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Corrosion and Inhibition of Ti-6Al-4V Alloy in NaCl Solution

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The electrochemical behavior of Ti-6Al-4V alloy in aqueous solutions of NaCl was studied using a variety of techniques, and the corrosion behavior of Ti-6Al-4V alloy was investigated at different concentrations of NaCl with and without the addition of bovine serum albumin and egg albumin. The morphology of the films that were formed was also examined by scanning electron microscopy (SEM).

Keywords: Ti-6Al-4V alloy, bovine serum albumin, egg albumin

1. INTRODUCTION

Corrosion resistance of titanium and its alloys in saline solutions, typical of physiological environments, is due to the formation of a protective oxide layer, mainly TiO_2, with a morphology that depends on surface and thermochemical treatment of orthopedic materials [1-3]. The Pourbaix diagram of titanium [4] reveals that the oxide film is stable over a wide range of potentials.

Titanium and its alloys also have a high strength to density ratio Because of all these advantages, titanium finds a wide variety of applications in, for example, electroplating, aviation, textile and paper production, and heat exchangers; there are therefore a large number of scientific papers dedicated to the study of corrosion and the passivity of titanium and its alloys in acidic media [5-19]. Ti-6Al-4V also has excellent specific tensile and corrosion resistance, and is mainly used for aircraft body and engine parts, for petrochemical plant materials and in surgical implants [20]. Localized corrosion, which usually results in pitting or crevice formation, is a multi-step process. It is generally accepted that the following four steps are involved in localized corrosion (i) adsorption of reactive anions on the oxide covered titanium surface, (ii) reaction of the adsorbed anions with the titanium cations in the titanium oxide lattice or with the precipitated titanium hydroxide, (iii) thinning of the oxide by dissolution; and (iv) direct attack of the exposed metal by the anions, perhaps assisted by an anodic potential. This is sometimes called pitting propagation [21-23]. The electrochemical behavior of Ti-Pd and Ti-6Al-4V alloys in 0.9% NaCl solution has been studied previously by single triangular potential sweep voltammetry, potentiodynamic polarization curves, and electrochemical impedance spectroscopy (EIS) techniques [24]. Williams et al. [25] studied the effect of serum proteins on the electrochemical behavior of metallic implants.

This work focuses on the effect of bovine serum albumin and egg albumin as corrosion inhibitors for Ti-6Al-4V alloy in NaCl solutions.

2. EXPERIMENTAL

2.1. Materials

Commercial titanium alloy (Ti-6Al-4V) was cut into circular electrodes and mounted into glass tubes of appropriate diameter with epoxy resin. The exposed circular surface area of the investigated materials was 1.54 cm^2.

The electrode was always pretreated by polishing the circular front surface with successive grades of emery paper down to 1200 grit, polishing with 1 µm diamond paste, washing with distilled water and ethanol and quickly inserting the electrode into the cell.

2.2. Electrochemical experiments

A conventional three-electrodes cell was constructed using a platinum sheet as the counter electrode and saturated calomel (SCE) as the reference electrode. Open circuit measurements were performed using an electronic multimeter (Type E scord – EDM 2116). Anodic and cathodic potentiodynamic polarization measurements and cyclic polarization measurements were performed for the Ti-6Al-4V alloy electrode using an electronic potentiostat (PGZ 301 Dynamic EIS voltammetry). Potentiodynamic polarization measurements were conducted at a scan rate of 2 mV/s, while cyclic polarization measurements were conducted at a scan rate of 10 mV/s. The test electrode surface was examined by scanning electron microscopy (SEM, model JEOL - JSM-5410, Japan), before and after immersion in the test solutions.

2.3. Solutions

The solutions were prepared from reagent grade chemicals and de-ionized water. Different concentrations of NaCl solutions [1×10^{-4} to 1 M], and different concentrations of protein additives [bovine serum and egg albumin] (0.25-1% v/v) were used.

3. RESULTS AND DISCUSSION

3.1. Open – circuit measurements

Fig. 1 shows the behavior of the Ti-6Al-4V alloy in aerated solutions of NaCl with concentrations varying from 1 x 10^{-3} to 1 M. Inspection of these curves shows that there is a general tendency for the immersion potential to shift steadily towards nobler values. This indicates formation of a passive film composed mainly of TiO_2 and additional oxides such as Al_2O_3 and V-oxides [26]. The extent of the potential increase depends primarily on the solution concentration, with more noble values obtained upon dilution.

