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THE USE OF X-RAY TECHNIQUES IN THE *IN SITU* STUDY OF CORROSION

Hugh. S. Isaacs
Brookhaven National Laboratory
Upton, NY 11973
U. S. A.

ABSTRACT. Applications of x-ray absorption and fluorescence techniques for *in situ* chemistry studies of passivity and localized corrosion have been described. X-ray absorption near edge structures showed that rapidly grown oxides on aluminum-chromium alloys incorporated chromium in the oxide. Repeated electrochemically induced changes between the chromium 3- and 6-valent state occurred without chromium dissolving. When the oxide was grown by small potential steps, the chromium dissolved when 6-valent chromate was formed. With iron-chromium alloys, dissolution of chromate took place but 6-valent chromium was also incorporated in the oxide. The 6-valent state was reduced on exposing the iron alloy to air. X-ray fluorescence measurements, in conjunction with energy dispersive analysis, have been used to monitor iron, chromium and nickel concentrations in solution. The concentrations and concentration gradients during localized corrosion of stainless steel were used to determine salt solubility and relative diffusion rates.

1. INTRODUCTION

Synchrotron x-rays sources make it possible to carry out *in situ* electrochemical measurements that could not be made using other available techniques. In general, *in situ* measurements, give real-time responses and enable direct unambiguous correlations with controllable variables. The removal and preparation of the samples for *ex situ* measurements can induce changes and introduce uncertainties. In addition there may be effects that develop during the measurement itself as many surface analytical techniques are carried out in and require exposure to vacuum.

There are many possible applications of x-ray absorption techniques to corrosion studies [1]. Two techniques will be described in detail here. They were chosen as they bracketed extremes in corrosion rates. Here the approach will be to simplify the corrosion aspects for the x-ray specialist and detail experimental factors in the x-ray applications for the corrosion scientist. Further details of the theory of x-ray absorption may be found in other chapters of this proceedings and examples of corrosion are usually close at hand.

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Corrosion processes have many facets with each metal and alloy system showing its own quirks and surprises but also distinct similarities. Problems are usually engineered around rather than solved because of the complexities arising from the solution chemistry within the corroding environment, sensitivity to the multitude of impurities at the corroding interface arising from both the metal and the environment, and the heterogeneities in the metal such as inclusions, grain boundaries and atomic defects.

The corrosion resistance of metals and alloys of industrial importance is accounted for by the formation of a passivating oxide layers that kinetically limits the oxidation of the metal. Corrosion currents may be as low as a few nA/cm^2 which are equivalent to a penetration rate of a less than a micrometer per year. The oxide layer is extremely thin having a thickness of only a few nanometers. The only metal that would not form an oxide or hydroxide layer when exposed to air-saturated water is gold, because of its thermodynamic stability. Even platinum is predicted to form a hydroxide in air-saturated water [2]. Thermodynamic stability, or cathodic protection, can be imposed with some metals by applying an external potential to hold the metal in a reducing regime, where the growth of oxide is prevented or reduction of any prior oxide present may take place.

The thickness of passive oxides increase as the potential of the metal is increased at a rate of about $1\text{-}3 \text{ nm/V}$ [3]. The upper limit of potential is determined by the properties of the oxides. With metals such as aluminum and tantalum, hundreds of volts can be applied when the oxide is insoluble in the electrolyte. With other metals the potential may be limited by the electronic conductivity of the oxide or changes in composition. The oxides on iron and nickel are electronic conductors and oxygen evolution takes place when the potential is increased above a critical value. The applied current and rate of oxygen evolution then increase exponentially with potential.

Increasing the potential may also increase the oxidation state of metal cation in the oxide and produce a more soluble species. The passive film then dissolves preventing further increases in passive layer thickness or even preventing any oxide from forming. Chromium is a notable example. The lower 3-valent chromium cation is highly insoluble and imparts an extremely protective oxide layer when used as an alloying element. However, at high potentials where the very soluble 6-valent chromium ion is formed, protection is lost and rapid dissolution of the chromium takes place.

