Determination of Surface Oxide Compositions on Alloy 600 Using

Rutherford Backscattering

A. L. Hanson, H. S. Isaacs, and H. W. Kraner

Brookhaven National Laboratory, Upton, New York 11973, USA

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ABSTRACT

The surface composition of oxides formed on Alloy 600 under conditions similar to those in the primary side of PWR heat exchangers has been studied as a function of potential using Rutherford backscattering and proton inelastic scattering. Electropolished samples of Alloy 600 were exposed at several potentials to a solution of $0.18M$ H_3BO_3 (2000ppm B) with $0.28M$ LiOH (1.4ppm Li) at 300°C for 450 hours. The potentials relative to an internal hydrogen electrode ranged from $-.09$ to 750 mV. RBS analysis showed little or no oxide formation on samples exposed at 0 mV. Above 0 mV oxide layers formed whose thicknesses increased with potential. In addition the RBS showed a significantly enhanced concentration of aluminum and silicon in oxide. Both the oxygen and the sum of the aluminum and silicon content appeared to maintain a fixed surface concentration independent of the oxide thickenss. Boron and lithium concentration were analyzed with proton inelastic scattering. No lithium was found in any sample. The boron concentration was found to follow the thickness of the oxide.

INTRODUCTION:

The nickel based Alloy 600 has been widely used in the nuclear power industry for heat exchanger tubing because of its high resistance to general corrosion, which is controlled by the formation of a passivating surface oxide layer. Only a few studies have been carried out on the composition of the oxide layer or how it is influenced by the presence of boron or lithium, which are generally added to the primary coolant. The presence of hydrogen or possibly oxygen would be expected to alter the potential at which the oxide grows which in turn may alter the susceptibility of the alloy to stress corrosion cracking. The corrosion of Alloy 600 is difficult to characterize since there are many factors affecting the performance of the alloy. These seem to include strong dependences on temperature (the iron dissolution peaking at roughly 200°C), physical state of the water (liquid or steam), impurities in the water, cover gas, surface roughness, and the potential of the particular surface influenced by the presence of dissolved oxygen, hydrogen, or other oxidizing or reducing species.

While corrosion from the secondary side is the major problem of steam generators, understanding the existing and possible future problems from the primary side is important. We previously reported (1) work studying corrosion products formed on electropolished Alloy 600 exposed to caustic solution at 315°C for 10 days in a nickel autoclave at several potentials. The autoclave had been pressurized at 1.38MPa with a %5H$_2$ 95%N$_2$ cover gas. That work showed an enhancement of

nickel on the surface with potentials of -90 mV and 0 mV; with the nickel layer being thicker at the more negative potential. Neither of these samples showed any significant oxide formation. At 170 and 225 mV a significant highly stressed oxide layer had formed with approximately a 50 at% metal concentration. The total oxygen content was not determined because the oxide was found to flake off the surface of the material. The basic stoichometry of the alloy was essentially maintained through the oxide without a major buildup of any specific element. At and above 270 mV, however, a duplex oxide was found. The oxide in contact with the solution was high in nickel, and the oxide adjacent to the the metal was high in chromium. A depletion of chromium was also found by McIntyre et al.(2) on exposing Alloy 600 to oxygen containing neutral and caustic solutions at 285°C. In their work there was apparently no major buildup of any minor alloying elements on their specimens prepared by abrasion and exposed to either deionized water at pH 7 or solutions of higher pH values with LiOH additives.

The purpose of this work was to characterize the effects of potential on the surfaces formed on Alloy 600 exposed to conditions similar to those of the primary side of PWR steam generators. The primary coolant consists of borated water (less than 4400 ppm boron) with a trace of lithium hydroxide (0.2 to 1.0 ppm Li) (3). The temperature of the water ranges from 290°C to 325°C with hydrogen added to the covergas to minimize the oxygen content. The concentration of boron in oxide films formed on type 316 stainless

steels have been measured after exposure to 340°C water with 1000 ppm boron. After about 600 hours the boron content of the oxide reached a stable value of about 0.03 $\mu g/cm^2$, or about 0.03 % of the corrosion film, a value similar to that in crud. This level was substantially lower than previous results which had maxia of 0.75 and 1.7 $\mu g/cm^2$ after about 300 hour exposures with and without 1 ppm Li as an additive (4,5).

