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INFLUENCE OF SOLUTION CHEMISTRY ON DISSOLUTION OF ARTIFICIAL PASSIVE FILMS

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The dissolution behavior of artificial Fe, Cr, and Fe/Cr passive films (sputter-deposited Fe/Cr oxide films on inert substrates) was studied by in situ X-ray absorption near edge spectroscopy (XANES). Low pH and presence of halides (Cl⁻ and F⁻) accelerate the dissolution due to the solubility of Fe oxides in these solutions. The presence of Fe(2+) in the oxide film strongly accelerates dissolution in acidic solution. For mixed Fe/Cr oxides, F⁻ leads to a selective dissolution of Fe oxide. Cr₂O₃ is not attacked by fluoride; hence if mixed oxide films contain a sufficient amount of Cr oxide, dissolution stop is obtained, probably by surface enrichment of Cr oxide. The composition of the oxide film is also crucial for its electrochemical stability. An increasing Cr₂O₃ content increases the resistance against reductive dissolution, increases the resistance in aggressive solutions (low pH, halides), but decreases the resistance against oxidative dissolution.

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INTRODUCTION

One key factor determining the stability of the passive state is the chemical and/or electrochemical dissolution behavior of passive films. However, most experimental approaches probe the behavior of an alloy/film system and hence it is difficult to obtain direct information on the properties of the passive film itself. This is the case especially in the presence of aggressive species in the solution, which can lead to pitting and thus to an attack of the underlying alloy. Therefore, in the present work, the dissolution behavior of oxide films was studied using thin, sputter-deposited oxide films ("artificial passive films") on an inert substrate (Ta). This approach is similar to earlier work by Sugimoto et al. (1, 2), who studied in acidic solutions the dissolution of thin Fe₂O₃-Cr₂O₃ films prepared by metalorganic chemical vapor deposition. In previous work we investigated the effect of the Cr₂O₃ content of mixed Fe-Cr oxide films on the electrochemical behavior (3), in continuation of previous work on thin iron- (4, 5) and chromium-oxide layers (6). In these investigations, in situ X-ray absorption near edge spectroscopy (XANES) measurements were carried out during the electrochemical experiments to monitor dissolution and changes in the valence state as a function of potential and solution chemistry. It was found that the electrochemical dissolution behavior strongly depends on

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the oxide composition. At low Cr oxide concentrations and with pure Fe oxide, the films dissolve when cathodically polarized, and are resistant to dissolution, when polarized in the anodic direction. At high Cr_2O_3 concentrations and with pure Cr oxide, dissolution occurs when the films are anodically polarized, but the films are stable against cathodic dissolution. In the intermediate Cr oxide concentration range, the oxides neither dissolve under anodic nor cathodic polarization. Hence, a critical composition range exists for the dissolution resistance of the oxide. An acidic environment was found to accelerate both anodic and cathodic dissolution, associated with chemical dissolution of the iron oxide. In the present work, the effect of solution chemistry on the dissolution behavior of such artificial passive films is studied in more detail.

EXPERIMENTAL

The oxide films were prepared by r.f. sputter deposition using oxide targets (Fe_2O_3 , Cr_2O_3 , $\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$ with $[\text{Cr}] = 10, 20, 50, 90\%$). The r.f. sputtering system has been previously described elsewhere (7). Before each deposition, the sputter chamber was evacuated to a pressure of 4 to 7 x 10^{-4} Pa. The deposition was carried out in pure Ar (99.998%). The oxide films were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and analytical transmission electron microscopy (TEM). The composition of the oxide film is near to that of the targets, with a slightly reduced Cr-content. All mixed oxides, as well as pure Cr_2O_3 show an amorphous structure, whereas Fe_2O_3 is deposited in a crystalline structure ($\alpha\text{-Fe}_2\text{O}_3$). Details of the characterization of the samples are given elsewhere (8, 9).

