Film Analysis of Alloy 600

TR-112776

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REPORT SUMMARY

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) surface analysis techniques performed on tubes removed from steam generators can provide clues to the local environment causing degradation.

Background

When alloy 600 steam generator tubes are pulled for examination, analysis of corrosion product chemistry on fracture faces and tube surfaces provides indirect evidence of the environment in the steam generator causing degradation. As the pH and oxidizing conditions of this environment change, different corrosion products become thermodynamically stable. AES and XPS surface analysis techniques can be used to identify composition and structure of corrosion deposits and film.

Objectives

To provide a database of reference film compositions over a broad range of pH values.

Approach

The project team exposed corrosion coupons and stressed C-ring samples of alloy 600 in reference environments covering the pH range of 3 to 10 at 315°C. The team obtained anodic polarization curves in each environment and determined stress corrosion cracking behavior and film compositions as a function of electrochemical potential (ECP).

Results

Results showed that film composition gives definitive identification of pH for all ECP values if the pH is above approximately 10 or below 5. At high pH, the surface is predominately pure nickel or nickel oxide/hydroxide. At low pH, the surface is predominately chromium oxide or hydroxide. At pH values between these extremes, results depend on the ECP. As long as the ECP was in the active region (< +50 mV) , there was a definitive correlation between the Ni/Cr ratio and pH.

Mill-annealed alloy 600 C-ring samples experienced stress corrosion cracking when polarized at 100 and 150 mV positive to the open circuit corrosion potential in a simple sodium chloride/sodium hydroxide environment at pH 10—but not in a complex environment containing silica and magnetite. Sensitized alloy 600 C-rings were only exposed to the complex environment and did not crack. Exposure of mill-annealed alloy 600 in a complex environment at pH 3 caused only severe wastage.

EPRI Perspective

Over the years, Auger and XPS analyses have been performed on pulled steam generator tubes from numerous plants. Analyses of corrosion films on tubes from older plants such as Trojan, Ginna, and Point Beach have shown films enriched in nickel, which implied a highly alkaline environment in regions of degradation. Over the years, as improvements in secondary water chemistry controls have been implemented, more recent analyses are suggesting that local environments could be neutral to slightly alkaline—yet, degradation at these lower pH values continues. Previous work has demonstrated that stress corrosion cracking is not only driven by the environment's pH but also by electrochemical potential. This work has noted that, for pH values in the neutral to slightly alkaline range, there is no simple correlation between film composition and potential. Thus, use of simple compositional factors such as Ni/Cr ratio derived from Auger analyses may have limited value in interpreting tube examination results. The challenge in future tube examination projects is to judicially use both compositional and structural analytical methods, such as XPS, to provide oxidation state information—in this manner, results can be interpreted in terms of both pH and potential.

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Keywords

Nuclear steam generators
Intergranular corrosion
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ABSTRACT

Reference films have been formed on alloy 600 by exposing samples to solutions and temperatures typical of those found in PWR steam generator crevices. The films, which were formed at constant electrochemical potentials (ECPs), were analyzed using surface analysis techniques. At high pH's the surface was predominately Ni or Ni compounds at all electrochemical potentials. In highly acidic conditions, the surface was predominately Cr or Cr compounds at all potentials. For pH's between highly acidic and caustic, the Ni/Cr ratio increased linearly provided with increase in pH provided the ECP was at open circuit or at slightly to moderately oxidizing values. Under these potential conditions, the ECP is in the active region of the polarization curve. This is believed to be the ECP range where most steam generators are operating.

SUMMARY

The crevice formed by the tube / tube support plate (tube / TSP) intersection in a pressurized water reactor (PWR) steam generator is a concentration site for nonvolatile impurities (referred to as hideout) in the steam generator water. The restricted mass transport in the small crevice volume prevents the species, which concentrate during the generation of steam, from quickly dispersing into the bulk water. These concentrated solutions have been a contributing cause of several forms of corrosion of steam generator tubes including intergranular attack / stress corrosion cracking (IGA / SCC), pitting, and wastage.

When alloy 600 steam generator tubes are pulled for examination, an analysis of the chemistry of the corrosion products on the fracture faces and OD provides clues to the local environment in the crevice or free span region, from which the section of tubing was removed. As the pH and oxidizing conditions of the aqueous environment change, different corrosion products become thermodynamically stable. Surface analysis techniques such as Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) combined with ion beam sputtering give the in-depth composition profile of these films. The valence state and compound identification can sometimes be provided by XPS.

In this program AES has been used to examine the composition of films formed on alloy 600 in reference environments. Two subsets of environments were used. In one subset solutions were used with 5 m NaCl, in which the pH was varied from 3 to 10 by adding HCl or NaOH. The second subset was designed to be prototypical crevice solutions. These solutions had 5 m NaCl, 0.5 m SiO_2, 0.1 m magnetite, and 0.25 m to 0.5 m K_2SO_4. The pH of the second subset was varied from 3 to 10 using different concentrations of H_2SO_4 and KOH.

Films were formed on alloy 600 at open circuit and at a constant electrochemical potential (ECP), which was anodic to the open circuit potential. The open circuit potential is the hydrogen equilibrium potential for 0.2 atmospheres of hydrogen. Potentials anodic to the open circuit ECP correspond to conditions of lower hydrogen activity or the presence of an oxidizing agent.

The results showed that the composition of films give definitive identification of the pH for all ECP values if the pH is above approximately 10 or below approximately 5. At the

high pH's the surface is predominately pure Ni or nickel oxide / hydroxide. At the low pH's the surface is predominately chromium oxide or hydroxide. At pH's between these extremes the results depend on the ECP. At the open circuit potential and at potentials a few 10's of millivolts higher, oxide film formation is not thermodynamically possible. For samples polarized at these potentials, it was found that a useful way to analyze the AES data was to normalize the atomic concentration of each alloy metal by dividing by the sum of Ni, Cr, and Fe atomic concentrations. When this was done, the normalized Cr concentration increased uniformly as the pH decreased. At potentials above those at which there was oxide formation, neither the Cr nor the Ni followed a predicable trend with pH.

The database for the prototypical crevice concentrations is not as extensive as that for the NaOH / NaCl / HCl subset, but the trends in the surface concentration were the same for both systems.

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INTRODUCTION

The crevice formed by the tube/tube support plate (tube/TSP) intersection in a pressurized water reactor (PWR) steam generator is a concentration site for nonvolatile impurities (referred to as hideout) in the steam generator water. The restricted mass transport in the small crevice volume prevents the species, which concentrate during the generation of steam, from quickly dispersing into the bulk water. The presence of a porous magnetite corrosion product from the support plate and deposits, originating from the feed and condensate systems, in the crevice further restrict mass transport. This flow restriction leads to the concentration of impurities from the steam generator water by a thermal/hydraulic mechanism.

The concentrated solutions in crevices have been a contributing cause of several forms of corrosion of steam generator tubes including intergranular attack/stress corrosion cracking (IGA/SCC), pitting, and wastage. The rate and type of corrosion are dependent on pH, specific anions, and the electrochemical potential (ECP). The exact composition of the crevice solution, causing damage to the tube, is not known since the crevices are inaccessible during operation of the steam generator. Clues about the crevice chemistry are provided when the chemistry of steam generator water is monitored on shutdown. The cessation of boiling in the crevice allows the crevice steam space to fill with water and the diffusion of concentrates out of the crevice into the bulk water. These species (called hideout return) are used as data in computer codes to calculate the crevice chemistry. However, this procedure has inherent uncertainties because the computer codes rely on hypothesized conditions and reactions in the crevice as well as incomplete databases.

When alloy 600 steam generator tubes are pulled for examination, an analysis of the chemistry of the corrosion products on the fracture faces and OD also provides clues to the local environment in the crevice or free span region, from which the section of tubing was removed. As the pH and oxidizing conditions of the aqueous environment change, different corrosion products become thermodynamically stable. Surface analysis techniques such as Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) combined with ion beam sputtering give the in-depth composition profile of these films. The valence state and compound identification can sometimes be provided by XPS.

This program aims to provide a database of reference film compositions. These films have been formed in environments with prototypic crevice species and concentrations over a broad range of pH's. The reference films can be used in identifying the crevice environment from tube examinations.

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EXPERIMENTAL

Test Material

The mill annealed alloy 600 tubing tested (Heat No. M5442) was manufactured by the Tubular Products Division of Babcock & Wilcox Company. Table 2-1 gives the composition. The tubing was in the mill annealed condition, time and temperature are proprietary, with a 15 mm OD and 1 mm wall thickness. The SCC behavior of this alloy has been in the MA and in the MA plus thermal treatment conditions has been characterized previously by B&W (1). This alloy was also used in the Rockwell program to evaluate the effectiveness of inhibitors for IGA / SCC (2).

Table 2-1
Chemical Composition of Alloy 600 Heat No. M5442 Test Material

C	Si	Mn	P	S	Ni	Cr	Cu	T	Fe	Al
0.047	0.11	0.38	0.007	0.005	74.42	15.71	0.01	0.24	8.6	0.28

A second heat of alloy 600 was tested as ¾ inch diameter tubing in the sensitized condition. This material was Heat No. 96834, which was specially prepared by B&W for EPRI to be susceptible to primary side water SCC (3). The chemical composition of the heat is given in Table 2-2. This relatively high carbon (0.04%) heat of alloy 600 had previously been given a final anneal of 1038°C. The tube was then heat treated in a vacuum furnace at 593°C for 18 hours. Sensitization was determined by the modified Huey test and by examination of the microstructure using the Dual Etch procedure. The microstructure had extensive carbide decoration of the grain boundaries. The Huey weight loss was 803 $mg / dm^2 / day$.

Table 2-2
Chemical Composition of Ally 600 Heat No. 96834

C	Mn	S	Si	Cr	Ni	Cu	Co	Fe
0.040	0.26	0.001	0.30	15.83	74.91	0.01	0.23	8.09

Test Environments

Both simple and complex test environments, which ranged from pH 3 to 11.2, were used. The pH 11.2 environment was a 50w/o NaOH solution. Table 2-1 gives the chemical composition and the MULTEQ calculations of the pH of the eight additional test environments. The simple environments were based on the HCl/NaCl/NaOH system. In this system the pH was adjusted by adding HCl and NaOH, and the NaCl activity was held constant at 5 m. The complex system was designed to simulate an hypothesized crevice environment. In this system the activities of NaCl, SiO_2 and Fe_3O_4 were held constant at 5.0, 0.5, and 0.1 respectively, while the pH was adjusted by varying the concentrations of sulfuric acid and KOH.

Table 2-3
Environments Used to Form Reference Films

		pH @ Temperature			
No.	**Chemistry**	**20°C**	**280°C**	**300°C**	**315°C**
1	5.000 m NaCl + 0.00122 m HCl	2.91	2.95	2.97	3.00
2	5.000 m NaCl	7.07	4.96	4.91	4.9
3	5.000 m NaCl + 0.45 m NaOH	13.8	9.5	9.5	9.3
4	5.000 m NaCl + 2.975 m NaOH	14.81	10.27	10.10	10.00
5	5.000 m NaCl + 0.500 m SiO_2 + 0.250 m K_2SO_4 + 0.430 m H_2SO_4 + 0.100 m Fe_3O_4	0.60	3.05	3.05	3.00
6	5.000 m NaCl + 0.500 m SiO_2 + 0.400 m K_2SO_4 + 0.059 m H_2SO_4 + 0.100 m Fe_3O_4	4.06	5.04	5.02	5.00
7	5.000 m NaCl + 0.500 m SiO_2 + 0.500 m K_2SO_4 + 0.555 m KOH + 0.100 m Fe_3O_4	8.30	9.33	9.14	9.00
8	5.000 m NaCl + 0.500 m SiO_2 + 0.500 m K_2SO_4 + 5.300 m KOH + 0.100 m Fe_3O_4	15.47	10.37	10.15	10.00

Potentiodynamic Polarization and Sample Preparation

All tests were conducted in a 750 ml nickel lined, alloy 718 autoclave. The autoclave head has six symmetrically spaced openings for fittings to accommodate 3.2 mm diameter Ni rods, which were electrically isolated form the autoclave. A cylindrical Ni counter electrode, which completely surrounded the test samples, was attached to one to the Ni rods. A second Ni rod was used as the reference electrode. Though the Ni reference rod may become coated with metal oxides which precipitate from solution, the coatings are porous and are not electrochemically active; thus, the reference potential should remain fixed by the hydrogen fugacity and pH. The remainder of the rods was used to suspend test specimens in the electrolyte.

Samples for potentiodynamic measurements and surface analysis were prepared by cutting "flag" specimens from the tubing. Each sample was a sector of the tubing one-fourth of the diameter and 12 mm wide with a 5 cm X 3 mm stem. The surfaces were polished to a final finish of 1 µm. The "flag" specimens were spot welded to the ends of the alloy 600 rods and suspended so that the same area was exposed to the solution in all runs. Two specimens were used for each potentiodynamic polarization curve, one for the cathodic potentials and one for the anodic potentials. A schematic of the setup is shown in Figure 2-1. Specimens were always positioned so that the solution level was 0.5 cm below the top of the stem. Up to four specimens for film analysis were prepared simultaneously. One specimen was at open circuit. The others were polarized potentiostatically using a Pine Instrument Co. Model AFRDE5 Bi-potentiostat. Specimens were polarized at several potentials above the corrosion potential for two days.

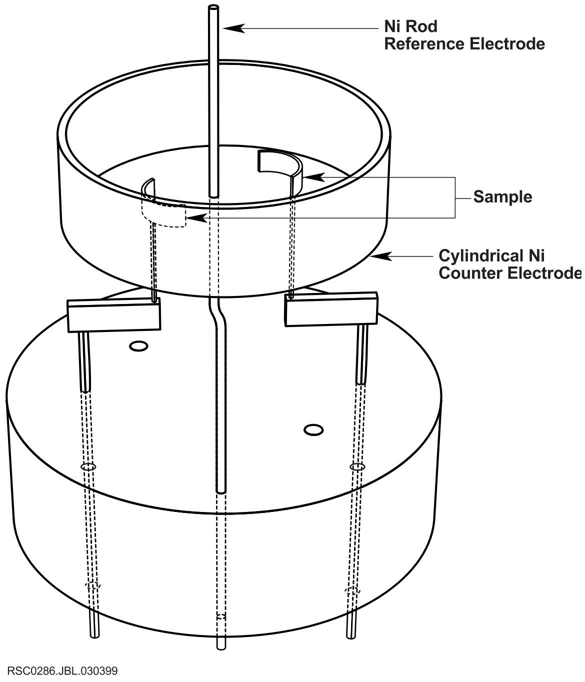

Figure 2-1
Schematic of the setup used to obtain polarization curves

Stress corrosion tests were performed using C-ring specimens. These specimens were prepared according to ASTM G38-73 and were strained to a constant deflection corresponding to a maximum stress at the apex of 150% of yield calculated according to

$$\Delta = s\ p\ D^2 / 4EtZ \qquad \text{(eq. 2-1)}$$

where s is the desired stress, Δ is the change of OD giving the desired stress, D is the mean diameter (OD – t), t is the wall thickness, E is the modulus, and Z is a correction factor for curved beams. Alloy 600 nuts and bolts were used to stress the samples.

Surface Analysis

Auger electron spectroscopy (AES) was used to obtain in-depth, elemental composition profiles for the films on specimens by sequentially sputtering by argon ion bombardment and performing Auger analysis. Preliminary results showed that long-term exposure to the slowly cooling solution causes changes in the surface chemistry and that rapid cooling of the autoclave is important to preserve the surface chemistry present at elevated temperature. Several procedures were tried including venting the solution while at temperature. Tests showed that the autoclave could be cooled at a sufficient rate with fans provided the heaters and insulation were removed immediately prior to terminating the test. During the first 15 minutes the temperature dropped approximately 150°C and reached room temperature in less than three hours. Potentials were not applied while the autoclave was cooling.

A Perkin-Elmer PHI Model 590 Scanning Auger Microprobe was used for the Auger examination. The analysis was performed using an electron beam excitation voltage of 3 KV, charging was sometimes observed at higher voltages. A 6 eV modulation voltage was used. Surfaces were analyzed with the electron beam rastered 60 mm X 40 mm. Individual grains were analyzed on fracture faces with a stationary electron beam defocused to a diameter of approximately 10 mm. Sputtering was performed with a 5 kV argon ion beam rastered over an area 2.7 µm X 4 µm, which gave a sputtering rate of approximately 5 Å / s.

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RESULTS

Figure 3-1 and Figure 3-2 show the potentiodynamic polarization curves for 50% NaOH and the pH 10 simple solution (Environment 4 in Table 3-1), respectively. The cathodic curve was obtained by scanning the potential from the rest potential to –50 mV. The anodic curve ranges for the rest potential to approximately 1000 mV. As the potential was made more anodic (scanned to higher potentials) from the rest potential, the current density increased rapidly. This type of current response with potential suggests the occurrence of film free dissolution (or active dissolution). The rapid decrease in current density after the anodic peak suggests the onset of passive film formation. After the rapid decrease, there is a broad potential range over which the current density is constant because the surface is protected by a passive film. At very high potentials, the dissolution rate again increases rapidly with potential as the passive film loses its protective quality and breaks down due to pitting.

