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Effect of Heat Treatment on the Electrochemical Corrosion Behavior of Ti- 15 V- 3 Al- 3 Cr- 3 Sn Alloy in HCl and NaCl Media

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Abstract: Titanium alloys are extensively used in Aerospace Industry. Presently, the alloy Ti-6Al-4V (α-β alloy) is widely employed while metastable β-alloys are gaining priority over α-β alloys. Metastable β-alloys can be aged for hardening by precipitation. But the corrosion properties of these alloys might get altered. Hence, the present studies are to investigate the effect of heat treatment on corrosion behavior of Ti-15V-Cr-3Al-3Sn (β-Ti alloy). The evaluation is carried out by polarization studies in various environments viz. HCl and NaCl with different concentrations. It has been observed that the corrosion property of β-titanium alloy is intact even after aging.
Keywords: A. Titanium; B. Polarization; C. SEM; D. XRD.

1. Introduction

Titanium alloys are candidate materials for Aerospace Industry due to their low density, high tensile strength values which are comparable to many of the super alloys used with exceptional corrosion resistance [1]. Based on the alloying elements added, two phases are stabilized, alpha (α phase) and beta (β phase). From this criterion, the titanium alloys are classified into α, α-β, and metastable β, depending on the phases stabilized and then there is unalloyed titanium (Commercially Pure Titanium) [2]. Among the alloys of titanium, Ti-6Al-4V which belongs to α-β class of alloys is most widely employed alloy [3], [4]. Whereas, metastable β alloys are gaining priority over the α-β alloys since these class of alloys offer the highest strength-to-weight ratios over any titanium alloy, though these have higher densities compared to other alloys of titanium [5], [6], [7]. Densities of the order of 4.70 to 4.98 g/c.c. are typical, with ultimate strength levels which range from 1,517 to 1,586 MPa [8]. In most aircraft structures, high modulus ranges are desired while these alloys fulfill this requirement with modulus ranging between 69 GPa to 76 GPa in their solution-treated condition and 103 GPa to 110 GPa in aged condition. These alloys are expensive, but due to their superior formability and strip producibility become cost effective than the α-β alloys [8], one such β-alloy is Ti-15V-3Al-3Sn-3Cr. In order to improve the structural efficiency of aircraft, it is necessary to increase the room temperature strength of Ti–15–3 from 1000 to 1080 MPa. The strengthening of Ti–15–3 is due to the precipitation of uniformly dispersed fine α-phase in the β-matrix [9]. After extensive investigations [9], an aging treatment of 540°C for 8 h and air cooled (AC) is selected for optimized mechanical traits of Aerospace Industry. Due to various phase transformations, the corrosion properties of the alloy can get altered [10]. In this paper, the effect of heat treatment on the corrosion properties of Ti-15V-3Al-3Sn-3Cr are evaluated using electrochemical techniques (Potentiodynamic Polarization Studies) and this evaluation was corroborated by Scanning Electron Microscopy, Energy Dispersion Spectroscopic Analysis and X- Ray Diffraction Studies.

Table 1. Composition of Ti-15-3 alloy and Ti-6-4 alloy (in % wt.)

Alloy	Ti	V	Cr	Sn	Al	Fe	C	N	H	O
Ti-15-3	75.492	15.1	3.0	3.1	3.0	0.18	0.008	0.027	0.003	0.009

2. Materials and Methods

2.1. Material

The alloy Ti-15-3 was supplied by M/s Kalva Engineers Pvt. Ltd., Hyderabad and their chemical compositions are shown in Table 1. Ti-15-3 material is obtained in sheet form and in annealed condition as per the specifications of ASTM B265.

The electrodes were cold mounted in epoxy resin, leaving 1 cm^2 of surface area for exposure (ASTM G1 Standards). The electrode surfaces were mechanically abraded using emery papers (80-2000 grit) followed by disk polishing with diamond compound polishing paste (1 μm).