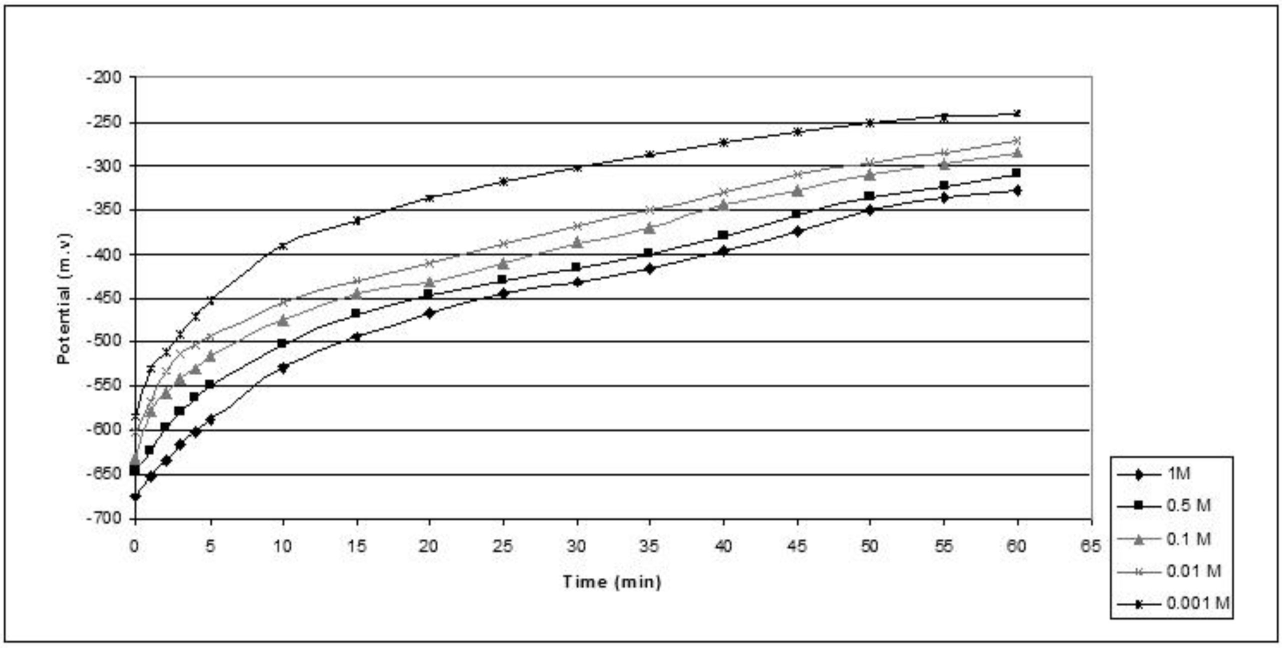


Figure 1. Variation of open-circuit potential of Ti-6Al-4V alloy electrode in NaCl solutions of various concentrations (1×10^{-3} – 1M) as a function of time.

3.2. Potentiodynamic polarization measurements

Potentiodynamic polarization measurements were used to determine the active-passive characteristics of Ti-6Al-4V alloy in different concentrations of NaCl solution. $E_{corr.}$, $I_{corr.}$, anodic, cathodic Tafel slopes and corrosion rates measured for the test electrode in different concentrations of NaCl (1 x 10^{-3} to 1M) with the help of potentiodynamic polarization technique are presented in Table (1). Fig. 2, represented a typical potentiodynamic polarization curves of Ti-6Al-4V alloy in NaCl solutions.