For most corrosion studies oxide thicknesses of about $1\text{-}3 \text{ nm}$ are of major interest. The chemistry of these extremely thin layers have been studied using a wide range of both *in situ* and *ex situ* techniques. These have been reviewed by Landolt [4]. Questions of interpretation always arise with *ex situ* methods as possible changes in the chemistry may develop on removal of the metal from its environment [5]. By far the greater number of studies have been carried out using ultra-high vacuum techniques which may lead to further changes [6,7].

When chlorides are present in solution, the passive oxide cover often loses its ability to prevent corrosion. Increasing the chloride concentration increases the probability of undermining the passive oxide. Corrosion initiates at only a few sites but once started, the localized corrosion is rapid [8]. The rate of metal dissolution within the localized corroding site is up to 8 orders of magnitude more rapid than that for the passive surface. Continued corrosion depends on maintaining the presence of high concentrations of the chloride

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corrosion products [9] at the localized corroding site. The chloride concentration is a balance between an increase, due to dissolution of the metal forming dissolved metal chlorides, and a loss by diffusion. If the concentration of the metal chloride drops too low, the metal can repassivate and localized corrosion stops.

When diffusion is slow, the concentration of dissolved metal chloride increases and supersaturates the solution. The metal chloride then precipitates and in a manner analogous to, but far less effective than the passive oxide, reduces the dissolution rate. The solubilities of the passive film and the salt layer may also differ by over eight orders of magnitude and offer one possible explanation for the extreme differences in corrosion rates exhibited by passivating metals.

Examples of cells and methods using x-rays to analyze the corrosion products on passive surfaces and under simulated localized corrosion conditions will be discussed, to indicate the approach taken in investigating the chemistry of these corrosion processes.

2. X-ray Absorption and Fluorescence Techniques.

At incident monochromatic x-ray energies that excite inner shell electrons to unoccupied levels, the absorption of photons increases rapidly and produces a step or edge in the absorption spectrum. After the inner shell is vacated, an electron from a higher shell drops into the inner shell and is accompanied by emission of an x-ray with a characteristic energy. With energy increases up to a few tens of eV, successive empty energy levels are filled by the excited electron. The position of the spectrum produced, or the x-ray absorption near edge structure (XANES), depends on the valency state of the excited element and its chemical bonding and incorporates multiple scattering effects associated with the ejected electron. The spectrum, by comparison with known standards, can be used to characterize the state of the particular element, be it in solution, as a crystalline solid or amorphous.

The XANES for Cr compounds in Figure 1A [10] clearly shows the changes for different valencies of the Cr atom. The position of the edge for metallic Cr is at 5989 eV and the measurements were calibrated and plotted relative to this value. By convention, the edge position was taken to be the first maximum in the derivative of the metal edge spectrum. Increasing the valency of the Cr increases the binding energy and the edge is shifted to higher energies. Of particular interest is the pre-edge peak of 6-valent Cr. It arises from a 1s to 3d transition which is allowed when the coordination of the absorbing atom lacks inversion symmetry as for example in tetrahedral coordination [11]. This peak clearly identifies the presence of 6-valent Cr.

A second example is shown for iron in Figure 1B [12]. The shift in the edge is again seen and as the valency varies from 0 to +3. The edge for all the 3-valent compounds are close together, but the shapes of the spectra differ and the compounds show broad peaks. In general, the shape of the spectrum depends on the particular compound and varies considerably even though the valency remains the same. The shape of the curves can be used as a "fingerprint" for the identification of a compound.

At energies higher than the XANES, the ejected electrons are weakly scattered and only single scattering processes are important. Interference between electron waves from the

Figure 1. A) XANES spectra of Cr metal and compounds relative to the Cr K edge at 5989 eV [10]. B) XANES spectra of Fe metal and compounds relative to the Fe K edge at 7112 eV [21].

absorbing atom and backscattered waves from neighboring atoms produce an extended x-ray absorption fine structure (EXAFS) from about 50 eV to up to about 1 keV above the edge. With amorphous materials EXAFS signals beyond the nearest neighbors are not observed. With small quantities of material, as with thin films, the EXAFS signals are generally too weak to analyze. However, efforts have been made to use EXAFS to determine the structure of passive oxide layers [13,14].

