

Corrosion behaviour of Ti–6Al–4V in phosphoric acid

V. B. SINGH, S. M. A. HOSSEINI

Department of Chemistry, Banaras Hindu University, Varanasi-221 005, India

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Ti–6Al–4V shows distinct active–passive behaviour in phosphoric acid over a wide concentration range. The cathodic polarization curves are similar over a wide range of acid concentration and temperatures. The alloy undergoes active dissolution and turns passive in the negative potential region followed by a wide range of passivity at all acid concentrations at different temperatures. Increasing acid concentration up to 11 M results in an increase in critical current density (i_{cr}). The passive current density (i_p) increases up to an acid concentration of 9 M while at 13 M i_{cr} and i_p decrease appreciably. A significant increase in both i_{cr} and i_p occurs with increase in solution temperature. The passive specimen remained stable for a long time when exposed to phosphoric acid under open circuit conditions.

1. Introduction

The strength properties and excellent corrosion resistance of titanium alloys make them suitable candidates for marine uses such as submersible vehicles and in risers in off-shore oil drilling. The high strength to weight ratio of titanium alloy also leads to automotive applications, such as auto and motor cycle racing. Titanium is also being used in the food industry [1], petroleum refining installations [2] and desalination [3].

Stainless steels and nickel-based alloys are being replaced by titanium alloys. For piping systems, where light weight or reduced wall thickness are important factors, an alloy with a greater design strength is desirable. Moreover, titanium and its alloys may also be employed in a variety of chemical plant and power generation condensers.

Titanium and its alloys have been subjected to several investigations of corrosion behaviour and the nature of the passive film [4–6]. The metal shows considerable corrosion in reducing acids. However, comparatively little is known about the performance of titanium alloy e.g. Ti–6Al–4V in phosphoric acid. The present study aims at examining the corrosion behaviour of Ti–6Al–4V alloy over a wide range of H_3PO_4 concentration and temperatures.

2. Experimental details

Titanium alloy (Ti–5.47Al–4.02V) sheet was cut into pieces of 2 cm^2 area. Prior to immersion in the electrolyte, the individual specimens were mechanically polished with different grades (1/0 to 4/0) of emery paper. After polishing, specimens were etched in an aqueous mixture of HF (2 v/o) and HNO_3 (4 v/o) for a few seconds at room temperature and washed with double distilled water. The specimens were finally degreased with acetone in an

ultrasonic cleaner. Acid solutions of different concentrations were prepared with double distilled water. The experimental set up and working procedures adopted were the same as reported [7–10] elsewhere. The solution was deaerated with nitrogen for 4 h. Prior to polarization, the working electrode was immersed in the solution between 30 to 120 min for stabilization of the open circuit potential. The polarization studies were performed potentiostatically (Pos 73, Wenking Model) in different concentrations of unstirred H_3PO_4 . The potential was varied in steps of 40 mV and steady-state currents were recorded. The influence of temperature was investigated between $20\text{--}50 \pm 1^\circ\text{C}$ for selected concentrations. The potential was recorded with reference to a saturated calomel electrode. The specimen surface was examined by SEM (Jeol 840A) after polarization. Impedance measurements were undertaken at different potentials (-300 , -100 , $+100$, $+300$, $+500$, $+700$, $+900$ mV) within the frequency range 5 Hz to 100 kHz using an EG and G Parc (model 378-3) Electrochemical Impedance System.

3. Results and discussion

It is seen from the curves (Figs 1 and 2) that the current density increases with increase in potential in the cathodic direction at each concentration, however, the nature of the curves remains the same. In general, the cathodic curves are similar in nature at both temperatures, indicating the same cathodic reaction may be of different rates. Cathodic Tafel slopes were found to be between 90 and 135 mV per decade which is close to the values reported [11] for the hydrogen evolution reaction (h.e.r.). Vigorous hydrogen evolution and unstable cathodic current were observed in concentrated acidic solution ($> 3\text{ M}$) and a higher temperatures.