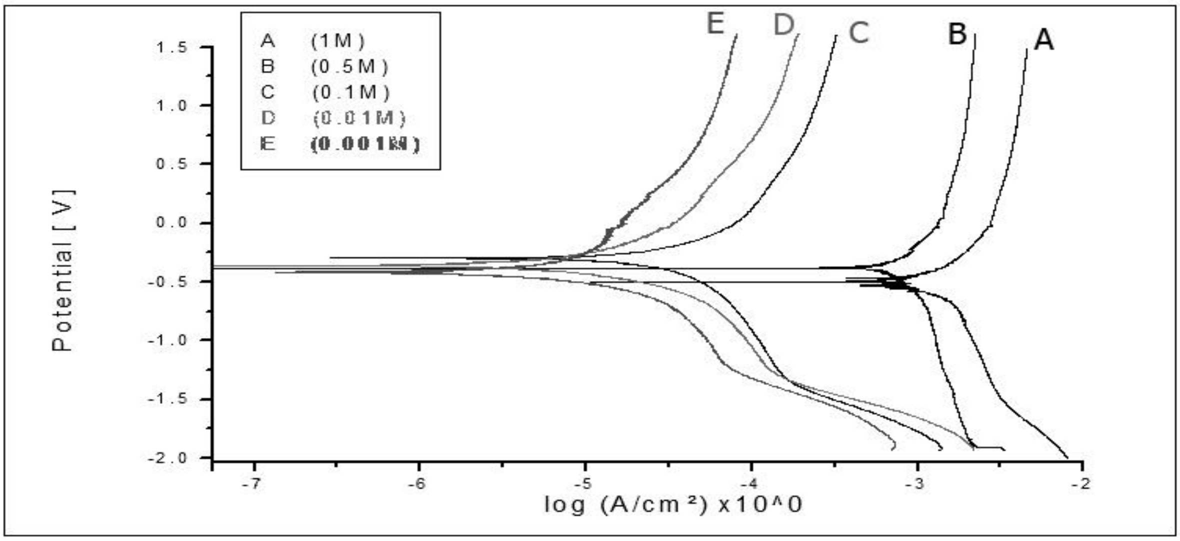


Figure 2. Potentiodynamic polarization curves of Ti-6Al-4V alloy electrode in NaCl solutions of various concentrations (1×10^{-3} – 1M) in NaCl solutions.

Table 1. The electrochemical parameters of (Ti-6Al-4V) alloy electrode in different concentrations of NaCl solution.

Electrode	Conc. M	$E_{corr.}$ mV	$I_{corr.}$ mA/cm^2	Tafel slopes		Corrosion rate (C.R.) µm/y
				β_a	β_c	
(Ti-6Al-4V) alloy	1	-754.1	2.1950	370.20	-222.10	86.63
	0.5	-769.7	0.0015	1087.8	-476.20	25.68
	0.1	-833.0	0.0003	764.70	-318.80	17.19
	0.01	-896.8	0.0001	408.40	-195.20	3.978
	0.001	-963.4	0.0001	398.00	-208.40	1.320

The dissolution of titanium occurs when it is in the tetravalent state under the steady state dissolution condition. Thus, it is likely that titanium tetrachloride is formed and covers the electrode surface. Lower valence titanium species may be formed as byproducts [27]. Fig. 2 and Table (1), demonstrate that the corrosion rate of Ti-6Al-4V alloy electrodes increases with an increase in the concentration of NaCl, with a concomitant shift in the corrosion potential to more positive values and an increase in the corrosion current.

3.3. Potentiodynamic cyclic anodic polarization measurements.

The cyclic polarization technique provides a qualitative view of pitting corrosion mechanism and it is a highly useful method for determining the susceptibility of metals or alloys to pitting when placed in a specific corrosive environment.

The cyclic polarization curves of the Ti-6Al-4V alloy electrodes in NaCl solution at various concentrations (1 x 10^{-4} - 1 x 10^{-2} M) are shown in Fig. 3, at a scan rate of 10 mV/s and in the potential range -1400 to 1400 mV (SCE) at 25°C. It is clear from Fig. 3, that the polarization curves have the same general features and are characterized by the appearance of active, passive and trans-passive regions.