With incident monochromatic x-rays fluorescence process may be used to measure x-ray absorption. The fluorescence is proportional to the absorption and the measurements are most useful in determining the edges of elements present in low concentrations. With polychromatic x-rays the fluorescence is used to determine the concentrations of particular elements. A broad polychromatic spectrum of the high intensity beam from the synchrotron is used and an energy dispersive detector is used to monitor the fluorescence [15,16]. Results using the energy dispersive measurements are shown in Figure 2 for a saturated solution above the dissolving edge of a salt covered stainless steel foil dissolving in chloride electrolyte. The $K\alpha$ peaks of the elements present are indicated.

Figure 2. Energy dispersive x-ray measurement of the solution at 50 μm above a salt-covered Type 304 stainless steel surface in a crevice dissolving in a chloride electrolyte showing the $K\alpha$ peaks of the elements present [20].

Figure 3. The mean free path for water, polystyrene and iron, as a function of x-ray energy, with the positions of the K shell binding energies for the elements shown [after 17].

In general, the absorption of x-rays increases with atomic number of the absorbing atoms and decrease with the x-ray energy. Figure 3 shows the mean free path of x-rays (or the thickness that attenuates the beam by a factor of $1/e$) as a function of energy in a polyester plastic, water and iron [17]. The positions of the K-edge binding energy for various elements are also indicated. At low energies the penetration depths are small. At energies close to the Cr edge, over 60% of the x-rays intensity is lost after passing through about 0.5 mm in water or the plastic and about 0.015 mm in iron. This limits the thicknesses of materials that can be used in construction cells. However, if heavy elements are to be studied, eg Mo, the thicknesses can be increase by a factor of about 30. The absorption depth also indicates difficulties in the study of passive oxides on surfaces. The oxide being a few nanometers thick, is considerably smaller than the penetration in iron and would swamp any attempts to measure the absorption by the oxide. In order to overcome this problem very thin layers of iron or iron alloys have been used where essentially all the metal is converted into oxide.

3. Experimental Configurations

A number of different experimental setups are shown in Figure 4. Standards for XANES are measured using the configuration shown in Figure 4A. The intensity I_0 of the monochromatic x-ray beam is monitored on passing through an ionization detector, or proportional counter, and the intensity I after being absorbed by a thin layer of the powdered standard material held between adhesive tape, about .015 mm thick, is again measured. The absorption is given by the logarithm of the I_0/I ratio as a function of the incoming energy. The results shown in Figures 1 and 2 were obtained in this manner and after subtracting background radiation extrapolated from below the edge, and for comparison, normalizing the edge step to unity. The edge step was obtained by extrapolating the absorption curve from well above the edge.

In order to study the chemistry of the passive oxide the setup shown in Figure 4B was used [18]. The Mylar electrode window used was angled at 45° to both the incoming monochromatic x-ray beam and the detector which in turn was at 90° to the beam. The position is important on reducing the background signals. The detector used was composed of an array of 13 energy-dispersive solid state detectors (Canberra). When the edges of two element were scanned, a fraction of the 13 detectors were tuned to the $K\alpha$ of each element. The $K\alpha$ emission is at a lower energy than the binding energy. A large background of the scattered

Figure 4. Schematic diagrams of x-ray measuring configurations.

(A) Transmission measurements of standards.

(B) Electrochemical cell for *in situ* XANES measurements of thin layer alloy electrodes deposited on Mylar windows using incident monochromatic x-rays and a 13-element fluorescence detector. The cell size was 70x50x25 mm [18].

(C) An cell for fluorescence measurements of concentrations of dissolved metals in solution within an artificial pit using polychromatic incident x-rays and an energy dispersive solid state detector [20].

Incident x-rays having values close to the binding energies are filtered out by tuning to the lower energy of the $K\alpha$ emission.