The polarization curve for the pH 9.3 solution (Environment 3) is shown in Figure 3-2. This is similar to those for the 50% NaOH and pH 10 solutions with the exception of two secondary peaks, one at approximately 0.4 V and one at approximately 0.65 V.

Figure 3-3 is the polarization curve for the pH 4.9 solution (Environment 2). This curve has an active peak followed by a passive region in which there is rapid fluctuation in the current. The average current density is approximately an order of magnitude higher than that in the curves for solutions at higher pH.

The polarization curve for the pH 3 solution (Environment 1) has no passive region. As shown in Figure 3-4 this curve increases exponentially with potential.

The polarization curves for the complex pH 10 and pH 9 environments, Environment 7 and Environment 9, are shown in Figures 3-5 and Figures 3-6, respectively. These curves are very similar to those shown in Figures 3-2 and 3-3 for the simple pH 10 and pH 9.3 environments. Both have active-passive types of behavior and the curve for Environment 9 (pH 9) has multiple peaks in the passive region like that for Environment 3, pH 9.3.

The polarization curve for the complex pH 5 environment, shown in Figure 3-7 is somewhat different from that for the simple pH 5 environment. The rapid fluctuations observed at potentials positive to the active peak in Figure 3-3 did not occur in the complex pH 5 environment. However, there is a well-defined abrupt increase in the current at approximately 0.2 V, which suggests that the film is breaking down by pitting.

Figure 3-8 shows the polarization curve for the complex pH 3.0 solution, Environment 5. This is almost identical to Figure 3-4. The current increases exponentially with potential up to approximately 0.2 V. But unlike Figure 3-4, it then reaches a limiting current plateau of approximately 0.05 A/cm^2 for potentials higher than 0.2 V.

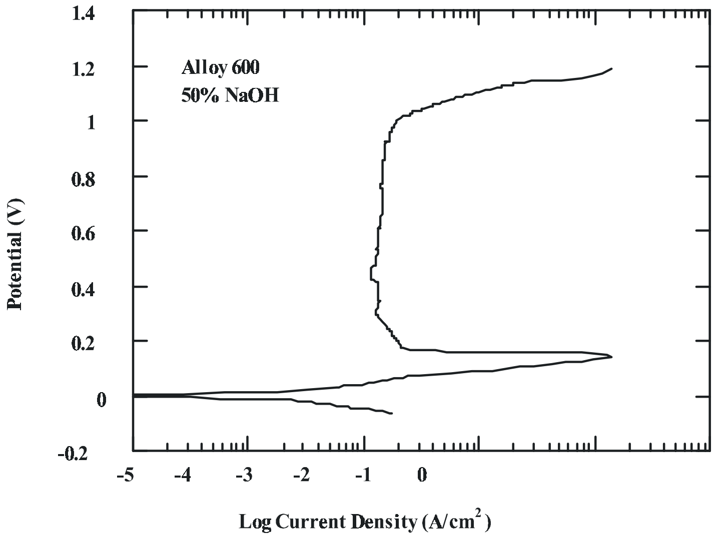

Figure 3-1
Potentiodynamic polarization curve of alloy 600 in 50% NaOH

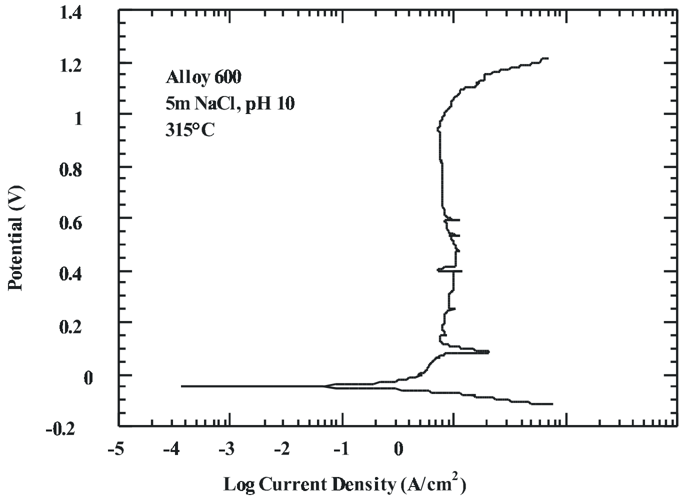

Figure 3-2
Potentiodynamic polarization curve of alloy 600 in 5 m NaCl +2 m NaOH at 315°C, pH = 10.0

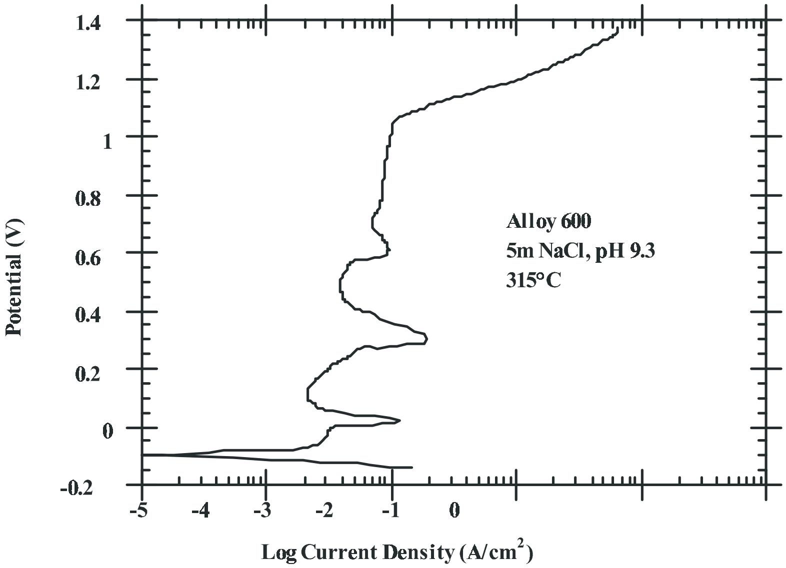

Figure 3-3
Potentiodynamic polarization curve of alloy 600 in 5 m NaCl + 0.105 m NaOH at 315°C, pH = 9.3

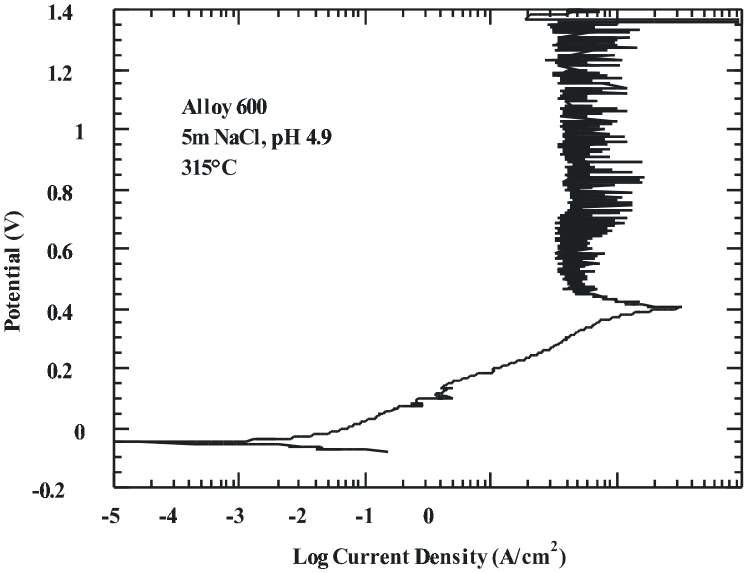

Figure 3-4
Potentiodynamic polarization curve of alloy 600 in 5 m NaCl at 315°C, pH = 4.9

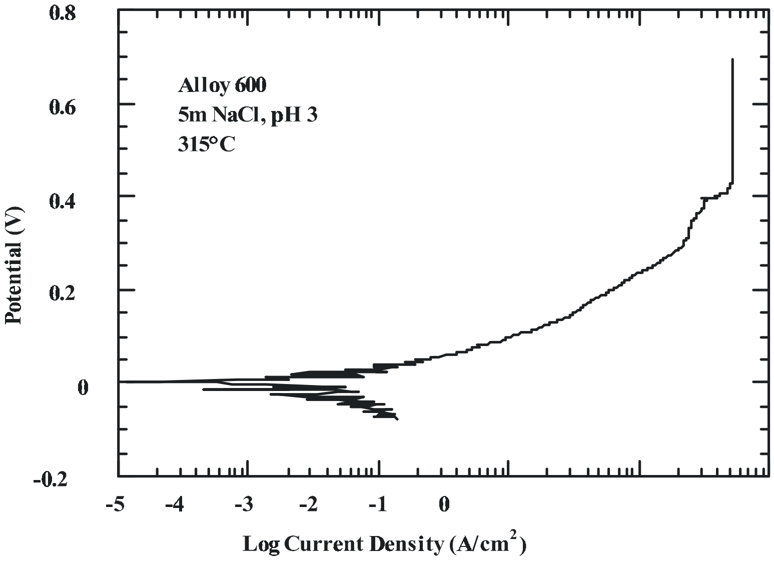

Figure 3-5
Potentiodynamic polarization curve of alloy 600 in 5 m NaCl + 0.00122 m HCl at 315°C, pH = 3

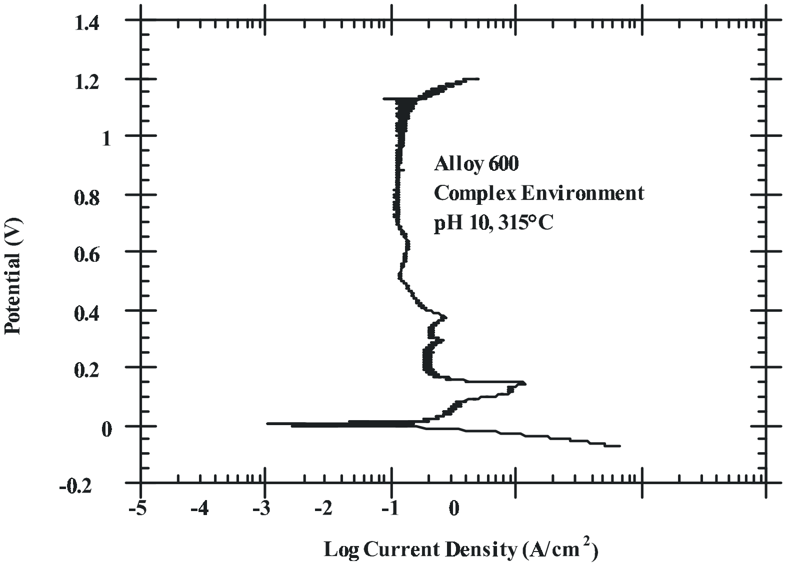

Figure 3-6
Potentiodynamic polarization curve of alloy 600 in the complex pH10 environment at 315°C

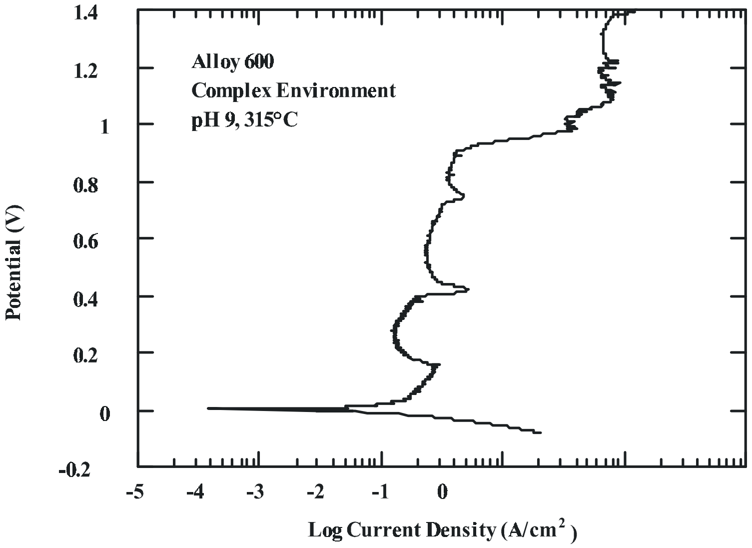

Figure 3-7
Potentiodynamic polarization curve of alloy 600 in the complex pH 9 environment at 315°C

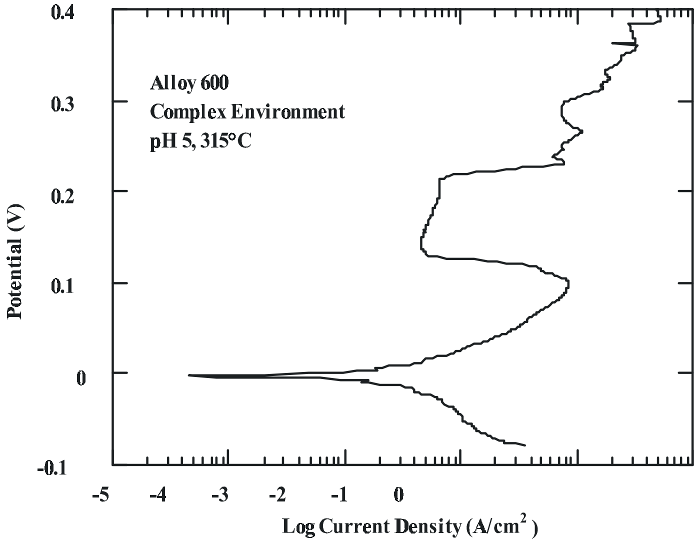

Figure 3-8
Potentiodynamic polarization curve of alloy 600 in the complex pH 5 environment at 315°C

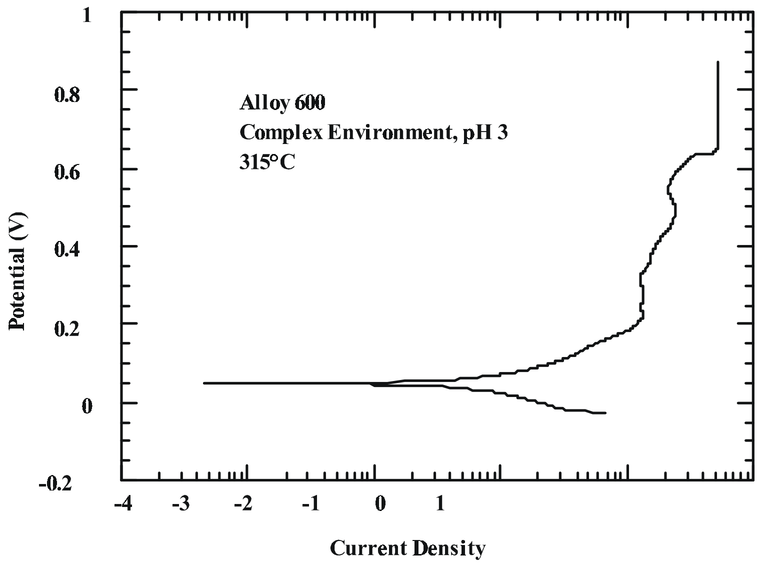

Figure 3-9
Potentiodynamic polarization curve of alloy 600 in the complex pH 3 environment at 315°C

Table 3-1 is the in-depth composition profile of the specimen exposed to the 50w/o NaOH solution, pH 11.2, at open circuit for 48 hours. This table is formatted such that the last column to the right gives the depth sputtered, the next three columns to the left give the relative atomic percent of the alloy metals normalized so that they add to 100%, and the remaining columns give the atomic percents of all the species detected. The surface has an oxide film less than 50 Å thick. After this is removed by sputtering, there is a pure Ni layer approximately 400 Å in thickness. The alloying metals, Cr and Fe, slowly increase to the levels in the bulk material as the next 3000 Å is removed by sputtering. Figure 3-10 shows the data for the normalized alloy metals in Table 3-1 in graphic form. Table 3-2 is a profile showing the in-depth composition of the surface film on an alloy 600 specimen, which has been exposed to the 50% NaOH solution for 120 hours at 315°C. The increase in exposure time from 48 hours to 120 hours has increased the depth of the pure Ni layer from approximately 400 Å to 800 Å. The depth of the layer in which Cr is below that in the bulk alloy is over 2 µm. Figure 3-11 is a graph of the normalized alloy concentrations in Table 3-20. The increase in exposure time causes an increase in the depth of the dealloyed layer, but no other changes in composition.

The next two tables and figures are also results from the 50% NaOH solution and show the effects on film composition by increasing the ECP. Table 3-3 is the composition profile of the specimen, which had been polarized 100 mV above the corrosion potential. The normalized in-depth composition of the alloy metals is given in

Figure 3-12. A 50 Å oxide film, which contains a large quantity of carbon contamination, covers a substrate dealloyed of Cr and Fe. Approximately 1500Å was sputtered from the surface before Cr reached the level in the alloy. Oxygen was detected to a depth of 3200 Å due to the existence of oxide in etch pits. Table 3-5 gives the composition of the film on the specimen, which had been polarized at 150 mV above the corrosion potential. This sample has an oxide film several micrometers thick. The film has a duplex structure with a nickel oxide outer layer and an Fe-Cr-Ni oxide adjacent to the substrate. The profile of the normalized alloy metals is shown in Figure 3-14.

