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## INVOLVEMENT OF SURFACE OXIDE FILMS ON IRON IN HALIDE-INDUCED PITTING

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**Abstract**—Bromide-induced pitting of Fe is triggered by a critical state of the passive oxide film. The state corresponds to a specific thickness of the oxide which depends on the concentration of bromide ions, but not the anodizing potential. In addition, pitting will only occur if the critical state is established in  $< 10$  s. The critical thickness for pitting is linearly dependent on the logarithm of the concentration of halide ions. Similar slopes are obtained for chloride and bromide ions, however, the critical thickness for  $\text{Br}^-$  is greater than for  $\text{Cl}^-$  at the same concentration, reflecting the more aggressive nature of the  $\text{Cl}^-$ . Once development of the passive film has passed the critical stage, pitting becomes very unlikely, even if the potential is held well above the pitting potential. Partial cathodic reduction experiments demonstrate that a thinner film does not pit more rapidly than a thicker film; instead more charge must pass for the thinner film to reach the critical state prior to pitting.

### INTRODUCTION

Pitting of Fe is induced by the presence of halides in otherwise non-aggressive solutions. Pitting will occur after an induction time,  $\tau$ , if the potential exceeds the critical pitting potential,  $E_c$  [1-4]. Both these quantities depend on the concentration of halide in solution, with a minimum concentration required for pit initiation. In general, the halides are aggressive in the order  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ . Despite numerous investigations, the mechanism of pitting remains a controversial topic [5].

In recent work, it has been demonstrated that  $\text{Cl}^-$ -induced pitting of Fe in pH 8.4 borate buffer solution is associated with a critical stage in the development of the passive film [6]. This state corresponds to a specific thickness of the oxide film which is independent of the applied potential, but dependent on the  $[\text{Cl}^-]$ . Since the passive film on Fe is formed with 100% efficiency in pH 8.4 borate buffer solution, a quantity  $Q_A(\text{pit})$ , the anodic charge passed prior to pitting, can be defined. A potential-independent  $Q_A(\text{pit})$  was shown to be consistent with the experimentally observed dependencies of  $E_c$  on  $[\text{Cl}^-]$  and of  $\tau$  on potential. The purpose of this paper is to show that these results also apply to  $\text{Br}^-$ -induced pitting of Fe. In addition, the minimum halide concentration required for pitting is explained in terms of a critical stage in the development of the passive film.

### EXPERIMENTAL

Fe samples were cut from zone-refined 99.99+ % Fe, obtained from Battelle Memorial Institute, and polished to 600 grit SiC. All samples were electropolished immediately before use. In pitting experiments, care was taken to interrupt the pitting at a very early stage, and the sample was electropolished before re-use. Results were checked by repeating some experiments with a sample which had not undergone pitting.

The reproducibility of the results indicated there was no effect of the previous pitting. After each pitting experiment the surface was examined, and the presence of pits noted. In some cases, waterline corrosion was observed: occasionally, both types of attack were visible on the same sample.

The standard solution used was pH 8.4 borate buffer containing 7.07 g of  $\text{H}_3\text{BO}_3$  and 8.17 g of  $\text{Na}_2\text{B}_4\text{O}_7 \cdot \text{H}_2\text{O}$  per liter. Using the equilibrium constants given by Pourbaix [7], the total concentration of anion equivalents is 0.0378 M. To obtain borate buffer solutions containing  $\text{Cl}^-$  or  $\text{Br}^-$ , a solution of 0.0378 M NaCl or NaBr was prepared, and mixed in various proportions with the borate buffer. This gave final solutions of a conductance equivalent to those of the pure borate buffer. Solutions were deaerated before use, and thermostated at 24°C. Potentials were measured relative to a 0.15N Hg/Hg<sub>2</sub>SO<sub>4</sub>/Na<sub>2</sub>SO<sub>4</sub> reference electrode (0.421 V *vs sce*, 0.661 V *vs she*). All samples were galvanostatically cathodically reduced before potential step anodization.

A Princeton Applied Research Model 173 Potentiostat with a custom modified Model 276 interface, connected to an IBM compatible computer, described previously [6], was used to control the potential.

