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Transpassive dissolution of iron in sulphuric acid solution

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Anodic oxidation characteristics of iron in 3, 10 and 12 mol dm^{-3} sulphuric acid solutions have been studied in the transpassive region. Dissolution current efficiency measurements have been carried out using potentiostatic current–voltage curves and solution analysis techniques. The current–voltage curves were split into metal dissolution and oxygen evolution curves assuming that the iron goes into solution as Fe^{3+}. The current density value in the passive region increased whereas the current density in the transpassive region decreased with the increase of sulphuric acid solution concentration. In order to obtain information about the nature of the films present on the surface, potential decay curves from different anodic potentials in the transpassive region have been recorded. It seems that there is no passive film present on the specimen surface in 12 mol dm^{-3} sulphuric acid solution and a better surface finish is obtained after the dissolution. Depth profile analysis of oxide films by the AES technique in 3 mol dm^{-3} sulphuric solution reveals that the sulphur concentration is maximum at the metal/oxide interface rather than at the oxide/electrolyte solution interface as required by an ion exchange mechanism for film dissolution.

1. Introduction

Much work has been carried out by different research workers on the passive films formed on metals [1] but much less attention has been paid to the behaviour of various metal electrodes in the transpassive region. Many reactions such as metal dissolution, oxygen evolution, passivation reactions etc. may simultaneously occur in the transpassive region thus causing a complicated electrochemical system. The electrochemical behaviour of a metal electrode in the transpassive region depends upon the nature of anions, the concentration of electrolyte and the anodic potential. It has been suggested that the dissolution of the passive films takes place in the transpassive region by an ion exchange mechanism [2] according to which the anion concentration in the film lattice should be maximum at the oxide/electrolyte solution interface.

In the present study, we have investigated the anodic behaviour of iron in sulphuric acid solutions of different concentrations in the transpassive region in order to obtain more information on the dissolution rate of the metal and its effect on the surface finish. Anodic polarization curves and solution analysis techniques have been used to obtain the dissolution current efficiency. An attempt has been made to obtain information about the nature of the oxide films formed on the surface of the electrode by recording the potential decay curves from different anodic potentials in the transpassive region. In addition, the Auger electron spectroscopy technique (AES) has been used to make a depth profile analysis of the oxide films present on the surface of the electrode to find out whether penetration of the electrolyte anions into the oxide film occurs.

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2. Experimental details

2.1. *Materials*

Pure iron specimens used in this investigation (supplied by Materials Research SA, Toulouse–Cedex, France) had the following composition.

Element	Al	Si	S	O	Cu	Cr	Fe
ppm	60	50	40	33	30	30	Major

All the chemicals used were of AR grade and the solutions were made by using conductivity water. Anodic polarization and potential decay curves were recorded in 3, 10 and 12 mol dm^{-3} sulphuric acid solutions. Depth profile analysis by the AES technique was carried out from specimens polarised in 3 mol dm^{-3} sulphuric acid solution only.

2.2. *Procedure*

The specimens were cut from rods and were 5.12 mm long and 5 mm in diameter to obtain an electrode area of 1 cm^2. The shape and the design of the specimens and connecting rods to make electrical connections were similar to those given by Greene [3]. The specimens were degreased and then mechanically polished up to 4/0 grade emery paper. The specimens were then heated in vacuum at 600° C for 3 h. The specimens were again polished after the heat treatment with 4/0 emery paper and then ultrasonically cleaned in acetone. The specimens were then wrapped in tissue papers and stored over silica gel in a dessicator. All the sulphuric acid solutions were pre-electrolysed for about 16 h and pure nitrogen gas was continuously bubbled through to deoxygenate the electrolyte solution. An electrolytic cell similar to that described by Greene [3] was used for the electrochemical study. All the potentials were measured against a saturated calomel electrode and the experiments were performed at room temperature (20 ± 2° C).