The advantage of the multiple detectors arises from the difficulties caused by the scattered radiation and the limitations of the detectors. The detectors can only respond to a maximum count rate independent of the incoming photon energy. Even though the energy discriminating detectors filters out the higher energy radiation, its presence generally determines the overall count rate. This then limits the count rate due the energies of interest. At higher count rates the "dead time" of the detector increases and the actual counting time or "live time" of the detector falls. Increasing the number of detectors increases the total count rate, and thereby decreases the counting times for a specific error margin.

The solution used in the cell shown in Figure 4B was a pH 8.4 borate buffer, deaerated with nitrogen [17-19]. The electrodes studied were thin metal or alloy layers sputtered onto a Ta or Nb substrate. The Ta or Nb substrates were of the order of 10 nm thick and were sputter-deposited on a 6 μm Mylar film. The 10 nm of sputtered Nb or Ta deposit acted as current carrier. The Mylar film was glued with epoxy across a cutout in a plastic container. The metal layers were controlled potentiostatically using a platinum counter electrode, and a mercurous sulfate reference electrode.

Figure 4C is the cell used for determining concentrations of elements using x-ray fluorescence [20]. In contrast to the chemistry studies using monochromatic beams, polychromatic x-rays are used because of the higher photon flux. The beam size was collimated to a diameter of the order of 0.02 mm in size and scanned across a sample to detect spacial variations in concentrations. An energy dispersive detector was again used but in these measurements the resolution was determined by that of the solid state detector. The emissions

detected relate only to quantities of the element and not to its chemical state. Again, to reduce the background signal from scattered radiation the detector is placed at 90° to the incoming beam. The "pin-hole" used to reduce the beam size down to its final size of 0.02 mm. The electrochemical cell was mounted on a stage that could be positioned in three dimensions with stepping motors and the area around where the beam entered the cell could be observed with the TV camera and microscope [15,16].

The cell was designed to measure concentration gradients in solution produced by dissolving stainless steel. The electrode was the cross section of a stainless steel foil 0.0137 mm in thickness, 2 mm in width and about 25 mm long. The foil was sandwiched between two pieces of 0.2 mm thick Mylar sheets with the foil protruding from one end. The other end was abraded after gluing to a solid square cylinder of methyl methacrylate. This solid was attached to a hollow square cylinder with a window cut out on one side that was positioned over the foil. The two square cylinders were attached with Teflon pressure sensitive tape. The solution was deaerated and stirred with helium and contained a platinum counter and a calomel reference electrode. The solid square cylinder served two purposes. It excluded solution from behind the cavity created when using standard solutions and still produced a clearly defined interface between the gas-stirred bulk solution and the solution in the cavity.

4. The Electrochemistry of Passive Oxides

X-ray absorption techniques have been used to elucidate the chemistry of passive oxide films. To demonstrate the methods, examples will be given based on studies on Fe-Cr and Al-Cr alloys. Alloying with Cr generally dramatically increases the corrosion resistance of many metals. At potentials where it forms a 3-valent atom it modifies and improves the properties of the oxide of the base metal, and being highly insoluble, may become the major component of the passive oxide. However, on increasing the potential the corrosion resistance due to the Cr may be lost or even further degraded, when under the highly oxidizing condition an extremely soluble chromate is formed with 6-valent Cr.

X-ray studies of the electrochemistry of Al-Cr alloys showed that the 6-valent Cr was retained in the oxide if the oxide was grown rapidly. The retained Cr was found to be electrochemically active, in that the valency could be repeatedly changed between the 3- and 6-valent states by changing the potential. Similar x-ray measurements also showed that 6-valent Cr was retained in the oxide on Fe-Cr alloy following chromate dissolution. However, on removing the electrolyte, the 6-valent Cr was reduced in contrast to what was found with the Al alloy.

Al-Cr ALLOYS

There has been recent interest in the corrosion resistance of Al alloys at concentrations exceeding the limits of solubility [22,23]. These alloys are generally amorphous and can be formed by co-sputtering the alloying element with the aluminum.

