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**ABSTRACT**

Interaction of thiosulfate with Alloy 800 was systematically investigated to obtain the kinetics in a neutral simulated steam generator crevice solution. Cyclic polarization showed that the pitting potential in a thiosulfate-chloride solution was much lower than in either a chloride solution or a sulphate-chloride solution, and thiosulfate selectively and distinguishingly degraded the oxide film on Alloy 800. The donor density of oxide film formed in a thiosulfate-chloride solution was slightly higher than in either a chloride-only solution or a sulphate-chloride solution. Even in the passivity range the material was degraded due to the slow interaction with S$_2$O$_3^{2-}$ with oxide, especially when the applied potential was close to the pitting potential. The UV-visible absorption spectra showed that thiosulfate formed a stable complex with Cu$^{2+}$, and their product was soluble in aqueous solution, which is possible evidence for the reaction, thiosulfate decreased the oxidation potential of Cu$^{0}$ to Cu$^{2+}$. Since the Cu$^{2+}$, an impurity in Alloy 800, normally accumulates at the grain boundary, especially at the triple points, thiosulfate induced corrosion is in the form of pitting or intergranular attack.

Keywords : Alloy 800, Thiosulfate, Passivity, Pitting Corrosion

1. Introduction

Thiosulfate (S$_2$O$_3^{2-}$) is one of the reduced sulfur species present in the corrosion products of steam generator (SG) tubing material in the nuclear industry. Research has shown that S$_2$O$_3^{2-}$ caused pitting, intergranular attacks or intergranular corrosion and stress corrosion cracking (SCC) on many kinds of materials. It has been reported that the S$_2$O$_3^{2-}$ ion induced pitting and SCC of type 304 stainless steel. Intergranular SCC (IGSCC) was found in 304 stainless steel (SS) due to S$_2$O$_3^{2-}$ and addition of Na$_2$S$_2$O$_3$ to 3.5% NaCl increased SCC susceptibility of type 316 stainless steel (SS), which was also observed by other groups. However, Gonzalez-Rodriguez et al. claimed that the addition of S$_2$O$_3^{2-}$ did not affect susceptibility of SCC on sensitized alloy. S$_2$O$_3^{2-}$ was found to shift the pitting potential of type 316 SS to more active values and to lead to formation of wider and more open pits on material surface. At the potential in the range of $-0.35$ to $+0.15$ V, both the anodic polarization curves and the microscopic observation indicated that S$_2$O$_3^{2-}$ participated in the electrochemical reactions. S$_2$O$_3^{2-}$ can also affect the materials used in the nuclear industry. Wang et al. found that the passive range and pitting corrosion potential of Alloy 800 in the solution containing both thiosulfate and chloride ions are lower than that in thiosulfate-only or chloride-only solutions or the sulfide + chloride ions.

S$_2$O$_3^{2-}$ can affect the materials used in the nuclear industry. Wang et al. found that the passive range and pitting corrosion potential of Alloy 800 in the solution containing both thiosulfate and chloride ions are lower than that in thiosulfate-only or chloride-only solutions or the sulfide + chloride ions. Z. Fang and R. W. Staehle investigated surfaces of Alloys 600, 690 and 800 after polarization over the potential range and found intergranular (IG) corrosion occurred mainly in a solution of SO$_4^{2-}$, sulfite (SO$_3^{2-}$), tetraethionate (S$_4$O$_6^{2-}$), and S$_2$O$_3^{2-}$, while S$^2-$ or HS$^-$ were found to produce pitting. The IGSCC or intergranular attack on sensitized Alloy 600 was confirmed by literature. Unsensitized Alloy 600 in S$_2$O$_3^{2-}$ ions was not susceptible to SCC when the potential was controlled at $-300$ mV$_{SCE}$ or at $+400$ mV$_{SCE}$ (SCE = saturated calomel electrode). Alloy 800 exhibited a high susceptibility to caustic SCC in the passive region at greater potentials than about $-0.30$ V$_{SCE}$, but was much less susceptible to SCC at potentials lower than approximately $-0.45$ V$_{SCE}$. S$_2$O$_3^{2-}$ is more detrimental than other impurities in water on the IGSCC of steel in a LWR environment, such as Cl$^-$ and F$^-$.

The initiation of SCC in sensitized Alloy 600 in aqueous Na$_2$S$_2$O$_3$ is much lower than that in Na$_2$SO$_4$ solutions, indication that S$_2$O$_3^{2-}$ is more detrimental to materials than S$_2$O$_3^{2-}$. Our previous work found that the detrimental effect of impurities containing sulfur at the reduced or intermediate oxidation level on the passivity of Alloy 800 depends significantly on the solution pH.