2.3. *Anodic polarization*

Firstly anodic polarization curves were recorded using a Wenking potentiostat (model 68FR05) and a Wenking Stepping motor Control (model SMP72). The current and voltage were continuously recorded on two single pen strip chart recorders. The specimen was initially kept in the electrolyte solution in the passive potential region (+ 1400 mV) for two hours. Due to the formation of passive films on the surface of the specimen the current decreased and became constant after some time. Then the anodic polarization curves were recorded at a scanning rate of 11 mV min^{-1}.

2.4. *Current efficiency measurements*

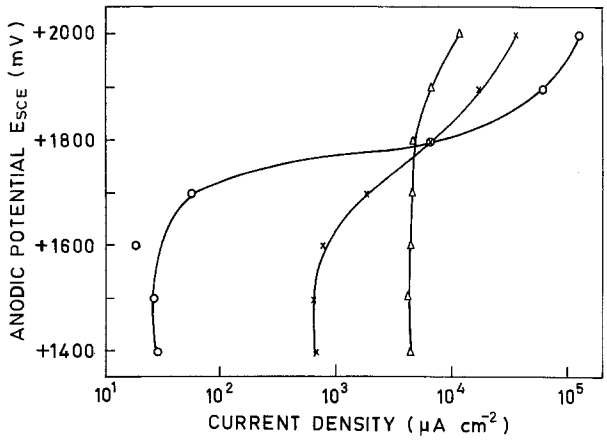
The anodic polarization curves were split into an oxygen evolution curve and an iron dissolution curve by the solution analysis technique. The specimen was kept in the electrolytic cell and a potential of + 2000 mV was applied for a certain time. A 10 ml sample of the electrolyte solution was then taken out and the potential was changed to + 1900 mV. This procedure was repeated until the potential was lowered in 100 mV steps to + 1500 mV. The samples of the electrolyte solution were quantitatively analysed for total iron and Fe^{3+}. It was also checked for the presence of Fe^{2+}. Total iron analysis was made by atomic absorption spectrometry (Perkin Elmer) and Fe^{3+} analysis by spectrophotometer (Cecil Instruments). The current efficiency for the dissolution of the specimen was calculated using Faraday's Law and considering Fe^{3+} as the ion produced from iron dissolution in the transpassive region.

2.5. *Potential decay curves*

The specimen was cleaned cathodically for 3 min and then kept at the rest potential for 30 min. Then a particular anodic potential in the passive–transpassive region was applied to the specimen for 15 min. The current was cut off and the potential decay curve was recorded on a strip chart recorder. When the potential had reached the open circuit potential value with the decay of the potential, the same specimen was used to record the potential decay curves at other anodic potential values after repeating the above mentioned procedure of cathodic cleaning and again keeping it at open circuit potential for 30 min.

2.6. *Depth profile analysis by AES*

The specimen was anodically polarized at a fixed



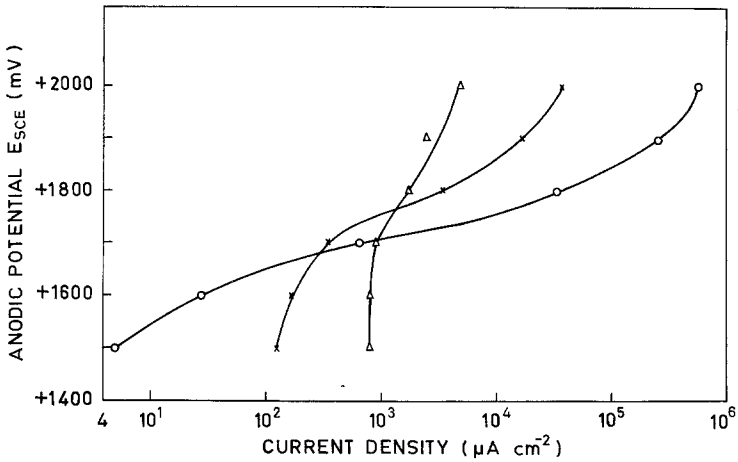


Fig. 1. (a) Iron dissolution curves during the anodic polarization of iron in different concentrations of sulphuric acid solution. (b) Oxygen evolution curves during the anodic polarization of iron in different concentrations of sulphuric acid solution.
○ 3 mol dm^{-3} H_2SO_4,
× 10 mol dm^{-3} H_2SO_4,
△ 12 mol dm^{-3} H_2SO_4.

