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AN AES AND SIMS STUDY OF THE INFLUENCE OF CHLORIDE ON THE PASSIVE OXIDE FILM ON IRON

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Abstract—The kinetics of passivation of Fe in pH 8.4 borate buffer solution at 0.0 V have been studied in both the presence and absence of 0.5 M Cl^- . Cl^- has no influence on the decay of the passive current with time over the course of several hours. Oxide films were examined by AES and SIMS for possible Cl^- incorporation into the oxide lattice. Neither technique was able to detect any Cl^- within the film. The same is true even above the pitting potential, which probably indicates that Cl^- incorporation into the oxide film is not a precursor to pit initiation. It also appears that Cl^- does not cause any film thinning.

INTRODUCTION

There is still controversy concerning the composition and structure of the passive oxide film on Fe and the mechanism by which the film breaks down. This situation persists in spite of the fact that many modern surface-analytical techniques have recently been brought to bear on the problem. In particular, there is a lack of agreement in the literature on the influence of Cl^- on the passive film [1–5]. According to some workers [1–3, 5], Cl^- causes a thinning of the passive film and this can lead to pitting if the potential is above a critical value. Another popular hypothesis for oxide film breakdown involves incorporation of Cl^- into the film lattice and a subsequent local depassivation [6]. While Auger electron spectroscopy (AES) [2] and X-ray photoelectron spectroscopy (XPS) [5] investigations did not reveal any Cl^- in the passive film exposed to Cl^- -containing solution, secondary ion mass spectrometry (SIMS) work [3, 4] seemed to indicate an increasing amount of Cl^- incorporation with time of polarization. Since SIMS has a very high sensitivity for Cl^- compared with AES and XPS, the results reported in the literature may not be contradictory. There are therefore still questions concerning the existence of Cl^- in the passive film and its role in local film breakdown and pit initiation.

In the present investigation, the influence of Cl^- on the passive oxide film formed on Fe in borate solution was studied both below and above the pitting potential. The objective was to gain a better understanding of the role of Cl^- on film formation and breakdown. AES and SIMS were used in an attempt to detect Cl^- in the oxide film, in much the same way as was previously done for Ni in $\text{Cl}^-/\text{SO}_4^{2-}$ solution [7].

EXPERIMENTAL

Pure zone-refined Fe (major impurities in atomic ppm: 30 O, 16 C, 8 Cr, 5 P, 5 S, 0.4 Si) was cut into discs of ~ 9 mm diameter. The anodizing solution was a deaerated equivolume mixture of 0.075 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ and 0.3 M H_3BO_3 [8] with a pH of 8.4, and the reference electrode was

Hg/Hg₂SO₄/0.1 M Na₂SO₄ (0.66 V *she*). All potentials quoted in the paper are with respect to the standard hydrogen electrode. The Cl^- concentration was adjusted by appropriate additions from a 4 M NaCl/borate stock solution. The temperature was $25 \pm 1^\circ\text{C}$.

The electrode pretreatment consisted of a 600-grit mechanical polish followed by electropolishing in a 20:1 acetic/70% perchloric acid mixture, and a 10 min cathodic polarization at -0.8 V to remove the air-formed film prior to an experiment. The potential was then stepped to the desired value in the passive potential range. The passive region extends from approximately -0.25 V to 0.85 V. After an experiment the sample was washed with doubly distilled water and blown dry with high-purity compressed air.

The surface analysis was carried out in a PHI 590 SAM (scanning Auger microprobe) system with a SIMS II attachment. For AES a primary electron beam of 300 nA and 5 keV at 30° off normal rastered over an area of 1 mm^2 and a CMA modulated at 4 eV were used. The peaks: Cl 181 eV, O 510 eV and Fe 650 eV were used. Details regarding the quantification have been published previously [9]. SIMS was conducted with 40% gating using the masses 18 (O^-), 19 (OH^-) and 35 (Cl^-). A PHI 04-303 differentially pumped ion gun with < 6.7 mPa Xe at 1 keV was used for sputtering. The ion beam was rastered over $1.5 \times 1.5 \text{ mm}^2$ for AES or $2.5 \times 3 \text{ mm}^2$ for SIMS; the incident angle was 33° with respect to the surface normal. The pressure at the sample during sputtering was ~ 500 nPa; the vicinity of the sample was pumped by a cold plate at 20 K [10].

Each batch of samples was analysed the same day and an electropolished sample was used for calibration purposes. The film on electropolished Fe consists of 1.7 nm of Fe₂O₃ [11].

RESULTS AND DISCUSSION

Figure 1 shows the decrease of current with time for Fe specimens polarized at 0.0 V in borate buffer solution containing 0 M and 0.5 M Cl^- . For comparison, the result obtained at 0.7 V in the absence of

Fig. 1. Current density–time curves obtained upon stepping the potential of an oxide-free Fe electrode to the desired anodic value in pH 8.4 borate buffer with and without 0.5 M Cl^- .

Fig. 2. Auger electron spectrum of an Fe specimen polarized at 0.0 V for 4.5 h in pH 8.4 borate buffer solution containing 0.5 M Cl^- . The position of the Cl peak and other major peaks are indicated. (Electron beam 5 keV with a current ~ 300 nA; modulation 4 eV peak-to-peak.)

Cl^- is also given. In all three cases the current decreases hyperbolically with time at the same rate, independent of potential as previously reported[12], and with no detectable influence of 0.5 M Cl^- .

To examine any influence of Cl^- in solution on the nature of the passive oxide film, Auger spectra were obtained from the films formed at 0.0 V. The spectrum from a film formed at 0.0 V for 1 h in the presence of 0.5 M Cl^- is shown in Fig. 2. There is no Cl^- signal evident in the spectrum, indicating that any Cl^-

present is below the limit of detection of the technique, namely 0.1 at. %. Auger depth profiles, shown in Fig. 3, indicate that films formed in Cl^- -containing and Cl^- -free solutions are essentially the same in terms of both composition and thickness. The oxide thickness is 2.2 nm in both cases as determined by thin-film analysis[13].