The oxide films were sputter-deposited onto Mylar (6 μm), which had been previously coated by sputter-depositing a thin layer of tantalum (20 to 30 nm) to establish a back contact to the samples. The electrochemical cell has been described previously (10, 11). XANES measurements were carried out *in situ* during the electrochemical treatment of the samples. The electrolyte solutions were continuously deaerated with a stream of Ar bubbles. The potentials were measured and are reported against a saturated mercury sulfate reference electrode (MSE, $\approx +0.4$ V (SCE)). A platinum wire was used as a counter electrode. The solutions were prepared from reagent grade chemicals and distilled water (Millipore Q, 18 $\text{M}\Omega$).

XANES measurements were carried out at Beamlines X10C and X19A at the National Synchrotron Light Source at Brookhaven National Laboratory. The energy scale was calibrated by taking the peak in the first derivative of a spectrum from an iron foil to be the position of the Fe K edge at 7112 eV and for chromium foil the Cr K edge at 5989 eV. The monochromator energy was periodically checked and was found to be very stable during the measurements. Spectra at the Cr and Fe K edges were collected sequentially. Data was collected with a 0.2-0.5 eV step size in the region near to the edge. The edge position was defined as the energy value at the half-height of the peak after background subtraction. The edge height was determined at an energy 100 eV above the edge after the background was subtracted out of each spectrum by extrapolating the curve fitted to the signal below the edge. *In situ* measurements on the electrochemically controlled samples were made using

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fluorescence detection set up with a Canberra 13-element solid-state detector. Further details of the geometry are given in reference (10) .

RESULTS AND DISCUSSION

Effect of solution pH

Figure 1 shows an example of the dissolution behavior of a thin Fe_2O_3 film during galvanostatic reduction in different solutions; shown is the thickness of the sample determined from the edge height of the XANES spectra as a function of charge density. Clearly, dissolution is accelerated in the acidic solution, whereas in the alkaline solution no change in the thickness takes place. A detailed study of the spectral changes (edge position) during the experiment revealed that the accelerated dissolution in the acidic solution is due to a chemical dissolution of the reduced iron oxide in addition to electrochemical dissolution, whereas in the alkaline solution a solid-state conversion into a ferrous hydroxide/oxide with no dissolution takes place. At potentials anodic to the reduction region ($\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$), Fe_2O_3 and Fe_3O_4 thin films dissolve chemically in strong HCl and H_2SO_4 (5) . The chemical dissolution rate is strongly pH-dependent: the higher the acid concentration, the faster the dissolution.

For pure Cr oxide films, dissolution was never found under cathodic polarization, independent of the electrolyte composition. On the other hand, under anodic polarization oxidative dissolution ($\text{Cr}^{3+} \rightarrow \text{Cr}^{6+}$) takes place. As illustrated in Fig. 2, the kinetics of oxidative dissolution of pure Cr oxides was found to be independent of pH. In all solutions studied, the oxidation reaction took place with a 100% current efficiency.

In the case of mixed oxides, the dissolution behavior strongly depends on the composition of the oxide film. Oxides with a high Cr oxide content are generally prone to oxidative dissolution, whereas oxides with a high Fe oxide content dissolve under cathodic polarization. A comparison with the pure iron and chromium oxides shows that even the addition of small amounts (10%) of the non-dissolving species retards dissolution. In borate buffer (pH 8.4), the mixed oxide films do not suffer from reductive or oxidative dissolution in a wide composition range. This is illustrated in Fig. 3 showing the dissolution rates for Fe/Cr oxide films as a function of the Cr_2O_3 content of the film during galvanostatic oxidation and reduction ($\pm 10 \mu\text{A}/\text{cm}^2$) in borate buffer. The dissolution rates were determined from the drop of the edge height of the XANES spectra during the experiment.

Figure 4 shows the effect of solution composition (borate buffer / 0.1 M H_2SO_4) on the dissolution rates of mixed Fe/Cr oxides as a function of the Cr oxide content during galvanostatic reduction (4a) and oxidation (4b). The composition range of high stability is strongly diminished in the acidic solution (0.1 M H_2SO_4). This can be attributed to chemical dissolution of iron oxide.