EXPERIMENTAL:

Rectangular samples, 10x20x0.8 mm in size, were cut from an as received annealed sheet of Alloy 600 with weight percent composition: 75.31 Ni, 14.59 Cr, 9.45 Fe, 0.33 Cu, 0.20 Mn, 0.20 Al, 0.20 Ti, 0.11 Si, 0.01 C and 0.001 S, determined by chemical analyses. These samples were electropolished in a mixture of 60% H_3PO_4, 20% H_2SO_4, and 20% H_2O, by volume, at 35 to 40°C with a cell potential of 15 volts. After polishing the samples were washed repeatedly in distilled water and dried after a methanol wash.

The electropolished samples were exposed in a borate solution of 0.18 M boric acid (2000ppm B) and 5 ppm lithium hydroxide (1.4 ppm Li) for 450 hours at 300°C in a nickel autoclave. The pH of the solution was 6.6. Prior to heating, the solutions were deoxygenated. The autoclave was pressurized at 9.7 MPa (1400 psi) with a 5% H_2 and 95% N_2 covergas. The samples were exposed at a series of controlled potentials using the technique of Seys and van Haute (6) as developed by Roberge et al. (7). The controlled potential range was -0.03 to

to 710 mV relative to a nickel electrode at its mixed or corrosion potential. A freely corroding Alloy 600 specimen also exposed in the borate solution gave potentials close to that of the nickel. The average potential of this sample was -0.09 mV. At the termination of the test the potential controls were switched off and the autoclave allowed to cool prior to removing the samples.

The samples were analyzed with Rutherford Backscattering Spectrometry (RBS), to study the relative elemental composition of the surface layers; SEM, to study the microstructure of the surfaces; and nuclear reaction analysis (NRA), to determine the boron and lithium content of the surfaces. The RBS measurements were made using a 2.8 MeV beam from the Brookhaven National Laboratory 3.5 MV electrostatic accelerator. The alpha beam size was 1 mm square, the scattering angle $165°$, and the energy resolution of the detector-analyzer system 14 keV. The typical He^+ currents were 30 nA and the total dose accumulated was approximately 50 µC. The energy of the system was calibrated with an ^{241}Am α source along with He^+ scattering edges from aluminum and copper. This type of analysis has been discussed thoroughly in the past and will not be reproduced here (for example see refs. 8,9).

Nuclear reaction analysis is a nondestructive technique mostly sensitive for the analysis of light elements. In this experiment, energetic protons were used to excite the nuclei of the target atoms. The nuclear reactions used for the analyses were the $^{10}B(p,p'\gamma)^{10}B$ and $^{7}Li(p,p'\gamma)^{7}Li$ inelastic scattering reactions. The resulting gamma

rays used in the analyses were the 2125- and 478-keV gamma rays from the boron and lithium, respectively. As has been discussed in detail previously (10,11), the gamma ray yield is directly proportional to the concentration of target atoms. In this particular experiment the resulting gamma rays were counted with a 90-cm^3 Ge(Li) detector, 14% efficient for Co-60 gamma rays, placed 4 cm from the target at 90° to a 3.4 MeV proton beam. Beam currents of 3 nA were used with counting times on the order of 1 to 2 hours.

RESULTS:

Microscopy:

All samples were examined with scanning electron microscopy to observe the surface morphology. The micrographs of the samples did not show any notable, visible features resulting from exposure. These results are in sharp contrast to the results from exposure to caustic solution (1) where etching was evident up to +70 mV and oxide formation did not develop until 170 mV. The oxide layers on the samples exposed to caustic solution were also poorly adhered to the surface and above 225 mV had a soluble outer layer. With the borate solution the oxides were thinner over most of the potential regions and there was no evidence of spalling up to potentials of 750 mV. In addition there was no development of the grain structure indicating that the oxides were far more protective than in the caustic solution.

Nuclear Reaction Analysis:

Boron was determined in each sample with nuclear reaction analysis. The results of the analyses are given in table I. Lithium can also be analyzed with this method, but the level of lithium in the surface layer was below the sensitivity limit of 0.05 $\mu g/cm^2$. This type of analysis does not give any depth information nor does it provide information on the element's chemical state. There was no measurable concentration of boron in the two 0 mV samples and only a trace in the sample exposed at 165 mV. The concentration shows a plateau as a function of potential between 250 mV and 500 mV and then starts to increase with potential.

