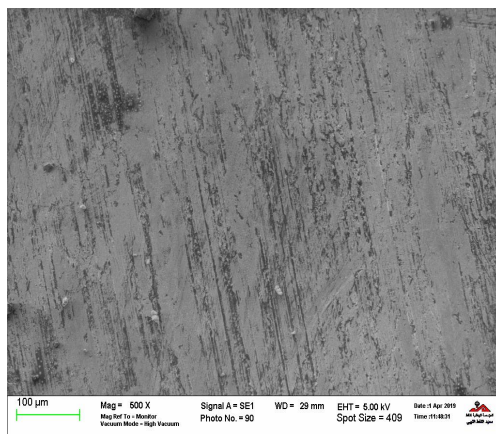


Figure 7: Secondary electron SEM image of as-received Ti specimen before immersion in acids.

Figure (8 and 9) show SEM images of AP and PO Ti samples immersed in 10% and 20% H_2SO_4 solutions, respectively. The image in Figure (8) differs with Figure (7) in white contrast that form on surface when as polished Ti is reacted with acid solution. The image in Figure (9) contains small surface voids. Such voids or pores may be formed in the passive oxide (which formed within 24-hour wait) by corrosion reaction upon immersing in acid solution.

In general, for PO Ti specimens, it is found that tiny surface pits form at mild corrosion conditions. As the solution corrosivity increases, the surface pits become more defined. The voids in passive oxide film for PO samples can result when hydrogen produced by acid reaction forming hydrides diffuses through the surface oxide [8].

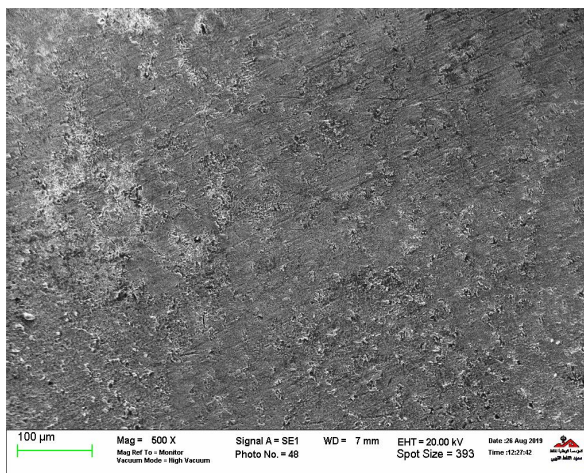


Figure 8: Secondary electron SEM image of AP Ti sample immersed in 10% H_2SO_4 acid.

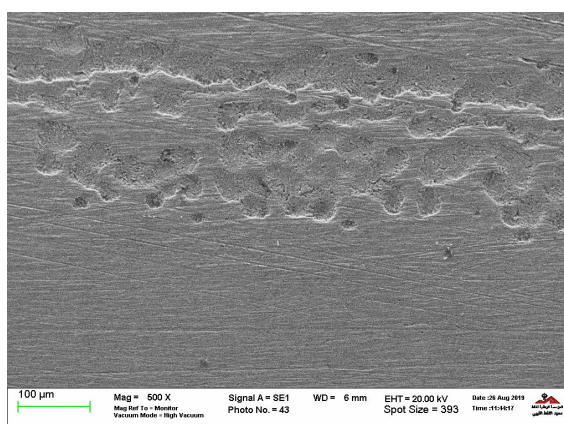


Figure 9: SEM image of PO Ti sample immersed in 20% H₂SO₄.

Galvanostatic polarization Tests

Galvanostatic OCP (i.e. open circuit potential vs. time) tests of AP and PO samples were performed in 10%, 20% and 30% HCl, HNO₃, and H₂SO₄ solutions. The results of AP case are shown in Figures (10-12), and of PO are shown in Figures (13-15). Table (4) summarizes the OCP start and finish after immersion in acid electrolytes for 1.5 hours' immersion time.

Tests in HCl

For AP Ti in 10% HCl (Figure 10), the OCP shifts slowly with immersion time to more noble (positive) direction. In case of 20% HCl (Figure 11), the curve tend to reach steady state from the start, and in the case of 30% HCl (Figure 12), the curve slowly shifts with immersion time in less noble direction before it levels off. It can be noticed that increasing the HCl concentration results in increase of corrosion activity. For OP Ti, treatment in 10% showed same trend as for AP case. In case of 20% treatment the trend is in noble direction while for 30% HCl the trend is in active direction. Thus for high concentration of 30% HCl, the oxide film is penetrated (pitted) allowing corrosion and hydriding to take place. This is of course manifested by the up and downs that occur in OCP curve as immersion time increases.

