Corrosion behaviour of Ti–6Al–4V alloy in concentrated hydrochloric and sulphuric acids

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Abstract

Open-circuit potential, polarization and electrochemical impedance spectroscopy (EIS) measurements were used to investigate the corrosion behaviour of Ti–6Al–4V alloy in H_2SO_4 and HCl solutions. The corrosion rate of the alloy was found to increase with increasing acid concentration. The corrosion behaviour of the alloy was compared to that of pure titanium in both acids. The results showed that the alloy is more corrosion resistant than pure titanium in the investigated solutions. The apparent activation energies of the corrosion process for titanium are lower than those of the alloy in the same solutions, which reflects the higher corrosion resistance of the alloy.

1. Introduction

Ti–6Al–4V alloy is widely used in the aerospace and aircraft industries for the manufacture of high-strength components [1]. The high strength to weight ratio of titanium alloy also leads to special applications, such as auto and motor cycle racing. In contrast to ferrous alloys which contain elements that became radioactive, titanium has an extremely short radioactive half-life, thereby permitting its use in nuclear reactors. Titanium exhibits excellent corrosion resistance in diluted acid solutions due to a protective passive film of TiO_2 but its corrosion rate is significant in media that dissolve the protective oxide film or limit its formation. Such media are mainly hydrofluoric acid, caustic solutions and uninhibited concentrated hydrochloric or sulphuric acid solutions.

The influence of acid concentration and/or temperature on the corrosion behaviour was examined for titanium in HCl, H_2SO_4 and H_3PO_4 [2, 3] and for Ti–6Al–4V alloy in H_3PO_4 [4, 5]. The aim of the present study is to investigate the corrosion behaviour of Ti–6Al–4V alloy in HCl and H_2SO_4 acid solutions using open-circuit potential, polarization and electrochemical impedance spectroscopy techniques. Also, a comparison study was made between the electrochemical behaviour of titanium and its alloy in these acid solutions at different temperatures.

2. Experimental procedure

Pure titanium (99.9%) and Ti–6Al–4V alloy of the composition (wt %); 5.70 Al, 3.85 V, 0.180 Fe, 0.106 O, 0.038 C and 0.035 N, were cut as cylindrical rods and mounted into glass tubes of appropriate internal diameter with epoxy resin. The exposed circular surface areas of the investigated materials were 0.315 cm^2 for titanium and 0.503 cm^2 for the alloy. Prior to immersion in the electrolyte, the electrodes were abraded using successively grades emery papers down to 2000 grit, then rubbed with a soft cloth until they acquired a mirror-bright surface and washed with triply distilled water. The electrolytic cell was an all glass double jacket three electrode cell. A platinum sheet was used as an auxiliary electrode. A Luggin probe saturated calomel reference electrode was employed; it contained an isolating stopcock to avoid contamination of the test solution by the chloride ions of the reference electrode. The test solutions were prepared from analytical grade reagents and triply distilled water. The measurements were carried out in naturally aerated solutions at a constant room temperature of ≈303 K. Some experiments were performed in the 298–333 K temperature range. The open-circuit potential of the mechanically polished titanium alloy was measured versus a saturated calomel electrode (SCE) by means of a valve voltmeter (Electronic Instruments Ltd., England). Polarization measurements were carried out at a scan rate of 1 mV s^{-1} using an EG&G (Princeton Applied Research) model 273A Potentiostat/Galvanostat interfaced to an IBM PS/3 computer. The electrochemical impedance spectroscopic investigations (EIS) were carried out using the IM5d-AMOS system (Zahner Electrik GmbH & Co., Kronach, Germany). The input signal was usually 10 mV peak to peak in the frequency domain 0.1–10^5 Hz. Before impedance or polarization measurements, the working electrodes were immersed in the test solution until a steady-state of the open-circuit potential was reached. Details of the experimental procedures were described elsewhere [6, 7].