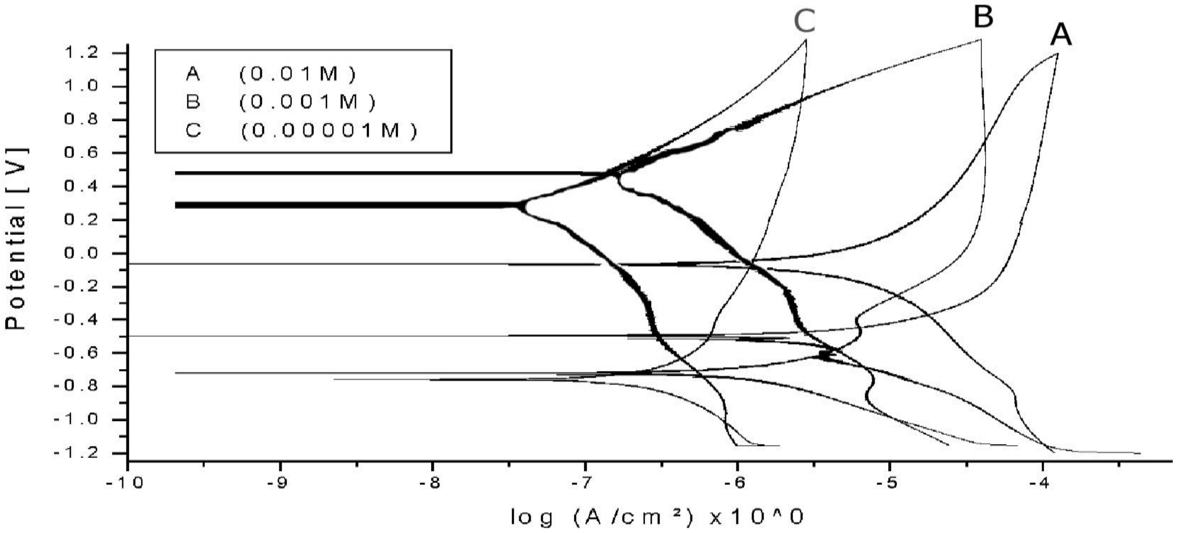


Figure 3. Cyclic anodic polarization curves of Ti-6Al-4V alloy electrode in different concentrations of ($1x10^{-4}$ – $1x10^{-2}$) sodium chloride solutions.

Table 2. The corrosion parameters of (Ti-6Al-4V) alloy electrode in different concentrations (1 x 10^{-4} – 1 x 10^{-2} M) NaCl solutions.

Electrode	Conc. M	$E_{corr.}$ mV	$E_{protect}$ mV	$I_{corr.}$ mA/cm^2	$I_{protect}$ mA/cm^2	I_{pit} mA/cm^2	Corrosion rate (C.R.) µm/y
(Ti-6Al-4V) alloy	0.01	-811.0	-0.7448	33.1876	5.233	4.279	388.1
	0.001	-808.0	-0.6892	28.4526	5.223	4.040	332.7
	0.0001	-771.4	-0.6336	8.8880	5.142	4.078	103.9

At a vertex potential of 1.4 V when the scan reverses its direction, the reverse scan went below the forward scan curve to form a big loop towards the low current density region. Materials characterized by this type of cyclic polarization curve are known to resist localized corrosion but are susceptible to both pitting as well as crevice corrosion in NaCl solutions. In general the pitting and crevice corrosion can be evaluated based on the formation of a loop and an evaluation of the Ti-6Al-4V alloy can be made based on the area of loops that form in the cyclic polarization curves. Generally the higher the loop area, the greater is the tendency towards pitting or crevice corrosion [28]. It is clear from Fig. 3 that the loop area is nearly invariant with concentration. It is concluded from the hysteresis loop observed during the reverse anodic scan that there exists the possibility of pitting. Pitting on the passive surface has been explained by a competitive adsorption mechanism in which chloride ions migrate to the metal/oxide film interface at the metal surface. At a particular chloride concentration, a pitting potential develops which is sufficient to displace oxygen from the protective oxide layer [29]. The corrosion parameters for the Ti-6Al-4V alloy electrode at different concentrations of NaCl ($1 \times 10^{-4} - 1 \times 10^{-2}$ M) are given in Table 2.

3.3.1. Effect of addition some proteins on the potentiodynamic cyclic anodic polarization of Ti-6Al-4V alloy in 0.01 M NaCl.

Inhibitors are often easy to apply and offer the advantage of use for in situ applications without a significant disruption of a process. However, there are several considerations to make when choosing an inhibitor [30]. The aim of this present section is to study the effect of some natural products, such as egg albumin and bovine serum, on the corrosion behavior of Ti-6Al-4V alloy electrodes. Albumin is a simple protein that is found in both plants and animal tissues. The most important albumins are egg albumin, which is found in the white part of eggs, and bovine serum albumin. These compounds are made of up to 385 amino acids. Compounds containing N and S have been shown to be very effective in inhibiting the corrosion of metals and alloys by adsorption onto the metal surface through these atoms lone pair electrons [31]. Figs. 4 and 5 illustrate the effect of different concentrations of egg albumin (0.25 - 1% v/v) and bovine serum (0.5 - 1% v/v) on the cyclic anodic polarization of Ti-6Al-4V alloy electrodes in 0.01M NaCl solutions. The corrosion parameters of Ti-6Al-4V alloy electrodes in 0.01 M NaCl solution containing different concentrations of both egg albumin and bovine serum are given in Table 3.