potential for one hour in 3 mol dm^{-3} sulphuric acid solution. The specimen was taken out of the cell, washed with distilled water and dried under a jet of argon gas. The specimen was then screwed to a specially designed stainless steel holder and was covered with a stainless steel cap in an argon gas atmosphere. Then the holder and the cap were sealed together with tape suitable for sealing in ultra high vacuum conditions. The sealed specimen was kept in an argon gas chamber till it was transferred to the chamber of the Auger Analyser (PHI545) on a specimen mount. The Auger chamber was evacuated to a vacuum of the order of 10^{-10} Torr. A primary 2 kV beam voltage was used. The sputter-etching of the specimen was performed at room temperature with a 500 eV argon ion beam having an ion current of about 10 mA at a pressure of 1×10^{-5} Torr. The stainless steel cap of the specimen was removed under vacuum conditions in the Auger chamber.

3. Results and discussion

3.1. *Polarization curves*

Anodic polarization curves of iron in 3, 10 and 12 mol dm^{-3} sulphuric acid solutions were split into metal dissolution and oxygen evolution curves and are shown in Figs. 1a and b respectively. In 15 mol dm^{-3} sulphuric acid solution, the current density was very low in the passive as well as transpassive region, i.e. 24 μA cm^{-2} at + 2000 mV and has not been plotted in Fig. 1. In the transpassive region both metal dissolution and oxygen evolution take place. The shape of the anodic polarization curve changes quite significantly when the concentration of sulphuric acid solution is changed from 3 to 12 mol dm^{-3}. The current density value in the passive region increases whereas the current density in the transpassive region decreases with the increase of sulphuric acid con-

Table 1. Dissolution current efficiency of iron in different concentrations of sulphuric acid solution at various anodic potentials

Anode potential E_{SCE} *(mV)*	*Percentage current efficiency*		
	3 *mol dm*$^{-3}$ H_2SO_4	10 *mol dm*$^{-3}$ H_2SO_4	12 *mol dm*$^{-3}$ H_2SO_4
+ 1500	82	83	83
+ 1600	40	82	85
+ 1700	8	84	84
+ 1800	16	66	72
+ 1900	18	50	72
+ 2000	18	47	70

centration. No passive region is obtained when the specimen is polarized in 12 mol dm^{-3} sulphuric acid solution and the passive film formed in 10 mol dm^{-3} sulphuric acid solution is either very thin or its structure is such that it provides a high current density value in the passive region. In other words, the passive film quality deteriorates as the concentration of sulphuric acid solution is increased up to 12 mol dm^{-3}. Further increase in concentration of sulphuric acid solution decreases the current density value in the passive as well as transpassive region very sharply.

3.2. *Current efficiency data*

The current efficiency data for the iron dissolution have been recorded in Table 1. In the case of 3 mol dm^{-3} sulphuric acid solution, the current efficiency is low in the transpassive region and the surface appearance even at + 2000 mV is dull. A better surface finish is obtained in 10 mol dm^{-3} sulphuric acid solution and the current efficiency is also increased. At 12 mol dm^{-3} sulphuric acid concentration, the current efficiency is further increased above + 1800 mV and the specimen is not dulled in appearance although no anodic brightening effect was produced. The use of a higher concentration of sulphuric acid (> 3 mol dm^{-3}) could be advantageous from the view point of surface finish. 10 and 12 mol dm^{-3} sulphuric acid solution analysis after dissolution at + 1500 mV showed only the presence of Fe^{3+} but in 3 mol dm^{-3} sulphuric acid solution it was found that Fe^{2+} traces were always present though in such a small quantity that it was difficult to estimate it quantitatively. It is not possible to explain why Fe^{2+} traces are present at + 1500 mV in 3 mol dm^{-3} sulphuric acid solution because Fe^{2+} should have changed to Fe^{3+} at this potential. Romashkan *et al.* [4] used a rotating disc method for the anodic polarization of iron in $NaClO_3$ solution and observed that in the beginning of the transpassive potential region, i.e. at lower current densities, Fe^{3+} is produced on dissolution of Fe. This has further been substantiated by Petit *et al.* [5] who reported that iron goes into solution only as Fe^{3+} in the transpassive region and that the electrode surface in the passive and transpassive potential region is covered by a layer of adsorbed species. The transition from passive to transpassive behaviour is governed by the rate of competitive adsorption and desorption reactions of passivating and depassivating anions. The passive film present on the iron surface is thought to be made up of Fe_2O_3 which give Fe^{3+} in the solution on increasing the anodic potential [6]. From the electrochemical study only it is very difficult to determine whether the passivation is due to a film of Fe_2O_3 or to a duplex film of Fe_2O_3 and Fe_3O_4.