Rutherford Backscattering Spectrometry (RBS):

RBS spectra from the samples is shown in figure 1. Each curve is identified with the potential at which each sample was exposed to the borate solution. All of the samples were held at their respective potentials except the -0.09 mV sample, which was allow to float; the -0.09 mV being its average potential. The conversion from channel to energy is 1.4 keV/channel. The leading edge of the 0 mV samples correspond to the surface concentration of nickel (channel 1520). The step at channel 1470 corresponds to the surface concentration of chromium, and the iron edge occurs at channel 1500. There are two lower energy edges in the spectra of the higher potential samples. The one at channel 1100 is from aluminum and/or silicon and the one at channel 700 is from oxygen.

The sample exposed at 740 mV shows a nickel edge that corresponds to a concentration of only 18 at%. The chromium does not appear at any significant concentration in this layer nor at any potential above 250 mV. It also shows an Al+Si surface concentration of 20%. Oxygen accounts for the remaining surface concentration as deduced from the height of the oxygen edge. The height of the edge was fairly constant on all the oxidized samples. Only the width of the oxygen "peak" and hence the thickness of the oxygen layer increased. The Al+Si edge increased in height until 415 mV indicating an increase in the surface concentration. After that most of the increase in the amounts were again due to increasing the width and hence the depth below the surface of the Al+Si layer. The amount of the Al+Si in the surface layer always followed the amount of the oxygen. There certainly is a correlation between the oxygen content, the Al+Si content, and the boron content. This is illustrated in figure 2, which is a plot of oxygen, Al+Si, and boron content as a function of potential.

DISCUSSION:

Samples of electropolished Alloy 600 exposed to borate solution show a considerably different behavior than samples exposed in a similar manner to a caustic solution. This experiment and the caustic experiment, reported earlier, exposed samples of Alloy 600 at different potentials to simulate the effects of oxidizing and reducing conditions which could arise by the presence of other impurities or galvanic effects in the primary and secondary sides, respectively, of

PWR steam generators. Samples exposed to the caustic environment experienced active dissolution and etching of the surface between -90 and 75 mV. In contrast, the samples exposed to the borate solution at 0 mV potential showed no etching or dissolution effects with the metal surface free of oxide.

At higher potential, with oxides present, a significant difference between the two experiments was the mechanical performance of the oxide layers. The oxide on samples exposed to the caustic environment displayed cracking, spalling, and dissolution of oxide layers after reaching 170 mV, becoming more pronounced at higher potentials. In contrast the samples exposed to the borate solutions showed no signs of cracking, spalling, or dissolution of the oxide layers even up to 740 mV. The effect of potential was to increase the thickness of the oxide present on the samples. In the caustic solutions the effects of potential were more complex and involved changes in the nature of the oxides as well as their internal stresses.

An extremely interesting result of this experiment was the enhancement of Al+Si in the surface oxide. As is illustrated in figure 2, the Al+Si concentration increases with potential. The concentration of aluminum and silicon in the base alloy is only .65 at% and with the higher potential exposures finish at approximately 52 (metal) at%. This increase would appear to occur with the dissolution of the other metallic alloying components leaving a relatively small fraction of the original nickel and most if not all

of the aluminum and silicon. As is also illustrated in figure 2 the Al+Si concentration increases as the oxygen content increases. These measurements demonstrated that for the 740 mV sample at least 5 mg/cm^2 of the alloy had dissolved. In the samples exposed to a caustic solution there was no increase in Al+Si since aluminum and silicon are soluble in caustic solutions. The loss of 5 mg/cm^2 of alloy is considerably higher than losses usually reported (12) and provides an indication of the large effects of a relative small increase in the potential of the surface. The sample exposed to 0 mV, as many other experiments measured, experienced no detectable (with RBS) loss of metal atoms.

The next qutestion to be asked is what are the chemical forms of the components of the surface oxide? Even though the techniques utilized in this experiemnt cannot determine the chemical state of the components we have enough information to make some comments about limits. The metal composition of the surface is only 38 at% and the oxygen makes up the majority of the balance. If the silicon were to be dissolved, leaving the aluminum-silicon conctentration to be 100% aluminum, the most probable form is Al_2O_3. This would then leave 1.8 oxygen atoms for each remaining nickel atom. The chemical form of nickel could not be NiO, but would have to be something on the order of $Ni(OH)_2$ and NiO. This type of surface layer has been reported in the past (2). If the aluminum-silicon concentration is 100% silicon (as SiO_2) then the nickel/oxygen ratio would be unity leaving NiO as a possible candidate. Of course, then any mixture of aluminum and

silicon would likewise lead to a mixture of nickel oxide and nickel
hydroxide.