It is reported that the S$_2$O$_3^{2-}$ detrimental effects are related to temperature. IGSCC of sensitized AISI SS304 was studied in aerated pure water and in chloride solutions with and without sulfide (S$^2-$) and S$_2$O$_3^{2-}$ anions at 50–200°C using the slow strain rate technique. At 50 and 100°C, the existence of S$_2$O$_3^{2-}$ or S$_2$O$_3^{2-}$ ions in Cl$^-$ solution increases the IGSCC. S$_2$O$_3^{2-}$ ions promote SCC at 150°C while S$^2-$ ions inhibit SCC; and both ions inhibit SCC at 200°C. The cracking rate observed on Alloy 600 increases with increasing temperature. Higher temperature accelerates the cracking, and possibly decreases the apparent threshold stress for cracking on Alloy 600.

Sulfur has many oxidation states, such as $-2$ in sulfide (S$^2-$), $0$ in sulfur (element), $+2$ in thiosulfate (S$_2$O$_3^{2-}$), $+2.5$ in tetraethionate (S$_4$O$_6^{2-}$), $+3$ in sulphite (SO$_3^{2-}$), $+6$ in sulphate (SO$_4^{2-}$) and so on. Under the reducing environments, the lower oxidation states, such as $-2$ and $0$ are more stable. The results of deposits and spectra...
taken from an energy dispersive X-ray (EDX) system confirmed the existence of reduced sulfur on alloy 600.\(^{15,26}\) X-ray photoelectron spectroscopy (XPS) revealed that primarily iron oxides in the passive film of 18-8 stainless steel were converted into sulfides in forms of FeS and FeS\(_2\), while elements of Cr and Ni still remained essentially as oxides/hydroxides.\(^{37}\) Cr-Ni-S particles were also found on Alloy 690 in some researches.\(^{38}\) The oxidation of FeS scales, gave rise mostly to Fe\(_2\)O\(_3\) and elemental S, with low yields of both S\(_4\)O\(_6\)^{2−} and S\(_2\)O\(_3\)^{2−}.\(^{39}\)

Alloy 800 is presently used as SG tubing material in nuclear industries which has very low sulfur levels. However, due to the usage of a reducing agent, such as hydrazine, it is thermodynamically possible that SO\(_4\)^{2−} in feedwater can be reduced by hydrazine at the operation conditions. It is also possible that SO\(_4\)^{2−} can be reduced by some elements in the alloy (e.g. Ni, Fe, Cr).\(^{40}\) Although SO\(_4\)^{2−} in feedwater has a very low concentration, it can change to reduced sulfur compounds, and these compounds can accumulate in the system and finally cause the material failure after tens of years service.\(^{1,37}\)

S\(_2\)O\(_3\)^{2−} is proved to be detrimental to SG tubing material, which is also well summarized in several reviews.\(^{36,41,42}\) However, how S\(_2\)O\(_3\)^{2−} interacts with Alloy 800 and how S\(_2\)O\(_3\)^{2−} initializes the corrosion are still not solidly confirmed in the publications. There is little amount of solid experimental results related to Alloy 800. It is important to understand what are the products generated from S\(_2\)O\(_3\)^{2−} that reacted with Alloy 800 and the kinetic information of those reactions. In this paper, the interaction of Alloy 800 with S\(_2\)O\(_3\)^{2−} has been studied, the S\(_2\)O\(_3\)^{2−} induced dissolution rates of alloying elements in Alloy 800 have been investigated, and the mechanism has been proposed based on the various experimental results.

2. Experimental

2.1 Chemicals and Sample Preparation

The compositions of the test solutions simulating the SG secondary side crevice chemistry conditions are listed in Table 1.\(^{59}\) All the chemicals used were reagent grade. Before experiments the solutions were filtered to remove any precipitate formed after they had been prepared for 24 h. The pH values of all the solutions were measured using a pH meter (AR50, Dual Channel pH/Ion/Conductivity Meter, Accumet Research, Fisher Scientific).