Sputtered Al-Cr deposits on Mylar were polarized in borate solutions under different potential schedules using the cell shown in Figure 4B, and the XANES was monitored. Slow increases in potential led to dissolution of the alloy. A series of Cr edge energy scans are shown in Figure 5A [24]. The edge heights were not normalized and were a measure of the

relative changes in the amounts of Cr present. The sample was a 2 nm thick 12%Cr deposit. After the first measurement at an open circuit potential of -1.08 Vm_{se} (measured versus a mercurous sulfate reference electrode), the potential was then held constant during the 3 minutes required for each scan and then stepped 0.1 V starting at -0.7 Vm_{se}. Changes in shape of the edges are compared with the standards in Figure 1A. The edge at open circuit was definitely metallic and remained so until a potential of about -0.3 Vm_{se} was reached. At -0.2 Vm_{se}, the edge position shifted to higher energies and the peak just above the edged increased, indicating a transition to a 3-valent Cr. The shape and magnitude of the edge remained the same until at 0.2 Vm_{se} the magnitude decreased and continued to decrease with each subsequent scan up to 0.6 Vm_{se}. Also associated with these spectra is the presence of a weak peak around 5992 eV. This peak arose because of the presence of 6-valent Cr as may be seen in Figure 1A. The presence of the higher concentrations of dissolving chromate was more readily seen during similar measurements on a pure Cr deposit or higher Cr contents in the alloy deposit. The presence of the chromate at the potentials were it would be expected to be the stable Cr species, increased currents from the potentiostat and the decrease in the edge height were all indicative of dissolution of the deposit resulting from the formation of soluble 6-valent Cr as chromate.

In contrast to the dissolution on slowly incrementing the potential, a single potential step to high potentials gave no significant dissolution of the Cr. In Figure 5B the edge for the

Figure 5. (A) *In situ* XANES spectra of a Al-12Cr thin film electrode under potential control. The thin film electrode consisted of 2 nm Al-12Cr on 10 nm Ta sputtered on Mylar. The XANES measurements were taken at the potentials shown on the right of the figure. The potentials were held at these values for the 3 min to record each curve and then stepped to the next higher potential [24].

(B) *In situ* XANES spectra of a Al-12Cr thin film electrode under potential control. The thin film electrode consisted of 2 nm Al-12Cr on 10 nm Ta sputtered on Mylar. The solid lines were XANES measurements of the alloy which took about 10 min to record. In (a) the alloy was first held for 12 min at open circuit, in (b) 7 min at 2.0 Vm_{se} and in (c) 6 min at -1.5 Vm_{se}. The dotted lines show superimpose XANES standards: (a) Cr metal, (b) K₂CrO₄, and (c) Cr₂O₃ [18].

initial open circuit exposure of an Al-12 Cr deposit, is shown by the noisy curve, a. The superimposed broken curve was for a Cr metal standard and indicated Cr was present as the metal. Curve b, shows the edge after the sample was polarized by stepping the potential from open circuit to 2.0 Vmse, and compares it with the broken curve for a K_2CrO_4 standard. The heights for the deposit were approximately the same as was seen in curve a, indicating little loss of Cr. The pre-edge peak due to 6-valent Cr for the sample attains a height of about 50% that of the edge. The peak height for the standard is about equal to the edge height. Hence 50% of the Cr is present was in the 6-valent state. On comparing the position of the edge with standards (Figure 1A) it was below that expected for the 6-valent state but considerably greater than for the metal. Hence, the remaining 50% was present in the 3-valent state. Curve c shows the edge after the sample was polarized to -1.5 Vmse. The corresponding curve for the Cr_2O_3

standard shows all the Cr to have been reduced from the 6- to the 3-valent state. The Cr in the rapidly grown oxide remained electroactive. On repeated stepping of the potential between 2 and -1.5 Vmse the changes in the Cr valency states between 3 and 6 could be repeated and also with no detectable losses of the Cr in the 6-valent state.