3. Results and discussion

3.1. *Open-circuit potential measurements*

The open-circuit potential of the mechanically polished alloy electrodes was traced over 3 h in H_2SO_4 and HCl solutions of different concentrations at 303 K. The potential decreases with time in the first few minutes indicating thinning of the native oxide film on the alloy surface, and reaches its steady state value within 20–30 min from electrode immersion in the test solution. The native oxide film thinning in concentrated sulphuric acid solutions was previously reported and a uniform dissolution followed by subsequent surface activation was discussed [8, 9]. The same behaviour for Ti and some of its alloys, namely, Ti-45% Nb and Ti-50% Zr in 5.0 M HCl at 37 °C was confirmed by the abrupt decrease of the open-circuit potentials as functions of time [10]. In 1.0 M HCl solution, the potential shows a positive shift with time due to thickening of the air-formed oxide film. The open-circuit potential of Ti–4Al–4V alloy in HNO_3 solutions was found to shift in the positive direction, indicating thickening of the passive layer and the film was found to consist of TiO_2 only [11]. The time needed for the open-circuit potential to reach a steady-state value decreases and the steady state potential shifts to more negative values with increasing acid concentration. These results indicate that the oxide film dissolves in more concentrated acid solutions leading to activation of the alloy surface.

It was reported that a hydride layer is readily formed on titanium when it is immersed in acid solutions of sufficient strength [12]. A hydride layer was found to form on the surface of titanium exposed to varying concentrations of HCl from 1.4 M to 9.9 M [13, 14]. The passive film on Ti–6Al–4V was found to dissolve in 5.0 M HCl, and a negative corrosion potential of ~−650 mV (SCE) was reported [15]. These results were explained on the basis of the formation of a hydride layer following the dissolution of the passive film. The hydride layer was found to prevent titanium surface attack and its structure was found to be a function of acid concentration [16].

3.2. *Polarization and impedance measurements*

The polarization curves of the alloy in sulphuric and hydrochloric acid solutions of different concentrations are presented in Figure 1a and b. The corrosion current density, I_{corr}, corrosion potential, E_{corr}, and corrosion rate in mpy of the alloy in both sulphuric and hydrochloric acid solutions of different concentrations were calculated and are presented in Table 1. It was previously reported that the corrosion of titanium or titanium alloys in sulphuric acid solutions is due to the dissolution of the material as Ti^{3+}. The formation of Ti^{3+} was confirmed analytically using spectrophotometric methods [17]. The presence of oxygen in the electrolyte oxidizes Ti^{3+} into Ti^{4+}. As the concentration of Ti^{4+} increases the corrosion rate increases up to a critical concentration at which TiO_2 is formed and the
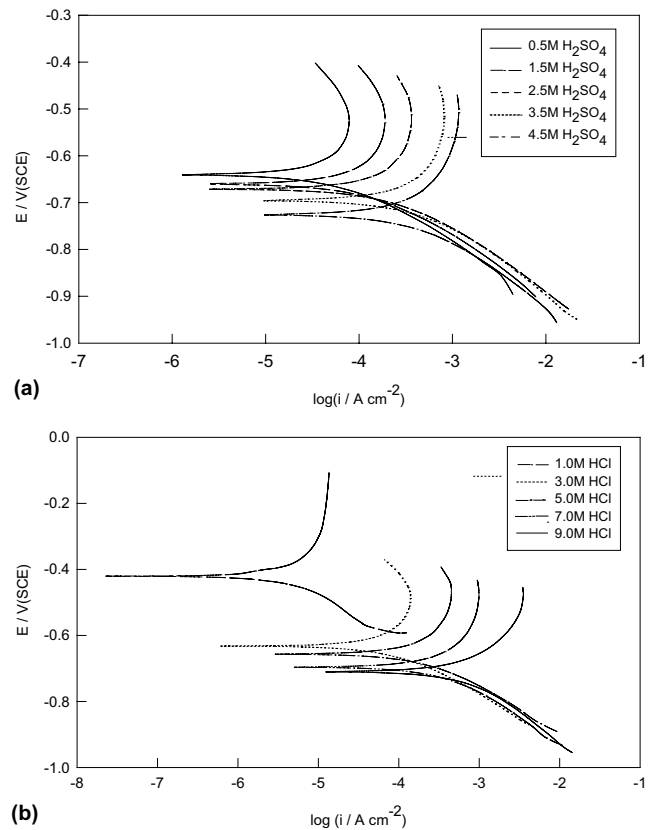

Fig. 1. (a) Potentiodynamic polarization curves of the alloy in H_2SO_4 solutions of different concentrations at a scan rate of 1 mV s^{-1} and 303 K. (b) Potentiodynamic polarization curves of the alloy in HCl solutions of different concentrations at a scan rate of 1 mV s^{-1} and 303 K.