2.2. Heat Treatment

Ti- 15-3 was received in a sheet form which was solutionized. The alloy was aged at 540^o C for 8 hours for optimized mechanical properties in a tubular furnace [9] under inert gas environment. However, beta-alloys are prone to surface oxidation, even in inert heat treatments. Hence, pickling was carried out [8]. The composition of pickling agent is 35 vol. % HNO_3, 5 vol. % HF and balance deionized water [11].

2.3. Electrochemical Experiments

All Electrochemical studies were conducted using CHI604D Electrochemical Analyzer supplied by M/s CH Instruments, USA. A conventional three-electrode cell was constructed using a platinum electrode as the auxiliary electrode and all the potentials were measured and reported with reference to a saturated Ag/AgCl/KCl electrode. Potentiodynamic polarization measurements were conducted at a scan rate of 10 mV/s. Each test was at least performed for 3 times until similar polarization curves were obtained.

2.4. Solutions

The solutions (NaCl, HCl) were prepared from reagent grade chemicals and de-ionized water. Test specimens were exposed to 0.5 M, 1 M and 2M NaCl and 1 M, 3M, 5M, 7M HCl solutions for 30 minutes.

2.5. Characterization

All the test specimens were characterized by Scanning Electron Microscopy (SEM, Model-VEGA 5 by TESCAN). The aged alloy was characterized for the chemical compositions of the two phases using Energy Dispersive Spectrometry (EDS, Model-X-act by Oxford Instruments). For this characterization, the aged alloy was etched in Krolls reagent, (6 vol% HNO_3, 2 vol% HF, Balance- H_2O). The Ti-15-3 in its aged form was evaluated for the phases present using X-ray diffractometry (PANalytical Instruments)

3. Results and Discussion

3.1. Potentiodynamic Polarization behavior

Cathodic and anodic linear sweep curves for Ti-15-3 and Ti-15-3 (Aged) recorded at a scan rate of 10 mVs^{-1} are presented in Figures 1 and 2, for different concentrations of HCl and in Figures 3 and 4, for different concentrations of NaCl. It has been observed that at all concentrations, the cathodic curves are similar for the alloy (as-received) and its aged condition in both HCl and NaCl media. When the anodic polarization starts, the current in the active region increases rapidly due to metal dissolution. As the potential increases positively, the rate of variation of the anodic current decreases and the curve merges into a more or less plateau [12].

Figures 1 and 2 compare the typical potentiodynamic polarization curves of the alloy and its aged form in HCl of different concentrations and similarly Figures 3, 4 compare the alloy and its aged form in NaCl of different concentrations. It has been noticed that E_{corr} determined from these curves (Figures 1, 2, 3, 4) are lower than those obtained from that of OCP measurements. This behaviour is expected, as the polarization tests were started at a cathodic potential relative to the corrosion potential, so that the passive film at the surface was at least partially removed due to the highly reducing initial potential [12], [13].