Tables 3-6 through 3-10 and Figures 3-15 through 3-19 are Auger results for specimens at different potentials while exposed to the pH 10 simple environment in Table 3-1. The specimen exposed at open circuit potential (Table 3-6 and Figure 3-12) and that polarized 25 mV (Table 3-7 and Figure 3-16) above the corrosion potential had a thin, nickel rich, oxide film 100 Å or less, covering a dealloyed substrate. The dealloyed layer extended a few thousand angstroms below the surface. The oxide films on the specimens, which had been polarized at 50 mV (Table 3-4 and Figure 3-16), 100 mV (Table 3-9 and Figure 3-18), and 150 mV (Table 3-10 and Figure 3-20), have substantial amounts of Cr and smaller Ni/Cr ratios than that of alloy 600. The thickness of the films formed at 50, 100, and 150 mV increased approximately in proportion to the increase in ECP. There was a lot of carbon contamination in the outer 50 Å of the film. There was no chloride or sodium in the film beyond that which could be explained by contamination.

The results for the pH 9.3 solution, Environment 3 in Table 3-2, are given in Tables 3-11 through 3-15 and Figures 3-20 through 3-24. These results show that films, which were formed on samples that had been at open circuit, at 25 mV, and at 50 mV were 50 to 100 Å thick with heavy carbon contamination. The Ni/Cr ratio in the films and in the underlying substrate was significantly higher than that in alloy 600. The dealloying in the substrate extended to a depth of over 0.5 µm. Table 3-14 and Figure 3-20 show the profile for the sample, which was polarized at 100 mV while exposed to the pH 9.3 solution. The thickness of the oxide film has increased significantly compared to those formed at lower potentials. The Ni/Cr ratio is near one for the outer 3200 Å of film, while Fe is the major metallic component of the oxide. Table 3-15 and Figure 3-24 give the Auger results for the sample, which had been polarized 150 mV above the corrosion potential. A film thicker than 2.5 µm covers the surface. The Ni/Cr ratio in outer several hundred Angstroms of the surface is near one. After approximately 1 µm of oxide is removed by sputtering, the Ni/Cr ratio in the oxide is near that of the alloy.

The surfaces of the specimens, which had been exposed to the 5 m NaCl solution (pH 4.9), were rich in Cr. At open circuit, Table 3-16 and Figure 3-25, the Ni/Cr ratio is almost 1/3. As the potential was increased the oxide film became thicker and the Ni/Cr ratio decreased. The film formed at 200 mV (Table 3-17 and Figure 3-26) contained over 65a/o Cr and that formed at 500 mV (Table 3-18 and Figure 3-27) had over 85a/o Cr.

The surface film on the specimen which had been exposed to Environment 1 (pH 3) was chromium oxide with between 3 to 5a/o incorporated chloride, as shown in Table 3-19 and Figure 3-28. The surface composition of the specimen, which had been polarized 100 mV below the open circuit potential, is shown in Table 3-20 and Figure 3-29. Decreasing the potential 150 mV below the open circuit potential changes the film from chromium oxide to a Ni-Cr oxide. A specimen was also examined which had been polarized 100 mV above the open circuit potential. Like the open circuit results, this film was also chromium oxide. However, a composition profile could not be obtained because the specimen charged after 200 Å were sputtered from the surface, making an Auger analysis impossible.

Table 3-21 and Figure 3-31 show the open circuit results for the pH 10 environment containing magnetite and the salts, Environment 8. The film contains no Cr and is a Fe-Ni oxide. All of the ionic species in the solution with the exception of sulfate are incorporated into the oxide film. Silicate and K are the incorporated species having the highest concentration.

The open circuit results for the pH 9 complex environment are shown in Table 3-22 and Figure 3-32. The outer 50 Å of film is depleted in Cr. After the outer 50 Å of the film are sputtered away, the film was a Fe-Cr-Ni mixed oxide. Table 3-23 gives the composition of the film formed in the pH 9 complex solution when the specimen was polarized 50 mV above the open circuit potential. Neither Cr nor Fe was found in this film, which was sputtered to a depth of 3200 Å. An analysis at greater depths in the film was not possible because of charging. The profile of the film formed on the sample in the pH 9 solution while polarized at 100 mV is shown in Table 3-24 and Figure 3-33. This oxide is also depleted of Cr, but has a significant amount of Fe. The oxides, which were formed at all three ECP conditions, had incorporated ionic species from the salts in the reference environment. Silicate and potassium were incorporated at the highest concentrations.

Table 3-25 and Figure 3-34 show the open circuit results for the pH 3 complex solution, environment 5. The oxide is duplex in structure. The outer layer is chromium oxide and the inner layer is a Cr-Ni oxide.

Table 3-1
Auger results for alloy 600 specimen exposed to 50% NaOH at 315°C for 48 hours

Atomic Percents					Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	C	Cr	Fe	Ni	
38.6	0.0	0.0	32.9	28.5	0.0	0.0	100.0	0
7.3	0.0	0.0	59.7	33.0	0.0	0.0	100.0	50
7.5	0.0	0.0	79.6	12.9	0.0	0.0	100.0	100
5.3	0.0	0.0	91.2	3.5	0.0	0.0	100.0	200
2.9	0.6	0.0	94.6	2.0	0.6	0.0	99.4	400
0.0	2.1	1.7	96.2	0.0	2.1	1.7	96.2	800
0.0	10.0	3.7	86.4	0.0	10.0	3.7	86.4	1600
0.0	17.6	7.9	74.5	0.0	17.6	7.9	74.5	3200
0.0	20.8	9.8	69.4	0.0	20.8	9.8	69.4	6400
0.0	20.9	10.0	69.1	0.0	20.9	10.0	69.1	12800

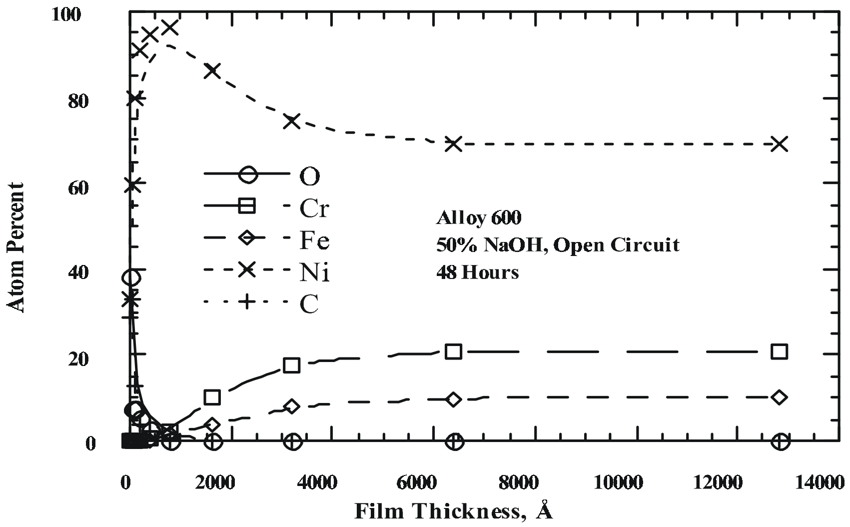

Figure 3-10
Auger in-depth composition profile of the surface of the specimen exposed to the 50% NaOH solution at open circuit

Table 3-2
Auger results for an alloy 600 specimen exposed to 50% NaOH at 315°C at open circuit for 120 hours

Atomic Percents					Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	C	Cr	Fe	Ni	
55.6	0.0	0.0	29.8	14.7	0.0	0.0	100.0	0
43.7	0.0	0.0	44.8	11.5	0.0	0.0	100.0	200
34.8	0.0	0.0	61.8	3.4	0.0	0.0	100.0	400
23.5	0.0	0.0	76.5	0.0	0.0	0.0	100.0	600
18.0	0.1	0.0	81.9	0.0	0.1	0.0	99.9	800
15.7	0.2	7.3	76.8	0.0	0.2	8.7	91.1	1000
13.2	0.6	6.9	79.3	0.0	0.7	8.0	91.3	1300
10.1	0.5	6.9	82.5	0.0	0.6	7.7	91.8	1600
8.7	0.8	6.7	83.7	0.0	0.9	7.4	91.7	2000
6.0	1.6	7.1	85.4	0.0	1.7	7.5	90.8	3000
5.1	2.4	8.0	84.5	0.0	2.5	8.4	89.1	4000
4.6	3.2	8.3	83.9	0.0	3.3	8.7	87.9	6000
4.5	3.8	8.1	83.6	0.0	4.0	8.5	87.6	8000
4.1	4.4	8.9	82.6	0.0	4.6	9.3	86.1	10000
4.0	5.5	8.9	81.6	0.0	5.7	9.3	85.0	12000
2.8	5.3	9.4	82.5	0.0	5.5	9.6	84.9	14000
2.4	7.2	10.6	79.7	0.0	7.4	10.9	81.7	22000

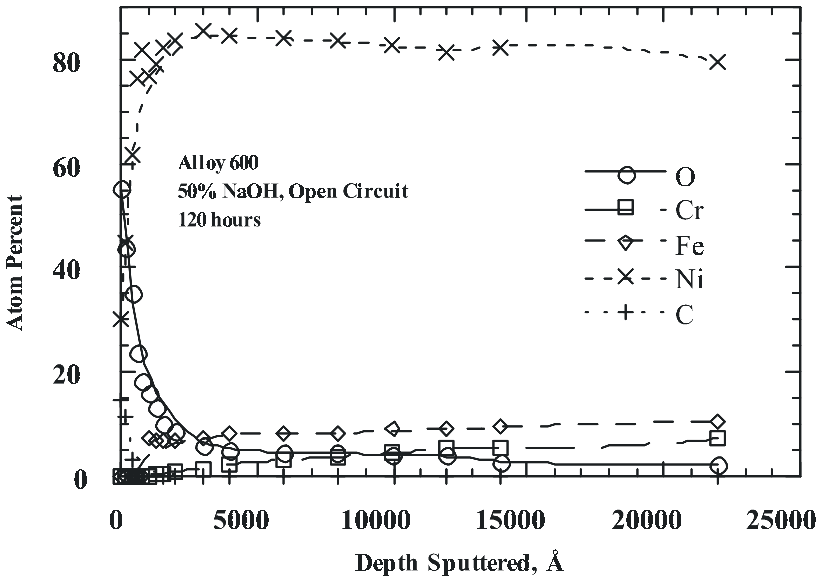

Figure 3-11
Auger in-depth composition profile of the surface of the specimen exposed to the 50% NaOH solution at open circuit for 120 hours

Table 3-3
Auger results for alloy 600 specimen exposed to 50% NaOH at 315°C at 100 mV above the corrosion potential for 48 hours

Atomic Percents					Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	C	Cr	Fe	Ni	
35.0	0.0	0.0	30.2	34.8	0.0	0.0	100.0	0
28.6	0.0	0.0	55.5	15.8	0.0	0.0	100.0	50
14.5	1.3	0.0	74.2	10.0	1.8	0.0	98.2	100
14.6	5.6	3.0	76.9	0.0	6.5	3.5	90.0	150
8.7	6.5	2.6	82.2	0.0	7.1	2.8	90.0	200
6.6	13.4	4.4	75.6	0.0	14.3	4.8	80.9	300
6.0	14.5	7.3	72.3	0.0	15.4	7.7	76.9	500
5.4	17.4	7.9	69.3	0.0	18.4	8.3	73.3	900
3.4	19.0	7.9	69.7	0.0	19.6	8.2	72.2	1600
2.2	19.1	9.1	69.5	0.0	19.6	9.4	71.1	3200
0.0	20.1	8.8	71.1	0.0	20.1	8.8	71.1	8000
0.0	20.7	9.3	70.0	0.0	20.7	9.3	70.0	18000

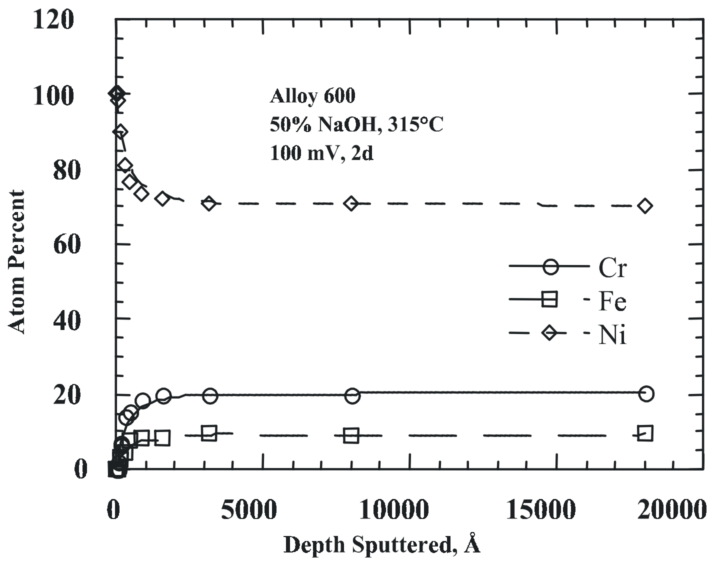

Figure 3-12
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to 50% NaOH at 315°C while polarized at 100 mV for two days

Table 3-4
Auger results for alloy 600 specimen exposed to 50% NaOH at 315°C at 150 mV above the corrosion potential for 48 hours

Atomic Percents					Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	C	Cr	Fe	Ni	
37.1	0.0	3.1	34.9	24.9	0.0	8.2	91.8	0
39.5	0.0	3.5	43.4	13.7	0.0	7.4	92.6	50
42.6	0.0	6.3	47.8	3.4	0.0	11.6	88.4	100
43.2	0.0	5.7	51.1	0.0	0.0	10.0	90.0	200
42.7	0.0	5.5	51.8	0.0	0.0	9.7	90.3	400
42.9	0.0	6.3	50.8	0.0	0.0	11.1	88.9	800
42.6	0.0	5.7	51.8	0.0	0.0	9.9	90.1	1600
43.4	0.0	5.4	51.2	0.0	0.0	9.5	90.5	3500
43.3	0.0	5.4	51.3	0.0	0.0	9.5	90.5	6400
42.7	0.0	5.3	52.0	0.0	0.0	9.2	90.8	12800
40.0	7.3	5.4	47.3	0.0	12.1	9.1	78.8	25000
42.4	7.6	3.5	46.5	0.0	13.1	6.2	80.7	40000
40.5	8.4	4.2	46.9	0.0	14.1	7.1	78.8	50000

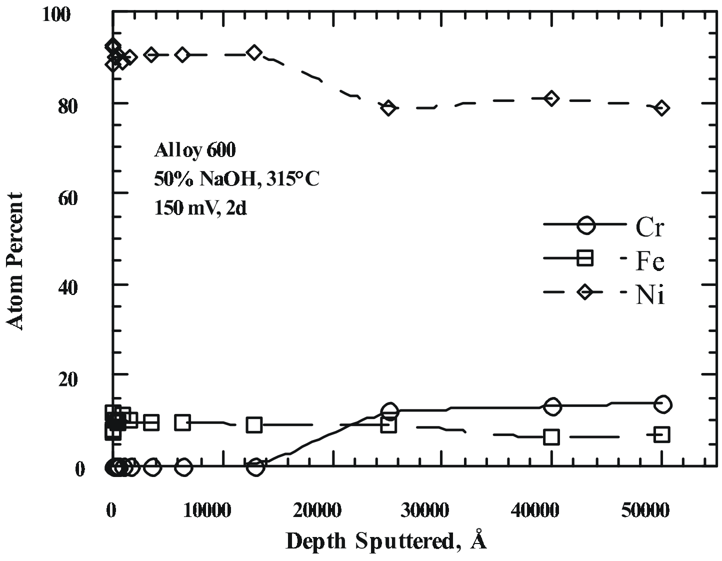

Figure 3-13
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to 50% NaOH at 315°C while polarized at 150 mV for two days

Table 3-5
Auger results for alloy 600 specimen exposed to pH 10, Environment 4 (Table 2-3) at 315°C at 100 mV open circuit potential for 48 hours

Atomic Percents					Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	C	Cr	Fe	Ni	
27.8	0.0	10.2	42.4	19.6	0.0	19.5	80.5	0
24.5	0.0	7.6	50.9	17.0	0.0	13.0	87.0	100
16.7	0.0	6.4	69.5	7.4	0.0	8.4	91.6	200
9.0	0.0	4.3	82.9	3.7	0.0	4.9	95.1	400
7.0	1.4	3.9	83.5	4.2	1.6	4.4	94.0	500
5.3	3.5	2.9	85.9	2.5	3.8	3.1	93.1	600
4.2	4.9	2.6	86.7	1.6	5.2	2.8	92.1	800
3.5	7.8	3.7	84.2	0.8	8.1	3.9	88.0	1200
2.1	12.3	4.7	80.9	0.0	12.5	4.8	82.6	2000
1.2	18.2	7.9	72.7	0.0	18.4	8.0	73.6	3600
0.0	25.0	8.6	66.4	0.0	25.0	8.6	66.4	6800
0.0	24.9	9.6	65.5	0.0	24.9	9.6	65.5	13200

