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Electrochemical behaviour of iron–chrome alloys in relation to pitting corrosion

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The polarization behaviour and pitting corrosion of Fe–Cr alloys of 7, 13, 18, 24 wt % Cr were studied. Potentiodynamic and galvanostatic measurements were performed in the absence and presence of Cl^-. As the Cr content increases the active dissolution current densities decrease while the passive range and transpassive current densities increase. Polarization parameters gave for the passive transition of the alloys a Cr concentration of $\simeq$ 13%. An increase of Cl^- concentration causes the progressive destruction of passivity. It interfered with O_2 evolution, and then destroyed the transpassive region. Still higher Cl^- concentrations initiated pitting corrosion as shown by the oscillations in potential of the galvanostatic polarization curves supported by visual observation. Results are discussed on the basis of competitive adsorption between the aggressive and inhibitor anions for the active sites on the alloys' surface.

1. Introduction

Pitting corrosion is one of the most insidious forms of localized corrosion of metals and alloys. It takes place at spatially separated anodic and cathodic areas of extremely important cathodic/anodic area ratio [1]. The propagation to perforation of a single pit would lead to complete structure failure.

Fe–Cr alloys are known to exhibit an exceptional resistance to pitting corrosion. This has been attributed to the presence of a protective passivating film [2–5]. A mixed oxide film of Fe and Cr is formed which is increasingly amorphous, and hence protective with the increase in the Cr content [3].

The present work studies the pitting of Fe–Cr alloys after the characterization of their polarization curves. These curves reflect the influence of the Cr content of steel over both their active and passive regions [4–9]. However, most of the previous studies either covered only the domain of low Cr contents or used values of Cr content which do not permit identification of the different transition limits of the alloy behaviour [10–12]. In the present work the polarization measurements performed over a wide range of Cr concentration in steel provide information both on active–passive transitions and pitting corrosion.

2. Experimental procedure

Four Fe–Cr steel alloys of the following composition (in wt %) were used:

Alloy	Cr	C	Si	Mn
I	7	< 0.12	0.5–1	< 1
II	13	< 0.12	0.7–1.2	< 1
III	18	< 0.12	1–1.5	< 1
IV	24	< 0.12	1–1.5	< 1

The electrodes cut in the form of sheets 2 mm wide and 2 cm long, were welded to thick Cu wires for electrical connection. The welds and the Cu connections were enclosed in tight fitting Pyrex glass tubing and sealed by neutral wax. The surface treatment of the electrodes involved their successive polishing 0, 00, 000 emery paper, degreasing with acetone and washing with distilled water, before being introduced into the deaerated test solution in the polarization cell.

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The polarization curves were determined in $0.1\,M\,H_2SO_4$ and in the presence of increasing amounts of Cl^- ions. In potentiodynamic polarization the cell used was previously described [13]. It is provided with a Pt counter-electrode and a Hg/Hg_2SO_4 reference electrode. The electrodes were subjected to a cathodic prepolarization treatment for 5 min at $-1.3\,V$ against Hg/Hg_2SO_4 reference electrodes. Potentiodynamic polarization then started at a rate of $10\,mV\,sec^{-1}$.

Galvanostatic polarization, on the other hand, was made in a cell similar to that previously described [14]. It was preceeded by a cathodic pretreatment of electrodes for 10 min at the polarization current of each experiment. Polarization measurements were made using an electronic potentiostat and galvanostat and an automatic recorder.

3. Results and discussion

3.1. Potentiodynamic polarization

Fig. 1a to d represents the potentiodynamic polarization curves of the alloys I to IV in the absence and presence of increasing Cl^- ion con-