The specimens were cut from Alloy 800 tubing (from Sandvik, heat number 516809) with a nominal wall thickness of 1.13 mm and an outer diameter (OD) of 15.88 mm, as received. The elemental composition of Alloy 800 is listed in Table 2. This tube section was then vertically cut into four equal specimens. The outside surface of each specimen was grounded with wet silicon carbide papers (Buehler Ltd.) in the following sequence: 320#, 600#, 800#, and 1200#, rinsed copiously with deionized water, acetone and ethanol, then dried in air. Then, the inner surface and the four edges of each specimen were sealed with epoxy leaving only the outside surface exposed for electrochemical tests, as shown in Fig. 1. The exposed testing area was about 3.118 cm\(^2\). Before all electrochemical experiments, the solutions were deaerated by high purity (99.99%) N\(_2\) for 1 hour except the experiment that investigated the effect of air on film degradation (shown in part 3.7) and thiosulfate decay due to a reaction with Alloy 800 samples in NC-2 (part 4). Nitrogen flow was kept on throughout the electrochemical measurements.

The experiments for testing the reaction rate of S\(_2\)O\(_3\)^{2−} with Alloy 800 were specifically designed. Six samples were prepared in these experiments, which are shown in Table 3. In order to determine the concentration of S\(_2\)O\(_3\)^{2−} that decreased with time, the concentration of S\(_2\)O\(_3\)^{2−} was noted everyday with UV-Visible Absorption Spectrometry (UV-Vis). Concentrations of Fe, Cr, Ni, Cu and Co were also determined using atomic absorption spectroscopy (AAS) at the 7th and 14th day after experiments started. The sample surface area was measured and the consumption of S\(_2\)O\(_3\)^{2−} was normalized to mol L\(^{−1}\) s\(^{−1}\) cm\(^{−2}\). The weight of Alloy 800 samples was also measured for the determination of weight loss.

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**Table 1.** Simulated CANDU SG crevice chemistry (unit: mol/L).

<table>
<thead>
<tr>
<th>ID</th>
<th>NaCl</th>
<th>KCl</th>
<th>CaCl(_2)</th>
<th>Na(_2)SO(_4)</th>
<th>Na(_2)S(_2)O(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC-0</td>
<td>0.30</td>
<td>0.050</td>
<td>0.15</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>NC-1</td>
<td>0.30</td>
<td>0.050</td>
<td>0.15</td>
<td>0.15</td>
<td>0.00</td>
</tr>
<tr>
<td>NC-2</td>
<td>0.30</td>
<td>0.050</td>
<td>0.15</td>
<td>0.15</td>
<td>0.075</td>
</tr>
</tbody>
</table>

**Table 2.** Chemical composition of Alloy 800 (mass%).

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Co</th>
<th>Ti</th>
<th>Cu</th>
<th>Al</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.017</td>
<td>0.46</td>
<td>0.5</td>
<td>0.012</td>
<td>0.001</td>
<td>21.87</td>
<td>32.78</td>
<td>0.01</td>
<td>0.48</td>
<td>0.02</td>
<td>0.29</td>
<td>0.016</td>
<td>43.2</td>
</tr>
</tbody>
</table>

**Table 3.** Experimental design for kinetics study.

<table>
<thead>
<tr>
<th>Solution ID#</th>
<th>Purging Gas</th>
<th>Role</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 800</td>
<td>Compress air</td>
<td>Reference</td>
<td>NC-2</td>
<td>NC-2</td>
<td>NC-2</td>
<td>NC-2</td>
<td>NC-2</td>
</tr>
<tr>
<td></td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Solution ID#</td>
<td>Compress air</td>
<td>—</td>
<td>NC-2</td>
<td>NC-2</td>
<td>NC-2</td>
<td>N(_2)</td>
<td>NC-2</td>
</tr>
<tr>
<td></td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>None (exposed to air)</td>
<td>None (exposed to air)</td>
</tr>
<tr>
<td>Role</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

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Figure 1. (Color online) A schematic diagram of Alloy 800 samples cut from alloy tube.
2.2 Cyclic Polarization (CP)

The samples were studied using cyclic polarization, which was carried out in a three-electrode cell. Alloy 800 samples were used as the working electrode (WE). A SCE connected with a Luggin capillary was used as the reference electrode (RE). For comparison with our previous results, all potentials in this paper have been converted to standard hydrogen electrode (SHE) potential scale. A Pt wire with Pt mesh was used as a counter electrode (CE). Normally the sample was preconditioned for 600 s at the initial potential (−0.46 V, SHE) unless otherwise stated. The potential scan rate was 1.0 mV s⁻¹. The solution was deaerated.