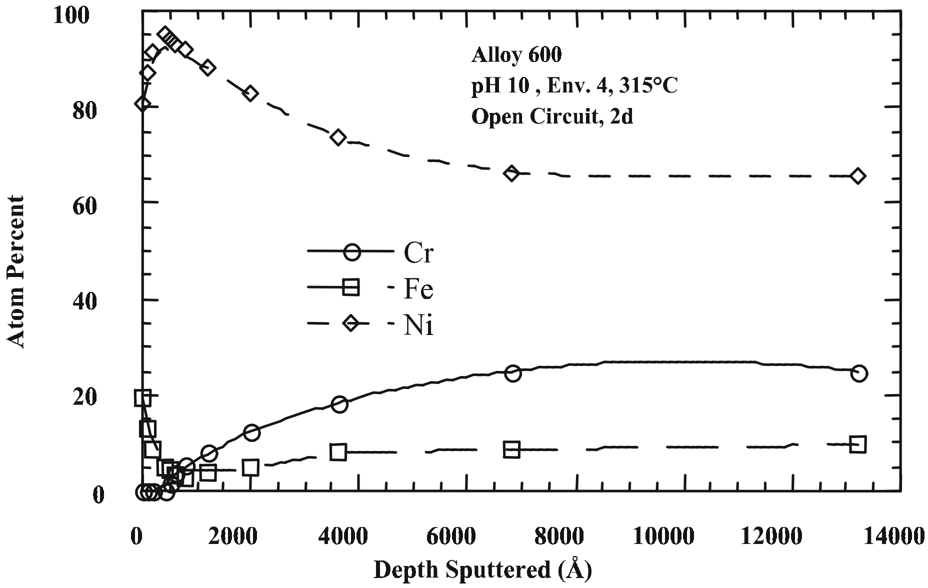

Figure 3-14
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to 5 m NaCl +2 m NaOH at 315°C while at open circuit for two days

Table 3-6
Auger results for alloy 600 specimen exposed to pH 10 environment (Table 2-3) at 315°C at 25 mV above the corrosion potential for 48 hours

Atomic Percents						Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	Cl	C	Cr	Fe	NI	
26.3	0.0	2.3	32.5	0.8	38.2	0.0	6.6	93.4	0
21.0	4.1	3.7	55.8	0.2	15.2	6.5	5.8	87.7	50
12.4	5.0	2.5	68.3	0.1	11.7	6.6	3.3	90.1	100
12.7	5.1	2.6	70.0	0.0	9.6	6.6	3.3	90.1	200
8.9	6.8	3.8	74.0	0.0	6.5	8.1	4.5	87.5	400
5.7	9.4	4.7	75.3	0.0	4.8	10.6	5.2	84.2	800
4.6	11.0	5.3	79.0	0.0	0.0	11.6	5.6	82.9	1600
3.7	14.4	6.2	75.7	0.0	0.0	14.9	6.4	78.6	3200
2.6	17.9	7.6	71.9	0.0	0.0	18.4	7.8	73.8	6400
1.6	20.6	8.6	69.2	0.0	0.0	21.0	8.7	70.3	12800

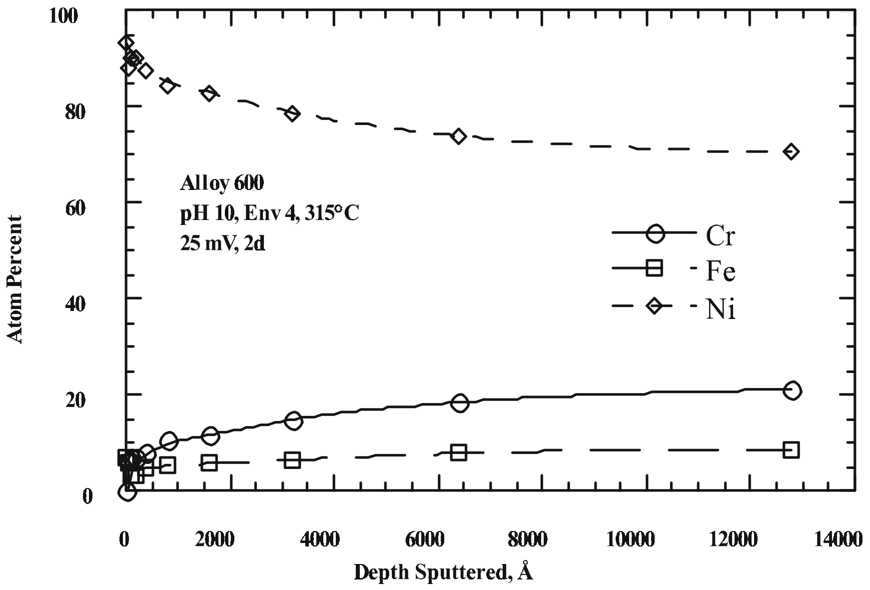

Figure 3-15
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to 5 m NaCl +2 m NaOH at 315°C while polarized at 25 mV for two days

Table 3-7
Auger results for alloy 600 specimen exposed to pH 10 environment (Table 2-3) at 315°C at 50 mV above the corrosion potential for 48 hours

Atomic Percents						Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	Cl	C	Cr	Fe	NI	
19.5	4.3	1.2	15.8	0.3	59.0	20.1	5.6	74.3	0
23.3	7.0	2.1	32.6	0.1	34.9	16.7	5.0	78.3	50
24.8	8.5	1.6	39.1	0.0	26.0	17.3	3.2	79.5	100
23.5	10.2	1.6	45.1	0.0	19.6	17.9	2.8	79.3	200
22.4	12.9	2.2	49.3	0.0	13.2	20.1	3.4	76.5	400
19.9	15.1	2.5	54.2	0.0	8.4	21.0	3.4	75.5	800
16.4	17.4	3.3	57.5	0.0	5.4	22.3	4.2	73.5	1600
12.6	18.0	4.7	61.6	0.0	3.1	21.4	5.6	73.0	3200
9.2	19.4	5.6	64.1	0.0	1.6	21.8	6.3	71.9	6400
4.6	21.4	7.3	65.8	0.0	0.9	22.7	7.8	69.6	12800
1.7	24.2	8.4	65.0	0.0	0.7	24.8	8.6	66.6	25600

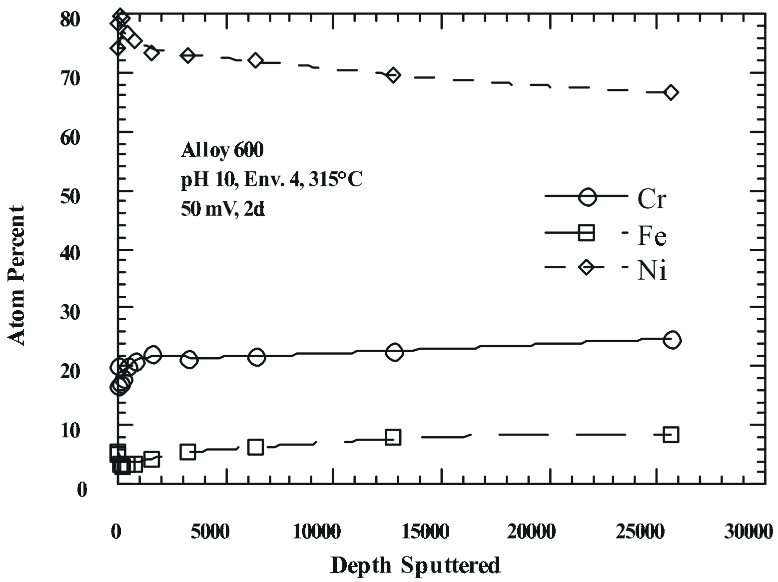

Figure 3-16
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to 5 m NaCl +2 m NaOH at 315°C while polarized at 50 mV for two days

Table 3-8
Auger results for alloy 600 specimen exposed to pH 10 environment (Table 2-3) at 315°C at 100 mV above the corrosion potential for 48 hours

Atomic Percents						Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	Cl	C	Cr	Fe	NI	
12.1	13.6	8.1	8.7	0.0	57.5	44.7	26.7	28.6	0
32.3	26.7	9.3	16.6	0.0	15.1	50.8	17.7	31.5	50
32.3	25.8	9.5	23.2	0.0	9.1	44.1	16.3	39.6	100
33.8	22.3	5.3	35.1	0.0	3.6	35.5	8.5	56.0	200
36.7	14.9	2.5	44.7	0.0	1.2	24.0	4.0	71.9	400
40.8	9.4	0.0	49.9	0.0	0.0	15.8	0.0	84.2	800
40.9	8.4	0.0	50.7	0.0	0.0	14.2	0.0	85.8	1600
42.4	9.2	0.0	48.4	0.0	0.0	16.0	0.0	84.0	3200
37.0	12.5	1.6	48.9	0.0	0.0	19.9	2.5	77.6	6400
5.2	19.9	8.2	66.7	0.0	0.0	21.0	8.7	70.3	12800

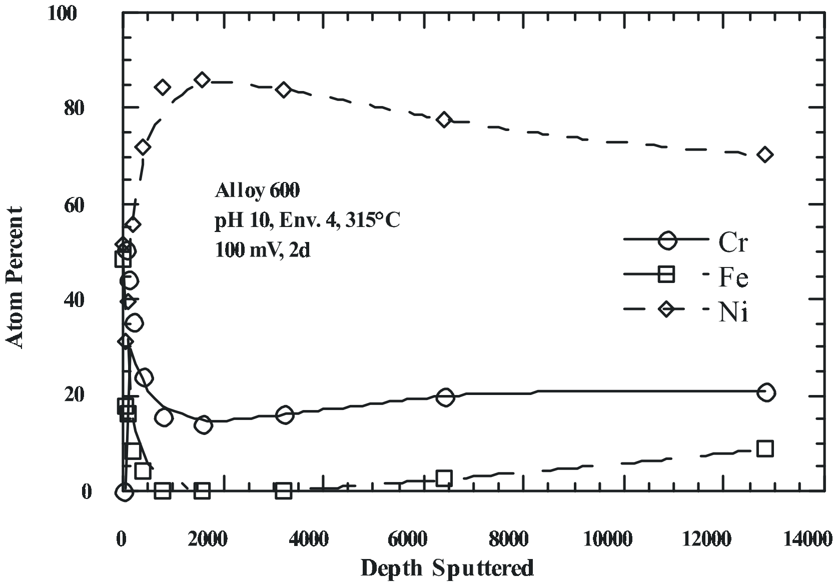

Figure 3-17
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to 5 m NaCl +2 m NaOH at 315°C while polarized at 100 mV for two days

Table 3-9
Auger results for alloy 600 specimen exposed to pH 10 environment (Table 2-3) at 315°C at 150 mV above the corrosion potential for 48 hours

Atomic Percents						Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	Cl	C	Cr	Fe	NI	
37.7	9.9	0.0	10.8	1.6	40.1	47.8	0.0	52.2	0
47.6	14.7	3.8	15.7	0.3	17.9	42.9	11.1	46.0	50
48.5	15.3	4.0	18.2	0.2	13.9	41.0	10.6	48.5	100
47.4	15.7	3.7	22.6	0.0	10.6	37.4	8.8	53.8	200
44.9	15.2	4.0	27.9	0.0	8.0	32.2	8.6	59.2	400
44.2	14.1	4.2	34.0	0.0	3.5	27.0	8.0	65.0	800
50.9	13.7	3.7	29.6	0.0	2.2	29.2	7.8	63.0	1600
44.4	9.1	2.3	44.2	0.0	0.0	16.4	4.1	79.4	3200
43.6	11.7	2.4	41.4	0.0	0.9	21.1	4.3	74.6	6400
30.6	18.9	4.1	46.3	0.0	0.0	27.3	5.9	66.8	12800
7.4	22.2	6.9	63.5	0.0	0.0	24.0	7.5	68.6	25600
11.4	20.9	7.7	60.0	0.0	0.0	23.6	8.7	67.7	51200

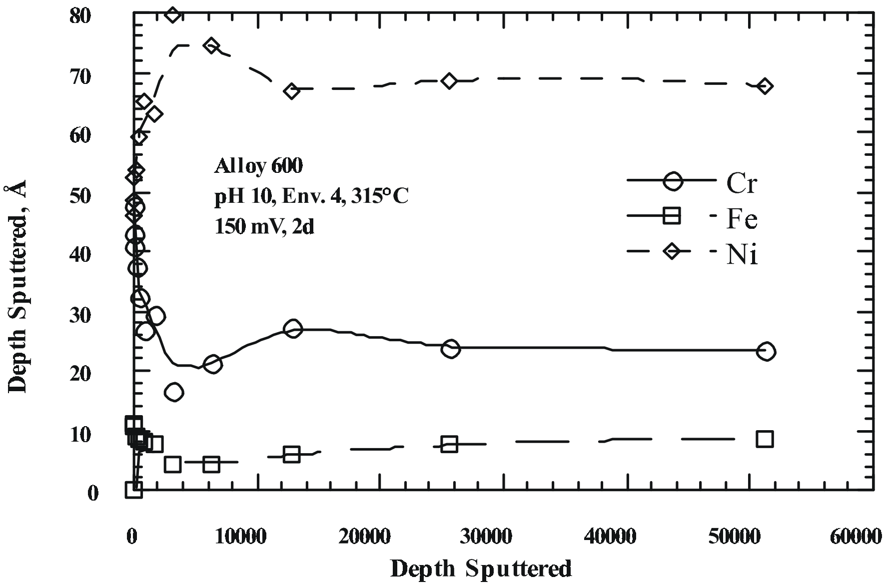

Figure 3-18
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to pH 10 at 315°C while polarized at 100 mV for two days

Table 3-10
Auger results for alloy 600 specimen exposed to pH 9.3 Environment 3 (Table 2-3) at 315°C at open circuit for 48 hours

Atomic Percents						**Normalized At%**			**Depth Sputtered, Å**
O	**Cr**	**Fe**	**Ni**	**Cl**	**C**	**Cr**	**Fe**	**NI**	
13.6	2.9	2.0	30.6	0.5	50.5	8.2	5.5	86.3	0
16.4	4.0	2.3	45.9	0.7	30.8	7.6	4.3	88.0	50
14.5	4.5	2.3	52.8	0.3	25.6	7.6	3.9	88.5	100
11.6	4.6	1.8	58.8	0.2	23.0	7.1	2.8	90.2	200
9.4	5.2	2.3	64.2	0.1	18.8	7.2	3.3	89.5	400
8.2	6.3	2.9	68.5	0.1	14.0	8.1	3.8	88.2	800
5.3	8.7	3.3	73.2	0.1	9.4	10.2	3.9	85.9	1600
4.4	11.5	4.2	74.1	0.0	5.7	12.8	4.7	82.5	3200
5.0	14.4	5.0	72.5	0.0	3.1	15.7	5.4	78.9	6400
4.2	17.4	5.4	70.7	0.0	2.3	18.6	5.8	75.6	12800
3.4	20.5	7.6	66.0	0.0	2.6	21.7	8.1	70.2	25600

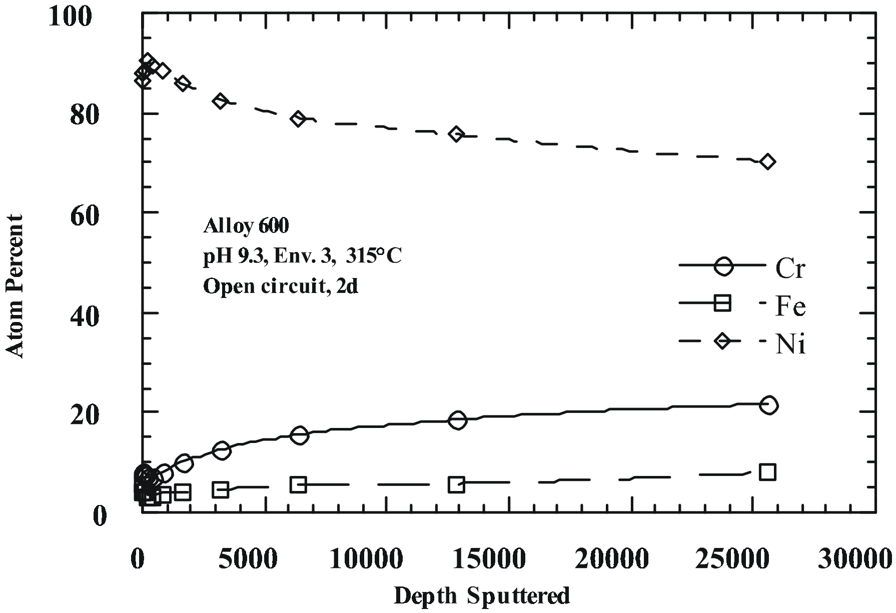

Figure 3-19
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to pH 9.3 at 315°C at open circuit potential for two days

