

IN SITU XANES DETECTION OF Cr(VI) IN THE PASSIVE FILM ON Fe-26Cr

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The passive film on sputter deposited thin film Fe-26Cr electrodes has been examined using the technique of *in situ* X-ray absorption near edge spectroscopy (XANES). During the X-ray spectroscopic measurements, the sample was maintained under electrochemical control in the pH 8.4 borate buffer electrolyte. The appearance of the distinctive Cr(VI) XANES pre-edge peak can be correlated with the transpassive wave in the cyclic voltammogram, and its disappearance with the corresponding reduction wave. The formation and reduction of Cr(VI) was reversible, and only small amounts were detected in the film. Cr(VI) in the passive film is not indefinitely stable, and it is completely absent after long periods of air exposure.

INTRODUCTION

The presence of Cr(VI) in the passive film on Fe-Cr and other stainless steel alloys has been postulated for many years. The transpassive peak observed on anodic polarization is often assumed to be due to the oxidation of Cr(III) to Cr(VI) because of the anodic potential at which the peak first appears. The presence of Cr(VI) in solution at these potentials has been confirmed (1), however, convincing evidence for the presence of Cr(VI) in the oxide film, from either *in situ* or *ex situ* techniques has been elusive. Clayton and Lu (2) have deconvoluted x-ray photoelectron spectra (XPS) to give a peak corresponding to Cr(VI), however, the presence of this peak is obscured by other overlapping peaks, and it is somewhat difficult to quantify. In addition, the peak disappears with time of exposure to the x-ray radiation, and thus Cr(VI) is thought to be subject to photoreduction (3). Hara and Sugimoto (4), using modulation spectroscopy, an *in situ* optical technique, identified an optical peak at 3.7 eV which they tentatively attributed to Cr(VI). This peak increased with the Cr concentration of the Fe-Cr alloys, however, it could also be attributed to Fe(II), making an unequivocal assignment impossible. In recent electrochemical studies (5), it has been shown that the characteristics of Cr(VI), which are present for samples passivated above a certain potential, are eliminated after a brief (15 min.) air exposure of the passivated sample. This suggests that Cr(VI) in the passive film on Fe-Cr alloys is not stable, and thus evidence for Cr(VI) should be sought using *in situ* techniques.

Long et al (6) showed that thermal oxide films (formed at 600°C) on Fe-25Cr contained Cr(VI) from *ex situ* XANES analysis. Davenport et al (7) have recently shown that anodic oxide films on Al-Cr alloys contained Cr(VI) by using XANES. In this case,

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the anodic films were examined *in situ* and under electrochemical control. In the present work, the *in situ* XANES technique has been used to demonstrate that Cr(VI) is present in the passive film on Fe-26Cr alloy at potentials in the transpassive region. The stability of Cr(VI) with respect to air exposure was also investigated.

EXPERIMENTAL

The experimental setup for the *in situ* XANES measurements has been described previously (7). Potentials are quoted with respect to a saturated mercurous sulfate reference electrode (MSE) and are accurate to ± 5 mV. The electrolyte was pH 8.4 borate buffer, deaerated with nitrogen bubbling. Bubbling was continued during the course of a XANES experiment to ensure that any dissolved reaction products (such as Cr^{6+}) were removed from the vicinity of the electrode and thus would not contribute to the observed spectra. The electrochemical cell design (7,8) allows for potential control of the working electrode, which consisted of a 6 μm Mylar film on which two metallic layers were sputtered. The lower layer consisted of 10-20 nm of Ta metal (used to provide good electrical conductivity) and the upper layer of 4-6 nm of Fe-26Cr. The samples were prepared using an Ion Tech sputter coater equipped with a getter pump (SAES), in order to reduce the oxygen contamination of the metal layers. Ar was used as the sputtering gas. The sputter rate was calibrated by sputtering thicker films and measuring the thickness with a Sloan Dektak II step gauge. Auger depth profiles confirmed that the film thickness was proportional to sputter time. The bulk Fe-26Cr alloy was prepared as discussed previously (5).