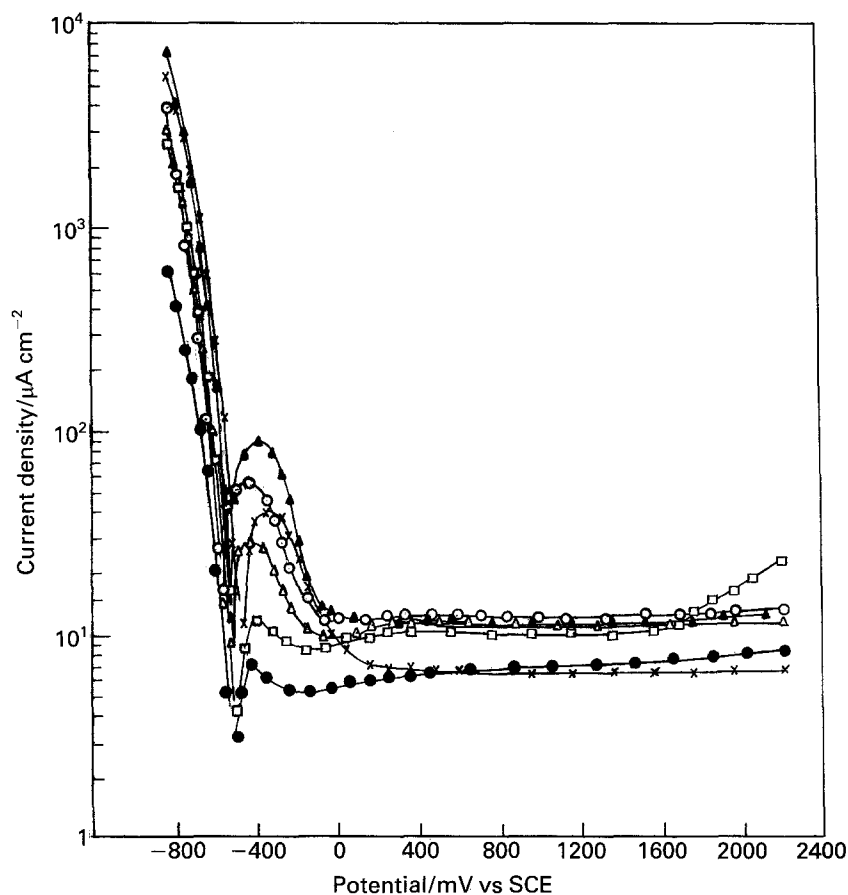


Fig. 1. Cathodic and anodic polarization of Ti-6Al-4V in different concentrations of H_3PO_4 at $30 \pm 1^\circ C$. Concentrations: (●) 1, (□) 3, (△) 5, (○) 9, (▲) 11 and (×) 13 M.

Interestingly a pink/purple colour developed in the electrolyte during cathodic polarization. The colour developed only at potentials more negative than -700 mV and disappeared with polarization in the

anodic direction (less negative). The appearance of the colour, indicative of trivalent titanium, can be ascribed to the reductive dissolution of some product or species on the surface of the working electrode or