Looking at the XANES spectra in detail during reduction reveals more information on the dissolution mechanism. Figure 5 shows the Fe edge with an expanded energy scale near to the edge region for a 10% Cr_2O_3 - 90% Fe_2O_3 sample during galvanostatic

reduction in borate buffer (5a) and in 0.1 M H_2SO_4 (5b). In order to compare the edge position for the dissolving sample, the spectra were normalized to unity edge height after background subtraction. Clearly, in the case of reduction in borate buffer, dissolution is accompanied with a shift of the edge position into the negative direction indicating a decrease of the average valency of the Fe oxide. However, during reduction in the acidic solution, almost no edge shift is found. Hence, the acceleration of dissolution in the acidic solution is due to the chemical dissolution of the reduced $\text{Fe}(2+)$ species. This behavior is very similar to the behavior of pure Fe_2O_3 films. In the case of higher Cr_2O_3 -containing oxide films, where no dissolution takes place during reduction in the acidic solution, an identical edge shift is found in borate buffer and in 0.1 M H_2SO_4 .

The role of $\text{Fe}(2+)$ in the oxide film in decreasing its stability has been already shown for pure iron oxide films, comparing the dissolution behavior of sputter-deposited films of Fe_3O_4 and Fe_2O_3 (5). In the case of mixed Fe/Cr oxide films, it is possible to convert the Fe species of the film into a lower valent state, since depending on the Fe/Cr ratio dissolution of the $\text{Fe}(2+)$ species does not take place. Hence, the dissolution characteristics of mixed Fe/Cr oxide films with a varying amount of $\text{Fe}(2+)$ in the oxide can be investigated. The XANES data enables a simultaneous monitoring of dissolution and average valency. An example of such a measurement is shown in Figs. 6,7. In Fig. 6 the XANES spectra are shown for a 20% Cr_2O_3 - 80% Fe_2O_3 sample during anodic potential steps in 0.1 M H_2SO_4 . Polarization from the open-circuit potential up to +600 mV does not lead to any dissolution. However, at higher anodic potentials dissolution of Fe is observed. The Cr edge XANES spectra show that at these potentials oxidative dissolution of Cr oxide takes place, and this results in a co-loss of the otherwise insoluble Fe oxide species. However, if the Fe oxide species in the oxide film is first converted into $\text{Fe}(2+)$ as seen from the edge shift during reduction in borate buffer (Fig. 7), then a subsequent exposure to 0.1 M H_2SO_4 at potentials lower than the Cr oxidative dissolution range leads to a fast dissolution of the Fe oxide.

Figure 8 shows a summary of a similar experiment on a 50% Cr_2O_3 - 50% Fe_2O_3 sample. This sample was again first reduced in borate buffer leading to a conversion of $\text{Fe}(3+)$ to $\text{Fe}(2+)$ without dissolution, and then exposed to 0.1 M H_2SO_4 . Subsequently, the potential was anodically stepped in 100 mV steps. In Figure 8, the edge height and edge position are shown as a function of potential during the anodic steps in H_2SO_4 . Clearly, dissolution of Fe takes place as long as the edge position indicates the presence of $\text{Fe}(2+)$ in the oxide. After all of the Fe has been oxidized to $\text{Fe}(3+)$, no further dissolution takes place. Hence, not only the Fe/Cr ratio in the oxide but the valency of the iron oxide as well has a major influence on the stability of the oxide film.

Effect of aggressive anions

Since halide anions lead to localized breakdown of passivity, it is of an interest to study their effect on the dissolution behavior of the oxide film. An XPS study by Khalil, Haupt and Strehblow on the effect of halide ions on the passive film on Fe has shown that a pronounced thinning of the passive film occurs in solutions containing Cl^- , Br^- , and I^- (12). Support for the dissolution of the passive film on iron in the presence of Cl^- in the solution was also given by a rotating ring-disc study by Heusler and Fischer (13). In the present work, the influence of Cl^- and F^- in the electrolyte on the dissolution behavior of

artificial passive films was studied. It is of a special interest to compare the effect of these halide anions, since it is well-known that a general attack of Fe takes place in fluoride solutions, whereas chloride leads to localized breakdown of iron passivity (14-16).