RESULTS AND DISCUSSION

Auger analysis of the sputtered films on Mylar substrates revealed that the Ta and Fe-26Cr layers contained significant amounts of C, present as carbide. Despite numerous efforts to reduce the C level in the metallic layers, it remained at approximately the same atomic concentration as the Cr. Samples sputtered onto Al foil or Si wafers under the same conditions contained much lower levels of C, but the thin film Al substrates could not be used for XANES analysis because the signal was destroyed by Bragg scattering from the substrate. Samples sputtered onto Kapton, another X-ray transparent polymer, showed similar levels of C contamination. Thus, it appears that Mylar or other polymers are sources for C contamination. Mylar samples were used in this work, and so the Fe-Cr alloy used in this study is rather heavily contaminated with C. Only the surface of the sample showed significant O, resulting from the air-formed film. No C was present in the oxide layer, either before or after electrochemical treatment. Auger analysis confirmed that the percentage of Cr in the Fe-26Cr metallic layer was as expected, and that after electrochemical treatment, a significant quantity of Fe-Cr metal remained, even for a 4 nm Fe-26Cr layer.

Cyclic voltammetry of slightly thicker sputtered layer samples was compared to that of the bulk material to ensure that the two electrodes behaved in a similar manner. A cyclic voltammogram on the Ta layer alone showed no peaks in the region of interest; thus the Ta acts as an essentially electrochemically inert substrate which is, however, required to maintain good electrical conductivity. Despite the significant C contamination of the

Fe-26Cr layer, the cyclic voltammetric characteristics (at 0.5 mV s^{-1}) of the thin layers were remarkably similar to those of the bulk Fe-26Cr alloy, as shown in Fig. 1. The second sweep on the thin film electrode shows all of the features of the sweep on the bulk material, namely an "active" peak at -1.11 V , a transpassive peak at about 0.27 V , oxygen evolution beginning at -0.61 V ; during the subsequent cathodic scan the features observed consisted of a cathodic peak at -0.27 V (corresponding to reduction of a higher oxide formed in the transpassive peak), a peak at -0.85 V resulting in reduction of the Fe-containing oxide, and finally hydrogen evolution beginning at -1.36 V . These peaks have previously been discussed in more detail (5). The first sweep, while exhibiting most of the expected characteristics, has a broadened and suppressed transpassive peak, and it seems likely that the first scan acts to "activate" the electrode surface. While the nature of the processes which occur in the first cycle are unknown, surface analysis revealed that they do not result in a reduction of the C contamination, nor any other detectable changes except in the Cr content of the oxide layer. It should be noted that an anodic activation of the sample was necessary to yield reproducible XANES spectra.

For reference, a series of XANES spectra of Cr standards are shown in Fig. 2. In general, the absorption edge moves to higher energy as the oxidation state of the Cr increases from zero to 6. Cr metal shows a plateau at about 5993 eV , while Cr(VI) has a very sharp and distinct peak at the same energy. This characteristic peak can be used to unequivocally establish the presence of Cr(VI) in a sample (6,7). The peak arises from Cr in a tetrahedral geometry (9). Since the passive film on Fe-26Cr is expected to consist of mixed Fe and Cr oxides and hydroxides, the presence of this peak is a fingerprint for Cr(VI).

