Effect of Thermal Treatment of Two Titanium Alloys (Ti-49Al & Ti-51Al) on Corrosion Behavior in 0.01 M Various Acidic Media

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Received: 10 May 2025; Received in revised form: 06 Jun 2025; Accepted: 12 Jun 2025; Available online: 18 Jun 2025 ©2025 The Author(s). Published by AI Publications. This is an open access article under the CC BY license (https://creativecommons.org/licenses/by/4.0/)

Abstract— In this paper, the effect of thermal treatment of (Ti-49Al & Ti-51Al) alloys on corrosion behavior in 0.01M of H₂SO₄, H₃PO₄, HNO₃ and HCl solutions was investigated. Potentiodynamic polarization measurements, were performed for the two alloys in 0.01 M acidic media at room temperature. The polarization curves indicated three regions. The first region, the active dissolution region was observed from – 2000 to ~ - 700 mV(SCE), the second region, signifying the transition from active dissolution to a passive state on the electrode surface and the third region, a trans-passive region, which the oxygen started to evolve and the current density increased sharply with further increase in potential. The results of potentiodynamic polarization curves, clearly indicate that the corrosion resistance for different alloys decreases as follows: a < f < e < d < b < c, this means that alloys (a, f and e), which have one phase structure (100 % γ), shows better corrosion resistance than alloys (d, b and c), which have dual phase structure ($\alpha + \gamma$). The surface morphology was examined by scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDX) of two alloys used to confirm the corrosion mechanism. The SEM results confirmed the corrosion of Ti-Al alloys due to uniform corrosion in 0.01 M HCl solution.

Keywords— Acidic media, Surface Morphology, Titanium alloys, Thermal Treatment.

I. INTRODUCTION

Ti is one of the most abundant metals on the earth and its alloys are commonly used in the shipping industry, chemical and medical industries due to its outstanding resistance, higher specific strength and corrosion [1]. Manufacturing of large cryogenic properties aeronautical titanium structural components by the wrought based traditional advanced manufacturing processes, has been recognized both technologically difficult and economically expensive [1, 2]. Ti alloys, as a kind of high strength ratio material widely used for the safety-critical components in the aero engines, exhibit microstructural sensitive fatigue performance when subjected to long term cyclic loadings [3].

A high-quality alloy of titanium is used to manufacture the thin-walled pipes of condensers, thin pipers of heat exchangers and mufflers of diesel engines in submarines [1]. They have been made faster in the marine industry, hydrocarbon extraction devices in the offshore petrolchemical industry, heat exchangers in desalination plants and cooling systems in seawater-cooled power plants [3]. High quality titanium alloys can operate for a long time even at a temperature above 600 °C. A huge amount of heat is generated during the machining of Titanium alloys due to its low machinability and thermal conductivity. Heat treatment mainly includes solution treating, surface treatment, annealing, aging and thermochemical treatment. Heat treatment, is a combination of industrial and metal working processes used to modify physical and chemical characteristics of a material. Heat treatment consists of

heating the materials at a predefined temperature to achieve the desired characteristics such as hardening and softening of the materials [1]. Heat treatment of Titanium alloys has been investigated by Peng Cao and Laichang Zhang [4]. Titanium and its Alloys: Metallurgy, Heat Treatment and Alloy Characteristics have been investigated [5].

Ti has two allotropic forms, high-temperature bodycentered cubic(BCC) β -phase and low temperature α -phase with a hexagonal-close-packed(HCP)structure. The transition from $\alpha + \beta$ to 100 % β - phase, occurred at ~ 882 °C for unalloyed Ti. α/β - alloys, this class of alloys is defined as the region between the boundary of the α alloys and the metastable β - alloys-marten site is formed when quenching from temperatures high in $\alpha + \beta$ phase filed or higher [5]. Titanium alloys that consist of only the alpha phase are commonly used in industrial applications where corrosion resistance is a primary concern [6].