Figure 9 shows a comparison of the Fe edge XANES spectra during galvanostatic reduction of 10% Cr_2O_3 - 90% Fe_2O_3 oxide film in borate buffer containing either 1 M NaCl (9a) or 1 M NaF (9b). A strikingly faster dissolution takes place in the presence of fluorides in the solution. The remarkably higher dissolution rate of the oxide films in presence of fluoride as compared to chloride may be due to the significantly higher tendency for complex formation of $\text{Fe}(3+)$ by F^- than by Cl^- (17).

In Fig. 10, the spectra of Fig. 9 are shown normalized and with an expanded energy scale near to the edge. Clearly, in both cases an edge shift towards more negative energies is found during the reduction. In contrast to this, as shown above, in an acidic solution almost no edge shift was found. This is in agreement with a remarkably higher solubility of $\text{Fe}(2+)$ species in acidic solutions as compared to $\text{Fe}(3+)$ (18). However, the behavior in the halide solutions suggests that compared with protons, a less specific effect of halides on $\text{Fe}(2+)$ than on $\text{Fe}(3+)$ takes place. For $\text{Fe}(2+)$ only little data is found concerning the halide complex formation; however the values reported in ref. (17) are in a similar range for $\text{Fe}(2+)$ and $\text{Fe}(3+)$. Hence, the increased dissolution rate of the oxide films by halides is due to complexation of both $\text{Fe}(2+)$ and $\text{Fe}(3+)$.

In Fig. 11, the influence of an addition of NaCl and NaF in the borate buffer on the dissolution rate during reduction is shown as function of the Cr_2O_3 content of the oxide film. The dissolution rates were determined from the drop of the XANES edge height during galvanostatic reduction experiments. For pure Fe_2O_3 , no acceleration of reductive dissolution is observed. However, it has been shown elsewhere that chemical dissolution of Fe oxide at potentials above the reductive dissolution region is enhanced in presence of Cl^- in acidic solutions (5). Also addition of NaF in acidic solutions very strongly accelerates dissolution of Fe_2O_3 . Hence, it is not a priori clear, why no effect of halide ions on the reductive dissolution rate could be found. However, in the case of mixed oxide films (which show a significantly lower dissolution rate in borate buffer as compared with pure Fe_2O_3) presence of Cl^- and even stronger F^- accelerates dissolution. In the case of pure Cr oxide, dissolution was found to be independent of the anion present in the solution ($\text{F}^-/\text{Cl}^-/\text{SO}_4^{2-}$). Thus the increase in the dissolution rate by halides observed for mixed oxide films must be due to their specific action on the Fe oxide component of the films.

Since halide / metal ion complex formation can be a major factor determining the dissolution rate of metal oxides, one has to consider the halide complex formation of $\text{Cr}(3+)$, as well. According to ref. (17), a strong tendency for $\text{F}^-/\text{Cr}^{3+}$ complex formation has been reported (for Cr^{3+} cations in solution). But as it has been pointed out by Strehblow (19), dissolution behavior of Cr oxide and complexing properties of Cr can be considered as a special case due to thermodynamic and kinetic reasons, which make Cr oxide films stable even in aggressive halide-containing solutions.

The specific action of halide anions on the Fe component of the oxide films is illustrated in Fig. 12. Here both the Fe and Cr XANES edge are shown during galvanostatic reduction of a 20% Cr_2O_3 - 80% Fe_2O_3 oxide film in borate buffer + 1 M NaF. For Fe

oxide, slight dissolution is observed in the beginning of the experiment. In the Cr spectrum, no dissolution can be seen. This suggests that fluoride is selectively dissolving Fe oxide out of the mixed oxide. Hence, it is possible that the surface layer becomes enriched with insoluble Cr oxide, and dissolution stop is obtained.