2.3 Mott-Schottky Measurements

The samples were studied using the Mott-Schottky analysis for the characterization of oxide film on the Alloy 800 surfaces, using a Gamry (PC-750) system. The RE and CE are the same as those in CP experiments. The potential scan started from 0.08 V, a little higher than the open circuit potential (OCP), with a scanning interval of 0.005 V. An ac signal with a frequency of 1000 Hz and peak-to-peak magnitude of 10 mV was superimposed on the scanning potential. The equivalent circuit for Mott-Schottky plots includes a resistance and a capacitance in series because the impedance of the capacitance of the space charge layer was much smaller than the charge transfer resistance of the passive film at high frequency. The resistance represents the solution resistance and the capacitance the space-charge layer in the passive films. Due to the high concentration of the ions in the test solutions the electric double layer at the electrode surface is converted to standard hydrogen electrode (SHE) potential scale. For comparison, the characterization of oxide films on the Alloy 800 surfaces was carried out in three different solutions (NC-0, NC-1, and NC-2) (Fig. 2). In each case the threshold current density was set at ~2.0 mA cm⁻², which reverses the potential scan. The experiments were repeated three times and similar results were observed. In all three solutions Alloy 800 suffered pitting corrosion or intergranular attacks. However, the pitting potential/oxide degrading potential in NC-2 (0.075 M S₂O₃²⁻) is 0.310 V_{SHE}, which is ~350 mV and ~580 mV lower than those in NC-0 and NC-1, respectively. These results indicate that S₂O₃²⁻ has a significant effect in enhancing the oxide film degradation on Alloy 800. A similar phenomenon also is found in a saturated ammonium chloride solution. S₂O₃²⁻ has less significant effect on the passive current density. The passive current density of the CP curves in NC-2 is only slightly higher than that on the CP curves in either NC-0 or NC-1.

2.4 Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

The solutions were collected after running experiments and acidified to a pH value of 3.0 with concentrated HCl (Certified ACS, Fisher Scientific) then analyzed using AAS or ICP-MS. The reference sample solution was also prepared and measured at the same time.

2.5 UV-Visible Absorption Spectrometry (UV-Vis)

The 0.01 mol L⁻¹ metal salts solutions were prepared as stock solution. They were diluted into 0.002 mol L⁻¹. The metal salts in solution with thiosulfate had the same final concentration as those in metal salts only solution. The stock solutions of cations investigated in this paper were listed in Table 4. The thiosulfate concentration was 0.075 mol L⁻¹ in both of the solution with metal salts and without metal salts. All the spectra of solutions were obtained under the same conditions: wavelength range 200–800 nm, sampling interval 0.5 s, slit width 1.0 nm, and time constant 0.1 s. All the tests were carried out by a UV-3600 series spectrometry with UVProbe software.

3. Results

3.1 Electrochemical behavior of Alloy 800

In order to investigate the electrochemical behavior of Alloy 800 in solutions without and with SO₄²⁻ or S₂O₃²⁻, cyclic polarization experiments were carried out in three different solutions (NC-0, NC-1, and NC-2) (Fig. 2). In each case the threshold current density was set at ~2.0 mA cm⁻², which reverses the potential scan. The experiments were repeated three times and similar results were observed. In all three solutions Alloy 800 suffered pitting corrosion or intergranular attacks. However, the pitting potential/oxide degrading potential in NC-2 (0.075 M S₂O₃²⁻) is 0.310 V_{SHE}, which is ~350 mV and ~580 mV lower than those in NC-0 and NC-1, respectively. These results indicate that S₂O₃²⁻ has a significant effect in enhancing the oxide film degradation on Alloy 800. A similar phenomenon also is found in a saturated ammonium chloride solution. S₂O₃²⁻ has less significant effect on the passive current density. The passive current density of the CP curves in NC-2 is only slightly higher than that on the CP curves in either NC-0 or NC-1.

3.2 Corrosion morphology

The samples after CP measurements in these three different solutions also were investigated using SEM. The results are shown in Fig. 3. Many pits with different diameters are formed on the surface of Alloy 800 treated in NC-0 (Figs. 3a and 3b). However, there are much less pits formed on the surface of Alloy 800 treated in NC-1 (Fig. 3c); only a few pits with much smaller diameters are formed (Fig. 3d). On the sample treated in NC-2 several corroded areas are formed, such as the one shown in Fig. 3e. The amount of pits formed in NC-2 (Fig. 3e) is much less than in either NC-0 (Fig. 3a) or NC-1 (Fig. 3c). Under higher magnification some small pits can be seen clearly around the big pit. These results indicate that the mechanism of S₂O₃²⁻-induced corrosion is distinct from the mechanism in either a chloride-only solution (NC-0) or a chloride-sulfate solution (NC-1). Due to the much lower pitting potentials in NC-2 than in NC-0 and NC-1, the pitting corrosion in NC-2 is initiated either by S₂O₃²⁻ alone or in cooperation with other ions in NC-2. It is assumed that S₂O₃²⁻ may interact with some low-content element(s) in this alloy therefore only a few corrosion regions on the surface are vulnerable.