Table 1. The corrosion parameters of TA6V alloy in H_2SO_4 and HCl solutions of different concentrations at 303 K

	R_p /kΩ cm^2	Corrosion rate, /mpy	I_{corr}, /μA cm^{-2}	E_{corr}, /mV
H_2SO_4 concentration (M)				
0.5	0.620	30.13	74.76	−639.2
1.0	0.451	44.79	111.14	−661.6
1.5	0.368	57.59	142.90	−659.1
2.5	0.210	90.93	225.64	−670.2
3.5	0.137	140.97	349.79	−681.4
4.5	0.134	164.53	408.27	−694.4
HCl concentration (M)				
1.0	21.55	0.920	2.280	−354.9
2.0	1.181	16.44	40.789	−612.8
3.0	0.588	32.67	81.056	−631.3
5.0	0.262	79.27	196.71	−655.7
7.0	0.175	131.40	326.06	−695.4
9.0	0.098	231.47	574.36	−709.7

alloy surface passivates [17, 18]. Therefore, a valency of 3 was used for the titanium ion to calculate the corrosion rate from the I_{corr} value [19]. It is clear from the obtained data that the increase in acid concentration results in an increase in corrosion rate.

Comparison of the corrosion rates of the alloy in HCl and H_2SO_4 solutions of the same concentration (Table 1) indicates that the rates are higher in sulphuric

than in hydrochloric acid solutions up to 3.5 M H_2SO_4 (or 7.0 M HCl). This indicates that the SO_4^{2-} anion has a stronger accelerating action on the active dissolution of the alloy than the Cl^- anion, which is in good agreement with results obtained for the corrosion of pure titanium [20]. At higher acid concentrations the corrosion rates in hydrochloric acid are higher than those in sulphuric acid. Also, it is clear from Table 1 that the polarization resistance of the alloy in 1.0 M HCl is notably high indicating that the alloy is passive in this solution. This result is consistent with the open-circuit potential measurements of the alloy in 1.0 M HCl.

The impedance results for the alloy in H_2SO_4 and HCl solutions of different concentrations are shown in Figure 2a and b as Bode plots. Bode plots are recommended as standard impedance plots, since all impedance data are equally represented and the phase angle, θ, is a sensitive parameter for any surface changes [21, 22]. This format enables the best data fitting to equivalent circuit models. The process of data fitting was carried out using a complex non-linear least squares procedure with minimum error and the program used enables data

Table 2. Comparison of the polarization resistance values of TA6V alloy in different acid solutions obtained from EIS measurements and polarization measurements at 303 K.

	Impedance			Polarization
	R_s /(Ω cm^2)	Phase /θ	R_p /kΩ cm^2	R_p /kΩ cm^2
H_2SO_4 concentration (M)				
0.5	1.177	79.1	0.905	0.620
1.5	0.463	78.6	0.405	0.368
2.5	0.367	77.0	0.196	0.210
3.5	0.347	75.8	0.132	0.137
4.5	0.337	75.1	0.101	0.134
HCl concentration (M)				
1.0	0.699	83.8	4.154	21.55
3.0	0.342	80.4	0.503	0.588
5.0	0.332	77.6	0.189	0.262
7.0	0.322	74.6	0.097	0.175
9.0	0.402	72.0	0.061	0.098

fitting in the required frequency range. The polarization resistance was calculated from the impedance data and was found to decrease with increasing acid concentration. Comparison of the values obtained from both the polarization and the impedance techniques shows that EIS measurements are in good agreement with polarization measurements (Table 2).

The corrosion behaviour of the alloy in 2.5 M H_2SO_4 and 5.0 M HCl was compared to that of pure metal. The corrosion parameters were calculated from both potentiodynamic polarization and impedance data, and consistent results were obtained. The calculated values for both the alloy and the metal are presented in Table 3. The alloy corrosion rates are slightly smaller than those for pure titanium in the same solutions. This may be attributed to the role of aluminum and vanadium as alloying elements. Aluminum modifies and shortens the potential range at which TiH_2 is formed and vanadium impedes its formation [23].

