IN SITU XANES STUDIES OF THE PASSIVE FILM ON Fe AND Fe-26Cr

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ABSTRACT

In situ x-ray absorption near edge structure (XANES) has been used to study the passive film on iron and Fe-26Cr thin films under potential control in borate buffer. The technique enables information on both valence state and the amount of material lost through dissolution to be determined. The passive films on both Fe and Fe-Cr are formed with negligible dissolution. On reduction, iron is lost from both films due to reductive dissolution. In the case of Fe, it has been determined that some of the iron in the film is reduced back to the metallic state. Concurrent monitoring of the Fe and Cr edges has shown that in the case of Fe-Cr, loss of iron leads to enrichment of Cr in the film.

INTRODUCTION

The chemistry of passive films formed on pure metals and alloys in aqueous electrolytes is the subject of much experimental investigation. Surface analytical work has been carried out using *e.g.* Auger, X-ray Photoelectron Spectroscopy (XPS) and Secondary Ion Mass Spectroscopy (SIMS), leading to a greater understanding of the composition of passive films. However, these measurements must be made *ex situ* in UHV and it has been demonstrated (1) that the passive film on Fe-Cr alloys is not stable when removed from an aqueous environment for *ex situ* examination. Thus, an *in situ* technique is to be preferred, particularly if it can yield deta:'ed information about the composition and valence states of elements in the film. These requirements are met by *in situ* X-ray Absorption Spectroscopy (2-4). In

the present work, X-ray Absorption Near Edge Structure (XANES) has been used to study the passive films on Fe and Fe-26Cr.

EXPERIMENTAL

The experimental setup for *in situ* XANES measurements has been described previously (3). The design of the cell ensured good potential control of the sample at all times. Potentials are quoted with respect to a saturated mercurous sulfate reference electrode (~0.4V(SCE)). The electrolyte was a pH 8.4 borate buffer. The solution was deaerated throughout the experiments by bubbling with nitrogen which also ensured that all dissolution products were removed from the vicinity of the electrode. The samples consisted of a 6μm Mylar film onto which ~100Å of Nb or Ta were sputtered to provide electrical contact. 20 or 40Å of the alloy under investigation (Fe or Fe-26Cr) was then deposited on top of the conducting layer. Measurements were made at Beamline X19A at the National Synchrotron Light Source. Data were collected in fluorescence geometry using a 13-element solid state detector (Canberra).

RESULTS AND DISCUSSION

Fig.1 shows a series of spectra collected at the iron K edge from a 40Å film of iron polarized cyclically in a borate buffer. It should be noted that the edges are not normalized so changes in the edge height represent quantitative changes in the amount of iron present. The initial curve was collected after cathodic reduction of the air-formed oxide film at -1.5V. The edge position and flat top to the edge is characteristic of metallic iron. On stepping the potential to -0.4V and then to +0.4V, the edge position shifts to higher energies and the top of the edge begins to sharpen into a peak (both are characteristic of oxides). The height of the edge at the right hand side of the figure does not change indicating that in the solution used (a borate buffer), oxidation of iron proceeds by a solid state reaction without any detectable dissolution. Reduction of the passive film on stepping the potential back to -1.5V results in a spectrum identical in shape to the first one, but the drop in the edge height indicates the dissolution of a significant

amount of iron. Spectra from the next cycle show that this process is repeatable a second time. Subsequent cycles do not show such clear behaviour, probably due to a loss of integrity of the very thin film. The loss of material during reduction suggests that the 3-valent oxide is reduced to the soluble 2-valent state which dissolved away leaving a bare metal surface. If this reductive dissolution process were 100% efficient, then it should be possible to reconstruct the XANES signal originating from the oxide alone by subtracting curve (d) from curve (c). The result of this subtraction is shown as (l). Its shape is characteristic of 3-valent iron oxides (2) but the negative deviation in the curve around 7120 eV indicates that Fe in the metallic state has been gained upon cathodic reduction. Approximate fitting of this curve indicates that the ratio of reductive dissolution to solid state reduction is in the region of 2:1.

The total amount of metal lost in each potential cycle is listed in Table 1. It is calculated on the following basis: it is assumed that the height of the Fe K edge for the as-deposited sample (which has a very thin air-formed oxide film), not shown, corresponds to 40Å of iron. If, for example, the edge height drops by 20%, this corresponds to a loss of iron equivalent to 8Å of metal. From Table 1, it appears that each potential cycle for pure iron involves the loss of approximately 7Å.