Table 4. The chemicals and volume used for UV-Visible Absorption Spectrometry.

<table>
<thead>
<tr>
<th>Stock</th>
<th>NaOH (mL)</th>
<th>H₂O (mL)</th>
<th>Final concentration (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂S₂O₃</td>
<td>~0.1−1.0</td>
<td>10</td>
<td>7.5 × 10⁻⁵</td>
</tr>
<tr>
<td>FeSO₄·7H₂O</td>
<td>10</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>Cr₂(SO₄)₃</td>
<td>10</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>NiSO₄</td>
<td>10</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>CoSO₄</td>
<td>10</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>CuSO₄·5H₂O</td>
<td>10</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>Sample</td>
<td>~0.2</td>
<td>10</td>
<td>~1.5 × 10⁻⁴</td>
</tr>
</tbody>
</table>

Figure 2. (Color online) Cyclic polarization curves of Alloy 800 in deaerated NC-0, NC-1 and NC2 solutions.
3.3 Semiconductivity

The oxide film of Alloy 800 is also studied using Mott-Schottky analysis in NC-0, NC-1 and NC-2 (Fig. 4). Figure 4a shows the Mott-Schottky plots of Alloy 800 in the three different solutions. Considering that the sign of the slope of Mott-Schottky plots in the most linear region, the passive films formed on the Alloy 800 is an n-type semiconductor.44 The slopes (kMS) in the linear regions of the curves were quite close to each other. For investigation in detail, the donor density is calculated using Eq. (1)45 and the results are shown in Fig. 4b.

\[
k_{MS} = \frac{2}{\varepsilon_0 \varepsilon N_D}
\]

where \(\varepsilon\) is the dielectric constant of the passive film, \(\varepsilon_0\) is the permittivity in vacuum \((8.85 \times 10^{-12} \text{ F/m})\), \(e\) is the charge on an electron \((1.60 \times 10^{-19} \text{ C})\) and \(N_D\) is the donor density. The dielectric constants of the oxides of main alloy elements, namely, Fe, Ni and Cr, are in the range 11.9 to 14.2.

The donor density of oxide film in NC-0 is \(\sim 1.00 \times 10^{22} \text{ m}^{-3}\) (with standard deviation (SD) 0.08 \(\times 10^{22} \text{ m}^{-3}\)), in NC-1 about 0.97 \(\times 10^{22} \text{ m}^{-3}\) (SD: 0.06 \(\times 10^{22} \text{ m}^{-3}\)), and in NC-2 about 1.3 \(\times 10^{22} \text{ m}^{-3}\) (SD: 0.1 \(\times 10^{22} \text{ m}^{-3}\)). The donor density of the oxide films in NC-0 and NC-1 are very similar. The donor density of oxide films in NC-2 is slightly higher than those in the other two solutions, indicating that S\(_2\)O\(_3\)^2\(^-\) interacts with the passive film. According to the physical-chemical process that takes place in passive film formation, cation vacancies are created in film-electrolyte interface and anion vacancies are created in metal-film interface. Cation vacancies are created by the reaction of metal cations with S\(_2\)O\(_3\)^2\(^-\) at the interface of oxide film/electrolyte since the binding of S\(_2\)O\(_3\)^2\(^-\) with cations in the oxide is stronger than that with sulfate and/or chloride. However, this interaction is not very strong, probably it is confined to the monolayer or at most several atom layers. As a result, the donor density of the oxide film in NC-2 is slightly higher than those in NC-0 or NC-1.

3.4 Effects of preconditioning on pitting susceptibility

The Alloy 800 sample was passivated at 0.24 V for 4 h in a deaerated solution and CP was carried out in deaerated solution. The results are shown in Fig. 5 (Curve a). Comparing with the native oxide film behaviour in the same solution (Curve b in Fig. 5), passive currents density of “a” is lower than that of “b”, and pitting potential of “a” is slightly higher than that of “b”. The passive currents density of “b” and “c” is almost the same value between 0.1 V to 0.3 V, and pitting potential of “c” is \(\sim 110 \text{ mV}\) lower than that of “b”. Under polarization potential of \(-0.46 \text{ V}\), the oxide film changes possible due to the reduction of oxide film and the Reaction 2 occurred on the surface. As a result, there is \(\sim 110 \text{ mV}\) of pitting potential difference between “b” and “c” in Fig. 5, indicating that the surface composition/properties are changed. A sulphur-containing passive film is less protective than oxide layer, as pointed out by Marcus et al.46

\[
8M + nS\(_2\)O\(_3\)^2\(^-\) + 6nH^+ \rightarrow 2M\(_2\)S\(_n\) + 4M\(_{n+}\) + 3nH\(_2\)O \quad (2)
\]