A series of XANES spectra on the thin layer electrodes under electrochemical control are shown in Fig. 3. The sample consisted of 4 nm Fe-26Cr on 10 nm of Ta sputtered on Mylar. While a thinner Fe-26Cr layer would result in an increase in the signal from the passive film relative to that from the Fe-26Cr metal, a thicker Fe-26Cr metallic layer ensures that the sample behaves as much as possible like the bulk material, which would not be the case if all of the metal was oxidized. Preliminary experiments showed that reproducible XANES spectra were only obtained after the sample had been activated by an anodic treatment, as suggested by the cyclic voltammograms. Thus, the sample was cathodically reduced at -1.5 V for 5 min. , then activated at 0.8 V for 5 min. , and finally cathodically reduced again at -1.5 V for another 5 min. An initial XANES spectrum, Fig. 3(a), was collected at the cathodic potential. It shows a plateau at 5993 eV , followed by a steeply increasing edge. Comparison with the standards (Fig. 2) suggests that the sample is composed of a mixture of Cr metal and Cr(III). The sample was then passivated by stepping to various anodic potentials and holding for 10 min. The XANES data collection (which required about 10 min. per spectrum) was started immediately after stepping the potential. There is no detectable change in the XANES spectra for the passivated (potentials $\leq 0.2 \text{ V}$) compared to the reduced surfaces. However, at a potential of 0.4 V (well into the transpassive peak), two features of the spectra change; a peak, as opposed to a plateau, appears at 5993 eV , and the main edge has a lower slope than at lower potentials. Both of these changes indicate that some of the Cr(III) in the film has been converted to Cr(VI). Although the slope of the main edge is not a simple measure of the oxidation state of Cr, consideration of the spectra of the standards (Fig. 2) indicates that a decrease in the slope would occur on the oxidation of a portion of the Cr(III) to Cr(VI), both because of the shift of the edge to higher energy, and because of the lower maximum absorption of Cr(VI). These features remain unchanged as the potential is increased to 0.5 V , and then decreased to 0.1 V . However, once the potential is decreased to -0.1 V (at the beginning of

the reduction peak), the peak at 5993 eV begins to diminish in size, and the slope of the main edge begins to increase. At -0.3V (through the cathodic wave) all evidence for Cr(VI) has disappeared from the XANES spectrum.

Electrochemical production of Cr(VI) in the anodic film on Fe-26Cr is reversible, as shown by the spectra in Fig. 3(h) to (j). After the Cr(VI) has been reduced at -0.3V, it can be reformed by an anodic treatment at 0.6V, and reduced again by a subsequent treatment at -0.3V. From Fig. 3(h) it is apparent that there is still a significant amount of metallic Cr remaining in the sample after these electrochemical treatments. Overall, a decrease in the edge height with time can be seen when spectra at similar potentials are compared. This indicates that there is some dissolution of the sample.

The insert shows a direct comparison between the average of spectra (e) and (i) (both at 0.6V) and the average of spectra (h) and (j) (both at -0.3V). This comparison makes the pre-edge peak attributed to Cr(VI) more distinct. The spectra shown in Fig. 3 were the result of about 10 minutes of data collection. In other experiments, not shown, spectra were improved in signal to noise ratio by increasing the collection time, however, the collection time was minimized for the illustrated series of experiments to reduce the dissolution of the sample.

The results of Fig. 3 clearly indicate that the production of Cr(VI) in the anodic film on Fe-26Cr is associated with the transpassive wave centered at 0.28V, and that Cr(VI) is reduced in the cathodic wave at -0.27V. Only small amounts of Cr(VI) are present in the oxide; if all of the Cr in the sample had been converted to Cr(VI), then the peak at 5993 eV would be expected to reach the height of the main edge (see Fig. 2). No attempt was made to quantify the Cr(VI) concentration for the following reasons. Firstly, the amorphous nature of the Cr(III) and Cr(VI) oxides in the passive film on Fe-Cr alloys might lead to changes in the details of the XANES features, and secondly, contamination of the metallic substrate by C could result in the presence of Cr₃C₂ spectra in addition to the expected spectra of Cr(0), which would complicate the fitting procedure.