### RESULTS AND DISCUSSION

#### *Experiments starting with a cathodically reduced surface*

In this series of experiments, the current-time transients obtained upon stepping the potential into the passive region were compared for borate buffer solutions with and without added NaBr. An example of such a series, using  $9.45 \times 10^{-3}$  M NaBr, is shown in Fig. 1. At potentials at or below  $-0.325$  V, no pitting and no waterline corrosion was observed on the sample, and the two curves were coincident. This indicates that the charge passed in the formation of the

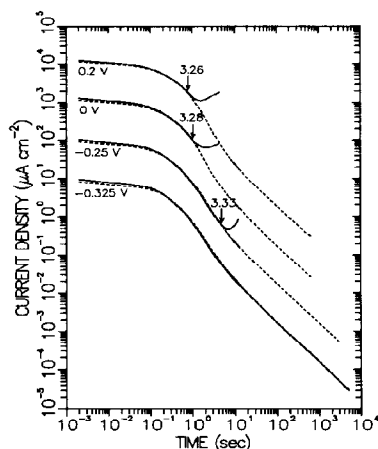


Fig. 1. Log  $i$ -log  $t$  profiles for various potentials in the passive region. The solid curves are the current transients observed for Fe in solutions containing  $9.45 \times 10^{-3}$  M NaBr in borate buffer, the dashed curves for Fe in pure borate buffer. The current density scale refers to the top curve, at 0.2 V. For clarity, at lower potentials the curves have been displaced by factors of ten. The arrows show the points at which the curves can be seen to diverge. The number above the arrow indicates the anodic charge, in  $\text{mC cm}^{-2}$ , which has passed to the point of divergence.

film in the presence and absence of  $\text{Br}^-$  is identical. At all potentials at or above  $-0.310$  V, the log  $i$ -log  $t$  profile in  $\text{Br}^-$ -containing solution showed a positive deviation from the curve in  $\text{Br}^-$ -free solution, indicative of pitting. For potentials between  $-0.310$  V and  $-0.30$  V both waterline and pitting attack were observed on the sample after the experiment. Above  $-0.3$  V, only pitting was observed. Therefore, for this system  $-0.325 < E_c \leq -0.31$  V, compared to the value of  $-0.32$  V obtained by Janik-Czachor[2].

As before[6], the first indication of pitting was taken to be at the point of deviation of the two log  $i$ -log  $t$  profiles, indicated by the arrows on Fig. 1. The corresponding integrated anodic charge,  $Q_A(\text{pit})$ , in  $\text{mC cm}^{-2}$ , is shown above the arrow. As was the case with  $\text{Cl}^-$  [6], the induction time for pitting decreased as the potential was increased, but the integrated charge remained relatively constant. The results of a large number of such experiments are shown in Fig. 2. Clearly, there is no systematic dependence of  $Q_A(\text{pit})$  on anodizing potential.

This series of experiments was repeated with various  $\text{Cl}^-$  and  $\text{Br}^-$  concentrations. In all cases, the value of  $Q_A(\text{pit})$  showed no systematic dependence on potential. Figure 3 shows a plot of the average value of  $Q_A(\text{pit})$  vs the logarithm of halide ion concentration. The points represent the average of 5 to 31 separate experiments at each concentration; the standard deviation of  $Q_A(\text{pit})$  varied from 0.2 to  $0.4 \text{ mC cm}^{-2}$ . The data show a reasonable linear correlation with the logarithm of the halide ion concentration, and the slopes are similar in the two cases. With increasing [halide], the solution is more aggressive and less anodic charge must pass before pitting begins.  $\text{Br}^-$  is obviously less aggressive than  $\text{Cl}^-$  since the data are shifted to higher values of  $Q_A(\text{pit})$ .

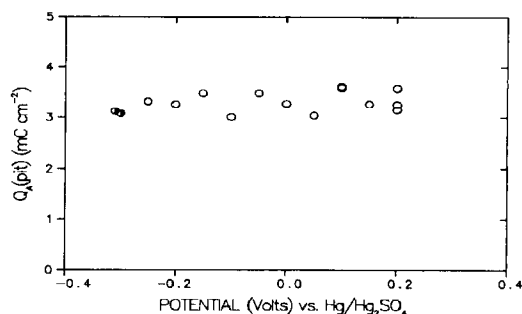


Fig. 2. The charge passed before the point of divergence of the log  $i$ -log  $t$  profiles (cf. Fig. 1) vs the anodizing potential for Fe in  $9.45 \times 10^{-3}$  M NaBr. The open circles represent experiments where pitting attack and no waterline attack was observed on the surface. The half open circles are for experiments where both pitting and waterline attack were visible on the same sample.