3.5 Stability of Alloy 800 at the passive potential region

During the passivation in NC-2 several potentials in the passive potential range of 0.00 V to 0.42 V were selected to study the stability of Alloy 800 with air-formed oxide film (Fig. 6). The
material is stable in NC-2 when the passivation potential on Alloy 800 is lower than 0.25 V, as shown in Figs. 6a and 6b. When the passivation potential increased to 0.34 V some sharp current peaks are observed on the current-time curve (Fig. 6c), which means that metastable pitting occurred on the surface. This value is significantly lower than the pitting potential of 0.42 V observed in CP curve (Fig. 5). When the potential increases further, such as at 0.39 V, the film is stable only for several seconds and then localized corrosion quickly happens on Alloy 800 surface in NC-2 (Fig. 6d).

Alloy 800 samples were treated by an anodic potential of 0.39 V until the current density reached 2.0 mA cm$^{-2}$. The corroded surface was investigated by using SEM and EDX, and the results are shown in Fig. 7. Figure 7a shows an overview on the surface, where there are tens of big pits observed. This kind of pitting regions has 4 on the total surface of 0.4 cm$^2$. The corroded area is quite small on the whole surface. One region is zoomed in and is shown in Fig. 7b. Both are similar as those observed in Figs. 3e and 3f. On another sample, the cross section of a pit is investigated (Fig. 7c). The pit depth is about 230 µm and the width is about 580 µm. At different region inside the pit, 3 points are selected to run EDX analysis and the results are shown in Fig. 7d. It is seen clearly that inside the pit, the sulfur peak is seen (Points 1, 2 and 3), and the maximum sulfur content is about 18 at%. There is no sulfur peak on the point 4, which stands the bulk material of Alloy 800. These results agree well with Lee et al. who found the reduction product to be sulfur. Also the ratio of Cr/Fe is higher at corrosion regions than at bulk material, indicating different dissolution rates of Cr and Fe. The Ratio of Ni/Fe is similar, which possibly means the similar dissolution rates of Fe and Ni. The oxygen content at the pitting region is quite higher than other regions.

3.6 Dissolution rates of metals of Alloy 800

Samples were polarized at 0.04 V, 0.14 V, 0.24 V, and 0.34 V in NC-2 for 14400 s, 14400 s, 6041 s, and 491 s, respectively. The electrolyte solutions were collected and acidified to pH $< 3$ to dissolve any precipitates formed in the electrolyte cells and analyzed using AAS (Fig. 8). The results report here have been transformed to the dissolution rate at unit time per unit surface area.

Due to the sensitivity limitation of the AAS instrument, Co is not found in all four solutions, possibly due to the lower content in this alloy. Fe, Cr and Ni are not found in the solution in which the sample treated at 0.04 V. Only Fe is found in the solution in which the sample is polarized at 0.14 V, indicating that Fe is the element most easily oxidized and thereby removes from the bulk material. According to the color of precipitations found in the solution, the oxidation state of Fe can be III, even at this low potential, since the Fe(II) is easily oxidized to Fe(III) by the oxygen in the air. At the 0.14 V potential the dissolution rate of Fe is about 0.08 $\times 10^{-12}$ mol L$^{-1}$ s$^{-1}$ cm$^{-2}$. It is expected that Fe dissolution rate at the corrosion region is much higher than this average value. At 0.24 V potential the dissolution rates of Fe, Ni and Cr are
7.2 \times 10^{-12} \text{mol L}^{-1} \text{s}^{-1} \text{cm}^{-2}, 5.8 \times 10^{-12} \text{mol L}^{-1} \text{s}^{-1} \text{cm}^{-2} and 1.7 \times 10^{-12} \text{mol L}^{-1} \text{s}^{-1} \text{cm}^{-2}, respectively, which are higher than those at 0.14 \text{V}. Thus the dissolution rate of Fe is close to that of Ni and both are higher than that of Cr. The results are consistent with those observed in the SEM and EDX experiments (Fig. 3).