From the experimental results presented in Figs. 4 and 5 and Table 3, it is clear that the corrosion potential ($E_{corr.}$) is shifted to more anodic values in the solutions containing egg albumin and bovine serum. The protection potential remained relatively constant at all concentrations of additives, while the corrosion current, pitting current and protection current decreased. It was also found that the hysteresis loop observed during the reverse anodic scan, which indicated the possibility of pitting corrosion, decreased as the concentration of egg albumin and bovine serum increased. Thus egg albumin and bovine serum behaved similarly to inhibitors. Inhibition efficiencies (I.E.%) were calculated from the equation:

$$\text{I.E.\%} = \frac{(C.R.)^o - (C.R)}{(C.R.)^o} \; x \, 100$$

where $(C.R)^o$ and $(C.R)$ are the corrosion rates in the absence and presence of the additives, respectively. The inhibitory action of the egg albumin and bovine serum may be attributed to the formation of a thick and relatively compact film at the Ti-6Al-4V alloy surface.

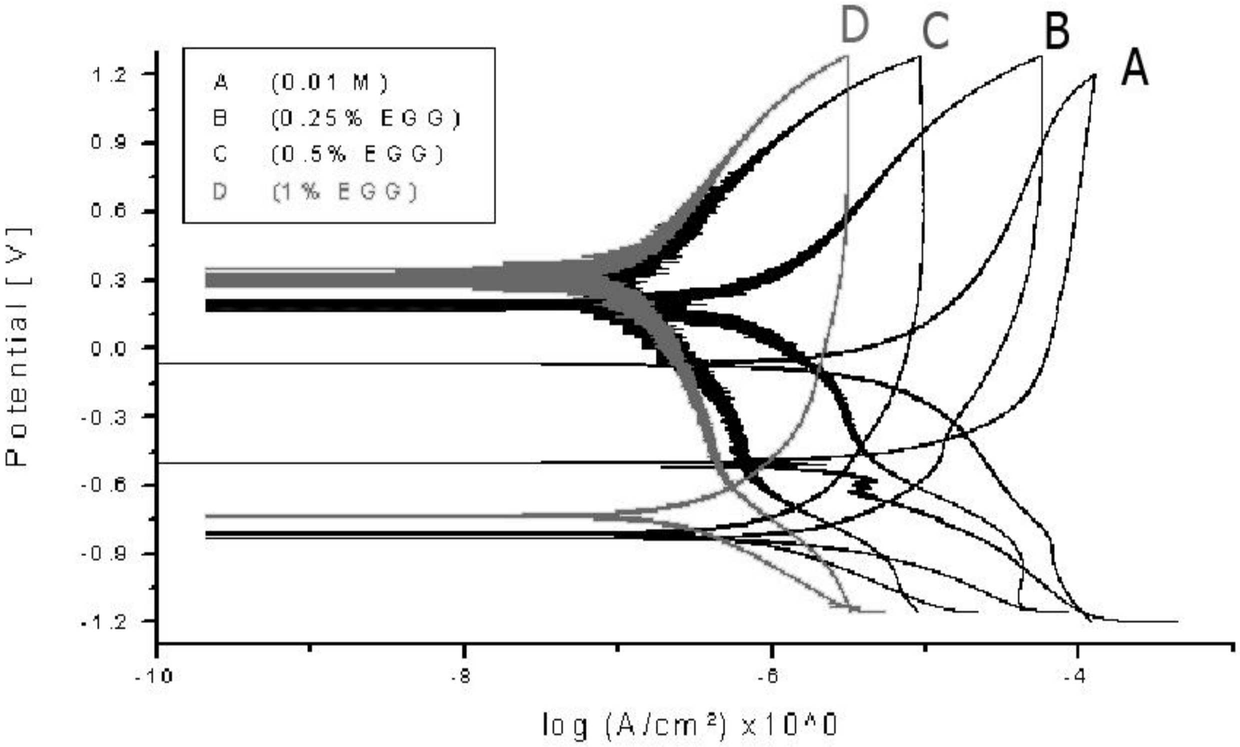


Figure 4. Cyclic anodic polarization curves of Ti-6Al-4V alloy electrode in (0.01M) NaCl with (0.25 – 1%) egg albumin.