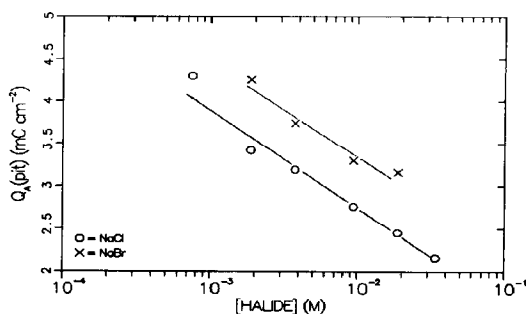


Fig. 3. Average values of  $Q_A(\text{pit})$  vs the concentration of halide ion present in solution.

The induction time before pit initiation (in a total of 169 experiments) was never greater than 10 s. In addition, pitting was not observed at potentials below  $E_c$ , even if the total charge passed exceeded  $Q_A(\text{pit})$ . This suggests that  $E_c$  can be operationally defined as the minimum potential at which  $Q_A(\text{pit})$  can be exceeded in less than 10 s. As indicated before[6], this is consistent with the commonly observed linear dependence of pitting potential on halide ion concentration[1-5]. The minimum concentration for pitting with both  $\text{Cl}^-$  and  $\text{Br}^-$  was also determined, and corresponds to the lowest concentration in Fig. 3. The value of  $Q_A(\text{pit})$  in both cases is close to  $4.25 \text{ mC cm}^{-2}$ , suggesting that pitting will not occur if the charge required exceeds  $4.25 \text{ mC cm}^{-2}$ . An anodic charge  $> 4.25 \text{ mC cm}^{-2}$  cannot be supplied quickly enough to permit pitting to begin, no matter how high the potential.

As in previous work, these results suggest that pitting is associated with a particular state of the oxide film, or a particular composition at the surface of the oxide[6]. It should be noted that the results could also be interpreted so that the induction time,  $\tau$ , is the critical parameter in pitting. Certainly,  $\tau$ , which depends on [halide] and the anodizing potential, influences the state of development of the oxide. To account for the present results, however, it would be

necessary for  $\tau$  to depend on potential in such a way that the film thickness at time  $\tau$  happens to be independent of potential. Additionally, this condition would have to prevail at every [halide]. In view of these constraints, the more probable interpretation is that a critical oxide film state (thickness) is necessary for pitting to begin, and is a function only of the [halide]. At the highest concentrations of  $\text{Cl}^-$  used, the value of  $Q_A(\text{pit})$  obtained corresponds to the first appearance of the outer phase on the inner phase[6]. At lower  $\text{Cl}^-$  concentrations, or in solutions containing the less aggressive  $\text{Br}^-$  ion, more of the outer phase is required to trigger pitting.

#### Experiments starting with a passive film-covered surface

The foregoing results suggest that pitting is associated with a particular stage in the development of the passive film. Previously, it was found that pitting will not occur readily if growth of the oxide film has already passed the critical stage before the sample is exposed to  $\text{Cl}^-$ -containing solution[6]. In this section it is shown that this result also applies to  $\text{Br}^-$ -induced pitting, and quantitative results are obtained.

In this series of experiments, a 2.99 nm thick passive film was formed by anodizing at 0.2 V for 5 min. in pure borate buffer, using the potential step technique. The sample was removed, rinsed and dried, and then immersed into a borate buffer solution containing  $9.45 \times 10^{-3} \text{ M NaBr}$  with a cathodic galvanostatic current of  $10 \mu\text{A cm}^{-2}$  applied. Reduction was continued for a given length of time before the potential was stepped to 0.2 V. The resulting current transient was compared to that obtained with reduction and anodization in  $\text{Br}^-$ -free borate buffer. Galvanostatic cathodic reduction has been shown to result in a layer-by-layer thinning of the passive film during the first potential arrest[8]. Thus, the amount of the passive oxide film remaining after the cathodic treatment could be varied in a systematic manner.