The above results show that marked differences in dissolution characteristics of the oxide on the alloy depending on how it was grown. Other studies, on deposits 2.5 nm thick were made using XPS [10,24]. It was found that the air-formed oxide layers on the alloys were predominantly Al oxide which tended to dissolved when the potential was slowly increased. The slow increase in potential to below where 6-valent Cr formed showed that Cr was further concentrated under the Al oxide. This suggested that when the potential was slowly raised and reached value at which the 6-valent Cr could form, only a thin Al oxide was present and was not sufficiently protective to prevent the metallic Cr from dissolving.

Figure 6. Cyclic voltamograms of Fe-26Cr bulk alloy and sputtered films in borate solution at a scan rate of 0.5 mV/s. The thin film electrode consisted of 25 nm Fe-26Cr on 25 nm Ta sputtered on Mylar. The arrows indicate the potentials at which the XANES measurements in Figure 8 were collected [19].

Fe-Cr ALLOYS

Stainless steels owe their corrosion resistance to the presence of Cr. There is a marked improvement when the concentration of Cr in Fe increases above about 13%. The passive film may alter when exposed to air prior to analysis or following exposed to vacuum and electron radiation when using Auger spectroscopy or XPS. Thus the composition of the passive film on stainless steels determined by *ex situ* techniques may not accurately reflect the composition of the *in situ* film [4-7].

Using a cell and sample design similar to that described above for the Al-Cr studies, the *in situ* behavior of Fe-26Cr has been investigated. Figure 6, from Bardwell et al [19], it has been shown, that there was agreement between the cyclic voltammetry for a sputtered and bulk electrode of the alloy in a pH 8.4 borate buffer solution conducted at 0.5 mV/s. At the most negative potentials hydrogen is the dominant cathodic reaction. The distinct hysteresis is associated with the reduction of the oxide which takes place at the most negative potentials. The first positive current peak on increasing the potential, was the formation of the passive oxide film. At higher potentials, the second positive current peak resulted from the dissolution of Cr as a chromate. Above this potentials the marked increase in current was due to oxygen evolution. The negative current peak, at the higher potentials were associated with the reduction of chromate in the oxide and, at the lower potential, the negative current peak was due to reduction of the iron in the oxide. These peaks have previously been discussed in more detail [5].

In Figure 6 the first cycle for the sputtered film differed from the second and subsequent reproducible cycles. The subsequent cycles more closely resembles the bulk alloy. For the sputtered alloy the passive film formation was distinct on the first cycle but the peak due to Cr dissolution was suppressed. On subsequent cycles the passive film formation peak was suppressed and the chromate dissolution peak was defined. The cause of the various differences between the first and second cycle has attributed to an enriched surface layer of iron over the sputtered Fe-Cr alloy films, which protected the Cr. The first scan displays an uninhibited passive peak due to Fe oxidation, but a reduced peak for chromate formation. On subsequent cycles the Fe oxidation is reduced but the chromate formation is developed as shown by the enhanced dissolution peak.

XANES measurements of the Cr edge for the Fe-26Cr alloy, in Figure 7, were taken after stepping and holding the potential at the values indicated. Each edge measurement were took 3 minutes. Here again the quantity of Cr can be deduced from distinct changes in the edge height and changes in valency, changes in position and shape of the spectra. The curves at -1.5 Vmse, followed open circuit exposure of the alloy on adding solution. Stepping the potential to regrow the passive film at -0.4 Vmse and to where chromate was expected to form, at 0.4 V, gave no major changes. Nor were changes seem on decreasing the potential to where the iron oxide was reduced on stepping to -1.5 V. Under these conditions it has been observed that Fe is lost to solution and only a fraction of the iron in the oxide deposits as metal [21]. It was only after the Fe oxide was reduced and the protection afforded by the enriched Fe overlayer was lost, did Cr then dissolved on the second potential stepping from -0.4 to 0.4 V. The edge scans at these potentials showed a distinct drop in the edge because of the dissolution of the Cr.

