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# *IN SITU* STUDIES OF PASSIVE FILM CHEMISTRY USING X-RAY ABSORPTION SPECTROSCOPY

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**Abstract**—The application of X-ray absorption spectroscopy to the study of passivation of thin metal films is discussed. Data are presented which demonstrate the effectiveness of the technique for monitoring both potential- and time-dependent data on valency and selective dissolution from passive films. It is shown that iron undergoes reductive dissolution from the passive oxide film on both pure iron and Fe–26Cr, in the latter case leading to enrichment of chromium in the passive film. Transpassive dissolution of chromium can take place on Al–Cr and Fe–Cr only after it has been enriched in the passive film by dissolution of the other alloying element. Rapid polarization of Al–Cr leads to trapping of electroactive chromium in the passive film.

#### INTRODUCTION

THE CHEMISTRY of passive films formed on alloys in aqueous electrolytes has been widely studied using a number of analytical techniques including Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy. However, since these techniques employ an electron signal, they can only be carried out in ultra-high vacuum, requiring removal of the aqueous environment and the electric field in which the passive film was formed. It is thus a subject of some debate as to whether the film studied in a vacuum is identical to that formed in solution. To overcome this problem, X-ray Absorption Spectroscopy (XAS), a photon- rather than electron-based technique, offers a method of studying passive films *in situ* in aqueous environments.<sup>1–11</sup> The advantage of this approach is that time- and potential-dependent data can be collected from a single sample. XAS can be used to study the valency of an atom using the X-ray Absorption Fine Structure (XANES), or its coordination using Extended X-ray Absorption Fine Structure (EXAFS).

While XAS is an effective method for making *in situ* measurements, it is not an inherently surface-sensitive technique. This problem is generally overcome by using a film of metal which is sufficiently thin that most of the metal is converted to passive film during polarization. In addition, the measurement geometry must take into account the limited penetration of X-rays through solutions. The earliest *in situ* measurements were carried out on thin films of iron, typically 2–4 nm in thickness, in an inflatable cell. <sup>3–6</sup> The cell was inflated to give good electrochemical control during film growth, and then deflated to give a thin layer of electrolyte for the XAS measurement once the steady state had been reached. A subsequent cell design completely avoided problems with thin electrolyte layers: the thin plastic on which the thin layer of metal was deposited was used as the window of a large electrochemical cell<sup>6</sup> through which the incident and fluorescent X-rays passed. This approach

proved to be effective both for EXAFS measurements<sup>7</sup> and time- and potentialdependent XANES measurements.<sup>8,9</sup> The alternative method for making surfacesensitive measurements of passive films *in situ* is to use the "RefIEXAFS" geometry in which the penetration of the X-rays into the bulk metal is suppressed by using very small incident angles (a few mrads).<sup>10</sup> However, in practice, this technique still leads to a substantial signal from the underlying metal.

In situ studies of passive films have generally used the EXAFS signal in an attempt to obtain the structure of the films.<sup>2-7</sup> However, recently the XANES signal has been used to investigate the time- and potential-dependence of valency in passive films on Fe–26Cr<sup>8</sup> and Al–Cr.<sup>9</sup> The importance of carrying out *in situ* measurements was highlighted in an experiment in which a passive film containing 6-valent chromium was emersed from the solution. Over a number of hours, all the 6-valent chromium was reduced to the 3-valent state.<sup>8</sup>

#### EXPERIMENTAL METHOD

The experimental setup for *in situ* XANES measurements has been described previously.<sup>9</sup> Potentials are quoted with respect to a saturated mercurous sulfate reference electrode [~0.4 V(SCE)]. The electrolyte was a pH 8.4 borate buffer. For measurements on Al–Cr, the solution was aerated, whereas for Fe and FeCr, the solution was deaerated throughout the experiments by bubbling with nitrogen to ensure that all dissolution products were removed from the vicinity of the electrode. The samples consisted of a 6  $\mu$ m Mylar film onto which ~100 Å of Nb or Ta were sputtered to provide electrical contact. Approximately 20–40 Å of the alloy under investigation (Al–12Cr, Fe, 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).

#### EXPERIMENTAL RESULTS

Figure 1 shows the chromium K edge for a film of Al–12Cr.<sup>9</sup> Curve (a) shows the spectrum from the sample at open circuit prior to electrochemical polarization.



FIG. 1. The Cr K edge measured during polarization of an Al-12Cr alloy (a) at open circuit, (b) after stepping the potential to +2 V, and (c) after subsequently stepping the potential to -1.5 V. The broken lines show standard compounds measured in transmission.<sup>9</sup>



FIG. 2. The Cr K edge for Al-12Cr at open circuit (OC) and after stepping the potential to 2 V. The time after the potential step is indicated.<sup>10</sup>

Superimposed on the data is the K edge from a pure chromium foil measured in transmission geometry. The coincidence of the two indicates that prior to polarization, chromium is present in the metallic state. On applying a potential of 2 V, the absorption spectrum displays a sharp peak below the edge ("pre-edge peak") which is characteristic of tetrahedrally-coordinated 6-valent chromium (as indicated by the superimposed spectrum from a power of  $K_2CrO_4$ ). The 6-valent chromium, normally a soluble species, is trapped in the passive film and is electroactive: it can be reduced to the 3-valent state (Fig. 1c) by stepping the potential to -1.5 V (as demonstrated by the superimposed spectrum of  $Cr_2O_3$ ). The spectra from the passive film have not been normalized: the height of the edge reflects the total amount of chromium present. The fact that the edge height does not change indicates that 6-valent chromium is not dissolved from the film. The valence state of the chromium can be further switched between the 3 and 6 states by stepping the potential between -1.5 and +2 V.

