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Publisher's version / Version de l'éditeur:

Corrosion Science, 35, 1-4, pp. 13-18, 1993

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THE GROWTH AND STABILITY OF PASSIVE FILMS

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Abstract—This paper will consider the growth and breakdown of passive oxide films on metals and alloys. Emphasis is placed on the use of surface-analytical techniques, particularly secondary ion mass spectrometry (SIMS) to characterize oxides formed on Fe and Fe–Cr alloys in ^{18}O -containing solutions, and to determine the oxide's stability to subsequent air exposure. It is found that the stability of passive films towards air exposure decreases with increasing Cr content of the alloy. Films formed on Fe in the passive potential range in borate buffer solution are stable towards *ex situ* exposure, whereas films formed on Fe–26Cr alloys are not stable to air exposure after passivation at any potential in the passive region. This result has implications for examining the thickness and composition of passive films on high-Cr alloys using *ex situ* techniques. Passive films play a critical role in the initiation of pitting and the processes which influence film breakdown on Fe in Cl^- -containing solutions are discussed. The results indicate that pitting is associated with a critical stage in the development of passive oxide films.

INTRODUCTION

THE NATURE of the passive oxide film on Fe, Fe–Cr alloys and stainless steels has been the subject of investigation for many years. *Ex situ* surface-analytical techniques such as secondary ion mass spectrometry (SIMS), Auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS) provide useful information regarding the nature and chemical composition of these electrochemically-formed films, and SIMS analysis of oxides formed in ^{18}O -containing solutions can be used to examine transport processes which take place during oxide growth as well as the oxide's stability to subsequent air exposure.^{1,2} This paper will emphasize the use of SIMS to examine oxides formed on Fe and Fe–Cr alloys.² The important role that anodic films play in the initiation of pitting will also be discussed.

EXPERIMENTAL METHOD

Fe and Fe–Cr electrodes were prepared as described previously.² Samples were electropolished before each experiment. Potentials were measured relative to a $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ reference electrode. The ^{18}O /SIMS technique for labelling and analysis is detailed elsewhere.²

EXPERIMENTAL RESULTS AND DISCUSSION

Cathodic reducibility of films

^{18}O /SIMS can be used to indicate the cathodic removal of oxide films on Fe and Fe–Cr alloys, e.g. the air-formed film can be produced by rinsing, and the passive film by anodizing in ^{18}O -enriched solution and these films can be subsequently reduced in non-enriched solution. The electropolish film and passive films on Fe in pH 8.4 borate buffer could be removed by potentiostatic^{1,3} or galvanostatic⁴ cathodic reduction at -1.46 V or $10\text{ }\mu\text{A cm}^{-2}$, respectively. However, for Fe–6Cr and

Fe–26Cr alloys the electropolish film could not be removed in borate solution, even with more vigorous cathodic treatment.² About 0.2–0.3 nm of oxide (~ 1 monolayer) remained on the surface. In contrast, samples reduced in 0.5 mol dm⁻³ H₂SO₄ according to the procedure of Frankenthal⁵ [10 min at -1.16 V (cathodic region), followed by 1 min at -0.94 V (active region)] showed an ¹⁸O level of 0.2% (the natural abundance) indicating that the electropolish film had been completely removed by electrochemical treatment in a more aggressive solution.

For film removal on Fe, the cathodic reduction profile showed two arrests, the first likely due to the reduction of the outer γ -Fe₂O₃ and the second representing reduction of Fe₃O₄.⁴ ¹⁸O/SIMS gave a measure of the oxide thickness as a function of cathodic reduction, and indicated that the initial stage of reduction resulted in a layer-by-layer rather than a patchwise reduction of the film.

Stability of passive films to air exposure

The air stability of passive films on Fe and Fe–Cr alloys can be determined from the analysed ¹⁸O level in the films compared with the known solution content.² A lower level than the solution content indicates instability to air exposure. The decrease in ¹⁸O concentration may be due to either film thickening upon air exposure, or to exchangeable oxygen in the film. *A priori*, it is not possible to distinguish between these possibilities. For Fe, where the prior electropolish film can be completely cathodically reduced, ¹⁸O/SIMS depth profiles of anodic films formed in ¹⁸O-enriched borate buffer showed an ¹⁸O level equal to that of the solution over most of the passive potential range. Only at very low potentials did the enrichment level decrease, indicating that the film thickened (and was therefore diluted with ¹⁶O) upon air exposure. The results are summarized in Fig. 1(a), where the total thickness (obtained from the SIMS interface using the Fe₃⁺ signal), and the corrected thickness, calculated from the film's ¹⁸O concentration (averaged over the total film thickness), are plotted as a function of anodic potential. Clearly, the film is influenced by air exposure only at -0.5 V and below. In this case it seems most likely that the films thickened upon air exposure because a constant thickness equal to the air formed thickness, ~ 1.7 nm, is reached upon air exposure at low potentials. This finding may well explain published Mössbauer data of Eldridge and Hoffman⁶ for films formed at low potentials (-0.75 V). Their Mössbauer parameters (particularly the isomer shift) were different for *in situ* and *ex situ* films and the likely reason is that the films underwent further growth upon air exposure and the spectral changes reflect this additional oxidation to a constant thickness, as seen in Fig. 1(a). At higher potentials where the films are stable in air, no difference was observed by Eldridge and Hoffman between the *in situ* and *ex situ* parameters of passive films.