3.3. *Potential decay curves*

The potential decay curves for Fe in 3, 10 and 12 mol dm^{-3} sulphuric acid solutions are shown in Figs. 2–4. In 3 mol dm^{-3} sulphuric acid solution, the first potential arrest, say E_1, is at about + 550 mV and the second potential arrest, say E_2, is at about − 490 mV which is very near to the open circuit equilibrium potential value. The time taken for the potential to decay up to the second potential arrest, say t, is recorded in Table 2. There is a sudden increase in the value of t at an anodic

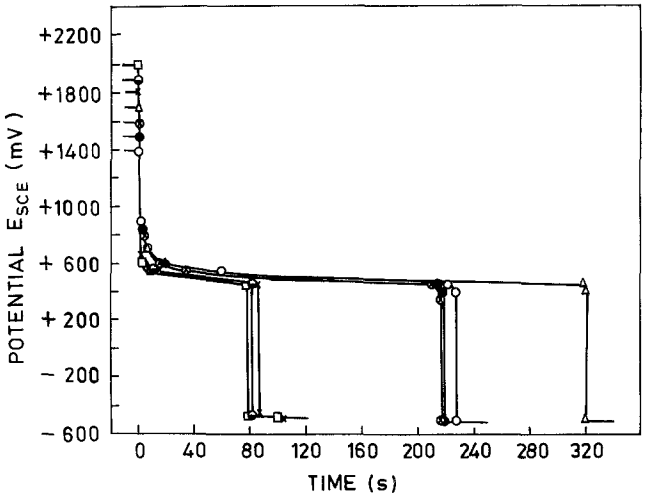


Fig. 2. Potential decay curves for iron from various anodic potentials in 3 mol dm^{-3} sulphuric acid solution. ○ + 1400 mV, ● + 1500 mV, ⊗ + 1600 mV, △ + 1700 mV, × + 1800 mV, ◒ + 2900 mV, □ + 2000 mV.

Table 2. Time, t, *taken for the potential to decay up to second potential arrest from various anodic potentials in different concentrations of sulphuric acid solution*

Anode potential E_{SCE} *(mV)*	*Time,* t (s)		
	3 *mol dm*$^{-3}$ H_2SO_4	10 *mol dm*$^{-3}$ H_2SO_4	12 *mol dm*$^{-3}$ H_2SO_4
+ 1400	227	10.3	1.4
+ 1500	218	12.0	1.8
+ 1600	216	14.4	2.3
+ 1700	320	10.7	2.6
+ 1800	86	8.0	2.9
+ 1900	80	4.8	3.2
+ 2000	78	4.5	3.8