CONCLUSIONS:

We have demonstrated that there are significant differences in
the performance of surfaces and their passivating oxides formed on
Alloy 600 depending on the type of environment the alloy was exposed
to. The oxides formed on the samples exposed to borate solution were
clearly more mechanically stable and thinner than the oxides formed
from exposure to caustic environments.   It is not clear if the
differences are simply that the caustic enviroment is more aggressive,
if the boron (or borate) in the oxide film helps in passivation, or if
the   nickel   compound   (probably   NiO   in   the   caustic   and
$NiO+Ni(OH)_2+Al_2O_3+SiO_2$ in the borate) formed is more stable. We also
have shown that the amount of corrosion is strongly dependent on the
potential   of   the   sample   with   respect   to   its   surroundings.

ACKNOWLEDGMENTS:

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Table I

Boron Concentration as a Function of Potential

Potential (mV)	Boron concentration ($\mu g/cm^2$)
$-.09 \pm 0.02$	NT
$-.03$	NT
165	<0.2
250	0.2 ±0.04
330	0.35±0.04
415	0.22±0.03
490	0.31±0.03
570	0.64±0.20
740	1.3 ±0.3

FIGURE CAPTIONS:

Figure 1. RBS spectra of the samples exposed to the borate solution at different potentials. The beam was 2.8 MeV α particles with the detector at 165°. The nickel edge is at channel 1520, the aluminum is at channel 1110 and the oxygen is at channel 700.