The mechanism of oxide growth on Fe can be studied by forming a film in non-enriched borate at e.g. -0.3 V where the film is air stable and then stepping the potential to say 0.1 V in ¹⁸O-enriched solution for additional growth.³ SIMS profiles show that the additional oxide grows by inward oxygen transport, likely by both lattice and short-circuit diffusion paths.

Thickness measurements from SIMS for Fe–6Cr alloys² are shown in Fig. 1(b). The error bar represents a thickness of 0.2 nm, the amount of unreduced prior film. Points separated by a distance greater than the error bar indicate samples where a decrease in enrichment is observed beyond that which would be expected due to the

FIG. 1. Thickness of the passive film on (a) Fe; (b) Fe-6Cr and (c) Fe-26Cr as determined from $^{18}\text{O}/\text{SIMS}$. The samples were passivated for 1 h in $\sim 8\%$ ^{18}O -enriched borate buffer solution. The circles indicate the thickness obtained after correction for the overall ^{18}O enrichment level in the film. The 'error bars' show a thickness of 0.2 nm in (b) and 0.3 nm in (c), or the difference that would be expected between the corrected and uncorrected thicknesses since 0.2 nm or 0.3 nm of prior film was not reduced. Sputtering was with 1 keV Xe.

irreducibility, thus indicating instability to air exposure. It is seen in Fig. 1(b) that the passive film on Fe-6Cr is influenced by air exposure at -0.2 V and below. The film, therefore, is stable to air exposure over a smaller potential range than was the case for Fe.

Data for Fe-26Cr alloys² are shown in Fig. 1(c). The error bar of 0.3 nm represents the upper limit for the amount of unreduced film. Clearly, the passive film on Fe-26Cr is not stable at any potential in the passive region. As seen in Fig. 1(b) and (c) for the Fe-Cr alloys, the corrected and uncorrected thicknesses steadily diverge as the potential becomes less anodic. In contrast to Fe, no constant thickness after air exposure is observed.

The above results have important implications for *ex situ* analysis of surface films on Fe-Cr alloys. Clearly, caution should be exercised in the interpretation of the data as the films may well have changed in the interval from removal from solution to installation in the UHV systems. As seen in Fig. 1, the results for the Fe-Cr alloys are quantitatively quite different from those for Fe. In the case of Fe, the unstable films

thicken up to a constant thickness, whereas for the Fe–Cr alloys, the corrected and uncorrected thicknesses steadily diverge as the potential becomes less anodic. An explanation which would be consistent with this behaviour is that the instability of passive films on Fe–Cr alloys to air exposure reflects the ability of the film to adapt to changing environmental conditions. For example, it is possible that some hydroxyl in the passive film on Fe–Cr alloys^{7,8} readily exchanges with water in the air (or water in the rinse solution, or even with water in the passivating solution). The presence of exchangeable hydroxyl would be consistent with the decrease in ¹⁸O enrichment observed by SIMS. A continuous increase in the concentration of exchangeable hydroxyl would explain the steady divergence of the corrected and uncorrected thicknesses with decreasing potential. In this model, which is similar in some respects to the views of others, including e.g. Okamoto,⁹ Revesz and Kruger,¹⁰ the passive film on Fe–Cr alloys is envisaged as flexible and labile. The ability of the passive film to accommodate environmental changes may be a factor in the superior corrosion resistance of Fe–Cr alloys. In contrast, the passive film on Fe, which contains no hydroxyl ions,⁷ is stable to air exposure over most of the passive region. This film is conceived to be a rigid, inflexible γ -Fe₂O₃/Fe₃O₄ layer which would, in fact, break down under a drastic change of environmental conditions, rather than subtly rearrange to respond to changing conditions.