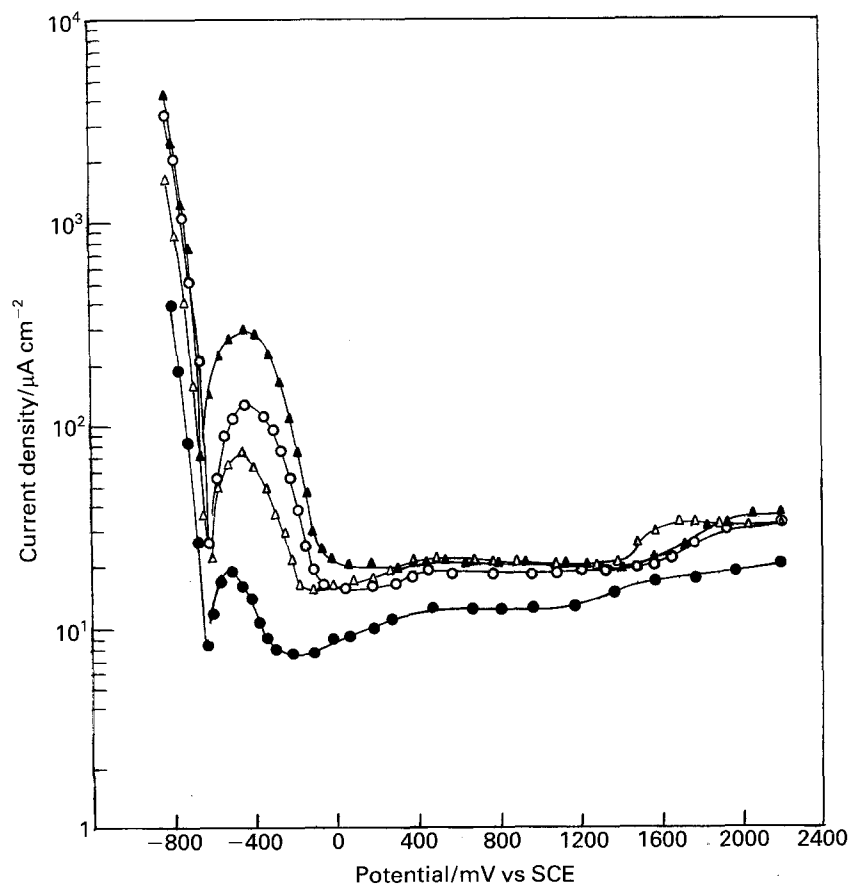
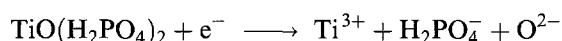


Fig. 2. Cathodic and anodic polarization of Ti-6Al-4V in different concentrations of H_3PO_4 at $40 \pm 1^\circ C$. Concentrations: (●) 1, (△) 5, (○) 9, and (▲) 11 M.

reduction of a complex species of titanium to a lower state, for example



It is observed from Figs 1 and 2 that alloy undergoes active dissolution over a wide range of phosphoric acid concentration at the different temperatures employed, i.e. the alloy first undergoes active dissolution and then becomes passive at negative potential. However, there is a slight shift in the critical potential for passivity (E_{cr}) towards the positive potential region with increasing acid concentration. Passivation is evident over a wide range of potential, with low values of the passive current density (i_p) in all acid concentrations. An increase in the critical current density (i_{cr}) is observed only up to 11 M acid and above this concentration it is found to decrease. The present results are similar to that reported for the metal and alloy in H_2SO_4 [14]. Slight variation in the passive current density with change in acid concentration suggests that the properties of the passive film formed at different acid concentrations are the same. Increase in the critical current density is pronounced when compared with the passive current density due to change in the concentration and temperature.

Low critical current density (i_{cr}) and lower passivity current density (i_p) are observed for the alloy in case of highly concentrated acid (13 M). This is possibly due to change in the structure of the phosphoric acid solution in comparison to medium or lower

concentration. In the dilute acid the phosphate ions are hydrogen bonded to the H_2O liquid lattice, but in highly concentrated acid solution, the phosphate ions are interconnected by hydrogen bonds. It has been reported [15] previously that the active and passive dissolution rates in 70% phosphoric acid are considerably higher as compared to the rates in lower/higher than 70% phosphoric acid. Though the proton activity in concentrated acid increased with increasing concentration, the critical current density and passivity current density decreased. However, the trend of variation of passivity current density with respect to concentration of the acid and temperature can be attributed to the variation in conductance [16] of phosphoric acid solution which increases with acid concentration and above certain concentration (~ 50 wt/o) it decreases.