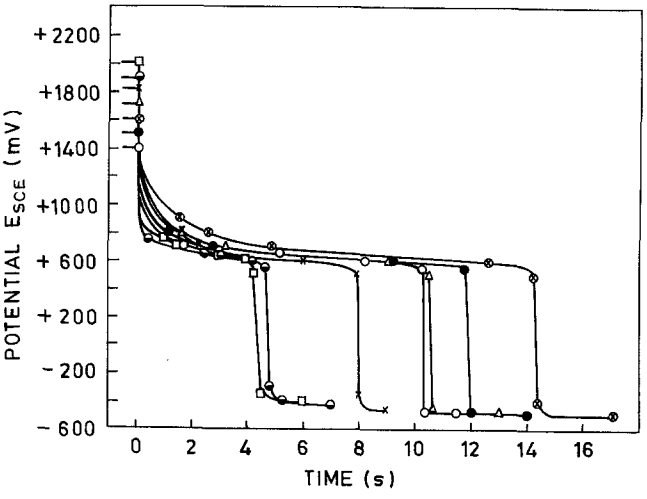


Fig. 3. Potential decay curves for iron from various anodic potentials in 10 mol dm^{-3} sulphuric acid solution. ○ + 1400 mV, ● + 1500 mV, ⊗ + 1600 mV, △ + 1700 mV, × + 1800 mV, ◒ + 1900 mV, □ + 2000 mV.

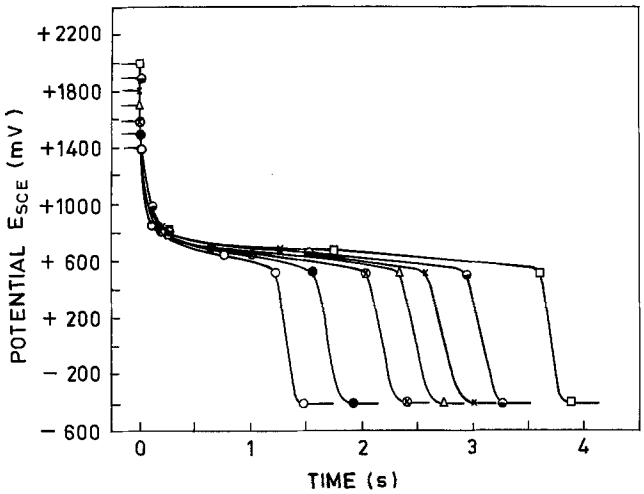


Fig. 4. Potential decay curves for iron from various anodic potentials in 12 mol dm^{-3} sulphuric acid solution. ○ + 1400 mV, ● + 1500 mV, ⊗ + 1600 mV, △ + 1700 mV, × + 1800 mV, ◒ + 1900 mV, □ + 2000 mV.

potential of + 1700 mV. At this potential the electrode is changing from the passive to the transpassive region and the dissolution current efficiency is minimum. At + 1800 mV the time t suddenly decreases to 86 s from 320 s at + 1700 mV. It seems, the dissolution of the oxide films is most difficult at this potential or the resistance of the passive film is maximum.

When the electrolyte concentration is increased to 10 mol dm^{-3}, the time t is reduced considerably in comparison to that in 3 mol dm^{-3} sulphuric acid solution. The first potential arrest shifts from + 550 to + 750 mV and the second potential arrest is obtained at − 450 instead of − 490 mV. The potential decay curve from + 1600 mV shows maximum time to reach the second potential arrest indicating that the quality of the passive film at this potential is improved due to adsorption of certain species from the electrolyte solution. In 10 mol dm^{-3} sulphuric acid solution the process of oxygen evolution is hindered because of the replacement of adsorbed water by adsorbed anions to some degree. In 3 mol dm^{-3} sulphuric acid solution the HSO_4^- concentration is more than the SO_4^{2-} concentration. In 10 mol dm^{-3} sulphuric acid solution the concentration of HSO_4^- further increases and the SO_4^{2-} concentration decreases. More HSO_4^- ions are expected to be present in the film at 10 mol dm^{-3} sulphuric acid solution hence making it ionically conductive. Thus the increased adsorption of HSO_4^- affects the anodic reactions. The potential decay from + 1400 mV (passive region) to open circuit equilibrium potential takes only 10.35 s suggesting that the passive film is very thin and ionically conductive in nature.

In 12 mol dm^{-3} sulphuric acid solution, the time taken to reach the second potential arrest goes on increasing with increase of the potential of the anode in the transpassive region. The first potential arrest is at + 800 mV and the time t at + 1400 mV is 1.40 s. At this high concentration of sulphuric acid, the concentration of HSO_4^- is quite high and the SO_4^{2-} concentration is very low. The passivity here is lost because of this high concentration of HSO_4^- and the decrease of OH^- concentration. Thus the behaviour of an anode in the transpassive region not only depends upon the metal/solution potential difference but also upon the nature of anion and anion/water ratio.