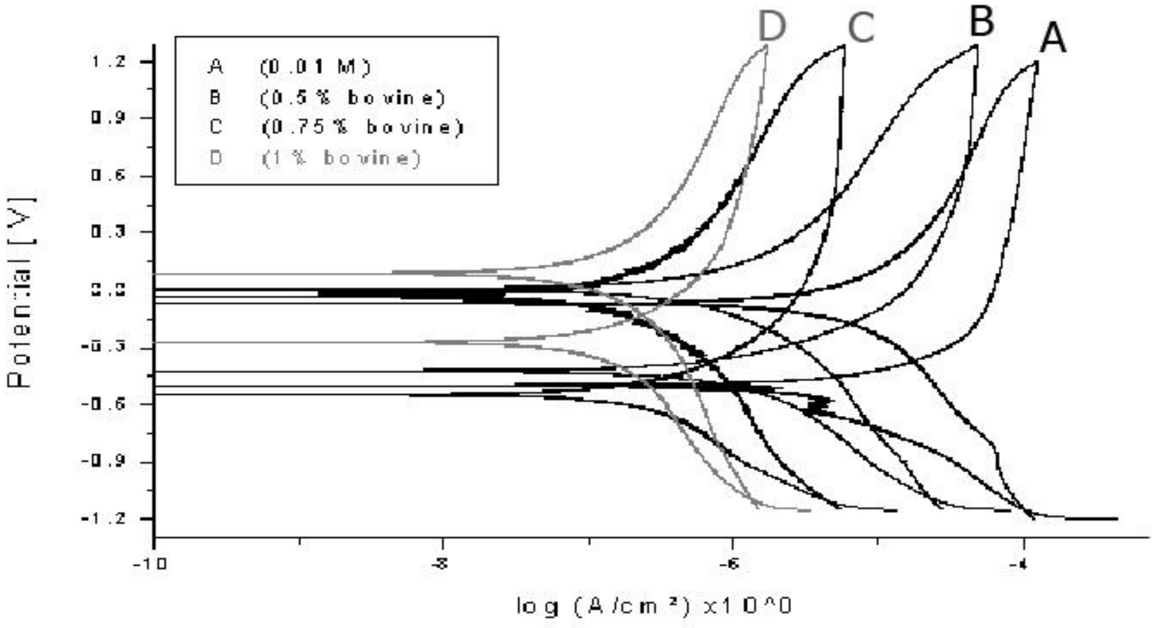


Figure 5. Cyclic anodic polarization curves of Ti-6Al-4V alloy electrode in (0.01M) NaCl with (0.5 – 1%) serum bovine albumin.

Table 3. The corrosion parameters of (Ti-6Al-4V) alloy electrode in 0.01M NaCl solution containing (0.25 -1 %) of egg albumin and (0.5 -1 %) of serum bovine albumin.

Type of proteins	Conc. %	E_{corr} mV	$E_{protect}$ mV	$I_{corr.}$ mA/cm^2	$I_{protect}$ mA/cm^2	I_{Pit} mA/cm^2	Corrosion rate (C.R.) µm/y	Inhibition Efficiency I.E. %
egg Albumin	0	-811.0	-0.7448	33.1876	5.233	4.279	388.1	-
	0.25	-786.6	-0.7401	4.26530	5.016	3.988	49.88	87.15
	0.5	-782.7	-0.6624	2.75300	4.899	3.980	32.16	91.71
	1	-761.6	-0.6614	2.08950	4.825	3.895	24.43	93.71
Serum bovine Albumin	0	-811.0	-0.7448	33.1876	5.233	4.279	388.1	-
	0.5	-770.6	-0.6225	3.59110	5.206	4.272	42.00	89.18
	0.75	-764.2	-0.6169	2.37560	5.200	4.257	27.78	92.84
	1	-669.4	-0.583	2.00250	5.186	4.057	23.42	93.96

3.4. Scanning electron microscope (SEM).

The main characteristic common to all metals and environments is the localized character of the corrosion nucleation. Preferred sites for such nucleation generally depend on the metal structure, which is associated with the presence of different phases, or to environmental pollutant deposition at discrete points, which results in the formation of a great number of small product nuclei that spread with exposure time until the surface is completely covered [32]. The barrier effect of the corrosion products of a metal in a given environment depends on the characteristics and properties of the film produced. Thickness, uniformity, compactness, porosity, solubility, fragility and adherence will condition the corrosion rate and morphology of attack to the underlying metal.