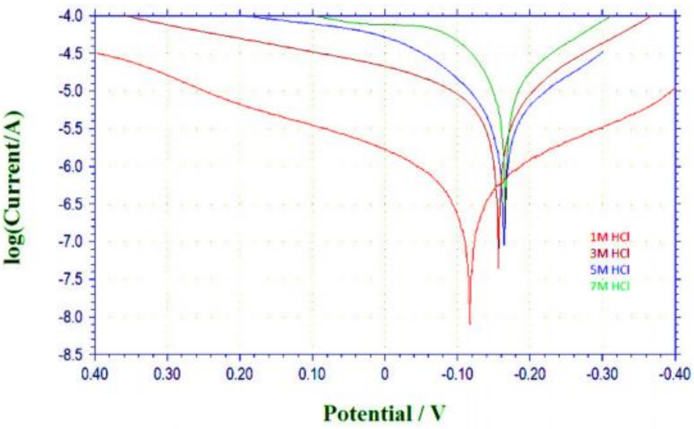

Figure 1. Tafel Plots for Ti-15-3 in different concentrations of HCl

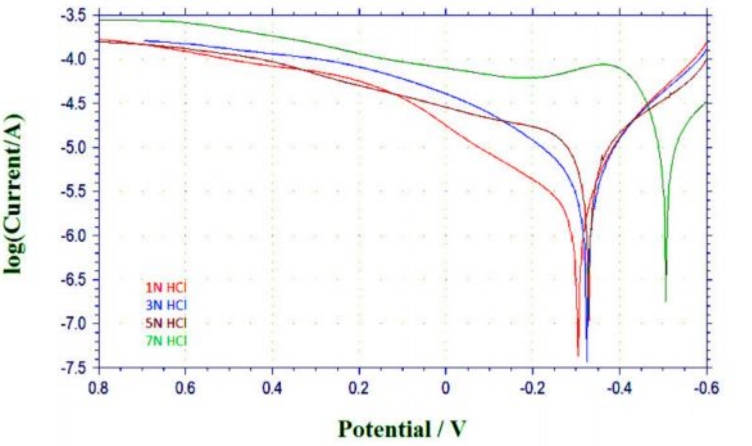

Figure 2. Tafel plots for Ti-15-3 (Aged) in different concentrations of HCl

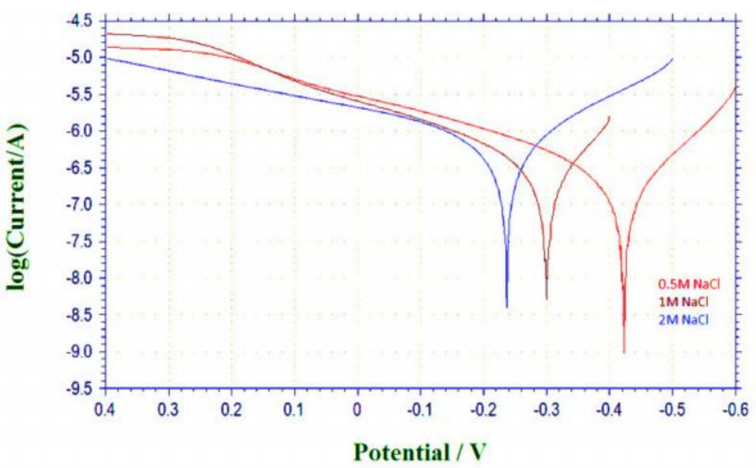

Figure 3. Tafel Plots for Ti-15-3 in different concentrations of NaCl

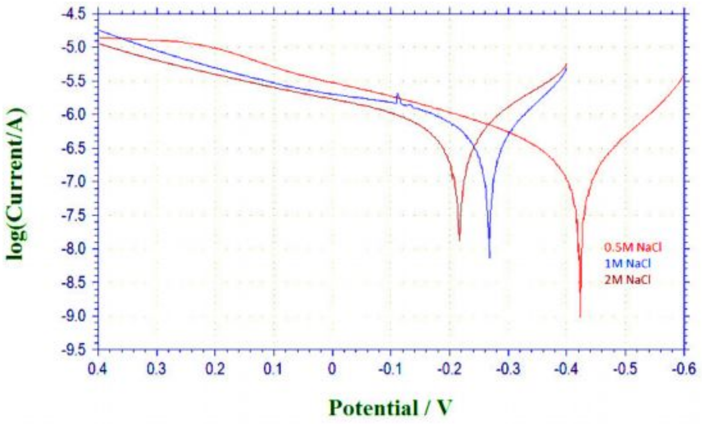

Figure 4. Tafel plots for Ti-15-3 (Aged) in different concentrations of NaCl

Valency of 3 was taken for the Ti ion for calculating the corrosion rate from the I_{corr} obtained from the tafel plots [14]. The corrosion rates of Ti-15-3 and its aged form in different concentrations of HCl and NaCl are shown in Tables 2 and 3.