Table 3-11
Auger results for alloy 600 specimen exposed to pH 9.3 Environment 3 (Table 2-3) at 315°C while polarized at 25 mV for 48 hours

Atomic Percents						Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	Cl	C	Cr	Fe	NI	
12.7	1.8	0.6	29.6	0.4	54.4	5.6	2.0	92.4	0
10.0	2.2	1.5	45.2	0.3	40.8	4.5	3.1	92.4	50
9.5	2.1	0.6	54.2	0.1	33.5	3.7	1.1	95.3	100
11.9	2.4	0.8	63.5	0.0	21.4	3.6	1.2	95.1	200
5.9	2.3	0.5	72.2	0.0	19.1	3.1	0.7	96.3	400
4.1	3.6	0.9	79.4	0.0	12.0	4.3	1.1	94.6	800
3.2	6.3	2.3	81.5	0.0	6.7	7.0	2.6	90.5	1600
4.9	10.7	3.4	77.8	0.0	3.3	11.6	3.7	84.7	3200
8.1	14.7	4.6	70.5	0.0	2.0	16.4	5.1	78.4	6400
11.3	18.4	5.3	63.3	0.0	1.7	21.2	6.1	72.7	12800
6.7	21.6	7.1	63.3	0.0	1.3	23.5	7.7	68.8	25600

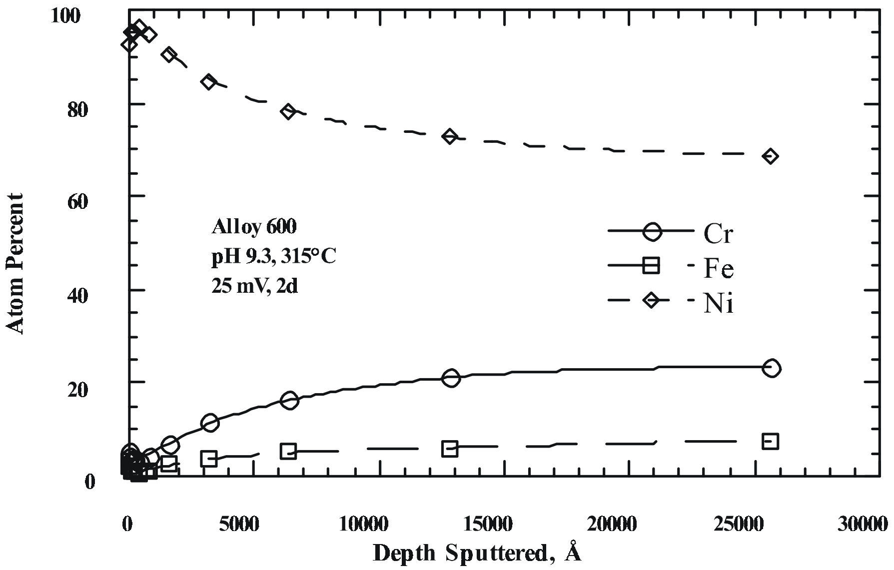

Figure 3-20
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to pH 9.3 at 315°C polarized at 25 mV for two days

Table 3-12
Auger results for alloy 600 specimen exposed to pH 9.3 Environment 3 (Table 2-3) at 315°C while polarized at 50 mV for 48 hours

Atomic Percents						Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	Cl	C	Cr	Fe	NI	
13.3	2.4	1.0	29.1	0.2	54.0	7.4	3.1	89.5	0
11.2	2.3	1.2	43.1	0.2	41.9	5.0	2.6	92.4	50
10.1	2.3	1.6	53.5	0.1	32.5	3.9	2.7	93.3	100
8.2	2.6	1.5	61.9	0.0	25.8	4.0	2.3	93.7	200
6.6	3.1	1.3	69.7	0.0	19.4	4.1	1.8	94.1	400
4.4	4.9	1.8	76.6	0.0	12.3	5.8	2.2	92.0	800
3.6	6.6	3.3	80.2	0.0	6.3	7.4	3.7	88.9	1600
4.2	9.7	4.4	78.3	0.0	3.4	10.5	4.8	84.7	3200
5.7	13.2	5.7	73.5	0.0	1.9	14.3	6.1	79.5	6400
5.7	16.1	7.0	71.2	0.0	0.0	17.1	7.4	75.5	12800
2.7	18.5	7.9	70.2	0.0	0.7	19.1	8.1	72.7	25600

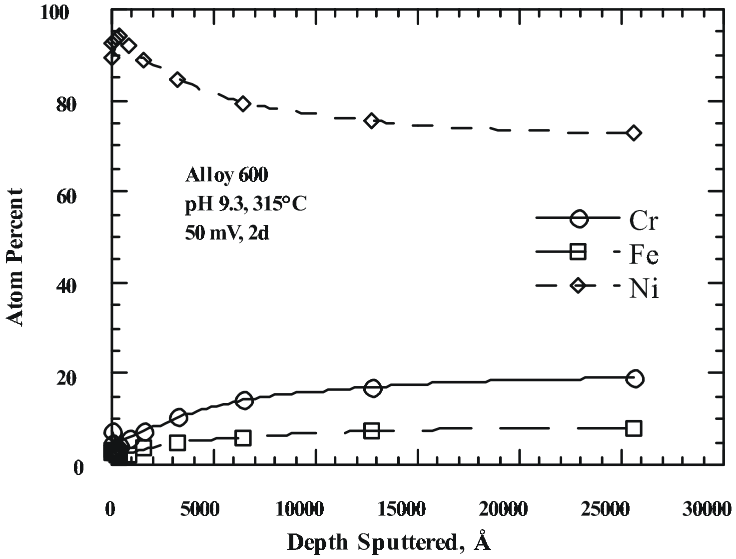

Figure 3-21
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to pH 9.3 at 315°C polarized at 50 mV for two days

Table 3-13
Auger results for alloy 600 specimen exposed to pH 9.3 Environment 3 (Table 2-3) at 315°C while polarized at 100 mV for 48 hours

Atomic Percents						Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	Cl	C	Cr	Fe	NI	
32.4	7.9	12.1	8.7	0.0	38.9	27.5	42.1	30.3	0
34.2	10.3	14.3	9.3	0.0	31.9	30.3	42.2	27.5	50
38.2	11.6	15.8	10.6	0.0	23.8	30.6	41.5	28.0	100
40.3	12.4	17.7	11.3	0.0	18.2	29.9	42.8	27.3	200
41.1	13.4	19.0	12.6	0.0	13.9	29.7	42.2	28.1	400
41.8	13.4	20.6	15.0	0.0	9.2	27.4	41.9	30.6	800
41.4	14.8	21.3	17.5	0.0	5.0	27.7	39.7	32.7	1600
42.3	14.7	21.0	18.9	0.0	3.1	26.9	38.5	34.6	3200
42.3	15.0	19.5	22.4	0.0	0.8	26.3	34.2	39.4	6400
40.9	15.0	15.3	28.4	0.0	0.4	25.6	26.1	48.4	12800
39.9	12.2	8.9	38.9	0.0	0.0	20.4	14.9	64.8	25600
41.3	11.3	5.7	41.8	0.0	0.0	19.2	9.7	71.1	51200

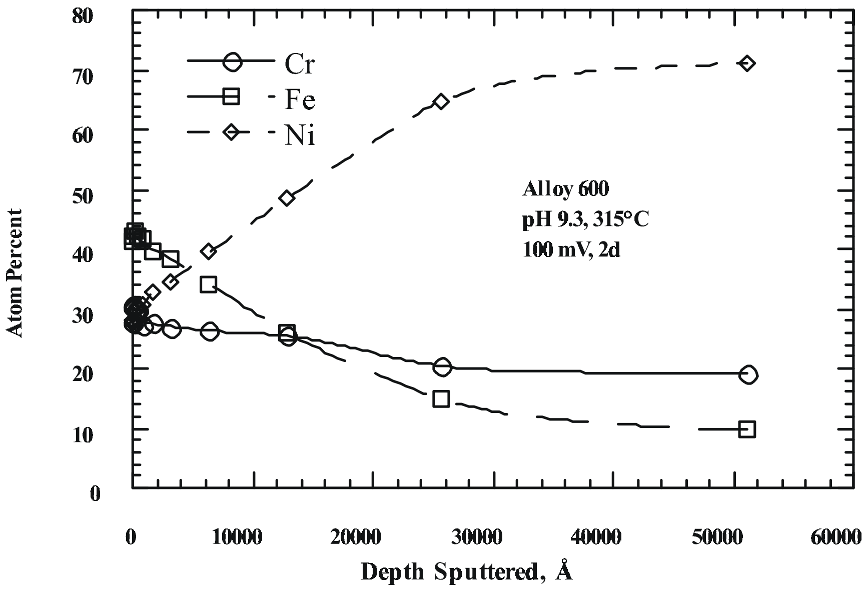

Figure 3-22
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to pH 9.3 at 315°C polarized at 50 mV for two days

Table 3-14
Auger results for alloy 600 specimen exposed to pH 9.3 Environment 3 (Table 2-3) at 315°C while polarized at 150 mV for 48 hours

Atomic Percents						Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	Cl	C	Cr	Fe	NI	
39.4	12.2	7.9	11.2	0.0	29.3	39.1	25.1	35.9	0
44.8	14.5	9.4	15.1	0.0	16.2	37.1	24.2	38.7	50
46.4	15.6	9.6	16.9	0.0	11.4	37.1	22.7	40.2	100
46.7	16.8	9.0	18.1	0.0	9.4	38.3	20.4	41.3	200
45.6	16.5	9.4	21.1	0.0	7.4	35.1	19.9	45.0	400
43.3	15.9	8.7	27.5	0.0	4.6	30.5	16.7	52.8	800
41.6	14.8	7.9	32.8	0.0	2.8	26.7	14.3	59.0	1600
41.3	12.0	6.6	38.2	0.0	1.9	21.1	11.7	67.3	3200
40.8	9.8	5.7	42.9	0.0	0.9	16.8	9.7	73.5	6400
40.5	10.5	4.8	43.7	0.0	0.5	17.8	8.2	74.0	12800
31.5	15.3	5.6	47.6	0.0	0.0	22.3	8.1	69.5	25600
12.7	18.6	7.4	60.7	0.0	0.6	21.4	8.6	70.0	51200

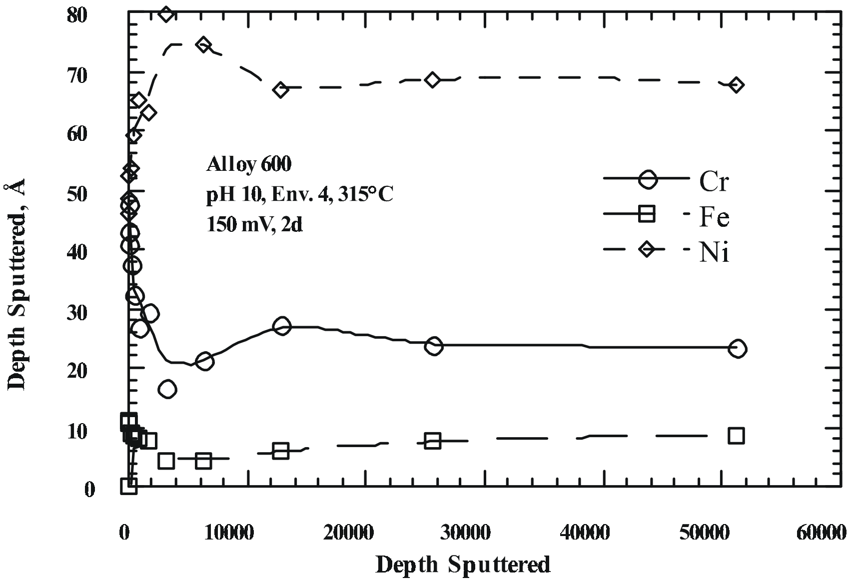

Figure 3-23
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to pH 9.3 at 315°C polarized at 150 mV for two days

Table 3-15
Auger results for alloy 600 specimen exposed to pH 4.9 Environment 2 (Table 2-3) at 315°C while at open circuit for 48 hours

Atomic Percents						Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	Cl	C	Cr	Fe	NI	
36.4	11.6	4.6	23.2	0.5	23.8	29.4	11.6	59.0	0
42.2	13.0	4.5	29.1	0.4	10.8	27.9	9.7	62.4	50
42.5	14.0	3.7	31.8	0.2	7.7	28.3	7.6	64.2	100
39.5	14.6	3.7	37.2	0.1	5.0	26.4	6.6	67.1	200
36.6	13.6	2.0	44.2	0.1	3.5	22.7	3.4	73.9	400
32.8	12.9	0.0	51.1	0.1	3.1	20.1	0.0	79.9	800
26.3	12.0	0.0	59.6	0.1	2.1	16.8	0.0	83.2	1600
22.9	9.1	0.0	65.5	0.0	2.4	12.2	0.0	87.8	3200
20.8	8.1	0.0	69.5	0.0	1.7	10.4	0.0	89.6	6400

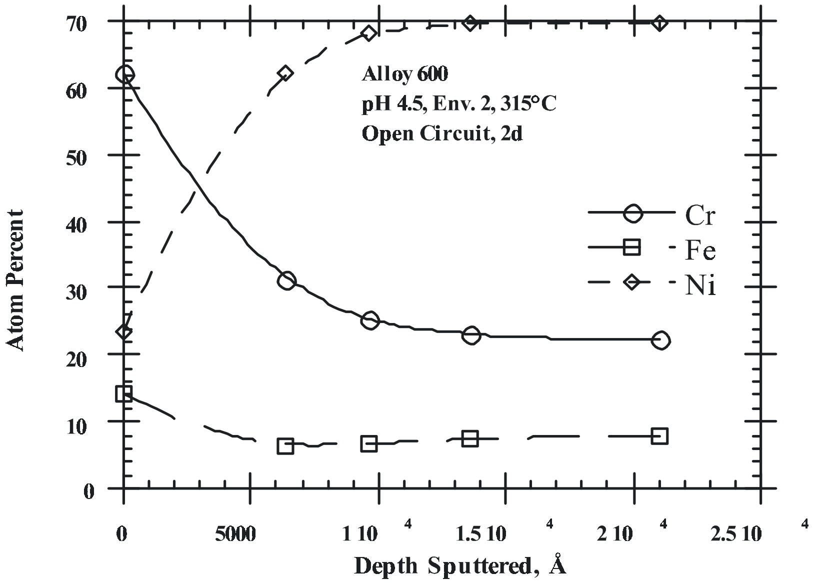

Figure 3-24
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to pH 4.5 at 315°C at open circuit for two days

Table 3-16
Auger results for alloy 600 specimen exposed to pH 4.9 Environment 2 (Table 2-3) at 315°C while at 200 mV above the corrosion potential for 48 hours

Atomic Percents						Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	Cl	C	Cr	Fe	NI	
45.3	19.9	3.9	5.0	2.8	23.1	69.2	13.6	17.3	0
49.7	23.5	4.2	6.1	2.3	14.2	69.4	12.5	18.1	50
50.0	24.7	4.6	7.1	1.9	11.6	67.8	12.6	19.6	100
51.1	26.2	4.1	8.4	1.4	8.8	67.7	10.5	21.8	200
50.3	27.8	4.1	9.8	1.3	6.7	66.7	9.8	23.5	400
50.7	27.1	3.7	12.5	1.1	4.8	62.7	8.4	28.9	800
48.7	27.2	3.0	16.5	1.1	3.6	58.4	6.4	35.3	1600
44.0	26.3	3.3	22.4	0.9	3.1	50.6	6.3	43.1	3200
36.7	25.3	3.4	31.4	0.6	2.5	42.0	5.7	52.3	6400
26.0	23.7	3.8	42.9	0.4	3.2	33.7	5.4	60.9	12800

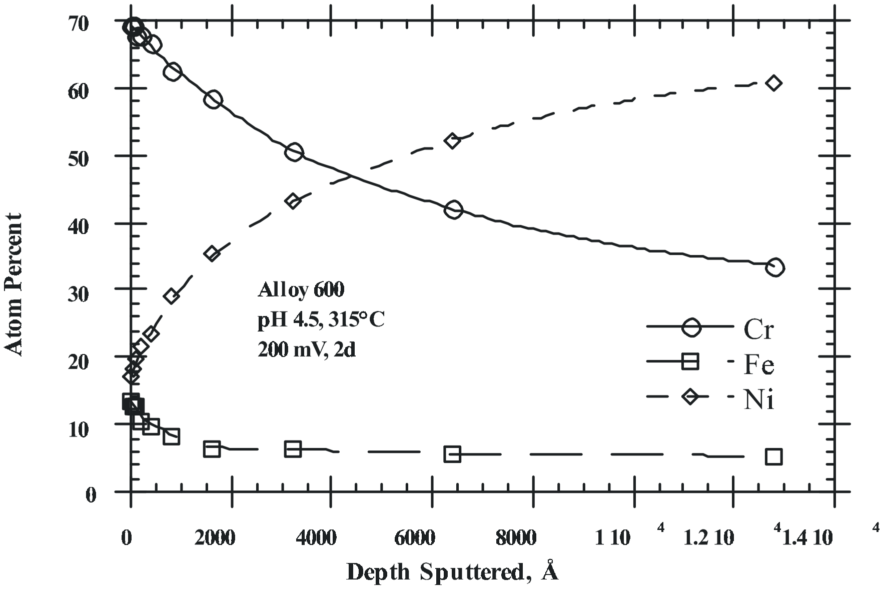

Figure 3-25
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to pH 4.5 at 315°C at 200 mV for two days