Aluminum also is an active metal, whose resistance to corrosion depends on the passivity produced by a

protective oxide film. Al is passive only in the pH range of about 4 to 9 [7]. The limits of passivity depend on the temperature and the form of oxide present, the various forms of aluminum oxide e.g.Al₂O₃ & AlO₂, all exhibit minimum solubility at about pH 5. At higher temperatures, thicker films are formed; these may consist of a thin structure less barrier layer next to the Al and a thicker crystalline layer next to the barrier layer [8]. A Critical Review on Heat Treatment of Aluminum Alloys [9].

The aim of this study, is to investigate the effect of the thermal treatment of two Ti-Al alloys on corrosion behavior in 0.01 M of different acids.

II. EXPERMENTAL

2.1. Materials

Two Ti alloys were used to evaluate the effect of thermal treatment. Chemical composition was determined by X-ray fluorescence and the surface area of Ti alloys are shown in Table 1.

| Samples | Ti | Al | Ν | 0 | Н | Si | Mn | Cr | Surface Area(cm ²) |
|-----------------|------|------|--------|-------|-------|--------|-------|--------|--------------------------------|
| I (Ti - 49 Al) | Bal. | 49.0 | 0.0057 | 0.115 | 0.001 | < 0.01 | 0.021 | < 0.01 | 1.54 |
| II (Ti – 51 Al) | Bal. | 51.0 | 0.004 | 0.114 | 0.003 | < 0.01 | 0.02 | < 0.01 | 1.54 |

Table 1: The chemical composition of the samples used, mass % & surface area

The two sample alloys, were prepared by argon arc melting (The arc melting process takes place in a cylindrical chamber that can be filled with argon gas after the air is evacuated by an integrated vacuum pump) with a non-consumable tungsten electrode, using high purity Ti and Ti chips (99.9 % Ti & 99.9 % Al) to make a 100 gm. button ingot. The chemical composition of the ingot was determined by X-ray fluorescence type ARL 9400. Switzerland. All samples were cut from the button ingots and wrapped with tantalum foil and used for heat treatment. They were treated with heat in a vertical furnace equipped with a vacuum system under high purity argon. Prior the heat treatment, the furnace was evaluated down to 5 x 10⁻³ pa and then back filled with argon. The previous circular electrodes were fixed to glass tubing with araldite adhesive. The electrical contact was made through a thick copper wire soldered to the inner side of the electrodes. Prior to each experiment, the surface of the working electrodes was performed by polishing with different grades of emery papers (800-1200), then diamond past (1 µm), washing by distilled water and ethanol, then quickly inserted in the cell. The counter electrode was

platinum sheet, and the potential was recorded relative to saturated calomel electrode (SCE).

Test solutions: 0.01 M of oxy and halogen acids which are sulfuric, phosphoric, nitric and hydrochloric acids.

2.2. Measurements and instruments

In order to study the effect of heat treatment on the microstructure and corrosion properties of the two alloys, three techniques were used: potentiodynamic polarization technique, scanning electron microscope (SEM) and energy dispersive x-ray analysis. Anodic and cathodic potentiodynamic polarization measurements were performed for the samples using electronic potentiostate (PGZ301 Dynamic EIS Voltammetry). The measurements were conducted at scanning rate 15 mV/s. All measurements were performed in freshly prepare aerated solutions at room temperature and the anodic E/log I curves were swept from (-2000 mV to +1500 mV). The morphology of titanium alloys, were examined before and after immersion in test solutions, using SEM. The identification of the elements present on the surface of specimen before and after immersion in 0.01 M

hydrochloric acid solutions and heat treatment, was using energy dispersive X-ray analysis.