CONCLUSIONS

The stability of artificial Fe/Cr passive films (sputter-deposited Fe/Cr oxide films on inert substrates) is strongly influenced by the solution chemistry.

- low pH and presence of halides (Cl^- and F^-) accelerate dissolution due to the solubility of Fe oxides in these solutions
- F^- leads to a selective dissolution of Fe oxide out of the mixed oxide
- Cr_2O_3 is not attacked by fluoride; hence if the oxide film contains a sufficient amount of Cr oxide, dissolution stop is obtained by surface enrichment of Cr oxide

Apart from the solution chemistry, the composition of the oxide film is crucial for its stability.

- an increasing Cr_2O_3 content increases the resistance against reductive dissolution
- an increasing Cr_2O_3 increases the resistance in aggressive solutions (low pH, halides)
- an increasing Cr_2O_3 decreases the resistance against oxidative dissolution
- an increasing Fe(2+) content in the oxide film strongly accelerates dissolution in acidic solutions

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Fig. 1 Thickness of a sputter-deposited Fe_2O_3 film as a function of charge density during galvanostatic reduction in different solutions. Thickness determined from the edge height of the XANES spectra.

Fig. 2 Thickness of a sputter-deposited Cr_2O_3 film as a function of charge density during galvanostatic oxidation in different solutions. Thickness determined from the edge height of the XANES spectra.

Fig. 3 Dissolution rate of sputter-deposited Fe/Cr oxide films as a function of the Cr_2O_3 content during galvanostatic reduction and oxidation in borate buffer, pH 8.4. Dissolution rates determined from the drop of the edge height of the XANES spectra during the experiments.

Fig. 4 Dissolution rate of sputter-deposited Fe/Cr oxide films as a function of the Cr₂O₃ content in borate buffer, pH 8.4 and in 0.1 M H₂SO₄
a) during galvanostatic reduction
b) during galvanostatic oxidation

Fig. 5 Normalized XANES Fe edge during galvanostatic reduction ($-10 \mu\text{A}/\text{cm}^2$) of a 10% Cr₂O₃ - 90% Fe₂O₃ oxide film in
a) borate buffer
b) 0.1 M H₂SO₄
Spectra a...c,d are consecutive spectra during the reduction.

Fig. 6 XANES spectra (Fe edge) of a 20% Cr_2O_3 - 80% Fe_2O_3 sample during anodic potential steps in 0.1 M H_2SO_4
a-f: 0 .. 600 mV (100 mV steps)
g-i: Consecutive spectra at +700 mV

Fig. 7 XANES spectra (Fe edge) of a 20% Cr_2O_3 - 80% Fe_2O_3 sample
a: open-circuit potential in borate buffer
b: after galvanostatic reduction in borate buffer
c,d: 0 mV in 0.1 M H_2SO_4

Fig. 8 Edge height and edge position of Fe XANES spectra as a function of potential for a 50% Cr_2O_3 - 50% Fe_2O_3 sample during anodic potential steps in 0.1 M H_2SO_4 after galvanostatic reduction in borate buffer

Fig. 9 Consecutive XANES spectra for the Fe edge of a 10% Cr_2O_3 - 90% Fe_2O_3 sample during galvanostatic reduction ($-10 \mu\text{A}/\text{cm}^2$)
a) in borate buffer + 1 M NaCl
b) in borate buffer + 1 M NaF

Fig. 10 Normalized XANES Fe edge of a 10% Cr_2O_3 - 90% Fe_2O_3 oxide film during galvanostatic reduction ($-10 \mu\text{A}/\text{cm}^2$)
a) in borate buffer + 1 M NaCl
b) in borate buffer + 1 M NaF

Fig. 11 Dissolution rate (determined from XANES edge heights) during galvanostatic reduction of Fe/Cr oxide films in borate buffer with additions of NaCl or NaF.
a) full scale; b) expanded scale

Fig. 12 Fe and Cr XANES spectra during galvanostatic reduction of a 20% Cr₂O₃-80% Fe₂O₃ oxide film in borate buffer + 1 M NaF