Table 3-17
Auger results for alloy 600 specimen exposed to pH 4.5 Environment 2 (Table 2-3) at 315°C while at 500 mV above the corrosion potential for 48 hours

Atomic Percents						Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	Cl	C	Cr	Fe	NI	
47.9	31.0	0.0	4.1	14.9	2.1	88.4	0.0	11.6	0
50.7	33.6	0.0	4.2	11.1	0.3	89.0	0.0	11.0	100
51.1	34.6	0.0	4.6	9.8	0.0	88.3	0.0	11.7	200
51.2	35.7	0.0	4.8	8.3	0.0	88.1	0.0	11.9	400
49.9	37.3	0.0	5.5	7.3	0.0	87.2	0.0	12.8	800
46.1	41.7	0.0	6.9	5.3	0.0	85.7	0.0	14.3	1600
39.2	47.1	0.0	9.5	4.2	0.0	83.3	0.0	16.7	3200

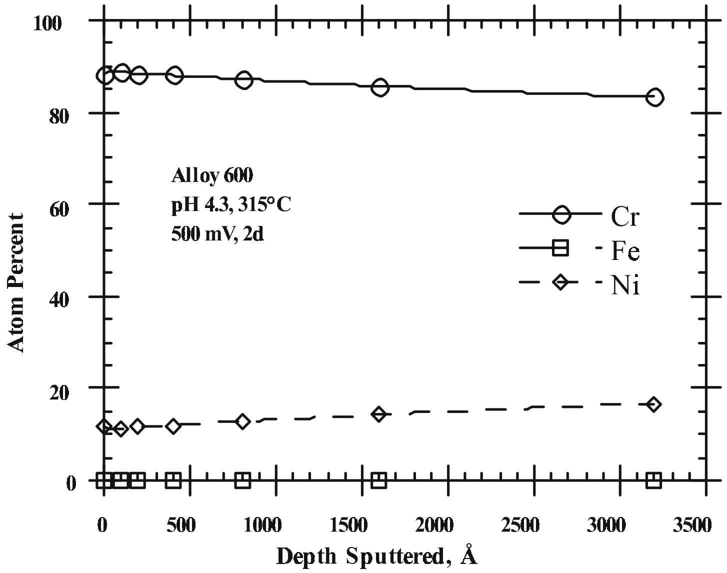

Figure 3-26
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to pH 4.5 at 315°C at 500 mV for two days

Table 3-18
Auger results for alloy 600 specimen exposed to pH 3 Environment 1 (Table 2-3) at 315°C while at open circuit potential for 48 hours

Atomic Percents						Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	Cl	C	Cr	Fe	NI	
75.9	12.7	0.0	8.5	2.9	0.0	59.8	0.0	40.2	0
69.5	15.4	0.0	12.7	2.4	0.0	54.8	0.0	45.2	100
64.4	15.5	0.0	13.8	2.0	4.3	52.9	0.0	47.1	200
63.2	14.6	0.0	16.9	1.9	3.4	46.5	0.0	53.5	400
55.0	14.6	0.0	25.7	1.5	3.3	36.2	0.0	63.8	800
43.4	14.3	0.0	38.7	1.1	2.5	27.0	0.0	73.0	1600
27.5	16.5	4.5	47.3	0.6	3.5	24.1	6.7	69.2	3200
13.3	19.6	7.2	55.2	0.2	4.3	23.9	8.8	67.3	6400
7.5	23.0	8.6	58.4	0.0	2.5	25.6	9.6	64.9	12800
0.0	25.4	9.2	65.5	0.0	0.0	25.4	9.2	65.5	25600

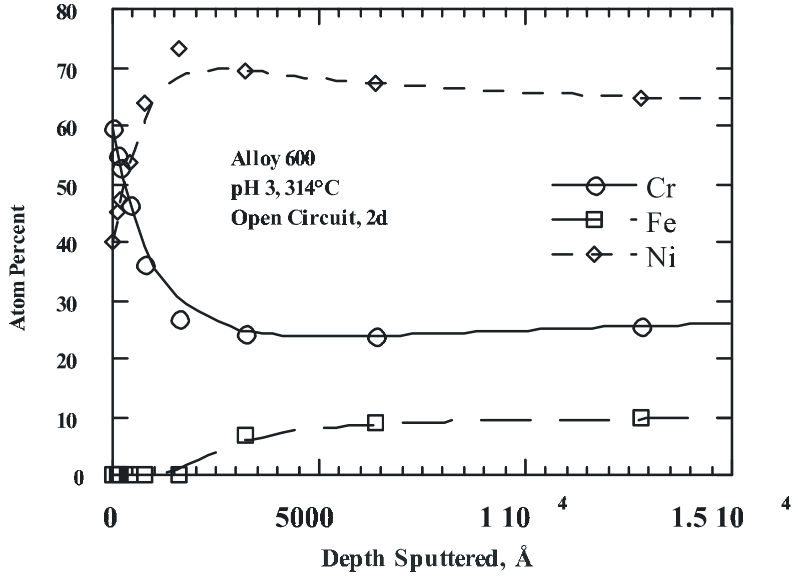

Figure 3-27
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to pH 3 at 315°C at open circuit for two days

Table 3-19
Auger results for alloy 600 specimen exposed to pH 3 Environment 1 (Table 2-3) at 315°C polarized 50 mV above the corrosion potential for 48 hours

Atomic Percents						Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	Cl	C	Cr	Fe	NI	
49.0	17.2	0.0	4.4	5.3	24.2	79.6	0.0	20.4	0
56.1	27.4	0.0	4.9	5.2	6.4	84.9	0.0	15.1	50
55.6	30.8	0.0	4.3	4.3	5.0	87.7	0.0	12.3	100
55.1	35.2	0.0	4.3	4.2	1.2	89.2	0.0	10.8	200
52.7	40.6	0.0	3.8	2.9	0.0	91.5	0.0	8.5	400
49.3	39.8	0.0	4.4	3.2	3.2	90.1	0.0	9.9	800
49.2	47.2	0.0	0.0	3.6	0.0	100.0	0.0	0.0	1600
51.0	46.0	0.0	0.0	3.0	0.0	100.0	0.0	0.0	3200
37.3	45.0	0.0	16.0	1.7	0.0	73.8	0.0	26.2	6400
9.3	32.6	7.7	50.2	0.3	0.0	36.1	8.5	55.5	12800
4.1	26.5	8.2	61.1	0.0	0.0	27.7	8.6	63.7	25600
0.0	26.0	8.8	65.2	0.0	0.0	26.0	8.8	65.2	31600

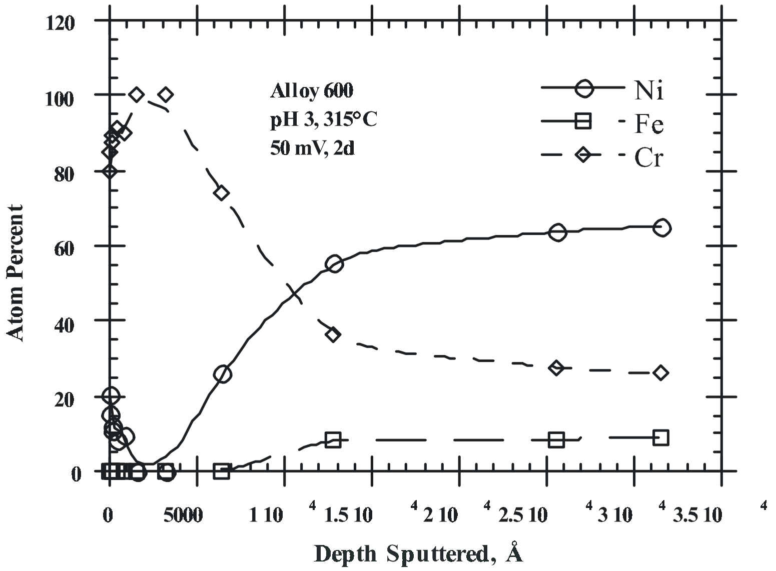

Figure 3-28
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to pH 3 at 315°C at 50 mV above the corrosion potential for two days

Table 3-20
Auger results for alloy 600 specimen exposed to pH 3 Environment 1 (Table 2-3) at 315°C polarized 100 mV below the corrosion potential for 48 hours

Atomic Percents						Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	Cl	C	Cr	Fe	NI	
43.8	14.4	0.0	14.1	5.2	22.6	50.5	0.0	49.5	0
49.7	15.6	0.0	23.2	2.8	8.7	40.2	0.0	59.8	100
44.3	21.1	0.0	27.0	2.3	5.3	43.8	0.0	56.2	200
40.9	21.8	0.0	31.7	1.3	4.2	40.8	0.0	59.2	400
35.5	19.0	0.0	40.3	1.2	4.0	32.1	0.0	67.9	800
25.2	12.8	0.0	55.1	1.4	5.4	18.9	0.0	81.1	1600
15.1	10.5	0.0	71.6	0.5	2.2	12.8	0.0	87.2	3200
9.4	13.9	4.4	69.9	0.3	2.1	15.8	5.0	79.2	6400
5.1	22.7	8.0	62.3	0.0	1.8	24.4	8.6	66.9	12800
0.0	24.0	9.0	67.1	0.0	0.0	24.0	9.0	67.1	25600

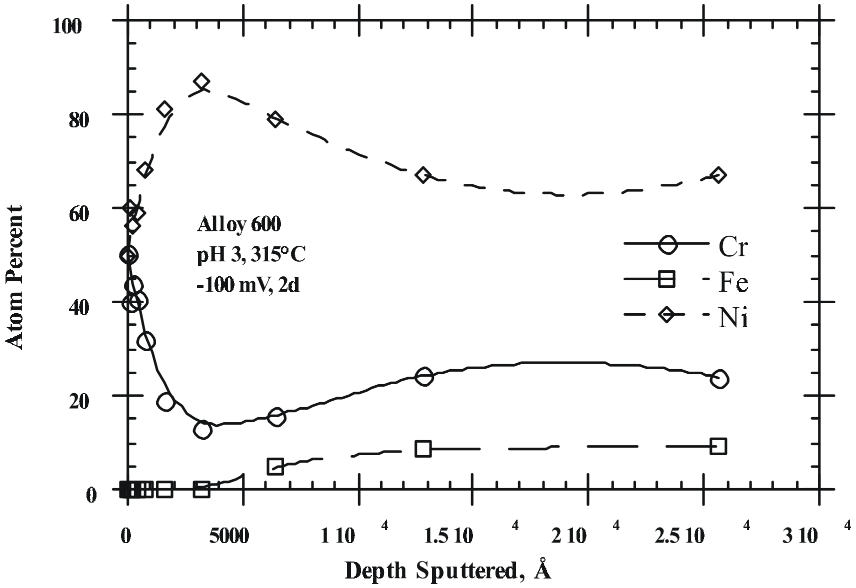

Figure 3-29
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to pH 3 at 315°C polarized 100 mV below the corrosion potential for two days

Table 3-21
Auger results for alloy 600 specimen exposed to pH 10 Environment 8 (Table 2-3) at 315°C at open circuit potential for 48 hours

Atomic Percents									Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	Na	C	K	Cl	Si	Cr	Fe	Ni	
40.2	0.0	3.9	16.7	1.4	23.0	4.2	1.7	9.0	0.0	18.8	81.2	0
39.0	0.0	4.1	19.6	1.2	19.3	6.2	1.2	9.5	0.0	17.3	82.7	100
41.7	0.0	4.7	19.4	0.7	16.4	7.0	1.0	9.2	0.0	19.5	80.5	200
42.2	0.0	3.0	18.2	0.0	20.5	7.2	0.9	8.0	0.0	14.3	85.7	400
45.0	0.0	4.8	17.6	0.0	15.5	6.9	1.2	9.0	0.0	21.3	78.7	800
45.1	0.0	4.4	17.7	0.0	13.1	7.5	1.1	11.2	0.0	19.7	80.3	1600
42.8	0.0	3.9	17.6	0.0	12.2	8.0	1.0	14.7	0.0	18.2	81.8	3200
42.1	0.0	4.6	17.2	0.0	10.2	8.3	0.7	17.0	0.0	21.0	79.0	6400
40.9	0.0	4.5	17.2	0.0	10.4	9.2	0.5	17.4	0.0	20.6	79.4	12800
42.3	0.0	4.6	17.1	0.0	16.3	7.0	0.6	12.0	0.0	21.0	79.0	25600
5.1	27.0	7.4	58.9	0.0	1.6	0.0	0.0	0.0	28.9	7.9	63.1	51200
4.3	21.3	8.0	66.3	0.0	0.0	0.0	0.0	0.0	22.3	8.4	69.3	52200
4.2	19.4	7.4	65.6	0.0	3.4	0.0	0.0	0.0	21.0	8.0	71.0	54200
3.5	21.2	7.7	67.6	0.0	0.0	0.0	0.0	0.0	22.0	8.0	70.0	59200
2.6	30.0	7.6	59.8	0.0	0.0	0.0	0.0	0.0	30.8	7.8	61.4	64200

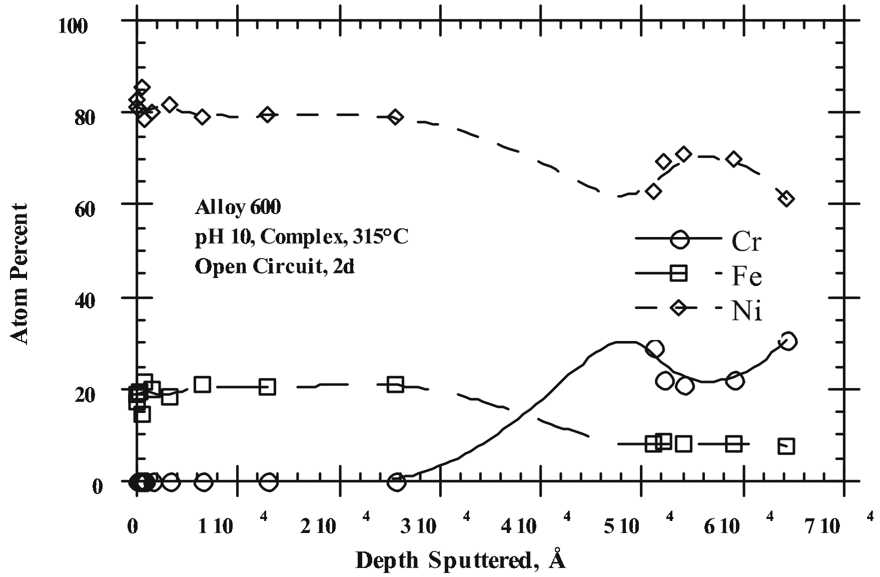

Figure 3-30
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to the pH 10 complex environment at 315°C at open circuit potential for two days

Table 3-22
Auger results for alloy 600 specimen exposed to pH 9 Environment 7 (Table 2-3) at 315°C at open circuit potential for 48 hours

Atomic Percents									Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	C	K	Cl	Si	S	Cr	Fe	NI	
30.5	0.0	0.0	17.5	18.9	3.9	4.0	24.9	0.2	0.0	0.0	100.0	0
37.9	0.0	3.1	17.8	2.9	12.0	2.2	23.9	0.2	0.0	14.7	85.3	50
34.1	3.9	3.0	13.7	3.3	10.3	0.9	30.5	0.2	18.8	14.7	66.5	100
34.6	5.5	2.2	9.9	1.7	11.5	0.9	33.5	0.2	31.4	12.5	56.1	200
33.0	6.5	3.7	12.3	0.8	10.6	0.7	32.3	0.2	29.1	16.2	54.7	400
33.1	7.3	4.4	16.8	0.8	9.4	1.0	26.5	0.7	25.6	15.6	58.8	800
28.1	11.0	5.7	28.2	0.8	6.4	0.8	18.4	0.7	24.4	12.7	62.9	1600
20.3	15.4	5.9	43.3	1.9	3.4	0.4	8.3	1.2	23.8	9.1	67.1	3200
9.0	20.7	7.2	56.1	2.6	0.8	0.2	3.4	0.0	24.6	8.6	66.8	6400
1.3	25.4	9.3	64.0	0.0	0.0	0.0	0.0	0.0	25.7	9.4	64.9	12800