III. RESULTS AND DISCUSSION

Surface heat treatment change the phases and grain size of the alloys are tabulated in Table 2. The surface morphology of the tested alloys as-received and after heat treatment, were shown in Fig. 1. Literature on the Ti-Al alloys, with and without surface treatment, showed corrosion problems [10]. Therefore, it is essential to understand the corrosion characteristics of Ti alloys in detail under different acidic solutions.

| Table 2. The heat treatment | conditions phases and | grain size of the h | eat treated allovs |
|------------------------------|-----------------------|---------------------|---------------------|
| 1 doie.2. The neur in cument | conditions phases and | grain size of the h | cui il cuicu uiloys |

| Alloy No. | Alloy composition | Heat treatment [* furnace cooled] | Phases | γ Grain size µm |
|-----------|-------------------|---------------------------------------|----------------|--------------------|
| a | Ti – 51 Al | As received | γ 100% | 22 |
| b | Ti-49 Al | Heat to 1435 °C for 5 minutes & f.c* | α2 25% + γ 75% | 430 |
| с | Ti – 51 Al | Heat to 1365 °C for 30 minutes & f.c* | α2 37% + γ 63% | 55 |
| d | Ti – 51 Al | Heat to 1365 °C for 3 minutes & f.c* | α2 15% + γ 85% | 60 |
| e | Ti – 51 Al | Heat to 1150 °C for 60 minutes & f.c* | γ 100% | 55 |
| f | Ti – 51 Al | Heat to 1200 °C for 10 hours & f.c* | γ 100% | 130 |

* furnace cooled





(a)



(c)



(d)



Fig.1: SEM morphology of tested samples, (a) as received Ti-51Al alloy, γ phase=100%, (b) Ti-49Al alloy, heat treated at 1435°C for 5 minutes, (c) Ti-51Al alloy, heat treated at 1365°C for 30 minutes, (d) Ti-51Al alloy, heat treated at 1365°C for 3 minutes, (e) Ti-51Al alloy, heat treated at 1150°C for 60 minutes, (f) Ti-51Al alloy, heat treated at 1200°C for 10 hours

3.1. Anodic and cathodic potentiodynamic polarization measurements

The potentiodynamic polarization measurements were performed for two alloys and carried out in 0.01 M of sulfuric, phosphoric, nitric and hydrochloric acids solutions at room temp., with a scanning rate 15 mV/s. Ranging from (-2000 mV to +1500 mV).

In the present part, potentiodynamic polarization is utilized to give information about the corrosion potential ($E_{corr.}$),

corrosion current density ($I_{corr.}$), anodic, cathodic Tafel slopes and corrosion rate for all tested alloys.

Consideration of the curves of Fig. 2, shows the variation of electrode potential with current density in 0.01 M of different tested acidic solutions at different heat treatment cycles. The electrochemical parameters determined for all tested alloys are summarized in Table 3.

| Alloy No. | 0.01 M Acids | Ecorr. | Icorr. | Tafel slopes | | Corrosion rate |
|-----------|--------------------------------|--------|-----------------------|--------------|--------|----------------|
| | 0.01 WI Aclus | (mV) | (mA/cm ²) | βa(mV) | βc(mV) | (C.R) μm/y |
| | H_2SO_4 | -629.3 | 0.0053 | 566.5 | -281.5 | 61.89 |
| | H ₃ PO ₄ | -634.5 | 0.0023 | 615.7 | -300.9 | 27.15 |
| а | HNO ₃ | -589.2 | 0.1108 | 509.4 | -949.7 | 129.5 |
| | HCl | -628.4 | 0.0038 | 525.9 | -328.2 | 44.34 |
| | H_2SO_4 | -818.8 | 31.2718 | 693.2 | -885.7 | 365.7 |
| h | H ₃ PO ₄ | -718.8 | 0.0050 | 497.9 | -280.1 | 58.18 |
| D | HNO ₃ | -789.4 | 0.0088 | 1086.5 | -265.4 | 103.0 |
| | HCl | -637.7 | 0.0592 | 732.5 | -705.0 | 692.5 |
| | H_2SO_4 | -696.0 | 11.7814 | 559.7 | -500.8 | 137.7 |
| c | H ₃ PO ₄ | -781.3 | 0.0031 | 463.8 | -280.6 | 36.02 |
| | HNO ₃ | -730.5 | 0.0044 | 677.9 | -301.8 | 51.32 |
| | HCl | -776.3 | 0.1788 | 400.1 | -883.8 | 209.1 |
| d | H_2SO_4 | -855.4 | 0.0092 | 1632.8 | -327.4 | 107.7 |
| | H ₃ PO ₄ | -735.9 | 0.0030 | 552.3 | -297.4 | 35.42 |
| | HNO ₃ | -670.5 | 0.0069 | 638.4 | -339.3 | 81.10 |
| | HCl | -629.5 | 0.0590 | 580.2 | -799.1 | 689.6 |
| e | H ₂ SO ₄ | -730.4 | 0.0086 | 1026.5 | -301.6 | 100.7 |