Table 2. Effect of HCl conc. on Ti-15-3, Ti-15-3 (Aged) corrosion behavior

Alloy	Conc.	E_{corr}	Corrosion Current (µA)	Corrosion Rate (mpy)	Cathodic Slope (mV/dec)	Anodic Slope (mV/dec)
Ti-15-3	1N	-0.12	0.606	**0.305**	-178.9	193.6
	3N	-0.16	6.11	**3.08**	-151.3	247.7
	5N	-0.18	15.87	**7.99**	-160.6	146.8
	7N	-0.20	25.18	**12.47**	-164.5	255.81
Ti-15-3 (Aged)	1N	-0.3	2.751	**1.386**	-130	295.85
	3N	-0.325	5.045	**2.54**	-150.3	226.75
	5N	-0.34	14.37	**7.23**	-225.7	392.1
	7N	-0.5	26.22	**13.2**	-224.71	235.8

Table 3. Effect of NaCl conc. on Ti-15-3, Ti-15-3 (Aged) corrosion behavior

Alloy	Conc.	E_{corr}	Corrosion Current (µA)	Corrosion Rate(mpy)	Cathodic Slope (mV/dec)	Anodic Slope (mV/dec)
Ti-15-3	0.5N	-0.42	0.073	**0.037**	-125.4	206.01
	1N	-0.27	0.455	**0.23**	-117.8	251.2
	2N	-0.22	0.516	**0.261**	-160.2	255.2
Ti-15-3 (Aged)	0.5N	-0.42	0.138	**0.07**	-125.47	206.5
	1N	-0.24	0.346	**0.175**	-102.92	215.19
	2N	-0.22	0.514	**0.26**	-168.06	233.10

With increase in concentration of HCl, the E_{corr} is shifting towards active side in both the cases, while, similar results were observed by A. S. Mogoda *et.al.* [15]. In Ti-15-3, the corrosion rate is low for 1N HCl. This may be due to the development of a passive layer on the surface of the electrode. But it has been observed that the corrosion rate increased from 7.747 * 10^{-3} mmpy (millimetre per year) to 78.23 * 10^{-3} (µmpy) when the concentration was increased from 1N to 3N HCl. This can be explained by breakage of the formed film due to high concentrations of Cl^- in the solutions [12]. The increase in corrosion rate is gradual from 3N onwards but not as significant as in the case of 1N to 3N, due to reduction in ionization of the solution at these high acid concentrations [16], [17], [18].

However, the situation is different in aged condition of the alloy (Ti-15-3). There has been no critical shift in corrosion ratewhen concentration was increased from 1N to 3N. The passive oxide film development and dissolution mechanisms might be different from that of the as-received alloy (Ti-15-3). Whereas, similar corrosion rates are noticed when the concentration was increased from 3N to 7N in both the cases which can be attributed to the reduction in ionization of the solutions at these high concentrations [16], [17], [18].

When the samples are tested in different concentrations of NaCl solution, as the concentration increases, it has been observed that the E_{corr} is shifting towards the nobler side in both the cases. The corrosion rates are very low, which can be due to the passive film development [19]. For both the alloys, comparable corrosion rates are observed which may be due to the development of a similar oxide film on Ti-15-3 and also on the aged condition of the alloy.

3.2. Characterization

3.2.1. X-ray Diffractometry:

An X-ray diffraction pattern (XRD) for Ti-15-3 in its aged condition is shown in Figure 5. It has been observed from the XRD pattern that the peaks validate the presence of two phases with HCP and BCC crystal structure, which could be attributed to the α-phase precipitated and the β matrix respectively [20].