Tests in HNO₃

Again, for the case of AP Ti in 10% and 30% HNO₃, the trend is slow and in noble direction while for 20% concentration the trend is in active direction. For OP (after 24 hour wait after polishing of Ti surface), slow reaction take place resulting in small changes in OCP trends for the three tested concentrations.

Tests in H₂SO₄

For the case of AP Ti in 10%, the trend is in active direction while for 20% and 30% concentrations the trend is in noble direction. For OP Ti surface, no reaction takes place for case of 10% concentration, and for 20% and 30% concentrations the initial noble values decrease slowly with time indicating an almost stable passive film. Hence it can be said that Ti has good corrosion resistance in HNO₃ followed by H₂SO₄ then HCl.

For OP Ti, when leaving the samples 24 hours in the atmosphere after polishing, the results of experiments indicate that the corrosion resistance of Ti in HNO₃ become better. It can be noticed that, the OCP corrosion potential is more positive than the as-polished (AP) samples. This is attributed to the fact that when samples exposed in air for 24 hours the passive oxide film layer is reproduced and Ti becomes more corrosion resistant.

Table 4: Summary of Galvanstatic OCP (mV vs. SCA) start and finish obtained from Figures 10-15.

	HCl Concentration			HNO ₃ Concentration			H ₂ SO ₄ Concentration		
	10%	20%	30%	10%	20%	30%	10%	20%	30%
AP, OCP start	-130	-100	-150	-215	70	60	+55	-62	-730
AP, OCP finish	-85	-100	-220	-195	60	75	+50	-8	-700
PO, OCP start	-215	-147	-105	120	-95	67	85	120	155
PO, OCP finish	-138	-95	-180	90	-92	75	85	105	135

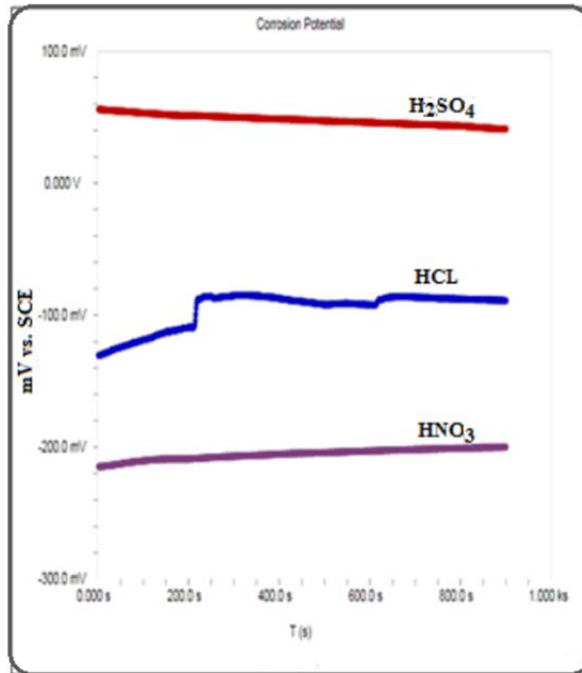


Figure 10: OCP test for AP Ti in 10% HCl, HNO₃ and H₂SO₄ solutions.