At 0.34 \text{V} the dissolution rates of Fe, Ni and Cr are 16 \times 10^{-12} \text{mol L}^{-1} \text{s}^{-1} \text{cm}^{-2}, 5.8 \times 10^{-12} \text{mol L}^{-1} \text{s}^{-1} \text{cm}^{-2} and 7.4 \times 10^{-12} \text{mol L}^{-1} \text{s}^{-1} \text{cm}^{-2}, respectively. Fe dissolution is still the most rapid among these elements in this alloy. The differences between metal dissolution rates cause the variation in resulting film compositions on treated Alloy 800.29

A small concentration of Cu is found in the solution when the sample is treated at 0.34 \text{V}, and the average dissolution rate is calculated to be \sim 4.6 \times 10^{-11} \text{mol L}^{-1} \text{s}^{-1} \text{cm}^{-2}, which is much lower than those of the three major alloying elements. However, since Cu initially has very low content in this material (0.02 mass%), the local dissolution rate of Cu is relatively higher than that of Fe, an indication of the strong interaction of S_{2}O_{3}^{2-} with Cu, showing that S_{2}O_{3}^{2-} aided Cu dissolution into NC-2.

### 3.7 Oxide film degradation rate in air

The samples were immersed in deaerated NC-2 for an hour and exposed to air for different amounts of time to investigate the film degradation rate in air. Figure 9a shows the result of no-contact with air, where the pitting potential is about 0.42 \text{V}. Figure 9b, Fig. 9c
and Fig. 9d are the results of samples contacted with air for 5 min, 30 min and 240 min, respectively. The pitting potential on these 3 curves are 0.22 V, 0.23 V and 0.35 V, respectively. It is clear that the surface with a thin film of S\(_2\)O\(_3^{2-}\) can be changed very quickly in the air and the oxygen plays an important role in the film degradation. Although the mechanism is unknown, it is expected that S\(_2\)O\(_3^{2-}\) degrades the oxide film with the assistance of oxygen. Because the sample stayed in the air for long time (e.g. 4 hours), the degraded region could be further oxidized and form an oxide film again which has a little higher corrosion-resistance ability. However, after 4 hours in the air, the pitting potential is still lower than it was without contact with air, which is possibly a clue that the products of S\(_2\)O\(_3^{2-}\) still affect the oxide film property. Similar work has been done by Hisaoka et al., who studied the stress corrosion cracking done by alpha-brass in solutions of Na\(_2\)S\(_2\)O\(_3\) and Na\(_2\)S\(_2\)O\(_3\) + NH\(_3\) and found that the stress corrosion cracking life is short under the corrosion environment in repetition of the dipping and drying test.49

4. Discussion

Due to its electronic structure, S\(_2\)O\(_3^{2-}\) has a stronger complex ability with heavy metals than sulfate and sulfite, such as Au and Cu.51,52 However, the interaction between S\(_2\)O\(_3^{2-}\) with Co, Cr, Fe and Ni is still unknown. Therefore, in our experiments, UV-Visible spectrometry was used to study the interaction of S\(_2\)O\(_3^{2-}\) and Ni is still unknown. Therefore, in our experiments, UV-Visible spectrometry was used to study the interaction of S\(_2\)O\(_3^{2-}\) and Ni. Comparing the absorbance curves of S\(_2\)O\(_3^{2-}\) without contact with air, which is possibly a clue that the products of S\(_2\)O\(_3^{2-}\) still affect the oxide film property. Similar work has been done by Hisaoka et al., who studied the stress corrosion cracking done by alpha-brass in solutions of Na\(_2\)S\(_2\)O\(_3\) and Na\(_2\)S\(_2\)O\(_3\) + NH\(_3\) and NaCl + NH\(_3\) and found that the stress corrosion cracking life is short under the corrosion environment in repetition of the dipping and drying test.49

Since the material studied in this project contains 0.02 mass\%, the S\(_2\)O\(_3^{2-}\) may interact with Cu in two ways and initiate the pitting corrosion. The 1st way is to form the coordinates of S\(_2\)O\(_3^{2-}\) with Cu(II), as shown in Reactions 3 and 4

\[
\text{Cu}^{2+} + \text{S}_2\text{O}_3^{2-} \rightarrow \text{Cu}(\text{S}_2\text{O}_3^{2-})
\]

(3)

\[
\text{Cu}(\text{S}_2\text{O}_3^{2-}) + \text{S}_2\text{O}_3^{2-} \rightarrow \text{Cu}(\text{S}_2\text{O}_3^{2-})_2^{2-}
\]

(4)