Table.3: The electrochemical parameters of Ti-Al alloys in different acidic in 0.01 M of different acidic solutions

| | H ₃ PO ₄ | -790.0 | 0.0042 | 607.0 | -321.5 | 49.68 |
|---|--------------------------------|--------|---------|--------|---------|-------|
| | HNO ₃ | -710.9 | 0.0060 | 712.0 | -323.2 | 69.97 |
| | HCl | -591.3 | 77.9468 | 488.2 | -1087.9 | 911.6 |
| f | H_2SO_4 | -595.1 | 7.0159 | 213.8 | -1517.1 | 82.05 |
| | H ₃ PO ₄ | -734.6 | 2.1003 | 705.2 | -722.1 | 24.56 |
| | HNO ₃ | -513.9 | 3.9133 | 238.8 | -1058.6 | 45.66 |
| | HCl | -724.6 | 8.4955 | 2273.6 | -453.5 | 99.36 |

Analysis of the polarization curves Fig. 2 and Table 3, show a similar character of potentiodynamic curves for as-received and heat-treated alloys and the values of the parameters are almost similar in received alloy in all acids.













(d)



Fig.2: Potentiodynamic polarization curves of the of tested alloys in 0.01 M of Acidic solutions,

(a) as received Ti-51Al alloy; (b) Ti-49Al alloy, heat treated at 1435 °C for 5 minutes; (c) Ti-51Al alloy, heat treated at 1365 °C for 30 minutes; (d) Ti-51Al alloy, heat treated at 1365 °C for 3 minutes; (e) Ti-51Al alloy, heat treated at 1150 °C for 60 minutes; (f) Ti-51Al alloy, heat treated at 1200°C for 10 hours

Data recorded in Table 3, reveal that the corrosion rate of all tested alloys depends not only on the acid used, but also on the surface heat treatment and immersion time. The effect of immersion time and temperature on the corrosion behavior of certain aluminum alloys was examined [11].

All polarization curves exhibit well-developed Tafel behavior in the active region with E α log I_a. The results obtained show that, the cathodic current density is due to hydrogen evolution. It is clear from the curves that, the polarization curves indicated three regions. The first region, active dissolution region was observed from – 2000 to ~ - 700 mV(SCE), where the potential-current relation was linear and well-defined Tafel slope.

The second region, signifies the transition from active dissolution to a passive state on the electrode surface. And the third region is a trans-passive region. The oxygen started to evolve and the current density increased sharply with a further increase in potential. Increasing the acid concentration, shifts the critical current density, and active-passive transition potential region toward the active direction [12-13]. So all tested acids follow the order:

$H_{3}PO_{4} < HNO_{3} < H_{2}SO_{4} < HCl$

Increasing the acid concentration, shifts the critical current density, active-passive transition potential region toward the active direction. The composition of the passive film for Ti-Al alloy formed in the different acids used is: the titanium oxide layer, which may be described as an n-type semiconductor [14]. The results of potentiodynamic polarization curves and Table 3, clearly indicate that the corrosion resistance for different alloys decreases as follows: a < f < e < d < b < c This means that alloys (a, f and e), which have one phase structure (100 % γ), shows better corrosion resistance than alloys (d, b and c), which have dual phase structure ($\alpha + \gamma$).

Regarding the (γ) grain size, it can be easily seen that as the grain size increases the corrosion resistance decreases (for alloys a, f and e). For alloys d, b and c, with $(\alpha + \gamma)$ phase structure by increasing the percentage of α phase, the corrosion resistance decreases. These results are in good agreement [15, 16], phosphate is formed on the oxide surface and prevents dissolution.

