APPLICATION OF IN SITU X-RAY ABSORPTION AND FLUORESCENCE MEASUREMENTS TO ANALYZE SOLUTIONS IN A SIMULATED PIT

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X-ray energy-dispersive spectroscopy has been used to study the compositions of metal ions in solutions developed during localized corrosion. An electrochemical cell was designed to simulate a corrosion pit, maintaining one-dimensional diffusion and fulfilling the requirements for x-ray fluorescence measurements. The working electrode consisted of a dissolving thin foil of Type 304 stainless steel sealed between Mylar sheets through which the x-ray beam passed. Concentration gradients within the artificial pit were quantitatively determined.

INTRODUCTION

X-ray absorption and fluorescence measurements offer a powerful method for the in situ study of chemical and physical changes during electrochemical and corrosion processes. The measurements offer a non-destructive in situ technique for analysis, in contrast to other surface analytical techniques, Auger and x-ray photoelectron spectroscopies, that require a vacuum and can induce chemical changes (1,2). High photon intensity monochromatic synchrotron x-rays have previously been used to investigate corrosion samples in air and under controlled electrochemical conditions. This technique is mainly used to determine the chemical nature of the elements, but the concentrations of individual elements can also be obtained.

Methods for analyzing the chemical composition and nature of the solutions within pits and crevices during active dissolution are being developed. In the present report, in situ fluorescence microanalysis using white x-rays and an energy-dispersive spectrometer (3,4) was carried out in order to determine the chemical compositions of the solutions within a one-dimensional artificial pit. This enabled simultaneous counting of the x-ray fluorescence from all the elements in stainless steel at each position of the sample and reduced the time required to obtain concentration gradients. Measurements of the concentration gradients of the major constituents of the alloy could be made more rapidly than with x-ray absorption measurements using monochromatic x-rays that must
ions, potential and pH as a function of depth within a pit using an actively dissolving metal site. Several investigations of pit and crevice solutions have appeared in the literature (9-11). Ives and Luo (10) measured concentration of chloride ions and inferred the presence of the metal-chloride complex ion FeCl\(^+\). Complex formation is also supported by x-ray scattering studies of solutions (12).

**EXPERIMENTAL**

The electrochemical cell shown in Fig. 1 was designed to simulate one-dimensional diffusion processes taking place in pitting or crevice corrosion. It consisted of a thin stainless steel foil, 2 mm wide and 0.018 mm thick, sandwiched between 0.3 mm thick Mylar sheets and sealed using an epoxy glue. The sandwich adhered to a 0.09 mm thick Teflon tape that formed the window to the cell and through which the x-ray beam entered. The upper cross-section of the steel strip was exposed to the solution. A 0.5 M HCl + 0.5 M NaCl solution was used. The steel was dissolved downwards at a constant potential of 600 mV (vs. SCE) leaving a rectangular shaped crevice. The composition of the stainless steel is shown in Table 1. Helium gas was bubbled into the bulk solution to stir it and thus avoid the concentration build-up of diffusing species at the mouth of the cavity.

The measurements presented here were carried out with high intensity white x-rays at the National Synchrotron Light Source Beamline X26A (3,4). A schematic diagram of the X26A x-ray microprobe beamline is shown in Fig. 2 (4). The beam size was collimated with a 20 \(\mu\)m "pin-hole". The cell was positioned with the plane of the foil at 45\(^\circ\) to the beam. The cell was held on a motorized stage and area or linear scans were made across the stainless steel/solution interface and across the artificial pit into the bulk solution. A 0.5 M NiCl\(_2\) + 0.8 M CrCl\(_3\) standard solution was used to examine the uniformity of the thickness within the artificial pit. The measurements of this known solution were also used to compared with the analysis based on the stainless steel foil used as a standard to determine the present accuracy of the experiments.
DATA ANALYSIS

It takes a finite time for the electronics of the solid state detectors to process a signal from a single photon. During this time, any other photons which are incident on the detector will not be collected. For high photon fluxes, this gives a significant "dead-time" so that counting only takes place for a measured fraction of the total time available. The number of counts are therefore normalized to this "live-time". This value is then divided by the current in the storage ring, which is proportional to the x-ray intensity that may vary during measurements.

Quantitative x-ray fluorescence analysis has been well established for many years and a number of possible methods of calibration are available. The basic principles were presented by Gigante and Hanson (13). Two methods are mainly used for quantitative analysis. The first is an empirical method exemplified by the multiple regression treatment of Lucas-Tooth and Pyne (14). This method calculates the absorption and scattering effects of each element present in a sample from the fluorescent intensities measured. Standards are required which are similar to the sample. The second is the fundamental-parameters method (15). This method derives the expected intensities from a sample composition and geometry and three sets of basic information: the x-ray spectral distribution of the incoming beam, the mass absorption coefficients for each element in the sample, and their fluorescence yields.

In this study, the fundamental-parameters method was employed to obtain calibration curves, and the reliability of this approach was investigated using known standards. A modified NRLXRF Fortran program (16) was used to calculate the theoretical fluorescent intensities of Fe, Cr and Ni as a function of concentration. The assumption for the composition was a homogeneous solution of FeCl₂ : CrCl₃ : NiCl₂ = 68.11 : 19.44 : 12.45, a composition ratio of the stainless steel foil. Table 2 shows the compositions and densities of the solution being used for the theoretical calculations. Minor elements such as C, P, Si, Cu, Mn and Mo were not included in the calculations. Relative calibration curves for the major metal cations calculated by the fundamental-parameter method are shown in Figure 3. The counts for each element do not increase linearly because of absorption and scattering effects, but the ratios of the elements only show deviations of less than 3% for the most concentrated solutions, indicating no marked preferential absorption for one element.