Measurements to determine the behavior of the 6-valent Cr in the passive film are

Figure 7. *In situ* XANES spectra of the Cr K edge for a Fe-26Cr thin film electrode under potential control. The thin film electrode consisted of 4 nm Fe-26Cr on 10 nm Ta sputtered on Mylar. The potential was held for 10 min at each value indicated while the XANES was collected [21].

shown in Figure 8. They were carried out after a first cyclic voltammetry scan to remove the iron layer present after sputter deposition. The potentials at which the sequence of measurements were taken are indicated by the arrows on the cyclic voltammetry curves in Figure 6.

Figure 8. *In situ* XANES spectra of the Cr k edge for a Fe-26Cr thin film electrode under potential control after a first potential step cycle. The thin film electrode consisted of 4nm Fe-26Cr on 10 nm Ta sputtered on Mylar. The potential was held for 10 min at a given value while the XANES was collected. The vertical dotted line is at the pre-edge peak, 5993 eV, associated with 6-valent Cr. The insert shows a comparison between the summed spectra of (e) and (i) (both at 0.6 Vmsec) and (h) and (j) (both at -0.3 Vmsec) [19].

The edge scans (a) to (c) show that on stepping the potential Cr was not lost until the potential was increased to 0.4, (d) and 0.6 V, (e), above the current peak for chromate formation. The height of the main edge was reduced due to loss of the Cr into solution. The a pre-edge peak (at 5993 eV) associated with 6-valent Cr can be discerned. Decreasing the potential to (f) and (g) produced no changes, and the pre-edge peak remained. On stepping below the peak to (h) the edge shape changed. There was on longer a clear indications of a pre-edge peak and also the height of maximum of the main edge increased. These two changes indicated a reduction of 6- to 3-valent Cr.

Changes in the edge shape on stepping the potential to (i) and (j) showed that 6-valent was again formed and was then reduced to the 3-valent state without any losses of total Cr. The features associated with the 3- and 6-valent states are more clearly seen on summing the higher and lower potentials as shown in the inset in Figure 8. Hence, the passive film on the iron alloy was also electroactive and showed similar behavior to that observed with the oxide formed on the sputtered aluminum alloy.

The stability of the 6-valent Cr state when incorporated in the iron oxide was also investigated. A sample with a passive oxide incorporating 6-valent Cr was washed with distilled water, and without drying, was exposed to air [19]. The near edge spectra are shown in Figure 9. The *in situ* measurement prior to removal was at 0.8 V and 6-valent Cr was present. At 1.5 h the 6-valent Cr was still present, but after 16.5 h it had disappeared. With dry samples reduction has been observed after 15 min [5]. Hence the 6-valent Cr was not stable and its presence cannot be maintained on removal of potential control even in the presence of oxygen in the air. In reducing environments or in vacuum, the rate of reduction can therefore be expected to be more rapid.

Figure 9. *In situ* and *ex situ* XANES spectra of a 6 nm film of Fe-26Cr. (a) *In situ* potentiostated at 0.8 V_{mse}, and *ex situ* after (b) 0.5, (c) 1.5 h and (d) 16.5 h, of air exposure. The vertical dotted line is at the pre-edge peak, 5993 eV associated with 6-valent Cr [19].

5. Localized Corrosion

In the presence of chlorides breakdown of passive films take place and the dissolution of the metal is rapid. The composition and nature of the solution that develops within the corrosion area is important as it determine the subsequent behavior. If the concentration continues to increase then a salt layer eventually precipitates on the metal surface and the rate of dissolution is controlled by diffusion gradients and the dissolution of the salt. If conditions prevail that lead to a drop in concentration, the solution becomes less aggressive and the actively dissolving surface will repassivate.

In order to simulate the chemical processes in solution during localized corrosion one-dimensional artificial pits have been used [9]. X-ray fluorescence measurements using white x-rays and an energy-dispersive spectrometer offer a powerful method for the *in situ* study of chemical and physical changes during electrochemical and corrosion processes. It 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.

The electrochemical cell shown in Figure 4A was designed to simulate one-dimensional diffusion processes taking place in pitting or crevice corrosion. A 0.5 M HCl + 0.5 M NaCl solution was used with a saturated calomel reference electrode (sce). The steel was dissolved downwards at a constant potential of 0.6 V_{sce} leaving a rectangular shaped crevice [20].