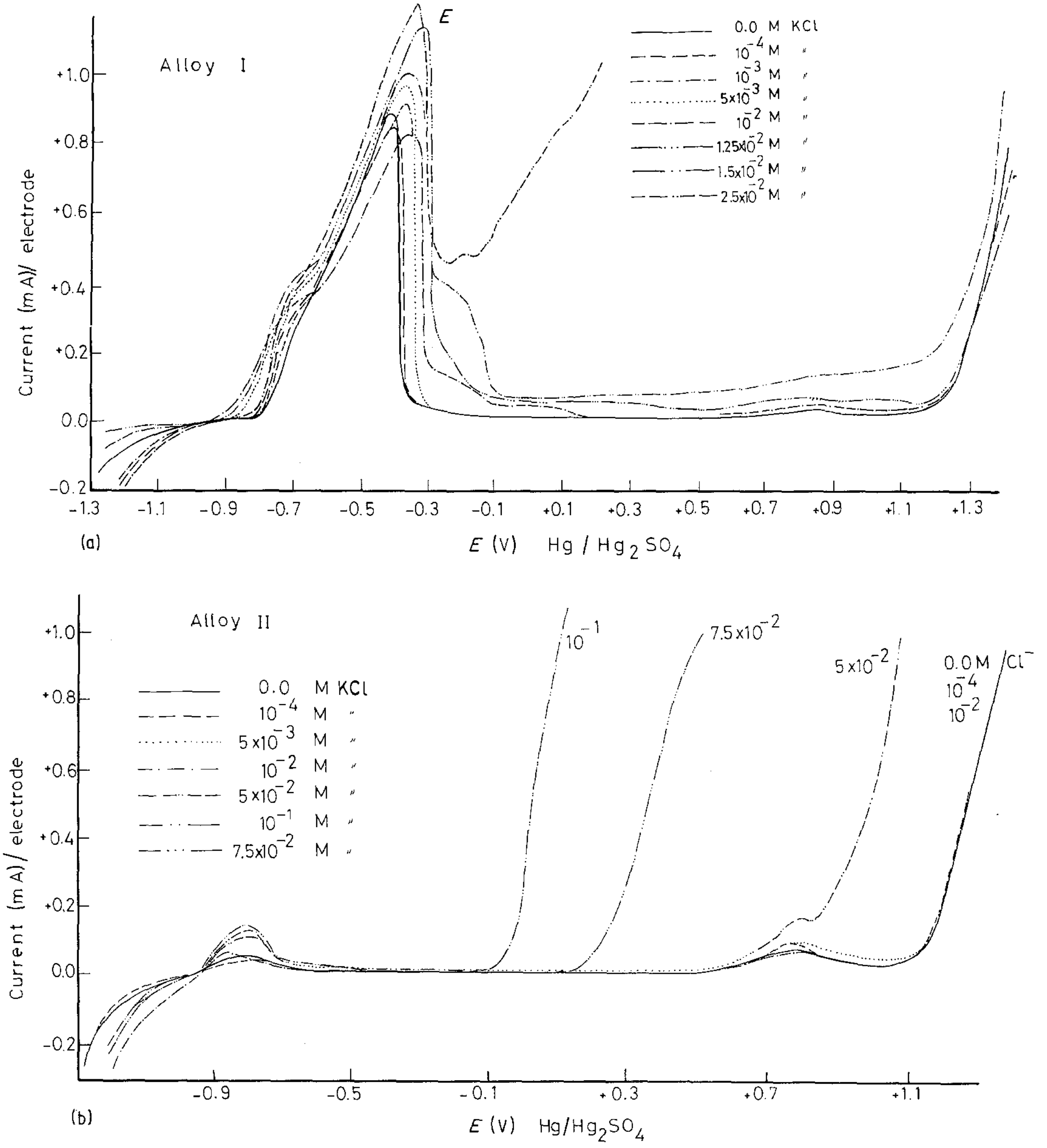

Figure 1 (a) to (d) Potentiodynamic polarization curves of Fe–Cr alloys I–IV in $0.1\,M\,H_2SO_4$ in the presence of increasing Cl^- concentrations.