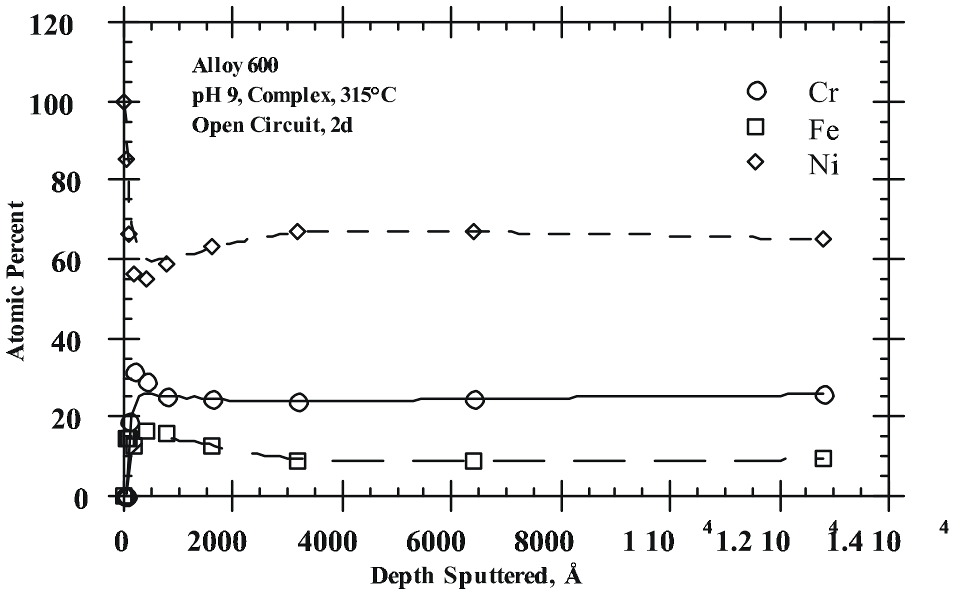

Figure 3-31
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to the pH 9 complex environment at 315°C at open circuit potential for two days

Table 3-23
Auger results for alloy 600 specimen exposed to pH 9 Environment 7 (Table 2-3) at 315°C at 50 mV above the open circuit potential for 48 hours

Atomic Percents									Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	Si	S	Cl	K	C	Cr	Fe	Ni	
40.8	0.0	0.0	20.6	3.4	2.0	11.5	7.2	14.6	0.0	0.0	100.0	0
35.8	0.0	0.0	13.2	26.1	2.2	6.9	15.9	0.0	0.0	0.0	100.0	200
35.7	0.0	0.0	11.7	29.7	2.6	4.7	15.6	0.0	0.0	0.0	100.0	400
40.8	0.0	0.0	13.4	19.0	2.7	5.6	18.5	0.0	0.0	0.0	100.0	800
25.8	0.0	0.0	9.2	49.5	2.0	3.0	10.5	0.0	0.0	0.0	100.0	1600
27.7	0.0	0.0	9.7	46.3	2.0	3.3	11.0	0.0	0.0	0.0	100.0	3200

Table 3-24
Auger results for alloy 600 specimen exposed to pH 9 Environment 7 (Table 2-3) at 315°C at 100 mV above the open circuit potential for 48 hours

Atomic Percents									Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	C	Si	K	S	Cl	Cr	Fe	NI	
37.4	0.0	3.8	11.3	9.6	23.4	8.5	0.5	5.3	0.0	24.9	75.1	0
34.1	0.0	3.7	9.5	3.0	32.0	13.6	0.6	3.6	0.0	27.9	72.1	100
34.0	0.0	4.4	9.1	3.2	33.3	13.5	0.8	1.7	0.0	32.7	67.3	200
33.0	0.0	4.4	10.5	2.1	32.7	14.1	0.7	2.4	0.0	29.7	70.3	400
32.4	0.0	4.4	10.9	2.1	32.4	14.7	0.6	2.5	0.0	28.8	71.2	800
32.7	0.0	4.4	10.8	2.1	32.3	14.6	0.6	2.5	0.0	28.8	71.2	1600
33.6	0.0	3.9	11.3	1.9	32.2	13.8	0.6	2.6	0.0	25.8	74.2	3200
33.0	3.4	2.8	10.1	1.8	32.7	12.8	0.8	2.5	20.7	17.4	61.9	6400
31.5	3.4	4.3	12.7	0.9	31.9	12.5	0.8	1.9	16.8	21.2	62.0	12800

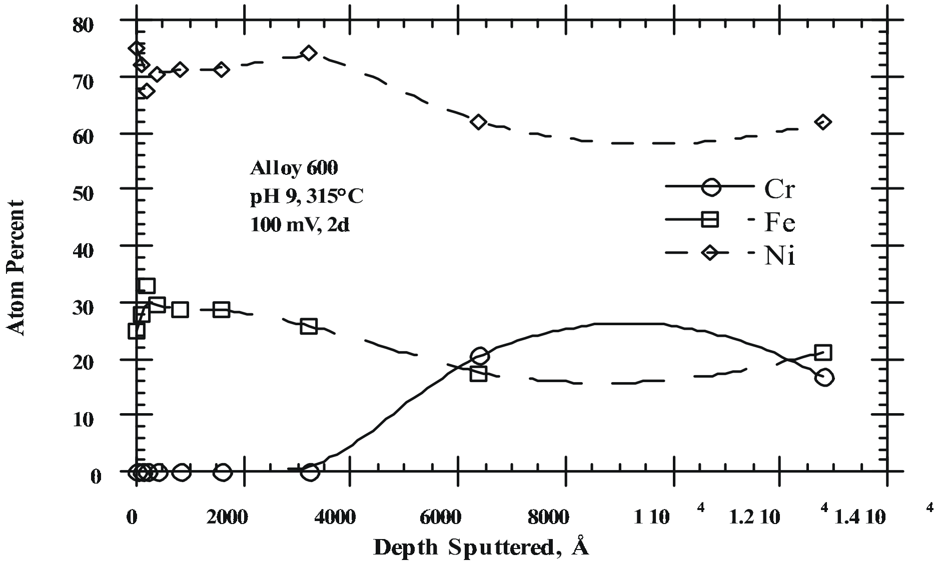

Figure 3-32
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to the pH 9 complex environment at 315°C at 100 mV for two days

Table 3-25
Auger results for alloy 600 specimen exposed to pH 3 Environment 5 (Table 2-3) at 315°C at open circuit potential for 48 hours

Atomic Percents									Normalized At%			Depth Sputtered, Å
O	Cr	Fe	Ni	Si	S	Cl	K	C	Cr	Fe	Ni	
58.9	33.5	0.0	0.0	7.6	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0
60.8	35.7	0.0	0.0	3.5	0.0	0.0	0.0	0.0	100.0	0.0	0.0	25
62.2	35.8	0.0	0.0	2.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	100
57.0	31.2	0.0	6.3	0.0	0.6	0.2	4.8	0.0	83.2	0.0	16.8	200
58.0	29.3	0.0	8.5	0.0	0.0	0.0	4.2	0.0	77.5	0.0	22.5	300
56.9	32.4	0.0	6.1	0.0	0.0	0.0	4.5	0.0	84.1	0.0	15.9	500
57.4	32.0	0.0	6.5	0.0	0.0	0.0	4.1	0.0	83.1	0.0	16.9	1000
28.8	14.1	0.0	25.6	21.7	7.8	0.6	1.4	0.0	35.5	0.0	64.5	2000
40.0	17.5	0.0	22.0	7.6	3.2	0.0	9.7	0.0	44.3	0.0	55.7	2500
26.3	21.0	0.0	27.8	2.8	12.5	0.4	9.2	0.0	43.1	0.0	56.9	3000
33.0	13.8	0.0	29.5	3.8	12.0	0.7	7.3	0.0	31.8	0.0	68.2	5000
32.8	17.1	0.0	26.9	3.7	11.8	0.8	6.8	0.0	38.9	0.0	61.1	6000
27.4	15.0	0.0	28.5	4.3	16.7	1.0	7.1	0.0	34.4	0.0	65.6	8000

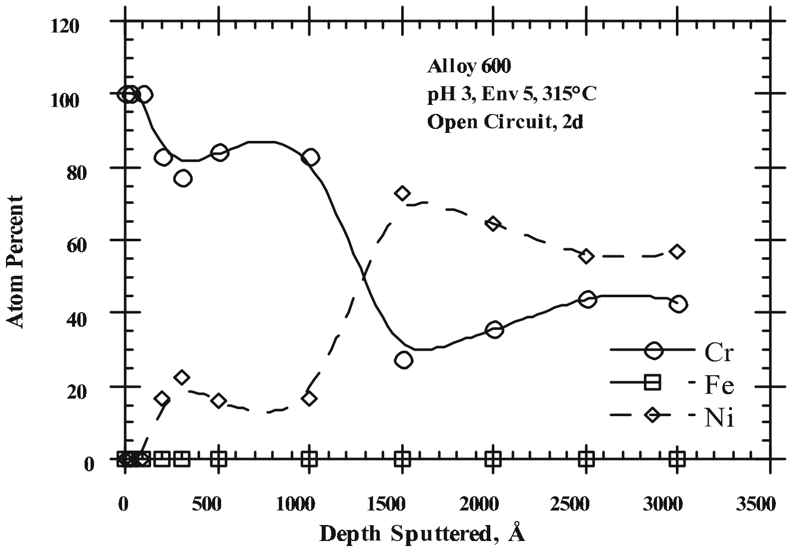

Figure 3-33
Profile of the relative amounts of Fe, Cr, and Ni in the film on alloy 600 exposed to the pH 3 complex environment at 315°C at open circuit potential for two days

The C-ring results for the two pH 10 environments are given in Table 3-26. The mill annealed material cracked only in the simple environment. Specimens were inspected after one week of exposure to the pH 10 simple environment and no cracks were observed. The next inspection was after three weeks of exposure and one of the two specimens, which had been polarized at 200 mV had a through wall crack. The third inspection was after the test had been underway for a total of five weeks, during which the second specimen, which had been polarized at 200 mV cracked. The final inspection was after seven weeks of exposure to the test solution. After this period a through wall crack was present in one of the two specimens which had been polarized at 150 mV. No tests were conducted on the sensitized specimens in the simple pH 10 solution. Neither the mill annealed nor the sensitized specimens cracked in the complex pH 10 solution after a seven-week test period.

Table 3-27 shows the results from the specimens exposed to the pH 3 complex environment. No cracks were observed, only severe wastage. The numbers in the columns are the decrease in the thickness after a two-day exposure.

Table 3-26
Results of C-Ring Tests in pH 10 Environments

		Mill Annealed		
ENVIRONMENT (TIME) / POTENTIAL, mV	0	100	150	200
Simple, pH 10, #4 (1 wk)	No SCC	No SCC	No SCC	No SCC
Simple, pH 10, #4 (3 wks)	No SCC	No SCC	No SCC	Thr Wall (1/2)
Simple, pH 10, #4 (5 wks)	No SCC	No SCC	No SCC	Thr Wall (2/2)
Simple, pH 10, #4 (7 wks)	No SCC	No SCC	Thr Wall (1/2)	
Complex, pH 10, #8 (7 wks)	No SCC	No SCC	No SCC	No SCC
		Sensitized		
Complex, pH 10, #8 (7wks)	No SCC	No SCC	No SCC	No SCC

Table 3-27
Results of C-Ring Tests in the pH 3 Complex Environment, Environment #5. Only general corrosion was observed. The numbers indicate the decrease in wall thickness, in mm

MATERIAL(TIME)/ POTENTIAL, MV	-200	-50	0	50	100
Mill Annealed (2 days)	0.17	0.46	0.17	0.46	0.42
Sensitized	–	0.63	0.2	0.38	0.33

4

DISCUSSION

The underlying hypothesis used in correlating film compositions on alloy 600 tubing with environmental chemistry is that thermodynamic considerations can be applied to relate oxide film compositions to the pH of the environment in which they were formed. Thermodynamic calculations summarized in Pourbaix diagrams (3,4) for Ni, Cr, and Fe metals exposed to high temperature water are a useful starting point. In these diagrams, Figures 4-1 through 4-3, Ni has the broadest range of solid stability at high pH's with nickel oxide having stability starting at mildly oxidizing potentials to approximately pH 15. Nickel metal is stable at all alkaline and caustic pH's at the reversible hydrogen potentials (line a) in the Pourbaix diagrams and at reducing potentials. Chromium is least stable having only soluble species predicted in the Pourbaix diagrams for highly alkaline to caustic solutions at both oxidizing and reducing conditions. The extent of the stability of iron at high pH's is between that of Cr and Ni. Iron has a band of potentials at both oxidizing and reducing conditions at high pH's where soluble $HFeO_2^-$ is predicted by the Pourbaix diagrams.

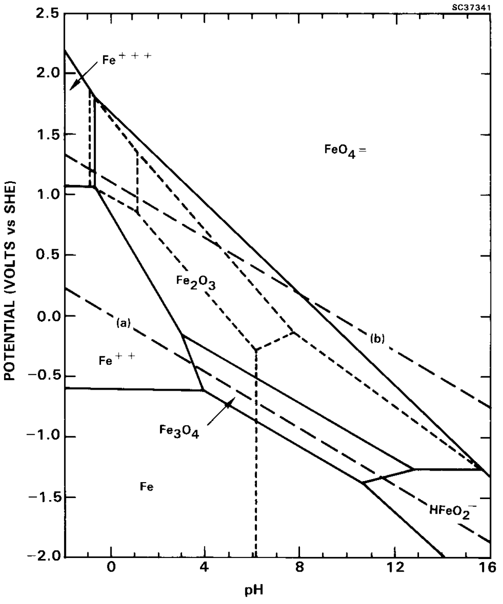

Figure 4-1
Potential-pH diagram for the Fe-water system (at 288°C) with dissolved species activities of 10^{-3} (4,5)

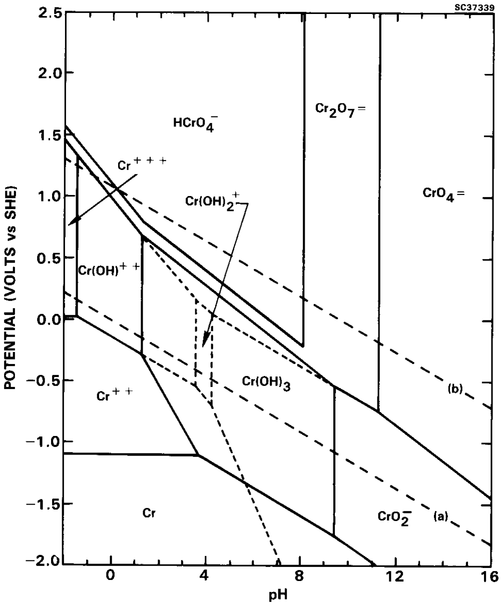

Figure 4-2
Potential-pH diagram for the Cr-water system (at 288°C) with dissolved species activities of 10^{-3} (4,5)

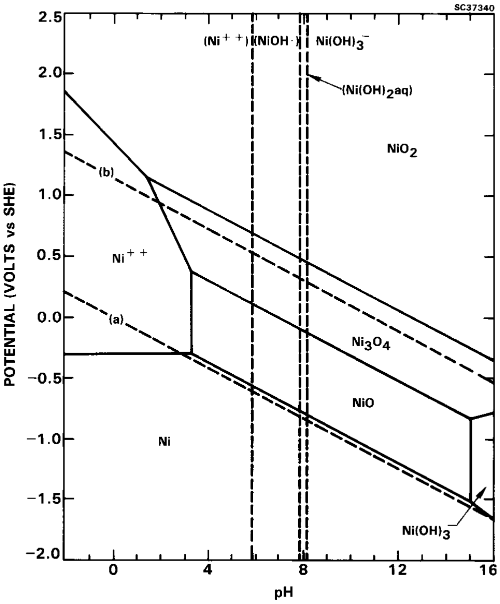

Figure 4-3
Potential-pH diagram for the Ni-water system (at 288°C) with dissolved species activities of 10^{-3} (4,5)

In order to locate a point on a Pourbaix diagram the ECP as well as the pH of the system must be known. In deoxygenated high temperature water, the corrosion kinetics of alloy 600 are under cathodic control. Under these conditions, the ECP is the reversible hydrogen potential, which is determined by the equilibrium reaction between dissolved hydrogen and water,

$$H_2 + 2OH^- = 2H_2O + 2e^-.$$

The reversible hydrogen potential at any temperature is given by

$$E_{H2/H+} = 2.303\ RT/F\ (\log a_{H+}) - 2.303\ RT/2F\ (\log p_{H2}),$$

where a_{H+} is the hydrogen ion activity in solution, p_{H2} is the partial pressure of hydrogen in atmospheres, and R,T and F have their usual definitions. Line (a) in the Pourbaix diagrams above give the reversible hydrogen potentials at 288°C for a hydrogen partial pressure of one atmosphere. At 288°C, the above equation becomes

$$E_{H2/H+} = -0.110\ pH - 0.056 \log p_{H2}.$$

Thus, assuming that the hydrogen activity remains constant, the ECP will decrease 110 mV for every unit increase in pH. Likewise, at constant pH the ECP will increase (become less negative) 56 mV for every order of magnitude decrease in the hydrogen concentration.