The nature of anodic curves at different temperatures is similar but temperature showed an influence on the current densities (i_{cr} , i_p) i.e. (Figs 3, 4). There is an appreciable increase in the current densities as the temperature is increased. The active dissolution range increased with temperature. The broadly similar curves at the different temperatures suggest similar reactions at the surface of the electrode, but with different rates. A stable and wide passivity range of potential was obtained in all concentrations of the acid at different temperatures. Apparent activation energy in the active and passive regions calculated from Arrhenius plot is shown in Figs 5 and 6. The activation energy in the active region, for the alloy

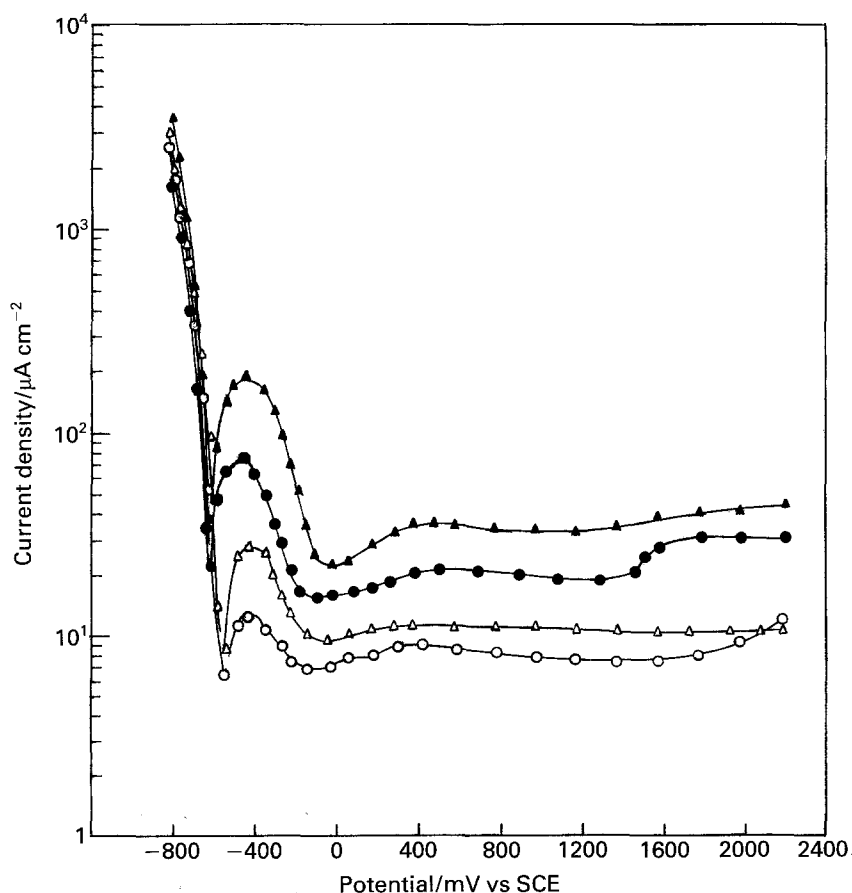


Fig. 3. Cathodic and anodic polarization of Ti-6Al-4V in 5 M H_3PO_4 at different temperatures. Temperatures: (○) 20, (△) 30, (●) 40 and (▲) 50°C.