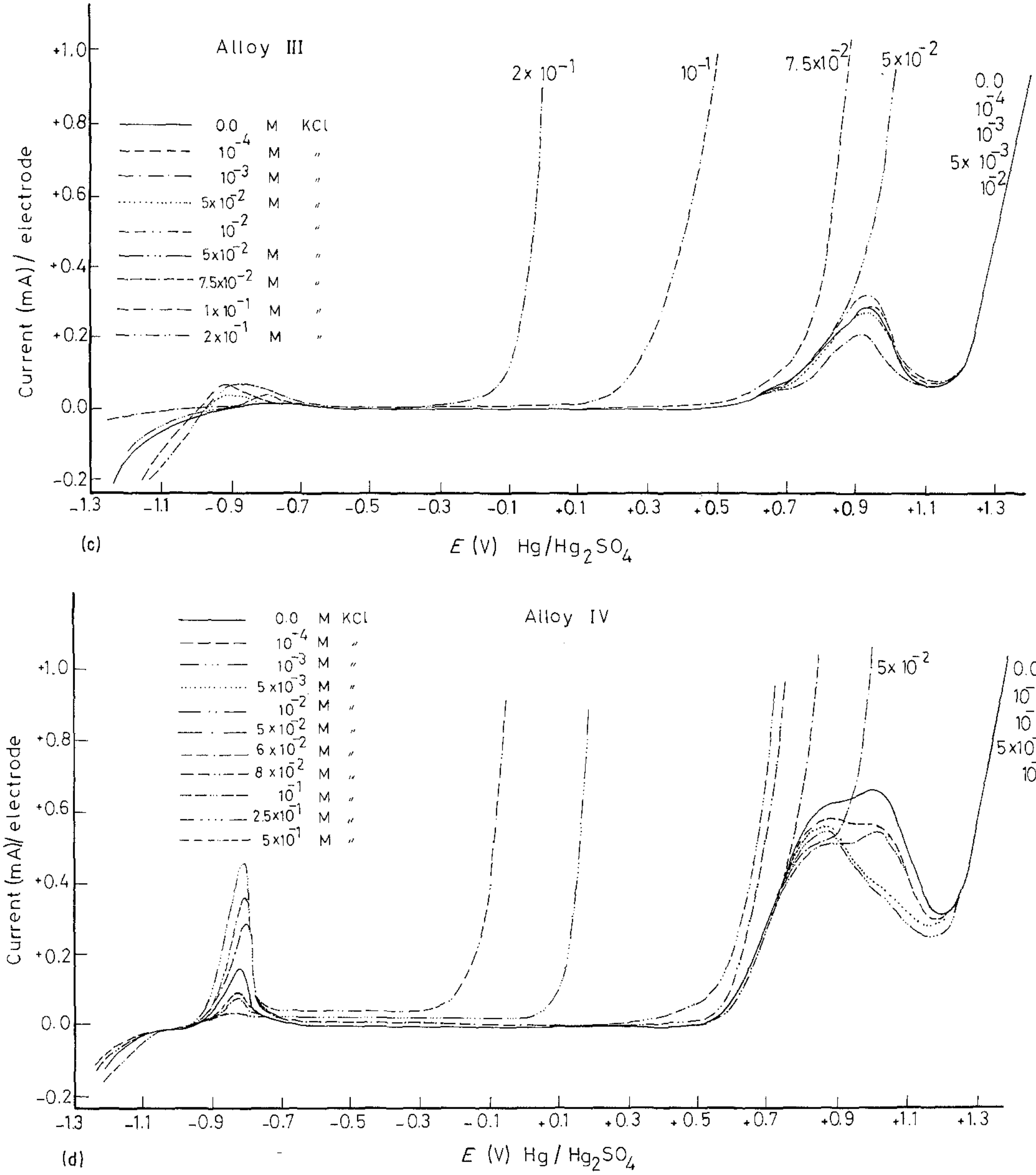

Figure 1 Continued.

centrations. In the case of Cl^--free solutions and those of low Cl^- ion concentrations, the current becomes zero at a more or less definite potential value different for each steel. At this point the rate of the cathodic reaction:

$$2\,H^+ + 2\,e^- = H_2 \qquad (1)$$

is equal to that of the anodic process of the type:

$$Fe = Fe^{2+} + 2\,e^-. \qquad (2)$$

When the electrode potential moves in the positive direction, the anodic process is favoured, while the hydrogen evolution reaction is hindered and soon ceases. Under these conditions the anodic current density is equivalent to the dissolution rate of Fe and Cr which would go in the solution in the same proportion as in the alloy. The current increases steadily with the potential until the peak potential E is reached. At E the actual passivating film starts to form on the electrode surface. When the film is continuous it interferes with the dissolution process and the current drops to approximately zero. As the potential is changed towards more positive values the current increases steeply at 1.14 V (against Hg/Hg_2SO_4) due to O_2 evolution on the passive anode. Before O_2 evolution the curves show a region of transpassivity. This region represents the dissolution of the Cr component of the alloy which would take place in the hexavalent state [15] according to:

$$2\,Cr + 7\,H_2O = Cr_2O_7^{2-} + 14\,H^+ + 12\,e^-. \quad (3)$$

The presence of higher Cl^- ion concentrations, on the other hand, increases the current density of the active dissolution slightly above that measured in Cl^- free solutions. It increases also the passive current density following the dissolution peak and causes the gradual disappearance of the transpassive region, (Fig. 1c and d). Still higher Cl^- concentrations result in the breakdown of passivity and the abrupt increase of current at lower potentials than in Cl^--free solutions.