Figure 4 shows the galvanostatic cathodic reduction profiles obtained in the  $\text{Br}^-$ -containing and  $\text{Br}^-$ -free borate buffer solutions. There is no significant difference in the two curves. Figure 5 shows the

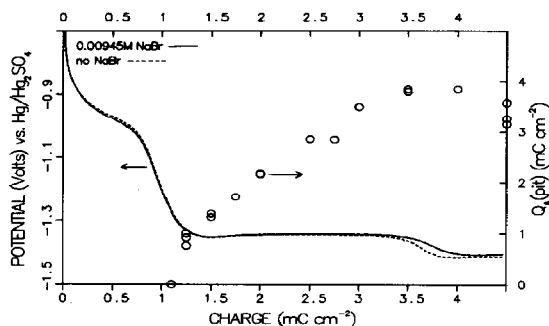


Fig. 4. Cathodic reduction profiles ( $10 \mu\text{A cm}^{-2}$ ) of a pre-formed passive film (anodized in  $\text{Br}^-$ -free borate buffer) in  $\text{Br}^-$ -containing and  $\text{Br}^-$ -free borate buffer solution. The circles show the amount of anodic charge passed prior to pitting during a potential step to 0.2 V, after partial cathodic reduction to the indicated extent.

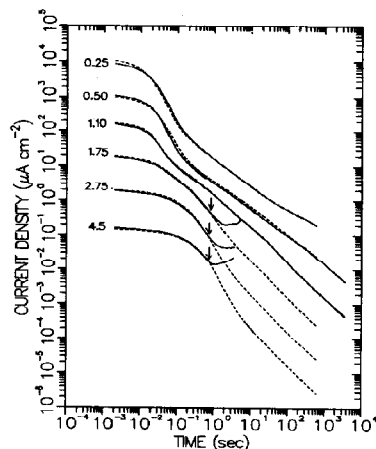


Fig. 5. Log  $i$ -log  $t$  profiles obtained upon stepping to 0.2 V after various extents of partial cathodic reduction in  $\text{mC cm}^{-2}$ , indicated by each curve. The solid curves are the current transients observed for Fe in solutions containing  $9.45 \times 10^{-3} \text{ M NaBr}$  in borate buffer, the dashed curves for Fe in pure borate buffer. The current density scale refers to the top curve, at  $0.25 \text{ mC cm}^{-2}$  of cathodic reduction. For clarity, the lower curves have been displaced by factors of ten. The arrows show the points at which the curves can be seen to diverge.

log  $i$ -log  $t$  profiles obtained at 0.2 V after different extents of cathodic reduction. For reductions of  $1.1 \text{ mC cm}^{-2}$  or less (see footnote in [6]), no deviation of the two curves was observed, indicating pitting was absent. For greater extents of cathodic reduction, multiple pits were present on the surface, consistent with the deviation of the two curves. Three examples are shown in Fig. 5. Despite the fact that the oxide film remaining on the surface is much thinner at  $2.75 \text{ mC cm}^{-2}$  than at  $1.75 \text{ mC cm}^{-2}$ , there is no significant change in the induction time prior to pitting. However, there is a significant increase in the charge passed prior to pitting. The results of a number of such experiments are shown in Fig. 4. Clearly, pitting does not occur with a shorter induction time even though the film is thinner, but instead must await the growth of the oxide to a critical state.

## CONCLUSIONS

Pitting of Fe by  $\text{Br}^-$  in borate buffer solution occurs when a critical state of the passive oxide film is reached within the first 10 s. of anodizing. This state corresponds to a specific thickness of the oxide film, which is dependent on  $[\text{Br}^-]$  but independent of potential. Pitting of Fe is triggered when the passive film develops the outer oxide layer. As the  $[\text{Br}^-]$  is decreased, more of the outer layer is required before pitting can begin. In addition, pitting is unlikely to occur once the critical state has passed, even if the potential is held above the pitting potential. The implications of these results for the mechanism of pitting will be discussed in detail in a forthcoming publication.

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