The presence of Cr(VI) in the passive film on Fe–Cr alloys has been postulated for many years. Difficulties in observing its presence by *ex situ* techniques may well be associated with its instability to air exposure. In collaboration with scientists at Brookhaven National Laboratory, *in situ* X-ray absorption near edge spectroscopy (XANES) has been used to establish the presence of Cr(VI) in the anodic oxide film on Fe–26Cr alloy.¹¹ The production of Cr(VI) was associated with the transpassive wave in the cyclic voltammogram, and its reduction with a corresponding reduction wave. The formation and reduction of Cr(VI) was reversible and only small amounts of Cr(VI) were detected in the film. Cr(VI) in the passive film was not indefinitely stable and was completely absent after many hours of air exposure. This is another example of the dynamic nature of films on Fe–Cr alloys which certainly undergo change on air exposure.

Breakdown of passive films

Recent work in our laboratory on Fe in neutral pH buffer solutions has indicated that the nature of the passive film is critically important in determining pit initiation.^{12,13} Pit initiation on Fe was found to be associated with a particular stage in the development of the passive film, corresponding to a specific film thickness, which was dependent on the halide ion concentration (Cl[−] or Br[−]), but not on the anodic potential. This critical stage of development was characterized by the amount of anodic charge which had passed prior to pitting.

Figure 2(a) shows some potentiostatic current transients for Fe in solutions with and without added Cl[−]. Below the pitting potential, the two curves are coincident. Above the pitting potential, after a certain anodization time, the two curves are seen to deviate. The charge passed to this point of deviation is defined as $Q_A(\text{pit})$. As seen in Fig. 2(b), $Q_A(\text{pit})$ remains relatively constant with potential even though the induction time for pitting decreases as the potential increases. As studied in complementary cathodic reduction experiments, once the development of the film had passed the critical stage, pitting became very unlikely, even if the potential was

FIG. 2. (a) Current transients for various potentials in the passive region. The solid curves are for Fe in solution containing 9.45×10^{-3} M NaCl in borate buffer and the dashed curves are for Fe in pure borate buffer. The current density scale refers to the top curve, at 0.1 V. For clarity, at lower potentials the curves have been displaced by factors of 10. The arrows show the points at which the curves can be seen to diverge, with the number referring to the integrated anodic charge, in mC cm^{-2} , which has passed to this point. (b) This anodic charge passed [$Q_A(\text{pit})$] before pitting occurred in 9.45×10^{-3} M NaCl as a function of anodizing potential. (c) SIMS [$\text{Cl}^-/(\text{Cl}^- + \text{Fe}^{16}\text{O}_2)$] signal depth profiles for films on Fe in Cl^- -free and Cl^- -containing borate buffer solutions. The data have been truncated at the oxide-metal interface. (d) Average values of $Q_A(\text{pit})$ as a function of [halide] in various buffer solutions.

held above the pitting potential. SIMS has been used to monitor the thickness and the halide content of the film during growth.¹⁴ During the induction time to pitting, the film was found to grow at the same rate in halide-containing and halide-free solutions and no incorporation of halide was detected in the film during the induction time to pitting.¹⁴ Figure 2(c) illustrates the Cl^- concentration in passive films formed in Cl^- -containing and Cl^- -free borate buffer under various conditions as determined by SIMS. Cl^- was present only on the surface of the samples, and its concentration did not depend on the presence of Cl^- in the solution, and whether pitting had or had not occurred.

The above results strongly suggest that the onset of pitting is associated with a particular combination of film thickness and [halide]. This is illustrated in Fig. 2(d), which shows average values of $Q_A(\text{pit})$, obtained for a variety of buffer solutions and

halide ion concentrations. Clearly, $Q_A(\text{pit})$ depends on the [halide], is independent of solution pH (between 7.4 and 8.4), and is strongly dependent on the identity of the solution species, both the nature of the halide ion (Cl^- or Br^-) and of the supporting buffer (borate or acetate). A larger value of $Q_A(\text{pit})$ is associated with a less aggressive solution, so Cl^- is seen to be more aggressive than Br^- , while 1 M acetate inhibits pitting compared with 0.4 M borate. Again, it is interesting to note that while chloride is not incorporated into the oxide film on Fe, it is readily incorporated into oxides formed on Fe–Cr alloys.¹⁵ This chloride incorporation into the film on Fe–Cr influences the open-circuit behaviour but is not a precursor for pit initiation.

CONCLUDING REMARKS

The technique of ^{18}O enrichment and SIMS analysis is a powerful method of studying oxide film growth, removal and film stability towards air exposure and breakdown. It was found that the *ex situ* stability of the passive film on Fe–Cr alloys decreased with increasing Cr content, which means that *ex situ* surface-analytical techniques must be used with considerable caution in investigating the composition of passive films on high Cr alloys. For Fe, the onset of pitting was observed to be associated with a particular combination of thickness of the passive oxide film and [halide], and not by a specific interaction between halide ions and the bare Fe surface. Thus, Fe is susceptible to pitting if, and only if, the oxide has reached a certain critical stage of growth.

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