The effect of the Cr content of the alloys on their polarization behaviour is shown by the following observations:

(a) the observed Tafel slope of the anodic dissolution of only alloy I ($\simeq$ 68 mV/decade) is similar to that of pure Fe in acidic chloride solution [16–18] i.e. the Cr content $\leqslant 7\%$ has no effect on the active dissolution behaviour of pure Fe;

(b) the passive range increases with the Cr content. The positive slope obtained for the linear change of the extent of passivity with the logarithm of Cr content represents the improvement of the passivating characteristics of the film formed;

(c) the increase of the Cr content increases the transpassive current density evidently due to the increased rate of Reaction 3 and shifts the transpassive peak potential towards more positive potentials as shown by Fig. 2a(1) and b(1), respectively;

(d) above a definite Cr content, the passivity of the Fe–Cr alloys increases remarkably as revealed by the curves of Fig. 2a and b. According to Fig. 2a the current density of the active dissolution peak, line 2, decreases and that of the transpassive peak, line 1, increases sharply at a Cr content of $\simeq 13\%$. At the same Cr content, Fig. 2b shows a considerable increase of transpassive peak potential, line 1, and change of active dissolution peak potential, line 2. The same limiting concentration of Cr has been observed by the open circuit potential measurements [19], where only the alloys of Cr content $> 13\%$ showed continuation of film growth instead of film destruction in the presence of Cl^- ions. It should be noted here that the Cr content of the film at the passive limit would vary with the anion in the solution but this is beyond the scope of the present article.

Relatively low Cl^- concentrations did not influence the passive behaviour of Fe–Cr alloys ($SO_4^{2-}/Cl^- = 10$ in the case of alloy IV, Fig. 1d).

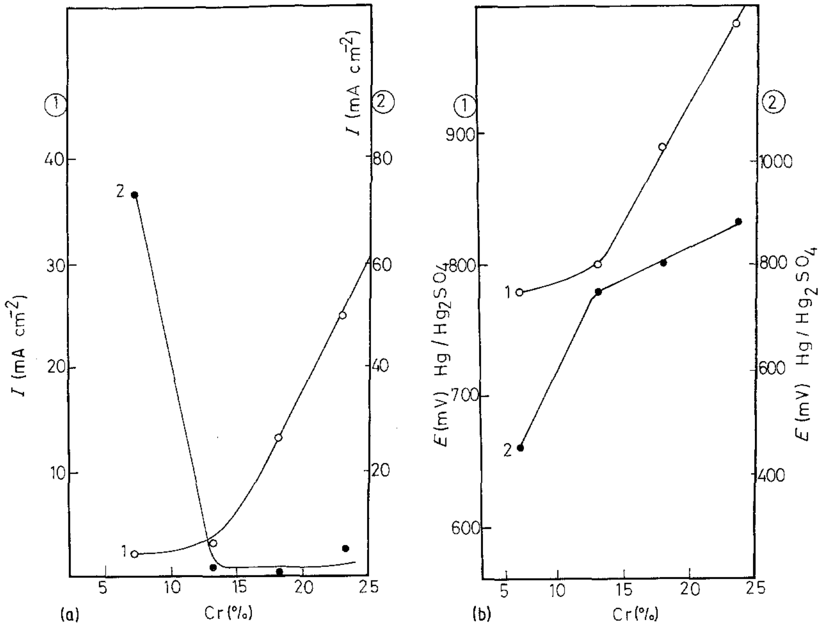

Figure 2 Effect of Cr content on (a, 1) current density of transpassive peak, (a, 2) current density of active dissolution peak, (b, 1) transpassive peak potential, (b, 2) active dissolution peak potential.