The time-dependence of the initial oxidation process is illustrated in Fig. 2.<sup>10</sup> The initial spectrum again shows chromium in the metallic state at open circuit. Subsequent spectra were collected during the indicated time periods after stepping the potential to 2 V. Initially, 3-valent chromium is formed (which is apparent from the shift in the edge position). Oxidation to the 6-valent state is a much slower process which takes between 30 min and 1 h.

In contrast to stepping the potential to 2 V, a slow increase in potential causes transpassive dissolution of chromium. Figure 3 shows data collected while the potential is increased in 0.1 V steps separated by the 3 min required to collect an edge spectrum. Little change is seen in the spectrum prior to +0.2 V where loss of chromium is apparent from the decrease in the height of the edge. A very small preedge peak due to 6-valent chromium may also be present at and above this potential.

Figure 4 shows a series of edges collected at the iron K edge from a 40 Å film of iron polarized cyclically in a borate buffer.<sup>11</sup> It should be noted that the edges are not



Fig. 3. The Cr K edge for Al-12Cr during stepwise increase in the potential from open circuit at 0.1 V intervals. Each spectrum took 3 min to collect.<sup>10</sup>

normalized and have not had any background subtracted 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 -1.5 V. The edge position and flat top to the edge is characteristic of metallic iron. On stepping the potential to -0.4 V and then to +0.4 V, the edge position shifts to higher energies and the top of the edge begins to sharpen into a peak (both characteristic of oxidation). Reduction of the passive film on stepping the potential back to -1.5 V



FIG. 4. The Fe K edge of 40 Å of Fe recorded on stepping the potential in the sequence indicated.<sup>11</sup>



FIG. 5. Fe-26Cr (40 Å) 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.<sup>11</sup>

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 indicate that this process is repeatable a second time. Subsequent scans do not show such clear behaviour, probably due to a loss of integrity of the very thin film.

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  $K_{\alpha}$  and Cr  $K_{\alpha}$  fluorescent photons. Figure 5(a) shows details of the Fe edge in a

polarization experiment identical to that shown in Fig. 4 for pure iron. The results are qualitatively similar: metallic Fe present at -1.5 V undergoes oxidation at -0.4 and +0.4 V without any loss of material, then undergoes significant dissolution as the sample is reduced back to -1.5 V. This behaviour is repeated on a second potential cycle (not shown). The chromium K edge, measured during the same two potential cycles, is shown in Fig. 5(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 -0.4 to +0.4 V).

#### DISCUSSION

The results from the Al-Cr system demonstrate that the passivation of the alloy depends on the polarization rate. Specifically, for a slow increase in potential, chromium undergoes transpassive dissolution whereas for a rapid step to a high potential, chromium is trapped in the passive film without any measurable dissolution and is electroactive, i.e. can be switched between the 3- and 6-valent states by stepping the potential between low and high values. Some recent preliminary RBS (Rutherford Backscattering) data<sup>12</sup> may provide a clue as to why the polarization rate might affect the transpassive dissolution of chromium. The air-formed film is predominantly alumina. A slow increase in potential results in selective dissolution of a small amount of aluminium leaving a passive film that is enriched in chromium relative to the initial air-formed film. It is possible that the presence of aluminium oxide protects the chromium in the film from transpassive dissolution. If this aluminium is selectively dissolved, then the chromium is susceptible to dissolution. This observation is consistent with results from Fe–26Cr described below where it is found that enrichment of chromium in the film by selective dissolution of iron is necessary for transpassive dissolution.

The data from pure iron indicate clearly that in the solution used (a borate buffer), oxidation of iron proceeds by a solid state reaction without any detectable dissolution. However, the oxide is not reduced to the metallic state. Instead, the 3valent oxide is reduced to the soluble 2-valent state which dissolves away leaving a bare metal surface. The data from Fe-26Cr are qualitatively similar: iron is only lost from the sample during reductive dissolution of the passive film. 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 passive film in a sufficient concentration for 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, there is now a sufficient concentration of chromium for transpassive dissolution to occur when the potential is stepped into the transpassive region. Thus data from Al-Cr and Fe-Cr both imply that chromium must be enriched in the passive film by selective dissolution of the other element for it to undergo transpassive dissolution.

In situ X-ray absorption spectroscopy of passive films on thin film electrodes is thus a promising technique for studying alloy passivation. In addition to providing *in* situ valency information, the thin metal film approach allows sensitive measurement of the quantity of material lost from the film during passivation and dissolution processes. In principle, it makes possible determination of 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) Polarization of Al-Cr at a slow rate leads to transpassive dissolution of chromium whereas stepping the potential to a high value traps electroactive chromium in the oxide film.

(2) Cathodic reduction of the passive film on iron leads to dissolution of the film rather than its reduction to the metallic state.

(3) 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.

(4) 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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