RESULTS AND DISCUSSION

An investigation of the dissolution characteristics of the sandwich type cell was carried out to ensure that a flat dissolving edge parallel to the mouth resulted from the mass transport-controlled dissolution process. The crevice was observed to be filled by a silica gel as subsequently determined with a scanning electron microscope. The gel
was formed from the silicon in the steel which expanded to occupy the volume of the dissolved metal. Similar effects were observed with 3% Si iron. Because of a five times greater amount of Si, the gel extruded from the crevice as dissolution proceeded. Ultrasonic cleaning of the crevice to remove the gel did not produce an observable difference in the concentration gradients across the boundary between first and second dissolution sequences. However, with or without removal of the gel, if the applied potential was turned off and the dissolving steel repassivated, subsequent dissolution often left remnants of steel under the passive surface that were undermined when the adjacent surface was reactivated. The remnants acted as obstacles to diffusion with major perturbation in the concentration gradients. Gradients were therefore measured during a single continuous dissolution of the foil.

Figure 4 shows a fluorescent spectrum of the solution inside the cavity immediately above the metal for counting times of 600 s. The counts under the Kα energy peak for each element (except Cu) were integrated and used to determine the concentration of each element. The Kβ peak was used for Cu because of the interference of the Ni Kβ and the Cu Kα peaks. The argon peak was from argon in the air. The source of the As and Br could be due to their presence as impurities in the plastic, the Teflon window or the epoxy glue. These were only observed after long period of counting (600 s) and were not seen when counting for 30 s. This does however show the capability of x-ray fluorescence microscopy to quantify trace impurities down to extremely low levels (3).

The relative integrated counts for Fe, Cr, and Ni as a function of distance above the steel/solution interface are shown in Figure 5, after normalizing for live-time and ring currents. Dissolution of the foil was stopped and the solution in the cell was replaced by the 0.5 M NiCl₂ + 0.8 M CrCl₃ standard. The fluorescence was then measured over the identical path taken in Figure 5. The results shown in Figure 6 were observed after the concentrations no longer changed. Variation of less than 5% within the crevice were attributed to thickness variations and a 10% decrease at its mouth due to an apparent constriction.

The concentrations obtained based on the stainless steel and the standard solution differed by about 10%. This could be due to changes in the beam or a number of instrumental factors which will be discussed elsewhere. This at present, is a major uncertainty in the determination of the concentrations above the stainless steel. In view of these differences, the early stage of the investigation and the need to assess the reproducibility of the measurements, an accuracy of the calculated concentrations should only be considered to be about 15%. The concentrations of Fe, Cr and Ni above the stainless steel based on these numbers are shown in Fig 7. The concentrations were derived from the data in Figure 5. The data were corrected for the variations in cell thickness (Fig 6), and the ratio of calculated and observed counts to obtain relative intensities. A conversion to the concentrations based on the calculated values in Fig 3 was then carried out.
The most concentrated solution obtained from the present x-ray fluorescence microanalysis was 4.1 M of total metal ions and the chloride concentration deduced from this value was 9.2 M. The saturated concentration of FeCl₂, CrCl₃, and NiCl₂ solution having the ratio of 68.11 : 19.44 : 12.45 was not found in literature. However, Hakkarainen (17) observed that approximately 10 M of chloride ions were contained in a saturated metal chloride solution dissolved by a Type 304 stainless steel in a HCl solution.

Distinct changes in the gradients for iron and chromium are apparent at high concentration and close to the dissolving steel. The changes are significantly smaller for the nickel ions. The increased slopes are a consequence of an increased viscosity of the concentrated solution, a decrease in diffusion coefficients or mobility of the ions and complex formation. These results and the consequence of the crevice chemistry on the growth and repassivation of pits will be reported elsewhere.

ACKNOWLEDGEMENTS

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REFERENCES

13. G. E. Gigante and A. L. Hanson, "Basic Principles of Synchrotron Radiation-
Induced X-ray Fluorescence (SRXRF)”, BNL-44768, Brookhaven National Laboratory, Upton, NY (1990).


Table 1. Chemical composition of a commercial stainless steel foil.

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<tr>
<th>element</th>
<th>wt%</th>
<th>atom%</th>
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<tr>
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<td>Mn</td>
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<td>S</td>
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<td>Fe</td>
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Table 2. The compositions and densities of the solutions used for the theoretical calculations.

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<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Cl</th>
<th>H</th>
<th>O</th>
<th>Density (g/cm³)</th>
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<td>52.06</td>
<td>1.45</td>
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Figure 1. A simulated one-dimensional pit used for x-ray fluorescence microscopy.
Figure 2. A schematic diagram of the X26A beamline.

Figure 3. Calculated fluorescent intensities of Fe, Ni and Cr in the solution mixtures having mole ratio of Fe : Cr : Ni = 68.11 : 19.44 : 12.45.
Figure 4. X-ray fluorescence spectrum taken immediately above the metal foil during steady state dissolution and 600 s counting time.

Figure 5. Normalized fluorescence counts as a function of position above the type 304 stainless steel foil.
Figure 6. Calibration of the cell with a standard solution of 0.5M NiCl₂ + 0.8M CrCl₃.

Figure 7. Derived concentration gradients of metal ions as a function of position.