As the Cl$^-$ concentration is progressively increased, however, the transpassive region decreases gradually until it totally disappears. At still higher Cl$^-$ concentrations the initiation of pitting corrosion is indicated by the large increase of current at potential less positive than that of O_2 evolution. Fig. 3 shows the variation of the pitting potentials, E_p, of the alloys as a function of the concentration of Cl$^-$ ion in solution. Invariably straight lines are obtained which satisfy the equation

$$E_p = a - b \log C_{Cl^-}. \qquad (4)$$

where a and b are constants and C_{Cl^-} is the chloride concentration. The slopes of these lines are lower the higher the Cr content of the alloys. The role of the Cl$^-$ ion and the pitting corrosion behaviour will be considered in some detail later for both the polarization techniques.

3.2. Galvanostatic polarization

Fig. 4a and b show the galvanostatic polarization curves of the Fe–Cr alloys II and IV, recorded at different current densities ranging from 0.36 to 66.67 mA cm^{-2}. The difference between the potential of the first step ($\simeq$ 0.14 V against NHE) and the normal potential of the system Fe/Fe^{2+}, i.e. -0.44 V, represents the activation overpotential associated with the electrode reaction [20, 21]. The higher the polarization current the shorter is the active dissolution step. Below definite polarization currents, which decrease with the increase of Cr content, the alloy electrodes exhibited active dissolution without passivation over the time span of the experiment. At higher values, however, a second oxidation step appears before the system attains O_2 evolution. This second arrest corresponds to the dissolution of Cr (Reaction 3).

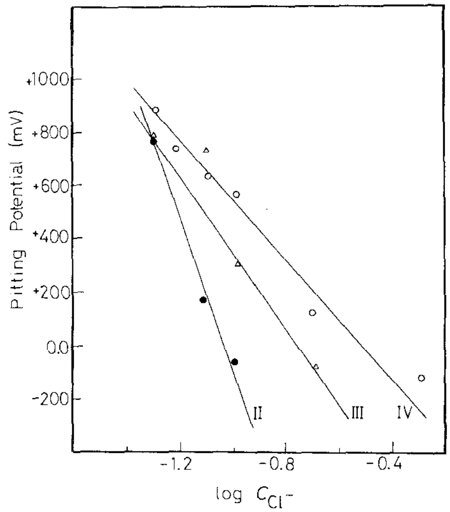

Figure 3 Variation of the pitting potential, E_p, of alloys II, III and IV with the concentration of Cl$^-$.

The effect of Cl$^-$ on the galvanostatic polarization behaviour of the Fe–Cr alloys is shown by Fig. 5a and b. At Cl$^-$ concentrations higher than certain minimum values, gradual destruction of passivity is recorded. First of all the step of O_2 evolution disappears, and the passive dissolution continues over the time of the experiment. In presence of higher Cl$^-$ concentrations, the potential oscillates with time after the primary passivity without attaining the passive dissolution potential. These oscillations in potential express the initiation of pitting corrosion. The potential shifts towards more active values. That passivity is impaired and that the alloy electrode suffered pitting corrosion is supported by visual observation of the electrode surface. Galvanostatic polarization results showed the same critical Cr content for the passive transition of the alloy behaviour as the potentiostatic measurements.

These results suggest the following mode of attack of Cl$^-$ to the passivity of Fe–Cr alloys. A minimum Cl$^-$ concentration is tolerated without damage of passivity. Such concentrations of the aggressive anion are supposed to exert no influence on the dissolution kinetics of the passive film formed on the alloy surface [22, 23]. Above these threshold concentrations, Cl$^-$ interferes with O_2 evolution reaction. The inhibition of the latter is apparently the result of the increased adsorption of Cl$^-$ at the high positive potentials. In the transpassive region where both $Cr_2O_7^{2-}$ and Fe^{3+} are obtained as anodic products, it is still possible for Cl$^-$ to adsorb. The two anions adsorb competively and for a high surface concentration of $Cr_2O_7^{2-}$, the adsorption of Cl$^-$ would be less probable and the $Cr_2O_7^{2-}$ would act as inhibitor of pitting corrosion in the same sense as SO_4^{2-}, ClO_4^- and NO_3^- [24, 25]. This explains the observed resistance of the transpassive region to pitting attack by Cl$^-$ up to concentrations higher than Cl$^-$/SO_4^{2-} = 1, alloy IV. However, as the concentration of Cl$^-$ is further increased, the transpassive region disappears and pitting corrosion is initiated since the adsorption of Cl$^-$ greatly reduces the overpotential of anodic dissolution of the alloy compared to the situation of O adsorption. Competitive adsorption of anions explains also the oscillations in potential of the galvanostatic polarization curves. These oscillations are attributed to alternate breakdown and repair of the passive film. Breakdown is caused by the aggressive Cl$^-$ ions, while film repair is caused by O_2 and SO_4^{2-} ions.