The equilibrium hydrogen concentration in the primary water is approximately 0.2 atmospheres. Hydrogen will diffuse from the primary side to the secondary surface. Since hydrogen is being continuously removed by steam, the upper bound of hydrogen in the crevice is assumed to be 0.2 atmospheres. Therefore, the cover gas used in this work contained 0.2 atmospheres of hydrogen. Assuming, as others have shown, that the Ni wire reference electrode is a hydrogen electrode, the open circuit potential is the hydrogen equilibrium ECP for a hydrogen concentration of 0.2 atmospheres. Then applying a potential above the open circuit or corrosion potential corresponds to a condition, which is equivalent to less dissolved hydrogen in the water, assuming that there are no oxidizing species present.

The Pourbaix diagrams provide a basis for explaining the kinetic phenomena observed in the polarization curves. The Pourbaix diagrams for Ni, Cr, and Fe, shown in Figures 4-1, 4-2, and 4-3, have regions at high and low pH's where soluble compounds are thermodynamically stable. A schematic of one of these regions is shown in Figure 4-4a, where the pH of the system is assumed to be the vertical line intersecting the horizontal and oblique lines representing the phase boundaries. Figure 4-4b shows how the polarization curve relates to the Pourbaix diagram. In this figure it is assumed that the hydrogen equilibrium potential, which is given by equation 4-3, is below M^{++}/M equilibrium potential. Thus, in Figure 4-4b, the open circuit potential is the equilibrium potential for metal deposition. At film-free conditions, metals dissolve with little impediment. As the potential is made more positive from the M^{++}/M equilibrium potential by environmental species or galvanic couples in a steam generator, the rate of dissolution increases rapidly with increase in the potential until the potential is reached where the oxide is thermodynamically stable. The onset of oxide film formation on the metal surface is accompanied by a step decrease in the dissolution current. Metals, which have a passive oxide film covering their surface, dissolve slowly and at rates which tend to be independent of potential (6). This region of potential independent dissolution can be shortened in extent by the onset of pitting if chloride ions are present. The regions and critical potentials on the polarization curve are labeled in Figure 4-4c.

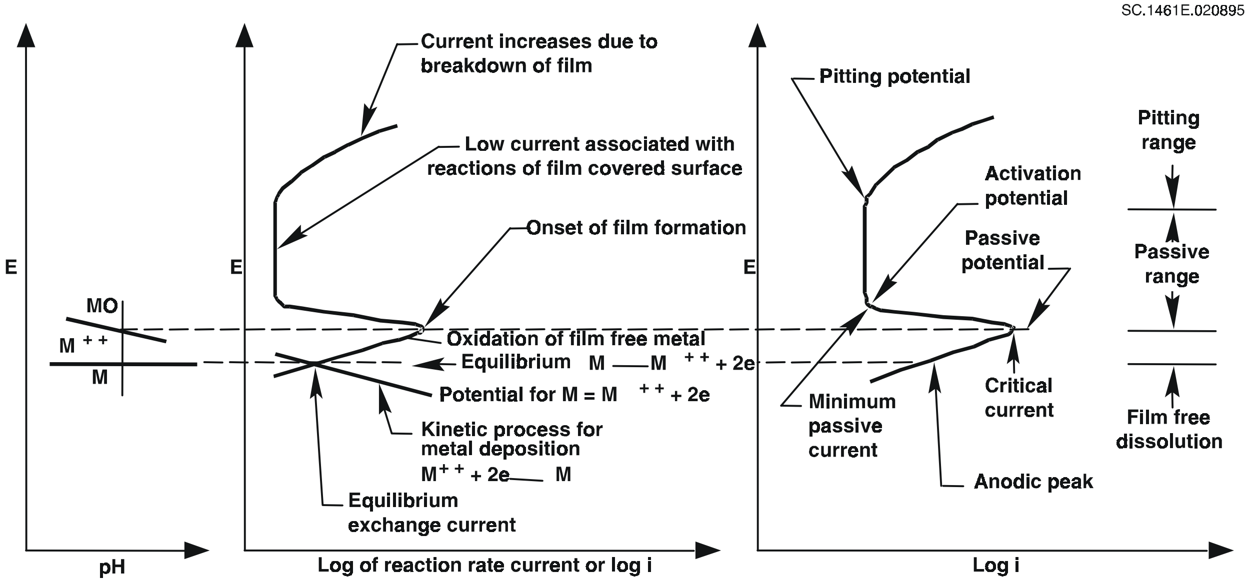

Figure 4-4
Schematic showing the relationship between (a) Pourbaix diagrams and (b,c) regions in polarization curves (6)

The polarization curves for the 50% NaOH solution and for both subsets of the pH 9 and pH 10 solutions follow the active-passive type of behavior shown in Figure 4-4. The polarization curve from the pH 5 complex solution also has active-passive type of behavior, but the passive region is shorter in extent because of the onset of pitting at the pitting potential. In the pH 3 solution only film free dissolution occurs although the Pourbaix diagrams suggest that oxide films should form at high potentials. Possibly film formation does not occur because the thermodynamic potential for the onset of oxide film formation is above the pitting potential. The results for the pH 4.5, 5 m NaCl solution appear to indicate that the region after the anodic peak is in the dynamic state of pitting and repassivation. The current density is higher than the passive current density, but lower than that which would exist if stable pit growth were occurring.

A secondary peak is observed in some of the polarization curves, which is between 0.4 and 0.5 V above the open circuit potential. This is possible from the oxidation of iron from the +2 to +3 oxidation state. An inspection of the Pourbaix diagram for Fe (Figure 4-1) indicates that the Fe_3O_4/Fe_2O_3 equilibrium potential is in the range where the secondary peak is observed.

Table 4-1 and Table 4-2 are a summary of the normalized Cr and normalized Ni contents at different pH's for the two subsets of environments. These tables give the normalized Cr and Ni contents in the film after the first 50Å have been removed by sputtering. This small amount of sputtering removes any contamination resulting from handling. Several general observations can be made from the results. These results indicate that at pH's above 9 or 10 (the pH of the 50w/o NaOH solution was 11.2) the surface composition is either Ni metal or nickel oxide/hydroxide. For environments having pH's 3 and below, the surface is predominately chromium oxide or chromium hydroxide. Between these two extremes in pH the Cr/Ni ratio is dependent on the ECP. The database for the complex subset of environments is not as complete as that for the simple one; however, the trends in the normalized Cr and Ni concentrations are the same for both environments.

Table 4-1
Normalized Ni and Cr surface concentrations, Ni%(Cr%), at the pH's and potentials tested. Results are for the NaCl/NaOH/Hcl simple system

Potential/pH	**11.4**	**10**	**9.3**	**4.9**	**3**
	Ni(Cr)	Ni(Cr)	Ni(Cr)	Ni(Cr)	Ni(Cr)
-100	—	—	—	—	51(49)
O.C.	100 (0)	81 (0)	86 (8)	24 (62)	60 (4)
25	—	95 (0)	92 (6)	—	20 (80)
50	—	74 (20)	90 (7)	—	0 (100)
100	100 (0)	29 (45)	30 (28)	—	—
150	100 (0)	52 (48)	36 (39)	—	—
200	—	—	—	17 (69)	—
500	—	—	—	12 (88)	—

Table 4-2
Normalized Ni and Cr surface concentrations, Ni%(Cr%), at the pH's and potentials tested. Results are for the complex subset of test environments

Potential/pH	10	9	5.0	3
	Ni(Cr)	Ni(Cr)		Ni(Cr)
O.C.	83 (0)	85 (0)	—	0 (100)
50	—	100 (0)	—	—
100	—	70 (0)	—	—

Figure 4-5 shows the change in the normalized Cr concentration as a function of pH for ECP regions in the polarization curve where there is no film formation. The concentrations plotted are the average of those measured at potentials at which film formation did not occur, i.e., the active region of the polarization curve. The normalized Cr concentration increased rapidly as the pH of the test environments was decreased from 10 to 3. Figure 4-6 shows the change in the normalized Ni corresponding to the normalized Cr concentrations shown in Figure 4-6. In both figures there were no test environments in the pH range from 5 to 9. A linear extrapolation was made in this region.

When the potentials were in the region of the polarization curve where the surface was film-free, the normalized Ni content decreased linearly as the test environments decreased from 10 to 3. The Ni content did not vary uniformly in potential region where there was film formation. The passive film formed in environments, which are caustic or highly acidic are Fe-Cr-Ni mixed oxides. Figure 4-5 shows that the environment need not be acidic for Cr to enrich on the surface. The Cr content of the surface at pH 9 is approximately that in the alloy. Chromium enriches on the surface in environments which are at mildly alkaline and neutral pH's.

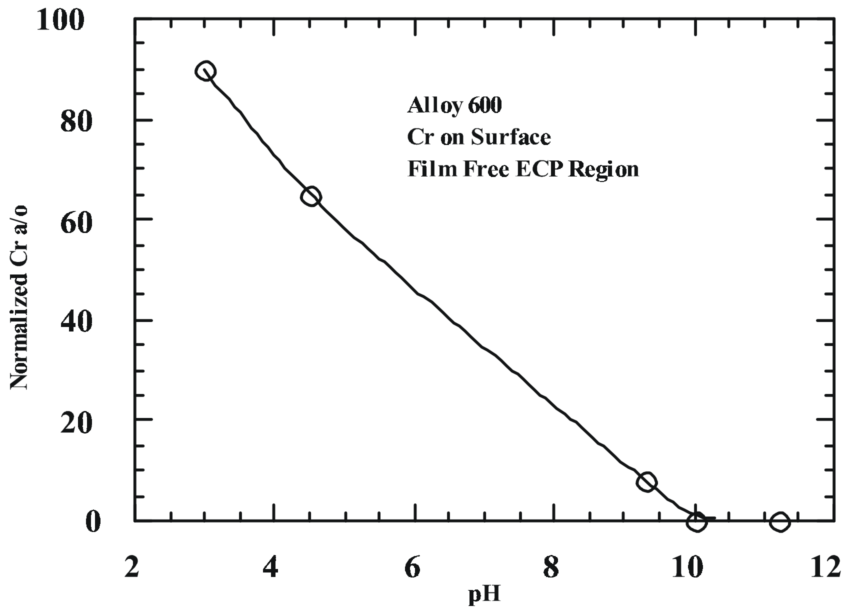

Figure 4-5
Effect of pH on the normalized Cr concentration on the surface of alloy 600 at potentials in the active region of the polarization curve

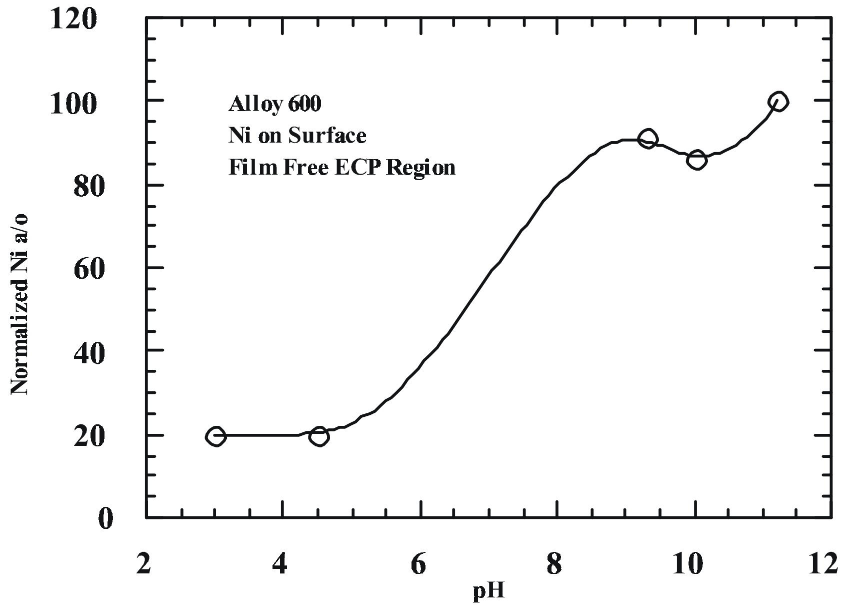

Figure 4-6
Effect of pH on the normalized Ni concentration on the surface of alloy 600 at potentials in the active region of the polarization curve

The effects of pH on the normalized Cr and Ni concentrations in the potential regime where there is film formation is shown in Figure 4-7. This behavior is more complex than that in the film free region because of the formation of Fe-Cr-Ni mixed oxides. In the high pH region it is clear that Ni increases rapidly and Cr decreases rapidly as the pH decreases. It is not clear what the trends are in the highly alkaline to neutral pH's because the test matrix did not include environments in this region.

There was no incorporation of Na ions nor chloride from the NaCl / NaOH / HCl subset of solutions except at pH 4.88 and 3.0. The oxide films formed in these environments had up to approximately 5a / o chloride incorporated. In the environments intended to represent prototypical crevice environments, there was substantial incorporation of K, chloride and silicate ions, particularly at pH 9 and 10.

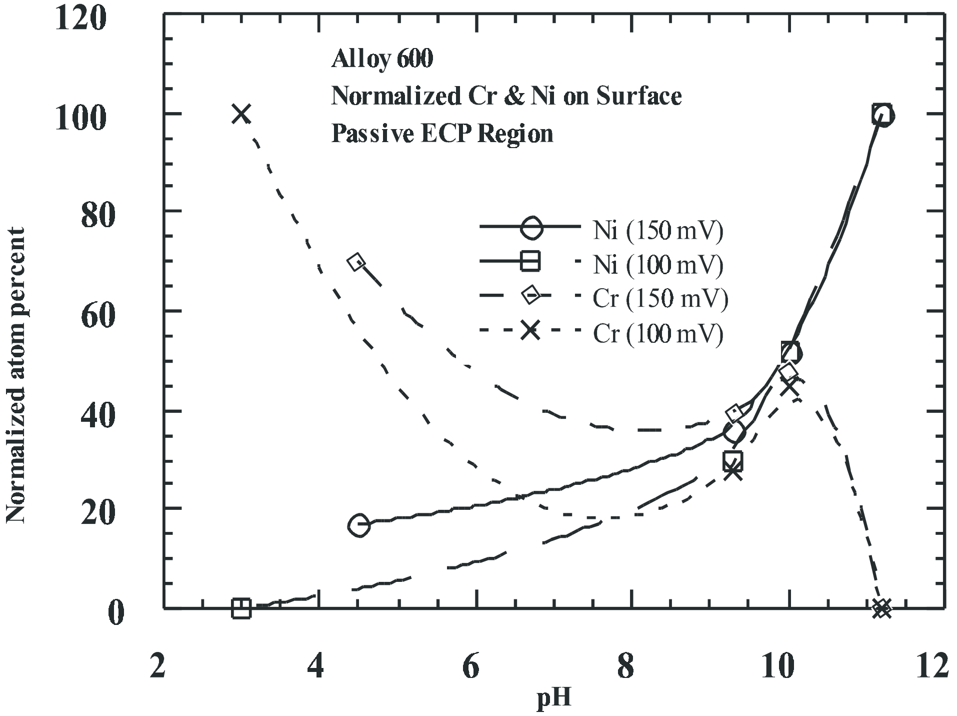

Figure 4-7
Effect of pH on the normalized Cr and Ni concentrations on the surface of alloy 600 at potentials in the passive region of the polarization curve

The C-ring results for the pH 10 solutions showed that pH is not the only environmental parameter controlling SCC susceptibility. SCC was observed in the specimens polarized at 150 and 200 mV while exposed to the pH 10 simple solution (Environment No. 4 in Table 2-1); however SCC was not observed in C-ring specimens exposed to the complex pH 10 solution (Environment No. 8 in Table 2-1). The potential dependence, in which SCC occurs at the transition potential between film free active dissolution and passive film formation, indicates that the passive film is a critical element. Apparently, the presence of one or more of the species in the complex solution, which are not in the simple solution, changes the chemistry of the passive film so that it is more resistant to the processes responsible for crack initiation and growth in the film rupture/anodic dissolution mechanism of SCC.

No cracks were observed in the C-rings exposed to the pH 3 solution. There was a decrease in the cross section thickness at all potentials. This indicates that the corrosion process is wastage in accordance with the polarization curves, which suggested film free dissolution occurs at all potentials. Thus, SCC is not possible if it is caused by a film rupture mechanism.

Conclusions

1. In solutions having pH 3 or less, which simulate crevice chemistries and temperature and have 5 m or higher concentration of NaCl, a passive film does not form on alloy 600 and wastage occurs.

2. In a pH 5 solution at 315°C having 5 m NaCl or higher concentration, pitting occurs on alloy 600.

3. Alloy 600 in solutions at pH’s 9 or higher, which simulate crevice chemistries and temperature, has ECP regions of film free dissolution and passive film formation.

4. Surfaces of alloy 600, which are exposed to crevice-like solutions at pH’s 10 or higher have a surface film which is predominately Ni or nickel oxides/hydroxides.

5. Surfaces of alloy 600, which are exposed to crevice-like solutions at pH’s 3 or less, have a surface film which is predominately Cr or chromium oxides/hydroxides.

6. The ratio of the atomic percents, Cr/(Cr + Ni + Fe), of alloy 600 on the surface increases uniformly as the pH decreases if the ECP is in the film-free dissolution potential range.

5

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