The presence or absence of Cl^- in the oxide film was next checked by SIMS. Figure 4 shows the raw SIMS depth profile for a sample polarized for 1 h at 0.0 V in

Fig. 3. Auger depth profiles of passive films formed on Fe after passivation at 0.0 V in borate buffer with and without 0.5 M Cl^- . The lines representing the results of both experiments are indistinguishable. Atom % concentrations were calculated from the measured peak-to-peak heights. (Sputtering was by 1 keV xenon.)

Fig. 4. Raw SIMS depth profile of the passive film formed on Fe at 0.0 V for 1 h in borate buffer with 0.5 M Cl^- showing both O^- and Cl^- signals. (Sputtering was by 1 keV xenon.)

the presence of 0.5 M Cl^- . Figure 5 gives the ratio of the negative chlorine signal (35 amu) with respect to negative oxygen (16 amu) as a function of depth for a variety of specimen treatments. While there is some scatter of results for the outermost part of the films, the profiles in Fig. 5 are essentially all the same and independent of whether or not Cl^- was present in the borate buffer solution. The increase in signal ratio at greater depths is simply due to the fact that the film/metal interface has been reached. Quantification of the SIMS data requires a sensitivity factor for Cl^- , and this is not presently available for an iron oxide matrix. However, if it is assumed that the Cl^- sensitivity factor is the same as that found for the Cl^- in NiO [7], then the amount of Cl^- present in these iron oxide films is < 0.001 at. %. It is therefore apparent that the amount of Cl^- incorporated into passive films

on Fe is negligible even when films are formed in 0.5 M Cl^- solution. The fact that the SIMS data is the same for films formed in the presence or absence of Cl^- suggests that the observed Cl^- signals are simply due to a very small amount of Cl^- surface contamination, perhaps arising from air exposure of the samples or being due to a low-level Cl^- background in the UHV instrument. The results are in contrast to those observed with nickel electrodes where substantial Cl^- incorporation occurred in both SO_4^{2-} and borate solutions[7]. It appears therefore from the results that Cl^- is not compatible with an iron oxide lattice. The findings are consistent with the observed lack of influence of 0.5 M Cl^- on the passivation behaviour (Fig. 1); if Cl^- could be incorporated into the iron oxide lattice it would probably influence the i - t characteristics. SIMS experiments, similar to those

Fig. 5. SIMS $\text{Cl}^- / (\text{Cl}^- + \text{O}^-)$ signal ratio depth profiles for oxide films on Fe after passivation in borate buffer with and without 0.5 Cl^- , after cathodic reduction in the same solution and after electropolishing (EP). (Sputtering was by 1 keV xenon.)

Fig. 6. AES oxygen depth profiles of oxide films on Fe formed after electropolishing (EP), after cathodic reduction and after polarization for 1 h at 0.7 V in borate buffer without Cl^- followed by polarization for 2 h at 0.0 V in borate buffer with and without 0.5 M Cl^- . As a reference the profile of the film formed after 1 h at 0.7 V is also given. (Sputtering was by 1 keV xenon.)

reported in Ref. 10, also indicated that oxide films formed either in the presence or absence of Cl^- were free of OH^- .

The pitting potential for Fe in pH 8.4 borate solution containing 0.5 M Cl^- is 0.05 V and caution had to be exercised when working above this potential in order to avoid massive pitting and/or the possibility of precipitated products on the surface. In an attempt to determine the influence of Cl^- on the character of the passive film above the pitting potential, samples were polarized at 0.15 V for 5 s and 30 s, the time being kept short to avoid extensive pitting. AES analysis of these films indicated that there was no Cl^- incorporation, in agreement with the results observed below the pitting potential. It thus appears that Cl^- incorporation into the oxide film lattice and pit initiation do not

go hand in hand, and other explanations have to be found for the role of Cl^- in pit initiation. Finally, a series of experiments was designed to investigate the possibility that Cl^- catalyses the dissolution of the passive oxide film, as has been suggested by some workers as the mechanism of Cl^- -induced pit initiation [1, 14, 15]. An oxide film was formed for 0.7 V for 1 h in the absence of Cl^- and the potential was then stepped to 0.0 V in both the presence and absence of 0.5 M Cl^- . The polarization was continued at 0.0 V for 2 h, after which AES oxygen depth profiles were obtained (Fig. 6). For reference purposes, profiles for a sample polarized at 0.7 V for 1 h and for two air-formed films are also given. The films on electrodes polarized for an additional 2 h at 0.0 V in solutions with and without Cl^- are identical, suggesting that the

presence of Cl^- in solution has no overall influence on the dissolution characteristics of the passive oxide film. These films are possibly slightly thinner than the film formed at 0.7 V, and $\sim 1/3$ thicker than the air-formed films. No Cl^- could be found in any of the films.

CONCLUSIONS

(1) Below the pitting potential, the presence of Cl^- in solution has no influence on the kinetics of passive film growth and development, as indicated by the $i-t$ profiles.

(2) AES of oxide films formed in 0.5 M Cl^- solution shows that the films are Cl^- free. The films display SIMS depth profiles which are identical to those obtained from films formed in non- Cl^- solution, demonstrating that Cl^- does not incorporate into the passive oxide film. Identical results are obtained when the films are formed for short time periods above the pitting potential. It thus appears that Cl^- incorporation into the oxide film is not a precursor or cause of pit initiation.

(3) Experiments performed below the pitting potential show that the presence of Cl^- does not cause thinning of the passive film in borate solution.

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