These views on the pitting corrosion behaviour of Fe–Cr alloys fit the models proposed by Leckie and Uhlig [24, 25] which attributed the pitting initiation and propagation in stainless steels to reversible adsorption of aggressive ions in competition with O_2 for sites on the alloy surface. Similar models were presented by Kolotyrkin [26, 27], Rosenfeld and Maximtschuk [28], and Brauns and Schwenk [29]. The change of the electrode potential in the positive direction introduces more Cl$^-$ into the double layer which displaces O ions and initiates pitting corrosion.

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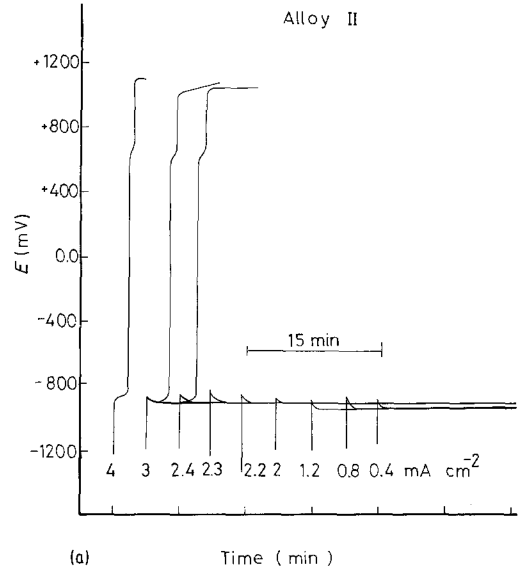

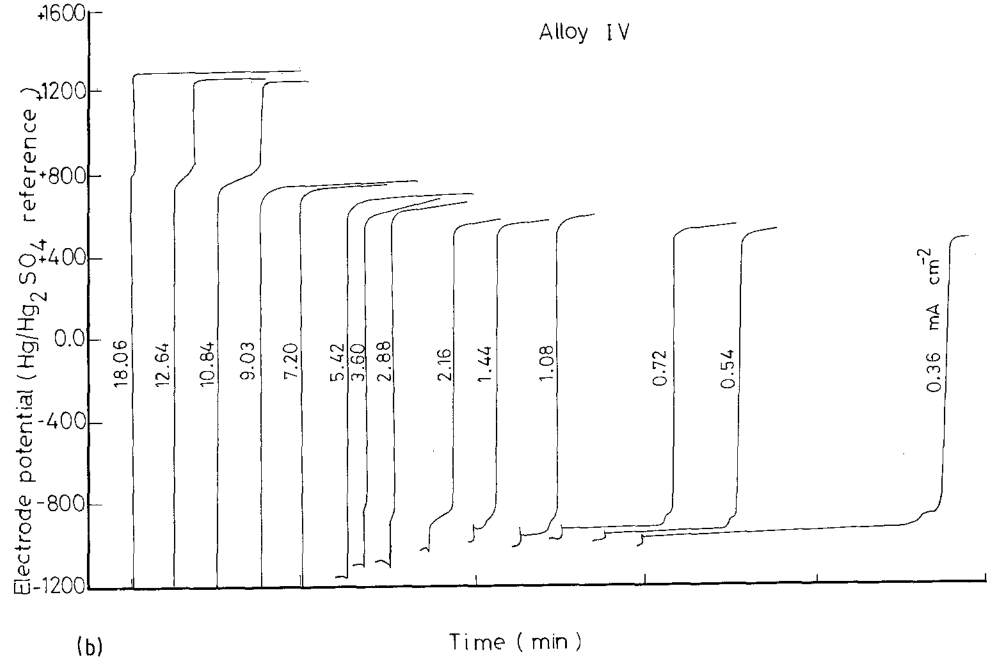

Figure 4 (a) and (b) the galvanostatic polarization curves of alloys II and IV in 0.1 M H_2SO_4 at different current densities.