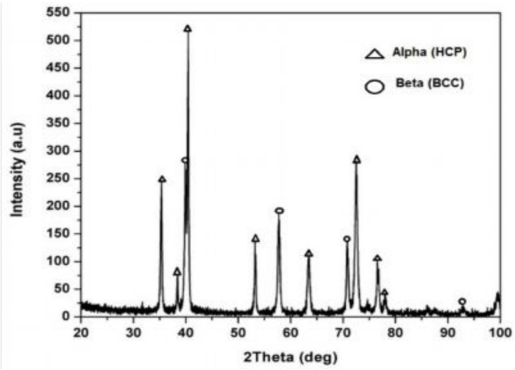

Figure 5. X-ray diffraction profile of Ti-15-3 (Aged)

3.2.2 Scanning Electron Microscopy:

The surfaces of Ti-15-3 and its heat treated form (aged) immersed in different corrosion media have been characterized using Scanning Electron Microscopy technique (SEM) [21]. However, no considerable change was observed in the morphology of the alloy surfaces which were immersed in different concentrations of NaCl solution. Hence, the electrodes tested in HCl solutions only are characterized for their surface morphologies, which revealed the following observations:

a. Surface Morphology of Ti-15-3:

The surface of the electrode immersed in 1N HCl solution (Figure 6) encountered insignificant corrosion than the surfaces of the electrodes immersed in 3N to 7N HCl (Figures 7, 8, 9). These results are in good agreement with the observations made from the polarization studies on Ti-15-3 (as discussed earlier).

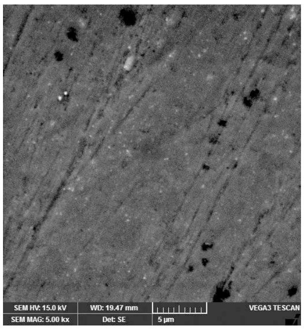

Figure 6. SEM micrograph of Ti-15-3, tested in 1N HCl showing insignificant corrosion.

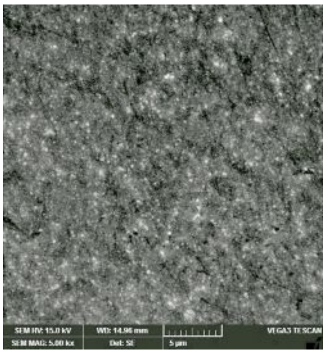

Figure 7. SEM micrograph of Ti-15-3, tested in 3N HCl showing considerable corrosion.

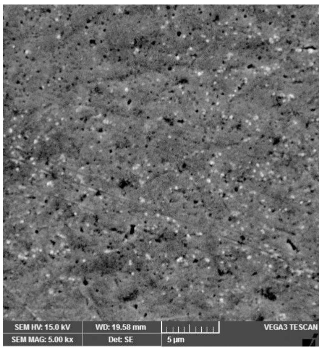

Figure 8. SEM micrograph of Ti-15-3, tested in 5N HCl indicating dislodging of the passive film.

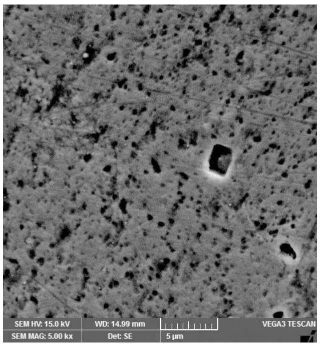

Figure 9. SEM micrograph of Ti-15-3, tested in 7N HCl, showing substantial damage of the surface

b. Surface Morphology of Ti-15-3 (aged):

The alloy (aged), immersed in 1N HCl was destroyed to some extent (Figure 10) and the increase in corrosion rate (which is not significant, as expected) of the electrode surfaces immersed in 3N to 7N HCl was observed from the Figures 11, 12, 13 which is supporting the observations made from the polarization studies on the aged form of the alloy (Ti-15-3).

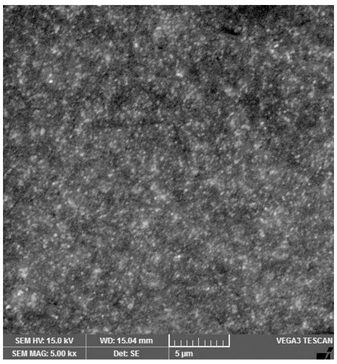

Figure 10. SEM micrographs of Ti-15-3(aged), tested in 1N HCl, showing negligible corrosion

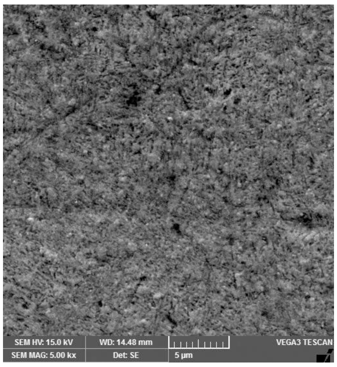

Figure 11. SEM micrographs of Ti-15-3(aged), tested in 3N HCl, showing signs of corrosion.