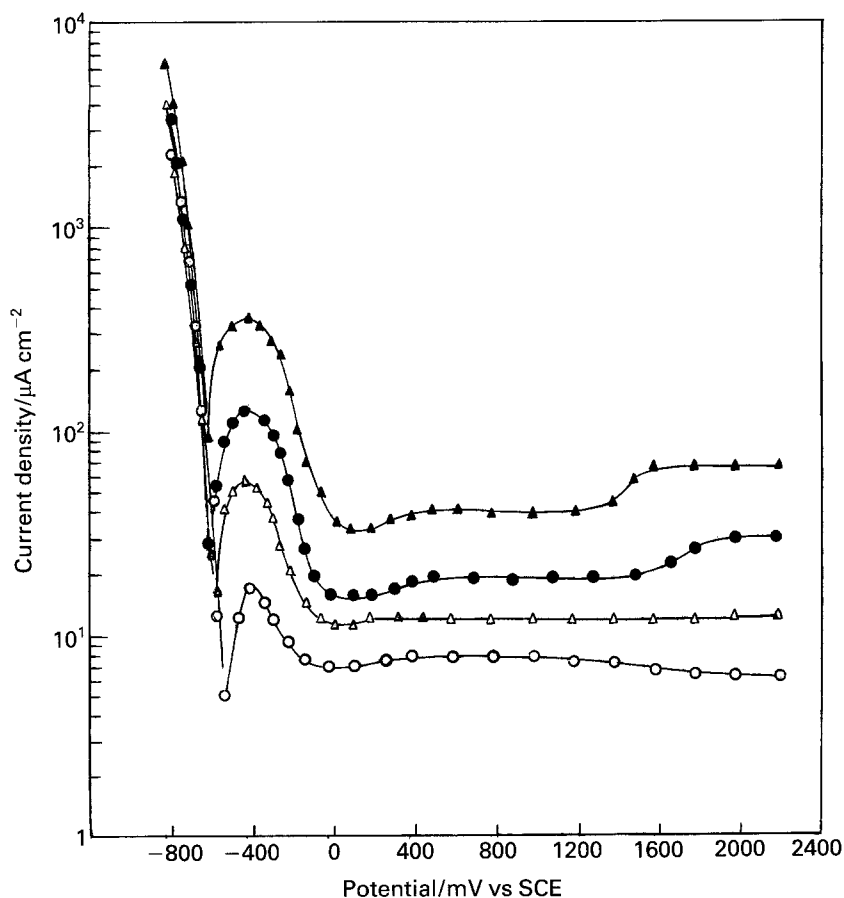


Fig. 4. Cathodic and anodic polarization of Ti-6Al-4V in 9M H_3PO_4 at different temperatures. Temperatures: (○) 20, (△) 30, (●) 40 and (▲) 50°C.

in this acid is higher than those in HCl and H_2SO_4 [17, 18]. Higher value of activation energy indicates that H_3PO_4 should be less corrosive than H_2SO_4 and HCl and such results have been reported [12, 13, 19] for corrosion behaviour of titanium and its alloy. The apparent activation energy obtained in the passive region may be considered to be associated with the complex processes/mechanisms that occur in this region.

To examine the performance of the passive specimens, after polarization, the specimens were left immersed in the same solution (1, 5, 9 and 13 M H_3PO_4) under the open circuit conditions for nearly 14 h and the o.c.p. was recorded in between. It was observed that the o.c.p. remained noble in comparison with the initial o.c.p. of the respective

specimens (unpolarized) and in most cases the difference was wide (> 600 mV). However, during the immersion period there was variation in the o.c.p. of the passivated electrodes, i.e. the o.c.p. tended to become less noble during the initial period (one hour) and after some time interval there was very little variation during the period of exposure. Again, the electrodes were anodically polarized (at +1500 mV) and the passivity current density against time plot was made (Fig. 7). The passivity current density in first few minutes dropped to very low value and after about 5 min it became practically constant. These values are comparable to the earlier one at the same potential. The o.c.p. values and i_p values after exposure reveal that the passive film remained protective in prolonged exposure in the acid. This