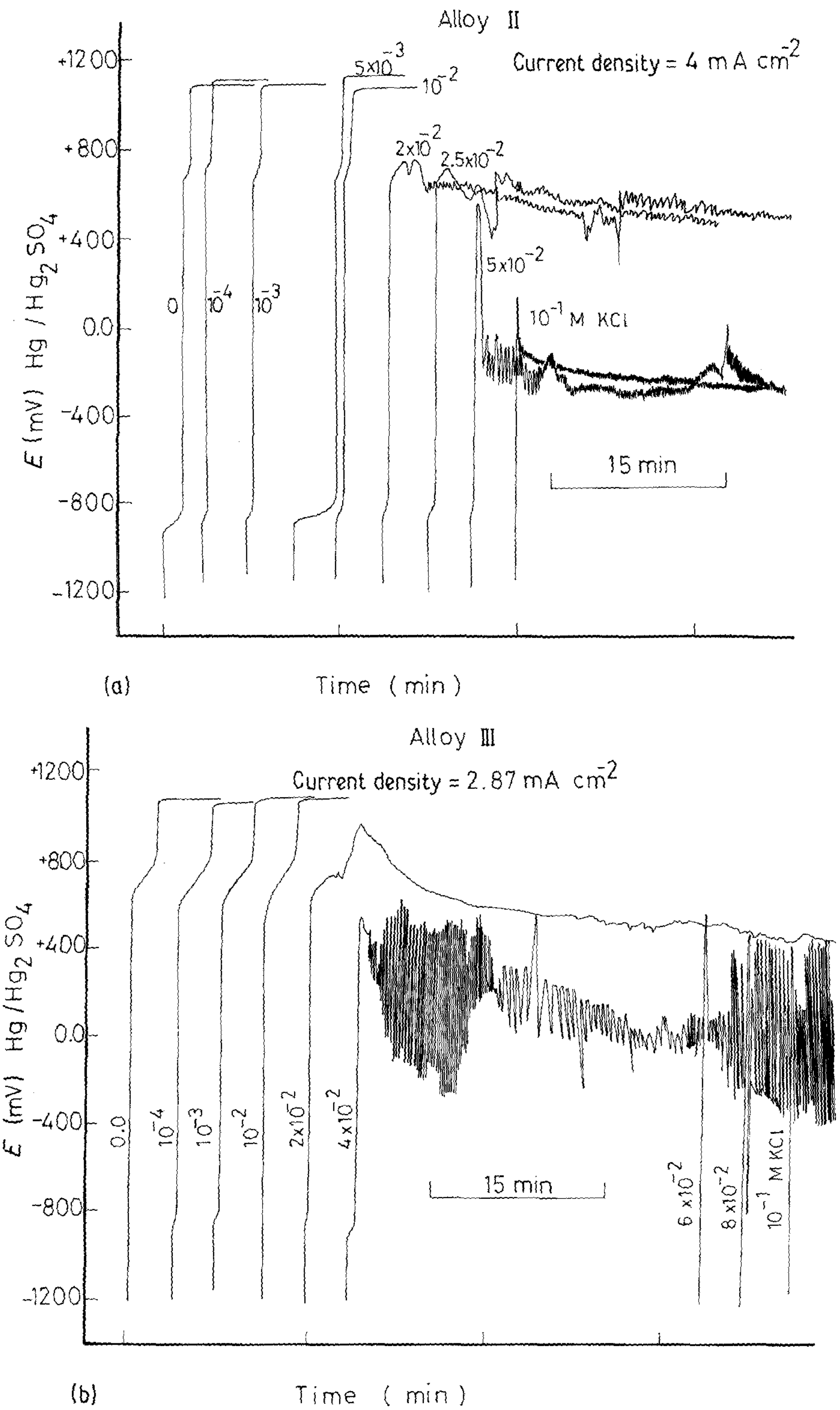

Figure 5 (a) and (b) effect of Cl$^-$ concentration on the galvanostatic polarization behaviour of alloys II and III.

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