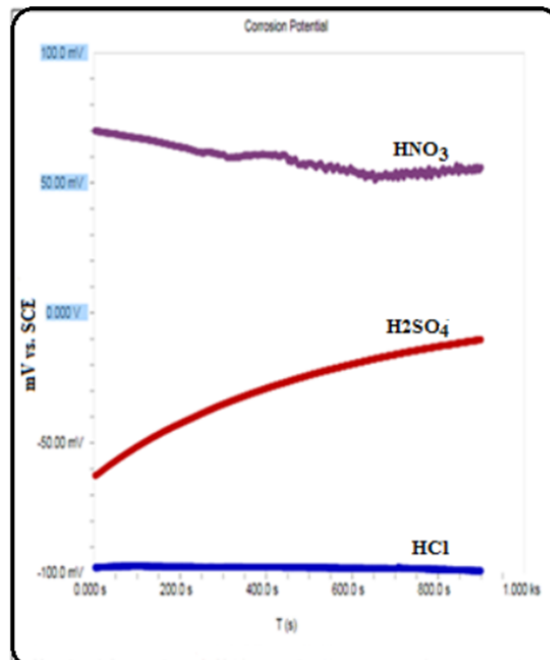


Figure 11: OCP test for AP Ti in 20% HCl, HNO₃ and H₂SO₄ solutions

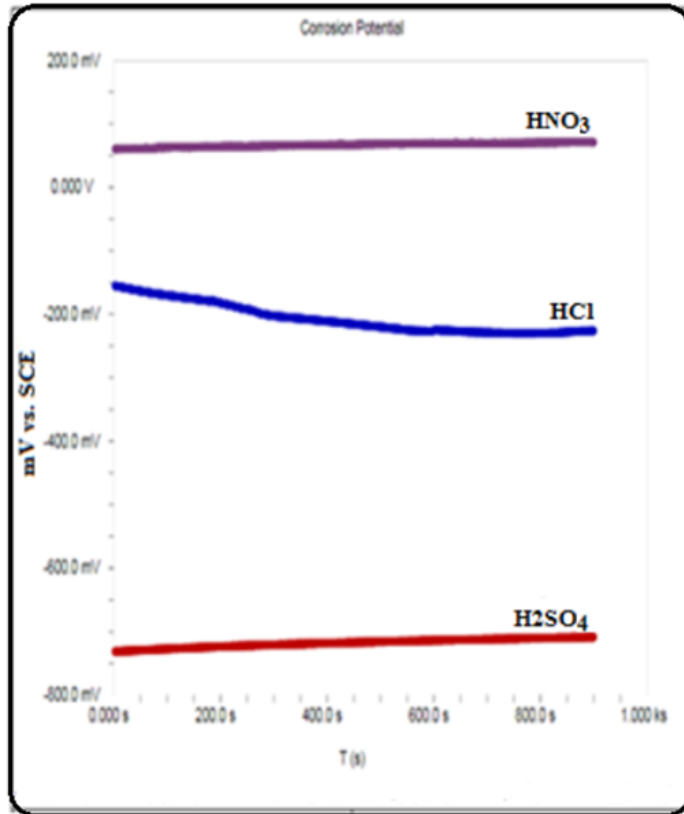


Figure 12: OCP test for AP Ti in 30% HCl, HNO₃ and H₂SO₄ solutions

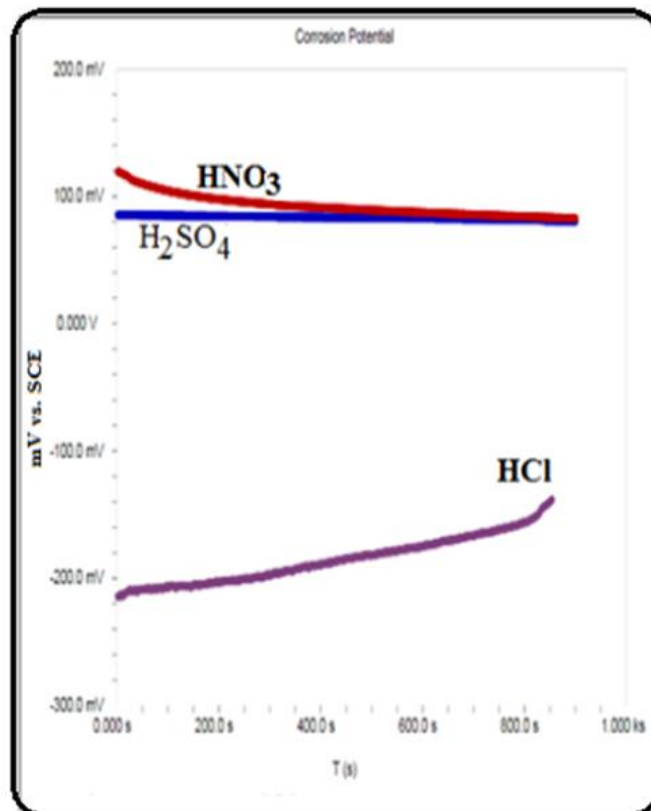


Figure 13: OCP test for OP Ti in 10% of HCl, HNO₃ and H₂SO₄

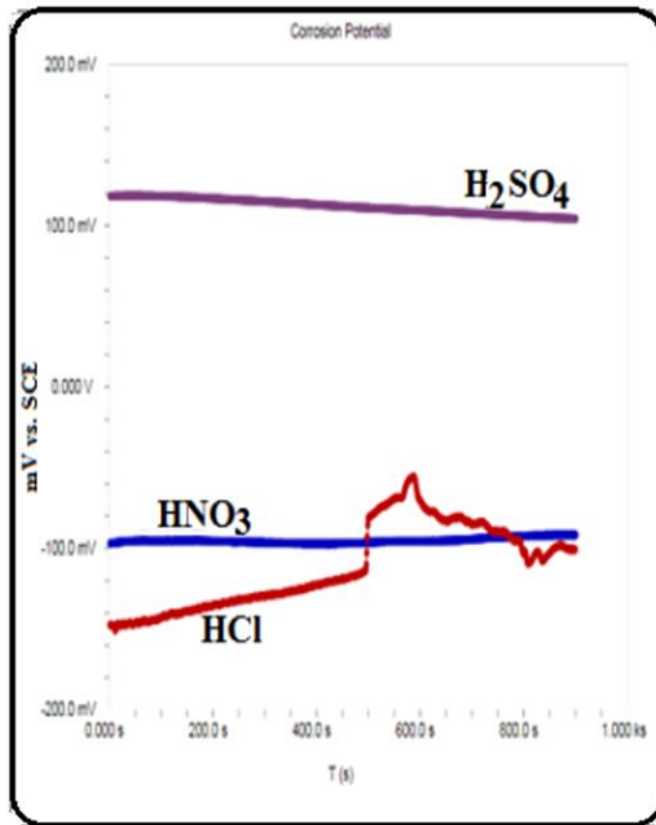


Figure 14: OCP test for OP Ti in 20% of HCl, HNO₃ and H₂SO₄

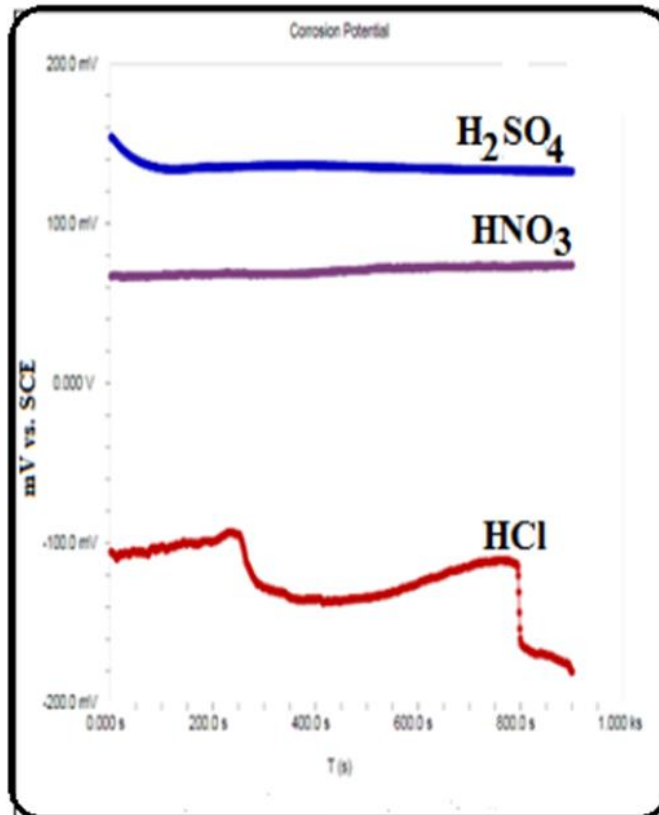


Figure 15: OCP test for OP Ti in 30% of HCl, HNO₃ and H₂SO₄

CONCLUSIONS

This study compared the corrosion behavior of titanium grade 2 in different acids of different concentrations at room temperature. Electrochemical galvanostatic polarization was used for the comparison. Under the experimental conditions of this study, the following conclusions can be drawn: -

- 1- In general, acidic environments are separated into two categories: oxidizing and reducing. It is found that titanium exhibits excellent resistance in nitric acid, which is categorized as an oxidizing acid. However, in the reducing hydrochloric and sulfuric acids, titanium exhibits moderate resistance only at low concentrations. Titanium exhibits limited corrosion resistance in dilute HCl. Higher concentrations of HCl are corrosive to titanium.
- 2- The electrochemical Galvanostatic experiments for AP (as polished) and PO (polished then oxidized) indicate that surface hydriding of titanium can be avoided only if oxide film is kept intact. Improper breaking of film promotes hydriding.
- 3- XRD pattern of an AP titanium sample immersed in 30% HCl revealed the existence of peaks that match well with typical peaks of cubic titanium hydride (TiH₂).

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