Figure 2. Amount of each element analyzed as a function potential. Oxygen=O, aluminum+silicon=*, and boron=Δ (which was multiplied by 10).
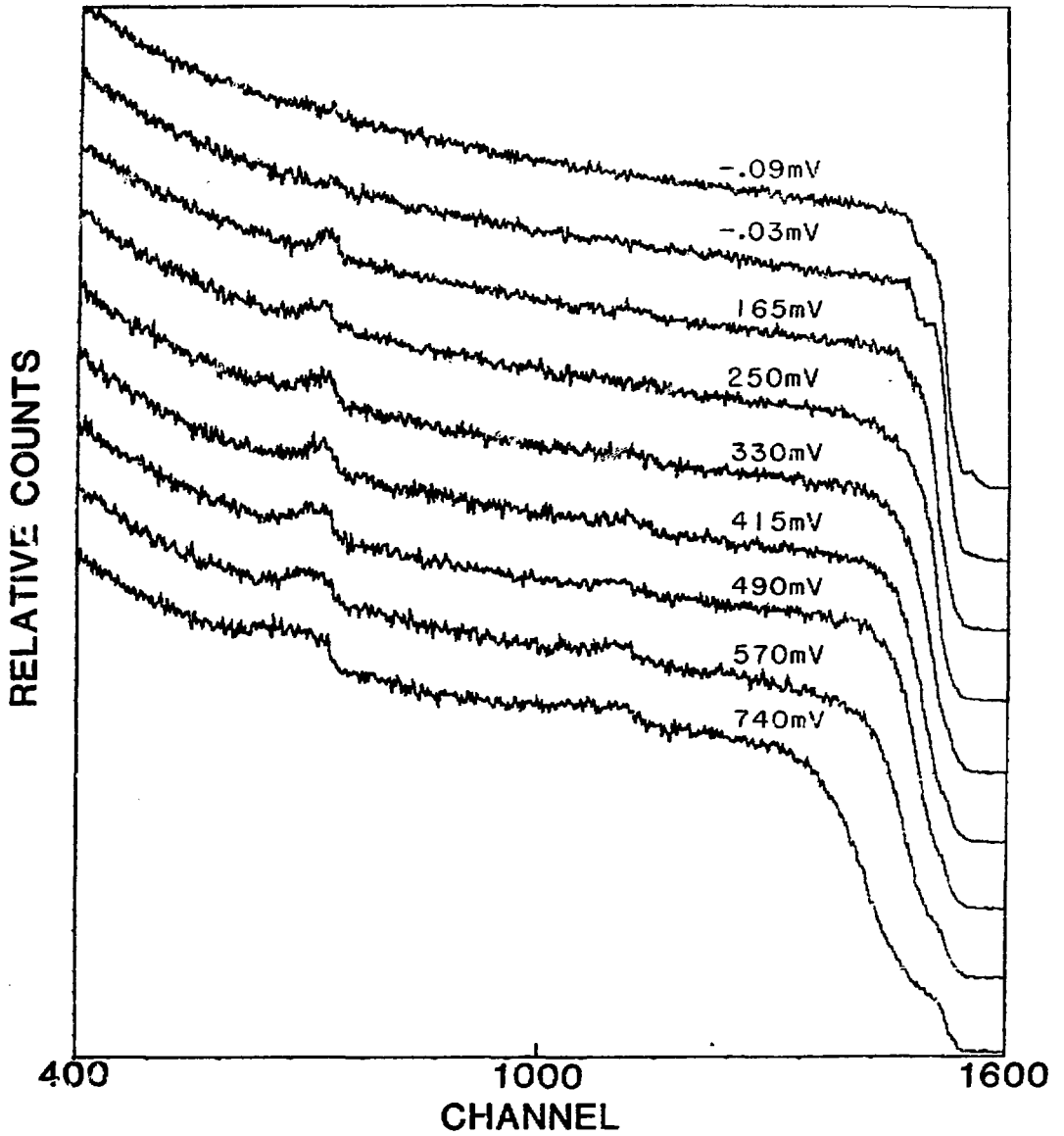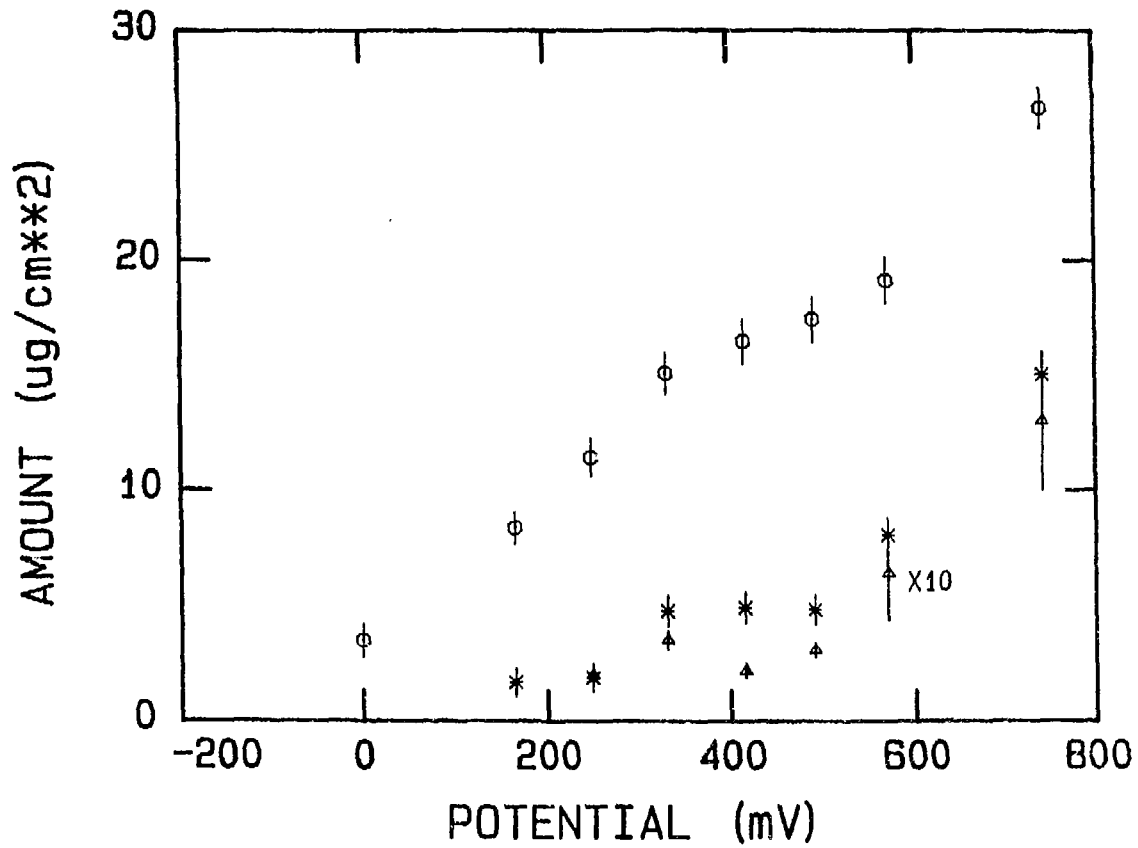
Figure 1

Figure 2