3.2. Spectroscopic analysis

3.2.1- SEM analysis

To confirm the corrosion mechanism of the Ti-Al alloys under various environmental conditions, the corroded specimens tested were observed under SEM, Fig. 3 shows the SEM images which describe the morphology of the corroded surfaces of tested electrodes after exposure to 0.01 M hydrochloric acid solution, at room temp. As can be seen the alloys corroded uniformly in 0.01 M hydrochloric acid solution, which is the reason for the corrosion of Ti-Al alloys under an acidic solution. SEM results are in good agreement with the potentiodynamic polarization data. Hence, SEM results confirm that, the degradation of Ti-Al alloys takes place due to uniform corrosion in the hydrochloric acid solution.

3.2.2 - EDX analysis

It is important to take into consideration, the percentages of the elements and oxide film formed on the surface of the alloys electrode. This percentages were obtained from elemental composition by energy dispersive x- ray analysis.

Fig. 4, shows the (EDX), for Ti-Al alloys tested in 0.01 M hydrochloric acid solution, at room temperature, it can easily show that, the corrosion products formed on the surface of the tested alloys, consist of TiO₂ and Al₂O₃ in addition to some chloride appears on the surface of samples heat treated Ti-51Al alloy at 1365 °C for 30 minutes (c) and heat treated Ti-51Al alloy at 1200 °C for 10 hours (f), that explained the healing process happened after uniform corrosion occurs.



Fig.(3): Surface morphology of heat treated Ti-Al alloys after corrosion tests in 0.01 M HCl solution, at room temperature, a) as received Ti-51Al alloy, (b) Ti-49Al alloy, heat treated at 1435 °C for 5 minutes,
(c) Ti-51Al alloy, heat treated at 1365 °C for 30 minutes, (d) Ti-51Al alloy, heat treated at 1365 °C for 3 minutes,
(e) Ti-51Al alloy, heat treated at 1150 °C for 60 minutes, (f) Ti-51Al alloy, heat treated at 1200°C for 10 hours



(a)



(b)



(c)

Int. j. chem. math. phys. http://www.aipublications.com/ijcmp/



Fig. (4): EDX spectra of tested samples: (a) as received Ti-51Al alloy; (b) Ti-49Al alloy, heat treated at 1435 °C for 5 minutes, in 0.01 M HCl solution; (c) Ti-51Al alloy, heat treated at 1365 °C for 30 minutes, in 0.01 M HCl solution; (d) Ti-51Al alloy, heat treated at 1365 °C for 3 minutes, in 0.01 M HCl solution; (e) Ti-51Al alloy, heat treated at 1150 °C for 60 minutes, in 0.01 M HCl solution; (f) Ti-51Al alloy, heat treated at 1200°C for 10 hours, in 0.01 M HCl solution

IV. CONCLASION

The following major findings are summarized:

- The effect of surface heat treatment on the corrosion behavior of two Ti alloys (Ti-49Al & Ti-51Al) was investigated by using potentiodynamic polarization technique, (SEM) and (EDX).
- 2- The potentiodynamic polarization measurements were performed for the two alloys and carried out in 0.01 M of sulfuric, phosphoric, nitric and hydrochloric acids solutions. The polarization curves indicated three regions. The first region, the active dissolution region was observed from 2000 to ~ 700 mV(SCE), the second region, signifying the transition from active dissolution to a passive state on the electrode surface and the third region, a trans-passive region, which the oxygen started to evolve and the current density increased sharply with further increase in potential.
- 3- The results of potentiodynamic polarization curves, clearly indicate that the corrosion resistance for different alloys decreases as follows: a < f < e < d < b < c, this means that alloys (a, f and e), which have one phase structure (100 % γ), shows better corrosion resistance than alloys (d, b and c), which have dual phase structure ($\alpha + \gamma$).
- 4- SEM results confirm the corrosion mechanism of Ti-Al alloys takes place due to uniform corrosion in hydrochloric acid solution.

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