A similar set of experiments was carried out for thin films of Fe-26Cr. One of the advantages of using a multi-element solid state detector is that different detector elements can be used to collect fluorescence data from different chemical elements. Thus iron and chromium K edges can be collected by scanning over both edges in a single spectrum whilst different detector elements collect Fe K_α and Cr K_α fluorescent photons. Fig. 2(a) shows details of the Fe edge in a polarization experiment on Fe-26Cr. The results are qualitatively similar to those found for pure iron: metallic Fe present at -1.5V undergoes oxidation at -0.4V and +0.4V without any loss of material, then undergoes significant dissolution as the sample is reduced back to -1.5V. This behaviour is repeated on a second potential cycle (not shown). However, the amount of iron lost in each cycle is ~2Å, considerably less than the ~7Å lost in the case of pure iron.

The chromium K edge, measured during the same two potential cycles, is shown in Fig.2(b).

Whilst the data are noisy due to the low concentration of chromium and the diminished number of detector elements used, it is clear that the data fall into two bands. All the spectra are roughly similar in shape, but there is a significant loss of chromium indicated by a drop in the edge height during the second potential cycle when the potential is raised into the transpassive region (increased from -0.4V to +0.4V). Concurrent monitoring of the iron and chromium edges demonstrates the interplay between the two elements in the film: on the first potential cycle, both elements are oxidized into the film. However, chromium is not present in the film in a sufficient concentration for significant transpassive dissolution to take place. During reduction of the oxide at the end of the first potential cycle, iron is lost by reductive dissolution leading to enrichment of chromium in the passive film. On the second potential cycle, the chromium is now no longer protected by the iron and is present in a sufficient concentration for transpassive dissolution to occur. This model is consistent with similar work carried out on AlCr alloys (5). In the presence of a protective alumina layer, chromium is trapped in the film but if the alumina dissolves, then transpassive dissolution of chromium can take place.

In situ x-ray absorption spectroscopy is thus a powerful technique for studying alloy passivation. In addition to providing *in situ* valency information, the approach allows sensitive measurement of the quantity of material lost from the alloy through dissolution or passivation. In principle, it is possible to determine which components of an alloy undergo selective dissolution, which are enriched in the passive film, and which are enriched under the film in the metallic state.

CONCLUSIONS

1.   Formation of the passive film on both iron and Fe-26Cr proceeds without any metal dissolution.

2.   Cathodic reduction of the passive film on iron leads to the loss of the equivalent of $\sim 7\text{Å}$ of metal in dissolution. The ratio of reductive dissolution to solid state reduction is approximately in the region of 2:1.

3. Cathodic reduction of the passive film on Fe-26Cr leads to the loss of only ~2Å of iron.

4. Transpassive dissolution of chromium from Fe-26Cr can only take place on the second potential cycle once iron in the film has undergone reductive dissolution leading to enrichment of chromium in the passive film.

5. *In situ* x-ray absorption spectroscopy of passive films on thin film electrodes is an excellent technique for obtaining quantitative data on valency and dissolution during alloy passivation.

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Figure Legends

Fig. 1. Fe K edge of 40Å of Fe on 100Å of Ta. The spectra were recorded on stepping the potential in the sequence indicated. Curve (l) is the difference between (c) and (d).

Fig. 2. 40Å of Fe-26Cr stepped through two oxidation/reduction cycles with the potential sequence indicated: (a) Fe K edge (only the first potential cycle is shown); (b) Cr K edge.

DISCLAIMER

Table 1.

Amount of metal lost during potential cycling measured from the edge height and converted into an equivalent thickness of pure metal.

edge measured	sample	sample thickness /Å	cycle	metal lost /Å ±1
Fe	Fe	40	1	8
			2	6
			3	2
	Fe	20	1	7
			2	2
	Fe-26Cr	40	1	2
			2	2
	Fe-26Cr	20	1	1
			2	3
Cr	Fe-26Cr	40	1	0
			2	2
	Fe-26Cr	20	1	0
			2	>3[†]
	Fe-26Cr	40	1[*]	3
			2	2

[*]Sample was "activated" by stepping to +0.8V and back down to -1.5V.

[†]Sample sat in the transpassive region for several hours due to problems with the synchrotron.

(a) −1.5V
(b) −0.4V
(c) +0.4V
(d) −1.5V
(e) −0.4V
(f) +0.4V
(g) −1.5V
(h) −0.4V
(i) +0.4V
(j) +0.8V
(k) −1.5V
(l) (c)−(d)

FLUORESCENCE (arbitrary units)

ENERGY (eV)

40Å Fe-26Cr

Fe K edge

-1500mV
-400
+400
-400
-1500

first potential cycle

ENERGY (eV)

7100   7120   7140   7160

FLUORESCENCE

40Å Fe-26Cr

first potential cycle

Cr K edge

second potential cycle

-1500mV
-400
+400
-400
-1500
-400
+400
+800
-400
-1500

FLUORESCENCE

ENERGY (eV)

5980   6000   6020   6040   6060

END

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