Finally, the air stability of Cr(VI) in the anodic film was investigated. Fig. 4(a) shows a XANES spectrum of a sample which had been treated at 0.8V, yielding clear indications of Cr(VI).^{*} The sample was then disconnected from the potentiostat, the solution drained from the cell, and the surface of the sample rinsed with water. XANES spectra were recorded after various times of exposure to the laboratory atmosphere (Fig. 4 (b) to (d)). While the characteristic peak at 5993 eV was still present after 1.5 hr. of *ex situ* exposure it had completely disappeared by 16.5 hr. Clearly, Cr(VI) is not indefinitely stable under these conditions. Compared with the previous procedure where the electrochemical characteristics of Cr(VI) disappeared after only 15 min. of laboratory ambient exposure (5), it was difficult to thoroughly dry the sample in the present series of experiments. Thus, it appears that the kinetics of the Cr(VI) reduction may be dependent on the ambient humidity. This possibility is currently under investigation.

^{*} It should be noted that this particular sample had undergone quite extensive electrochemical treatments, which, in general would be expected to result in a depletion of Fe from the sample. Thus, the effective Cr content of the alloy may be larger than 26%, yielding a larger Cr(VI) signal at 5993 eV than for the previously discussed sample, which had not been cycled as extensively.

CONCLUSIONS

XANES has been used to establish the presence of Cr(VI) in the anodic oxide film on Fe-26Cr alloy. The production of Cr(VI) is 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 anodic film is not indefinitely stable to air exposure and is completely absent after many hours of air exposure.

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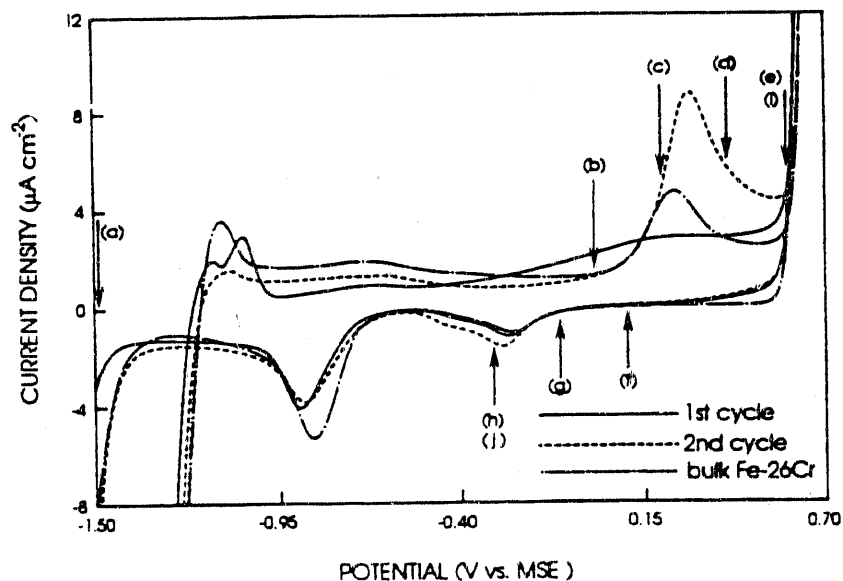


Fig. 1. Cyclic voltammograms (0.5 mV s^{-1}) for Fe-26Cr bulk alloy and thin film electrodes. The thin film electrode consisted of 25 nm of Fe-26Cr on 25 nm of Ta sputtered onto Mylar. The bulk electrode was reduced as described previously (5), while the sweep was begun at -1.44V for the thin film electrode. The arrows refer to potentials at which the XANES spectra shown in Fig. 3 were collected.