Figure 2 shows a fluorescent spectrum of the solution inside the cavity immediately above the metal for real-time counting of 600 s. The counts under the K α energy peak for Fe, Cr and Ni were integrated and used to determine their fluorescence intensities. The argon peak was from argon in the air. The source of the As and Br peaks could be due to impurities in the plastic, the Teflon window or the epoxy glue. These possibilities were not pursued as

Figure 10. A) Variations of fluorescence intensities for Fe, Cr and Ni as a function of position above the cross section of a dissolving Type 304 stainless steel foil 0.014 mm thick. The depth of dissolution of the foil was 2.1 mm. The bulk solution was 0.5 M NaCl+0.5 M HCl [20].

B) Variations of concentration of Fe, Cr, Ni and the total of these elements, above the cross section of dissolving Type 304 stainless steel, derived from the results in Figure 10A [20].

they were only observed after long period of counting time (600 s) and were not seen when counting for real-time 30 seconds. This does, however, indicate a major application of x-ray fluorescence technique which is the quantitative analysis of trace impurities [15,16].

Figure 10A shows the intensities as a function of height above the stainless steel/solution interface at a current density of 64 mA/cm² [20]. The iron shows a increased slope close to the dissolving interface and again at the mouth of the artificial pit.

The relative intensities of the observed fluorescence is a complex function of the x-ray cross sections, the relative positions of the binding energies of the elements and their emission energies. Quantitative x-ray fluorescence analysis has been well established for many years [25] and a number of possible methods of calibration are available. Two main methods are used for quantitative analysis. The first is an empirical method exemplified by the multiple regression treatment of Lucas-Tooth and Pyne [26]. 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 method calculates the expected intensities based on a fundamental-parameters method [25-28]. This method derives the expected intensities from a given sample composition, 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 computer program [28] was used and referenced to the known concentration of the iron in the stainless steel in order to convert the measured normalized fluorescent intensities of Fe, Cr and Ni to solution concentrations.

The derived concentrations variations are shown in Figure 10B. The total concentration of metal ions is also given as a function of distance from the steel surface. The saturation value for the steel was 4.75 molar and a corresponding chloride concentration was 10.4 molar. This value is in agreement with the value of Hakkarainen [29] who observed that approximately 10 M chloride ion was required to give a saturated metal chloride solution on dissolving Type 304 stainless steel in HCl.

The relative Fe:Cr:Ni weight per cent ratios in the saturated solution at the metal interface were 67 : 22 : 11 compared to ratios of 68.7 : 18.2 : 13.1 in the metal. The differences in the ratios resulted from unequal the mass transfer rate for the ions in solution. The mass transfer includes an electromigration contribution in addition to diffusion, but as the contribution is not known, the results have been treated in terms of effective diffusion rates. The effective integral diffusion rates calculated from the concentrations at the metal/solution interface, the depth of the crevice and the current density. The values obtained were 6.0, 5.2 and 4.7 10⁻⁶ cm²/s for the ions or chloride salts of nickel, iron and chromium respectively. These values are close to published results for nickel chloride diffusion coefficients [30] and indicate that only a small electromigration contribution was present.

The concentration gradients in Figure 10B were clearly non-linear with increased

slopes close to the dissolving metal interface and close to the mouth of the crevice. This behavior shows that the differential diffusion coefficients have a maximum at intermediate concentrations around a total metal ion concentration of about 2.5 M. Once again this behavior is consistent with diffusion coefficients of many salts [31,30]. Nickel chloride solutions show a maximum diffusion coefficient but at a lower concentration of 1.5 M [30].

6. CONCLUSION

Two applications of high intensity x-ray methods have been presented to indicate ways to study corrosion processes. They demonstrate but a few uses of x-ray methods. There are many other approaches with advantages and possibilities that complement or may not be met, using other techniques. In particular, with electrochemical processes, including corrosion where the processes can easily be turned on and off there will, in the future, be many more *in situ* investigation that can effectively elucidate the chemistry taking place.

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