The impedance data of titanium and Ti–6Al–4V alloy after 3 h immersion in 2.5 M H_2SO_4 and 5.0 M HCl solutions were fitted to an equivalent circuit model in the frequency domain 0.1 Hz to 10^5 Hz. The equivalent circuit model representing the surface properties of titanium and its alloy in 2.5 M H_2SO_4 and 5.0 M HCl solutions consists of a parallel combination of a resistor, R_p, representing the charge transfer (corrosion) resistance, and a capacitor, C, representing the electrode capacitance, in series with a resistor, R_s, representing the ohmic drop in the electrolyte [7, 24]. Figure 3a and b represent the computer fitted values and experimental impedance data of the alloy and pure titanium in 2.5 M H_2SO_4. These figures show only one phase maximum, which suggests that the time constant of the passive film RC circuit is much greater than that of the double layer RC circuit. Accordingly, the influence of the double layer is comparatively negligible.

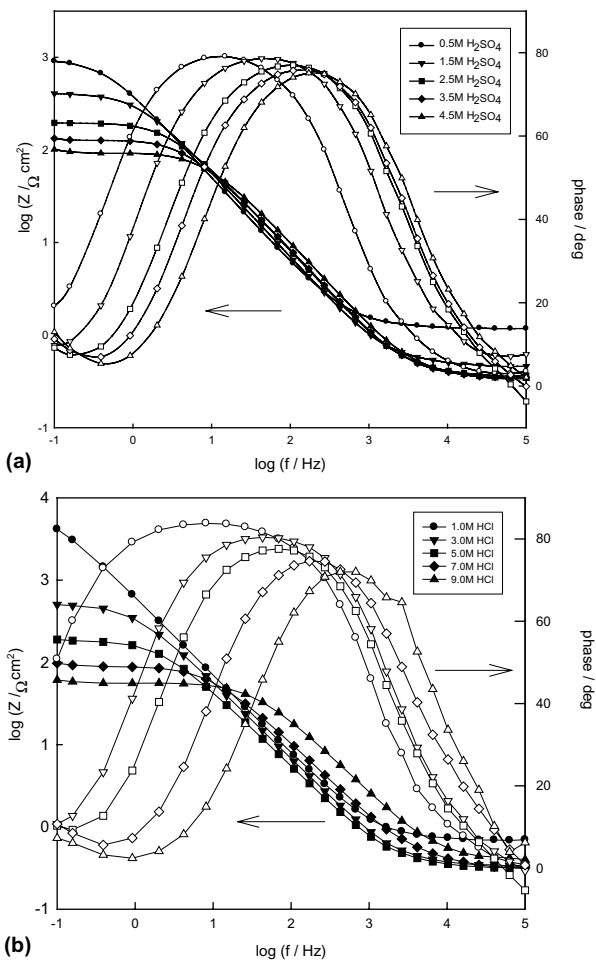The deviation of the experimental values of impedance and phase angle from the fitted values gives further

Fig. 2. (a) Bode impedance plots of the alloy after 180 min of electrode immersion in H_2SO_4 solutions of different concentrations at 303 K. (b) Bode impedance plots of the alloy after 180 min of electrode immersion in HCl solutions of different concentrations at 303 K.

Table 3. Corrosion parameters of TA6V alloy and pure titanium in 2.5 M H_2SO_4 and 5.0 M HCl at 303 K

Acid solution	Alloy				Titanium			
	Polarization			Impedance	Polarization			Impedance
	E_{corr} /mV	I_{corr} /$\mu A\ cm^{-2}$	R_p /$k\Omega\ cm^2$	R_p /$k\Omega\ cm^2$	E_{corr} /mV	I_{corr} /$\mu A\ cm^{-2}$	R_p /$k\Omega\ cm^2$	R_p /$k\Omega\ cm^2$
2.5 M H_2SO_4	−670.2	225.6	0.210	0.196	−602.4	253.0	0.171	0.169
5.0 M HCl	−655.7	196.7	0.262	0.189	−611.2	228.6	0231	0.159

evidence of the non-homogeniety of the passive film on the electrode surface [25]. After applying the fitting procedure, the mean error in the electrode impedance and the extent of deviation in the phase angle, θ, for each electrode in different solutions were calculated and are presented in Table 4.