To confirm the degradation mechanism of the Ti-6Al-4V alloy after being corroded in NaCl solution, the electrode was observed under a scanning electron microscope. Figs. 6 to 8 illustrate the surface morphology of Ti-6Al-4V alloy specimens after potentiodynamic cyclic anodic polarization treatment in 0.01 M NaCl in the presence and absence of egg albumin and bovine serum albumin. Fig. 6 shows the morphology obtained after a cyclic anodic polarization measurement in the range of -2000 to 1500 mV (SCE) at scan rate 10 mV/s in 0.01 M NaCl solution. It is evident from the SEM image that a large number of pits were formed on the surface of the specimen, therefore it is concluded that the alloy degrades due to pitting corrosion.

The optical micrographs showing the effect of different concentrations (0.25 and 1%) of both egg albumin and bovine serum albumin in 0.01 M NaCl is illustrated in Figs. 7 and 8 (A and B). The micrographs reveal that both proteins form a good protective film on the alloy surface at both low and high concentrations. Additionally, the protein bovine serum behaves as a corrosion inhibitor as it significantly slows down both the cathodic and anodic half reactions during active corrosion. This confirms the higher inhibition efficiency of bovine serum relative to egg albumin.

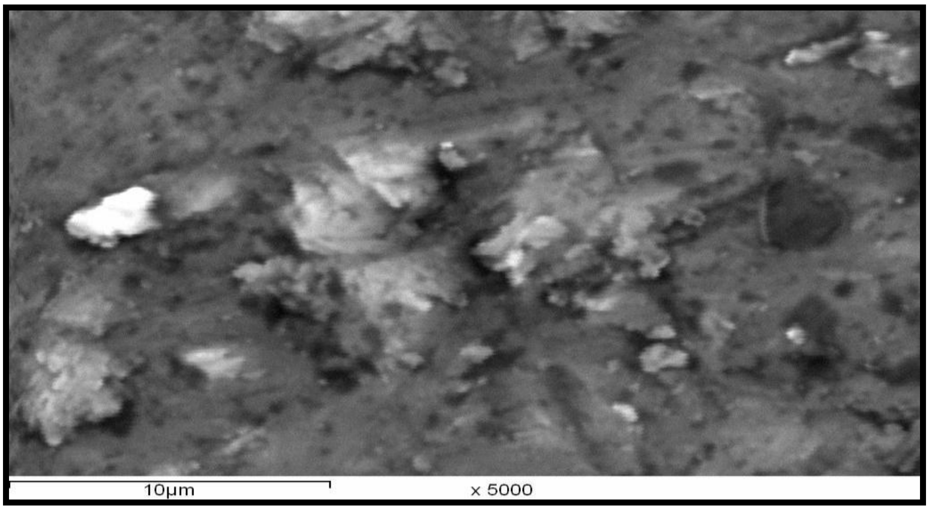
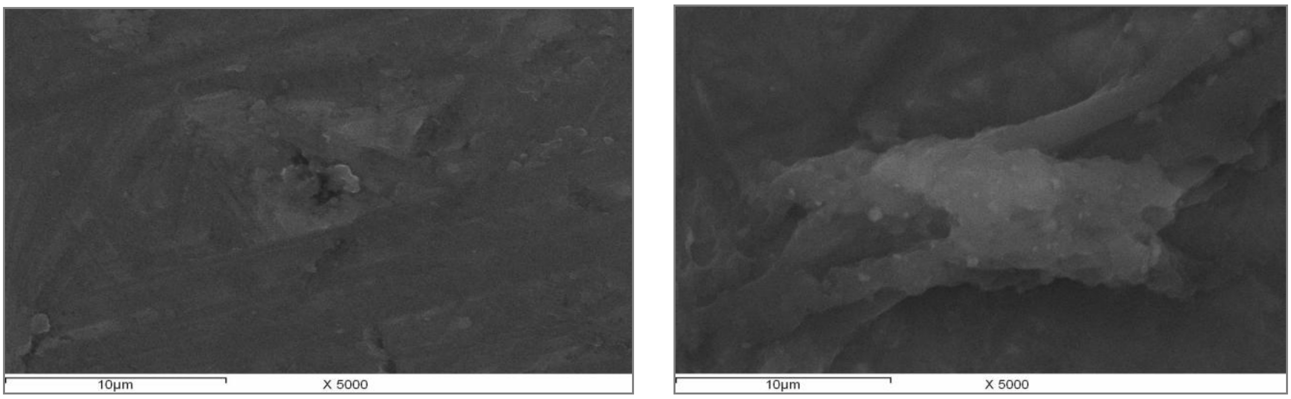
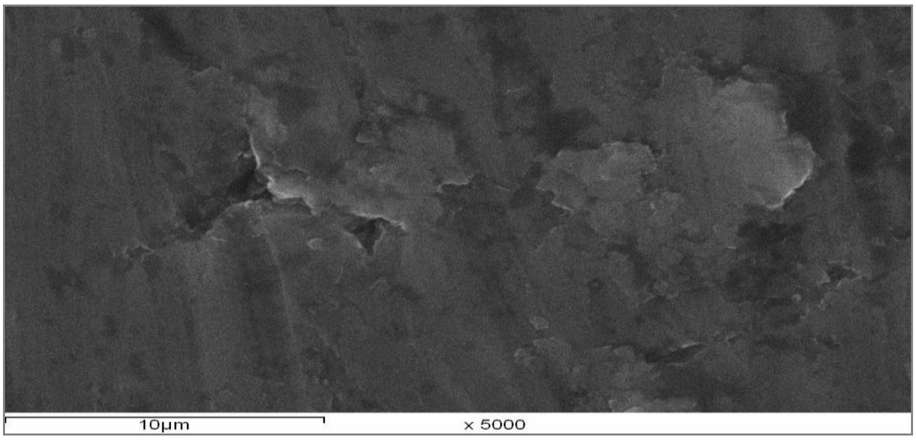