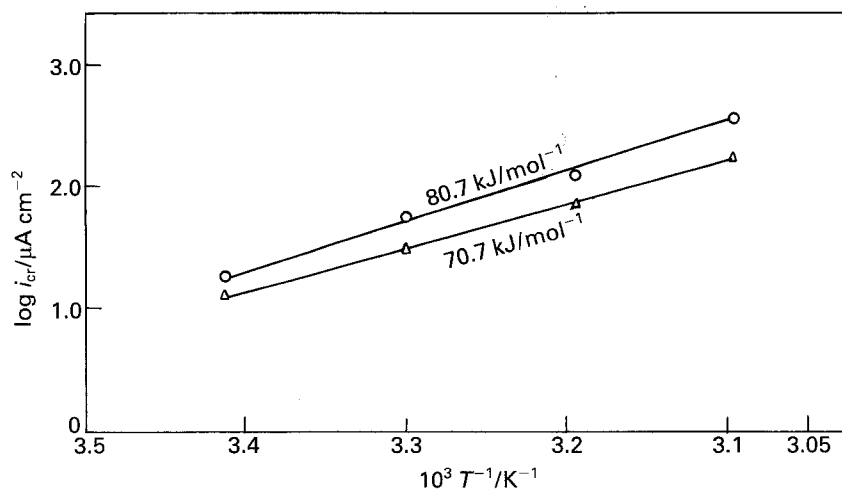


Fig. 5. Arrhenius plot for Ti-6Al-4V. (△) 5M, (○) 9M.

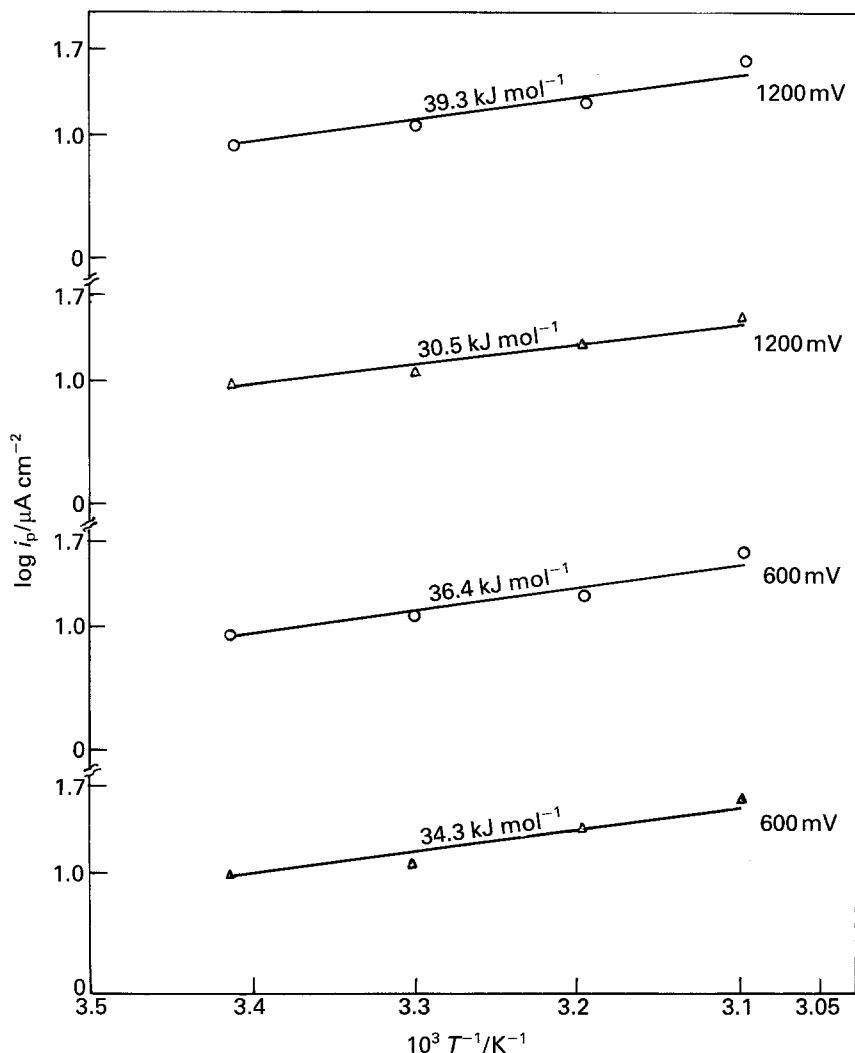


Fig. 6. Arrhenius plot at different potential for Ti-6Al-4V. (Δ) 5 M H_3PO_4 , (\circ) 9 M H_3PO_4 .

suggests that the insulating properties of the film did not change even if the dissolution of the anodic film has taken place to some extent under the o.c.p. condition.