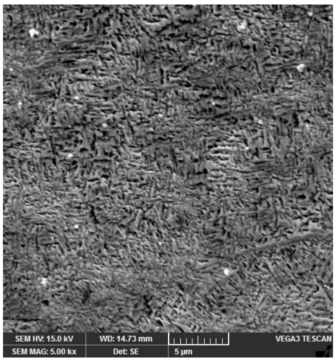

Figure 12. SEM micrographs of Ti-15-3(aged), tested in 5N HCl, revealing two distinct phases.

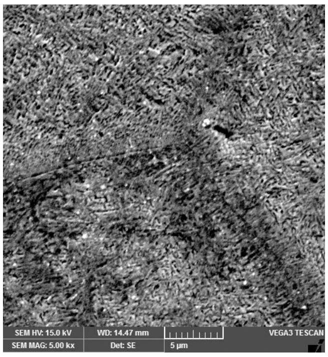

Figure 13. SEM micrographs of Ti-15-3(aged), tested in 7N HCl, indicating severe corrosion.

3.2.3 Energy Dispersion Spectroscopic Studies:

Energy Dispersive Studies (EDS) were conducted on the aged alloy, for characterizing the chemical compositions of the β-matrix and the grain boundary precipitate and the results are shown in Table 4.When a single phase alloy is aged for a dual phase structure, so as to improve its mechanical properties, the aged alloy ought to become more corrosion prone than the single phase structure [22]. On contrary, the corrosion behavior of the alloy is almost similar in its as-received and aged condition. This advantage of sustained corrosion resistance can be attributed to the high vanadium content in the grain boundary precipitate (Table 4).The grain boundary precipitate, which is meant to be α phase, has similar vanadium content as that of β matrix though vanadium is a β stabilizer [23]. Sizeable percentage of vanadium even in α phase resulted in the corrosion resistance of the aged alloy which is more or less similar to the as-received alloy.

Table 4. Chemical Compositions of phases in the aged Ti-15-3 alloy

	Composition (%wt)				
	Al	**V**	**Cr**	**Sn**	**Ti**
β-matrix	3.59	14.14	3.14	3.35	Bal
Grain boundary precipitate	3.64	13.77	2.44	3.40	Bal

4. Conclusions

HCl environments are more corrosive for Ti-15-3 alloy (as received) and its aged condition than NaCl environments. With increase in concentrations of the solutions viz. HCl and NaCl, the corrosion rate is increasing. In HCl, the E_{corr} is drifting towards the active side while in NaCl, E_{corr} shift is towards the nobler side. Corrosion rate of Ti-15-3 in 1N HCl is low, whereas, for 3N a sudden increase has been observed followed by a gradual increment from 3N to 7N HCl. In the aged condition of Ti-15-3, corrosion rate is higher when compared to Ti-15-3 in 1N HCl and no critical increase in corrosion rate was observed from 1N to 3N HCl (as in the case of Ti-15-3). The increase in corrosion rate is similar to that of Ti-15-3 at increased concentrations (3N to 7N). The corrosion rates are quite low and are similar in NaCl solutions for Ti-15-3 and its aged condition. Scanning Electron Micrographs of the alloy (Ti-15-3) and its aged form confirm the above conclusions. The corrosion rates of the Ti-15-3 in its as received form and in its aged form are almost similar which could be attributed to comparable vanadium percentages in both phases (grain boundary precipitate, α phase and β matrix).

5. Acknowlegments

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