Figure 6. Surface morphology of Ti-6Al-4V alloy in 0.01M NaCl solution.

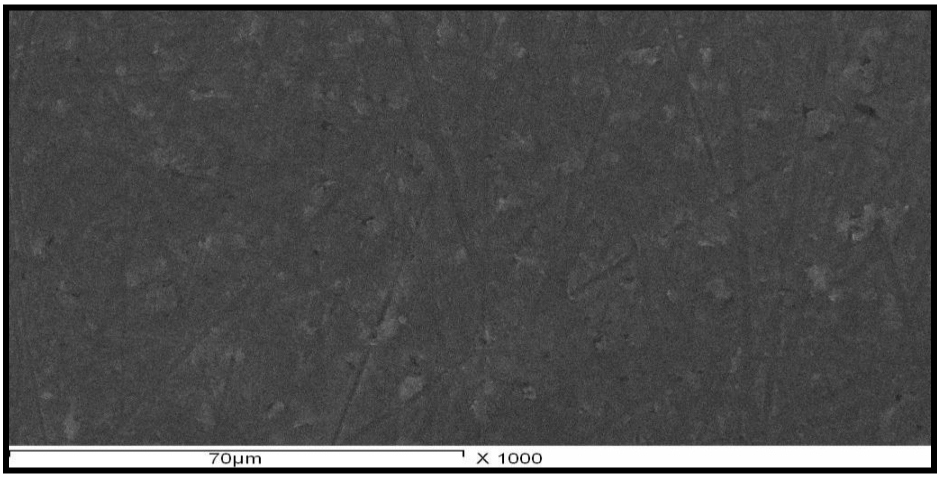


A **B**

Figure 7. Surface morphology of Ti-6Al-4V alloy :(A) in 0.01M NaCl solution + 0.25% egg albumin. (B) in 0.01 M NaCl solution + 1% egg albumin.



A



B

Figure 8. Surface morphology of Ti-6Al-4V alloy:(A) in 0.01M NaCl solution + 0.25% bovine serum albumin.(B) in 0.01 M NaCl solution + 1% bovine serum albumin.

4. CONCLUSIONS

The electrochemical behavior of Ti-6Al-4V alloy has been studied in NaCl solutions using different techniques. From the results of open-circuit potential measurements of Ti-6Al-4V, a general tendency for the immersion potential to shift steadily towards nobler values indicated formation of a passive layer of TiO_2 and additional metal oxides. It was also found that $E_{corr.}$ was shifted to more positive values and that $I_{corr.}$ increased with increasing NaCl concentration. Potentiodynamic cyclic anodic polarization measurements for Ti-6Al-4V alloy in NaCl solutions showed active, passive and trans-passive regions, with the reverse scan starting below the forward scan curve, indicating that the alloy was susceptible to pitting corrosion. The effect of addition of increasing concentrations of some proteins on the corrosion of Ti-6Al-4V alloy was also investigated using the potentiodynamic cyclic anodic polarization technique. The egg albumin and bovine serum behaved similarly as corrosion inhibitors. The inhibitory action of the additives may be attributed to the formation of a thick and relatively compact film at the Ti-6Al-4V alloy surface. These results were confirmed by using scanning electron microscopy.

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