The corrosion reaction occurring at the surface of passive film of the alloy appears to be dissolution/formation reaction during the exposure and polarization in phosphoric acid. Thus, the film may be

composed of two layers which differ in their chemical composition. A two stage dissolution process of the oxide film on titanium has been reported [20]. The decline in the o.c.p. at an early stage of immersion of the passivated specimens points to a two stage dissolution process of the film possibly because of some structural defect in passive film induced by alloying elements in titanium in comparison to the pure metal as a result of which the i_p values were slightly higher for the alloy than the metal [14].

Impedance measurements were performed in the frequency range 5 Hz to 100 kHz at different potentials. The complex impedance diagram was plotted which did not give ideal semicircle. The deviation can be ascribed to the possibility of incorporation of electrolyte ions into the passive film which causes deviation from stoichiometry and produces a variation of resistance along the length of the passive layer. A plot of reciprocal capacitance against formation potential (Fig. 8) shows that the alloy like other valve metals [21] yields a linear dependence. The linear relationship is consistent with a constant mean electrostatic field in the passive film; it can be ascribed that the linear dependence of reciprocal capacitance on applied voltage may result because the series capacitance depends linearly on the voltage.

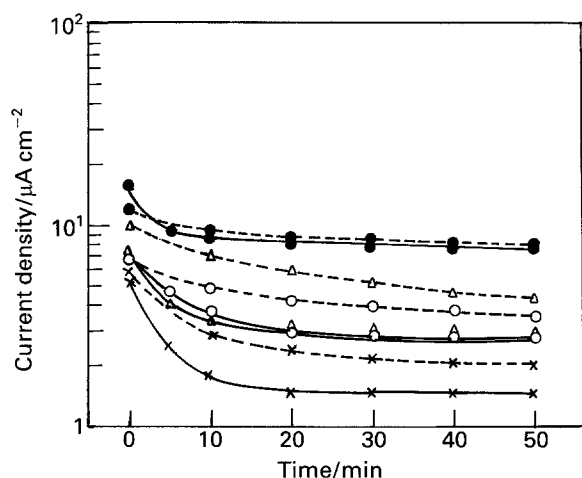


Figure 7. Plot of passivity current density (at +1500 mV) against time in 1, 5, 9 and 13 M at 30°C. Concentrations: (\circ) 1, (Δ) 5, (\bullet) 9 and (\times) 13 M H_3PO_4 .

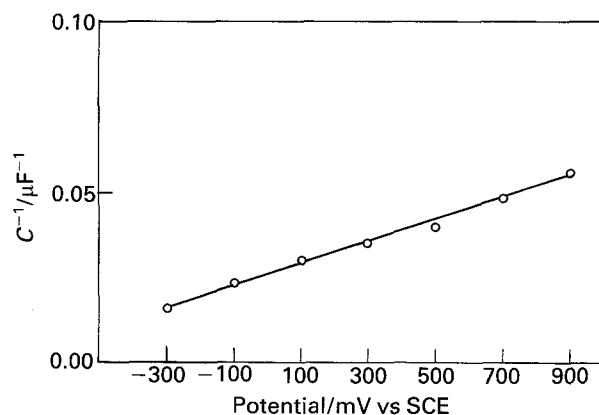


Fig. 8. Dependence of reciprocal capacitance on the potential of formation.

4. Conclusions

Ti-6Al-4V exhibited active-passive behaviour in phosphoric acid over a wide range of concentration and temperatures. The critical current density increased with increase in acid concentration up to 11 M acid. The increase in i_{cr} is appreciable in comparison to i_p with increase in the acid concentration and temperature. The passivated alloy remained stable even in prolonged exposure in this acid and transpassivity behaviour was not observed. Impedance studies yielded a linear relationship between reciprocal capacitance and formation potential of the passive film like other valve metals. The corrosion behaviour of the alloy is similar to the pure Ti and is quite comparable.

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