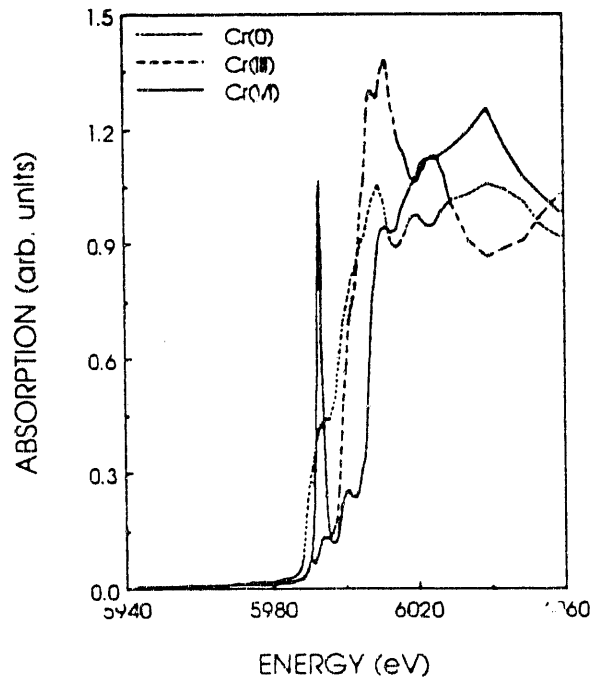


Fig. 2. XANES spectra of Cr foil (Cr(0)), and Cr_2O_3 (Cr(III)) and K_2CrO_4 (Cr(VI)) powder standards. The spectra have been background subtracted and normalized at an energy of 6180 eV, where the EXAFS features are damped out.

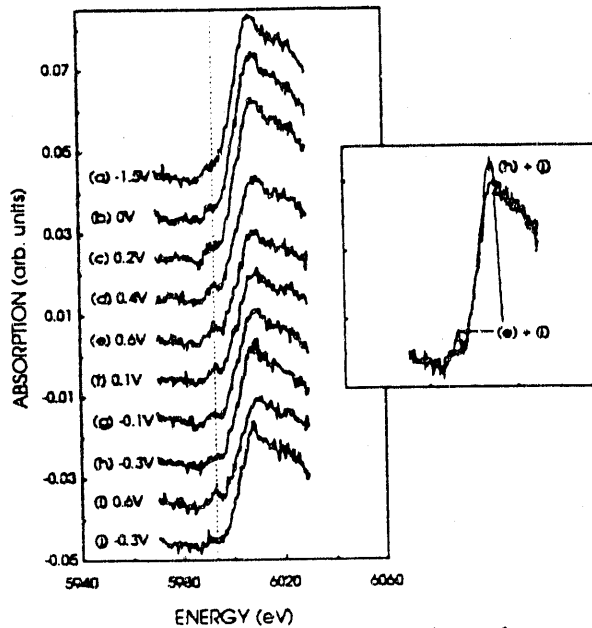


Fig. 3. *In situ* XANES spectra of a Fe-26Cr thin film electrode under potential control. The thin film electrode consisted of 4 nm Fe-26Cr on 10 nm of Ta sputtered onto Mylar. The vertical dotted line indicates 5993 eV, which is the position of the pre-edge peak clearly associated with Cr(VI). The insert shows a direct comparison between the average of spectra (e) and (i) and the average of spectra (h) and (j).

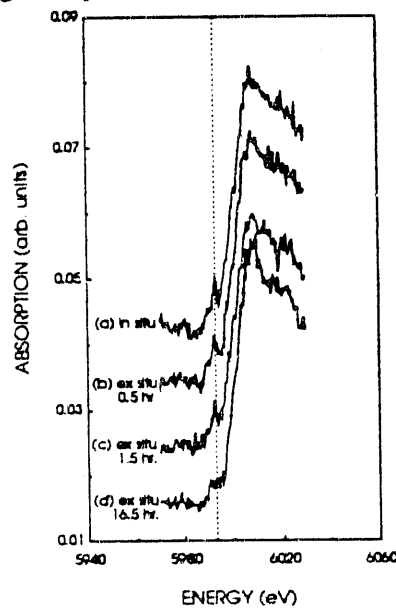


Fig. 4. *In situ* and *ex situ* XANES spectra of a thin film Fe-26Cr electrode consisting of 6 nm of Fe-26Cr on 20 nm of Ta sputtered onto Mylar. (a) *in situ* potentiostated at 0.8V, and *ex situ* (b) after 0.5 hr., (c) after 1.5 hr., and (d) after 16.5 hr. of air exposure. The vertical dotted line indicates 5993 eV, which is the position of the pre-edge peak clearly associated with Cr(VI).

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