3.4. *Depth profile analysis*

A concentration depth profile analysis by the AES technique of the specimens kept at + 1400 and + 1700 mV for 1 h in 3 mol dm^{-3} sulphuric acid solution has been shown in Figs. 5 and 6. Similar curves were obtained for the specimens kept at an anodic potential of + 1500 and + 1900 mV. The purpose of this experiment was to find out whether the anions can penetrate through the anodic films or not and whether the concentration of sulphur is maximum at the metal/oxide interface or at the oxide/electrolyte solution interface. It is evident from Fig. 6 that the sulphur maximum is at the metal/oxide interface in the transpassive region (+ 1700 mV). Though care has been taken to avoid atmospheric oxidation of the specimen dur-

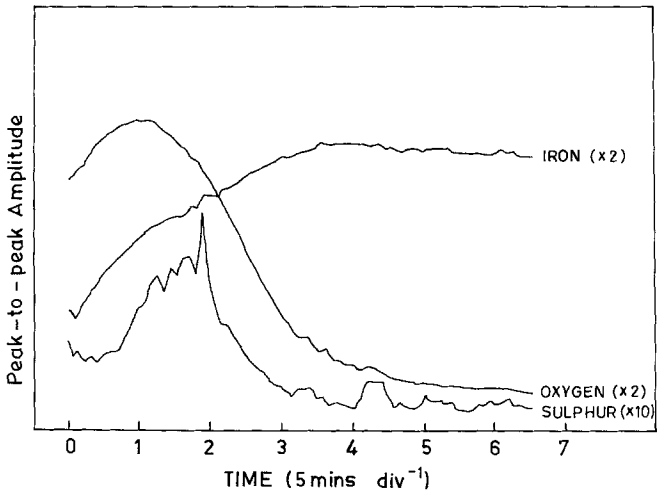


Fig. 5. Depth profile analysis of oxide films formed on iron in 3 mol dm^{-3} sulphuric acid solution at + 1400 mV.

ing transportation from the electrochemical cell to the AES chamber, the possibility of this occurring cannot be completely ruled out when the specimen is anodically polarized at + 1700 mV. The possibility of atmospheric oxidation is much less when the specimen is anodically polarized in the passive region (+ 1400 mV) for 1 h because then a thick passive film is obtained on the surface (Fig. 5). In both figures the sulphur maximum has been found at the metal/oxide interface thus indicating that the sulphate ions penetrate through the anodic films and accumulate at the metal/oxide interface. This is in agreement with the results reported in the literature for anodic films on nickel in the presence of nitrate ions [7] and for TiO_2 films in perchloric acid [8]. The occurrence of a sulphur maximum at the metal/oxide interface suggests that the ion exchange mechanism is not applicable for film break down otherwise the sulphur maximum would have been obtained at the oxide/electrolyte solution interface.

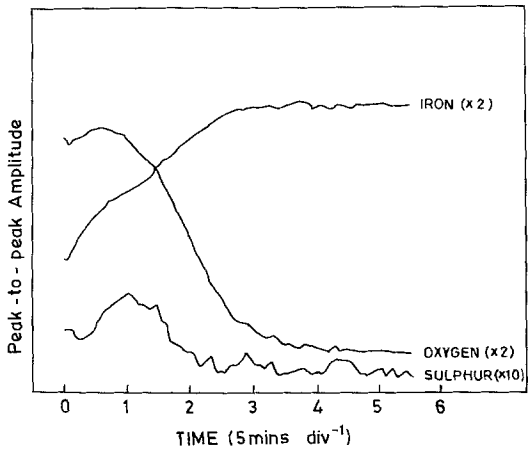


Fig. 6. Depth profile analysis of oxide films formed on iron in 3 mol dm^{-3} sulphuric acid solution at + 1700 mV.

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