During the cathodic polarization of the alloy a hydride film is formed which enhances the kinetics of hydrogen ion reduction as detected from the lowering of the hydrogen overvoltage [26]. This hydride film undergoes dissolution during forward anodic polarization and a mixed oxide film of Ti_2O_3 and TiO_2 is formed which causes the passivation of the alloy [27, 28].

3.3. *Effect of temperature*

The corrosion of the alloy and pure titanium was studied over a temperature range from 298 to 333 K. The rate of corrosion increased with temperature. The relation between the corrosion current density, I_{corr}, and temperature obeys the Arrhenius equation [29]:

$$\frac{d\log I_{corr}}{d(1/T)} = -\frac{E_a}{2.303R} \tag{1}$$

where E_a is the apparent activation energy of the corrosion process, R is the gas constant (8.31 J mol^{-1} K^{-1}) and T is the absolute temperature (K).

Figure 4a and b represent the Arrhenius plots for the alloy and Ti in 2.5 M H_2SO_4 and 5.0 M HCl. The apparent activation energies of the corrosion process for the alloy and titanium are 33.9 and 28.1 kJ mol^{-1} in 2.5 M H_2SO_4 and 46.7 and 29.7 kJ mol^{-1} in 5.0 M HCl, respectively. The apparent activation energies for the alloy are higher than those of pure titanium in the same solutions. This provides further evidence for the higher corrosion resistance of the alloy compared to pure titanium.

4. Conclusion

The open-circuit potential of the Ti–6Al–4V alloy in concentrated sulphuric and hydrochloric acid solutions decreases with time indicating the dissolution of the native oxide film and activation of the alloy surface. The alloy corrosion rate increases with the increase of
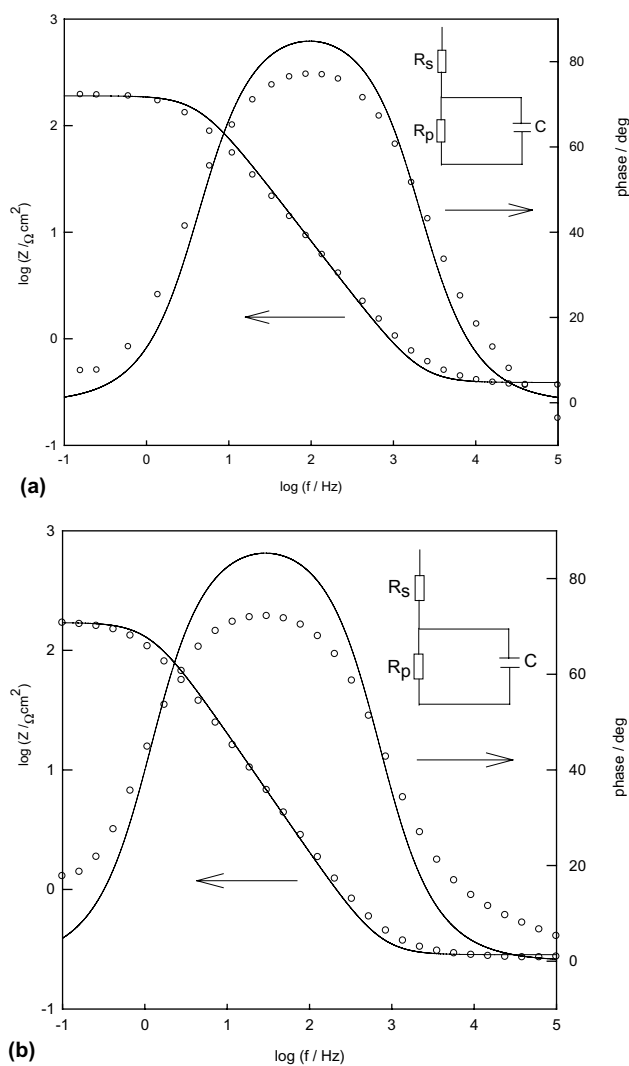

Fig. 3. (a) Experimental (ooo) and theoretical (- - -) impedance data of the alloy after 180 min immersion in 2.5 M H_2SO_4 at 303 K. The insertion is the equivalent circuit model [R_p=polarization (corrosion) resistance, C=electrode capacitance and R_s=ohmic drop in the electrolyte]. (b) Experimental (ooo) and theoretical (- - -) impedance data of the alloy after 180 min immersion in 5.0 M HCl at 303 K. The insertion is the equivalent circuit model [R_p=polarization (corrosion) resistance, C=electrode capacitance and R_s=ohmic drop in the electrolyte].

the acid concentration. In 1.0 M HCl, the open-circuit potential of the alloy is shifted to more noble values and its polarization resistance is large. The alloy is more resistent to corrosion than pure titanium in the same solution and the apparent activation energy of the alloy

Table 4. The experimental impedance data and the computer fitted values of TA6V alloy and titanium in 2.5 M H_2SO_4 and 5.0 M HCl solutions after 180 min of electrode immersion

|	Experimental values			Computer fitted values		
	R_s /Ω cm^2	Phase /θ	R_p /Ω cm^2	R_s /Ω cm^2	C /μF cm^{-2}	R_p /Ω cm^2
	2.5 M H_2SO_4					
Alloy	0.366	77.0	196.2	0.389	193.26	189.9
	Mean error in impedance = 2.5%					
	Mean error in phase = 1.1°					
Titanium	0.273	78.6	169.3	0.284	784.13	170.5
	Mean error in impedance = 2%					
	Mean error in phase = 0.9°					
	5.0 M HCl					
Alloy	0.332	77.6	189.0	0.345	304.6	184.3
	Mean error in impedance = 2.3%					
	Mean error in phase = 1.0°					
Titanium	0.323	74.60	158.8	0.334	1236.2	156.2
	Mean error in impedance = 1.9%					
	Mean error in phase = 0.9°					
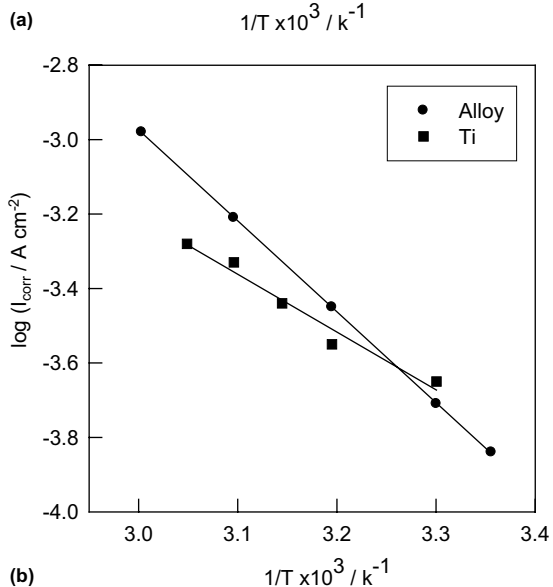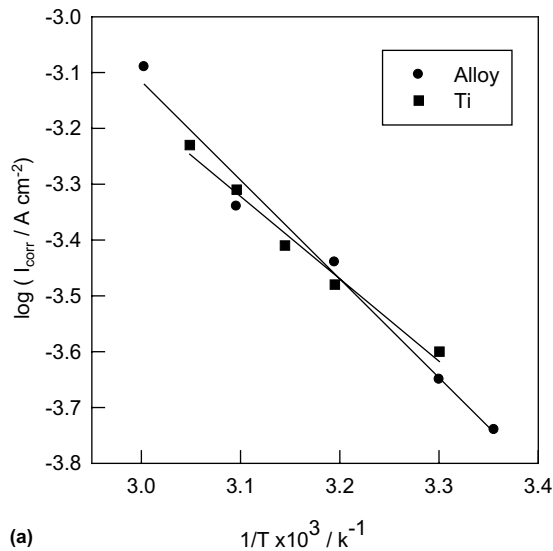
Fig. 4. (a) Arrhenius plots of the corrosion of the alloy and pure titanium in 2.5 M H_2SO_4 solution. (b) Arrhenius plots of the corrosion of the alloy and pure titanium in 5.0 M HCl solution.

corrosion process in 5.0 M HCl is larger than in 2.5 M H_2SO_4.

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