The 2nd way is that S\(_2\)O\(_3^{2-}\) can accelerate the oxidation of Cu to Cu(II). The principle is depicted as the following. For a half reaction:

\[
\text{Cu}^{2+} + 2e \rightarrow \text{Cu}
\]

(5)

The Nernst Equation can be expressed as the following:

\[
E = E^\circ + \frac{RT}{nF} \ln \frac{C_{Cu}^{n+}}{C_{Cu}}
\]

(6)

where, \(E\): potential of half reaction; \(E^\circ\): formal potential of half reaction, \(R\): gas constant, \(T\): temperature in Kelvin scale, \(n\): electron number involved in the half reaction (here \(n = 2\)), \(F\): Faraday constant, \(C_{Cu^{n+}}\): oxide state concentration, and \(C_{Cu}\): reduced state concentration.

Due to the coordination reaction which happens between O and L (legend), such as:

\[
\text{Cu}^{2+} + mL \rightarrow \text{Cu}^{2+}L_m
\]

(7)

The complex formation constant can be expressed:

\[
K = \frac{[\text{Cu}^{2+}L_m]}{[\text{Cu}^{2+}][L]^m} \Rightarrow [\text{Cu}^{2+}] = \frac{[\text{Cu}^{2+}L_m]}{K[L]^m}
\]

(8)

Combined Eq. (6) with Eq. (8), the following equation can be obtained:

\[
E = E^\circ + \frac{RT}{2F} \ln C_{Cu^{n+}} - \frac{RT}{2F} \ln C_{Cu}
\]

\[
E = E^\circ + \frac{RT}{nF} \ln \left(\frac{[\text{Cu}^{2+}L_m]}{K[L]^m} \right) - \frac{RT}{2F} \ln C_{Cu}
\]

\[
E = E^\circ - \frac{RT}{2F} \ln [L]^m - \frac{RT}{2F} \ln [\text{Cu}^{2+}L_m] - \frac{RT}{2F} \ln C_{Cu}
\]

(9)

Therefore, if the formation constant is large enough, \([\text{Cu}^{2+}L_m] = C_{Cu^{2+}}\), and \(E^\circ = 0\), \(\frac{RT}{2F} \ln K[L]^m < E^\circ\). Therefore, the metal can be
oxidized more easily, such as Cu in this case. Under these two kinds of impact, the pitting precursors or pits form on the oxide film.

The interaction rate between $\text{S}_2\text{O}_3^{2-}$ with Alloy 800 in simulated crevice chemistry was investigated at an open circuit potential. The samples were immersed into NC-2 solution and the $\text{S}_2\text{O}_3^{2-}$ concentration was monitored periodically and the results are plotted in Fig. 11. One sample was immersed in NC-2 exposed in air (black square), the second one was in NC-2 purging with N$_2$ (red circle), and the third was in NC-2 bubbled with compressed air (blue triangle). The $\text{S}_2\text{O}_3^{2-}$ concentration consumption was normalized to per square centimeter. The $\text{S}_2\text{O}_3^{2-}$ consumption increases with time in all 3 solutions, which were calibrated using the blank solutions. However, $\text{S}_2\text{O}_3^{2-}$ consumption is relatively the highest in the solution with compressed air and the lowest in the solution degassed with nitrogen. Therefore, it can be concluded that oxygen increases the reaction rate of $\text{S}_2\text{O}_3^{2-}$ with Alloy 800. In the deaerated solution with nitrogen, the consumption increases with time, and reaches a stable value ($\approx 0.086\%$/cm$^2$) on the 9th day. In the air-saturated solution, the stable value ($\approx 0.090\%$/cm$^2$) is reached on the 7th day. The stable value (0.098%/cm$^2$) is reached in the compressed air solution on the 5th day and the consumption rate has still increased a little after the 5th day. This observation possibly indicates that the oxygen concentration is an important factor which can accelerate the interaction of $\text{S}_2\text{O}_3^{2-}$ and Alloy 800.

The interaction between $\text{S}_2\text{O}_3^{2-}$ and Alloy 800 possibly includes the chemical absorption of $\text{S}_2\text{O}_3^{2-}$ on the material surface and the reaction of $\text{S}_2\text{O}_3^{2-}$ with some elements of the material, such as iron, nickel, chromium and copper. As mentioned above, although the copper content is very low in this material, the interaction between copper and $\text{S}_2\text{O}_3^{2-}$ can not be ignored due to the strong interactions between copper and $\text{S}_2\text{O}_3^{2-}$. The reactions of $\text{S}_2\text{O}_3^{2-}$ with Alloy 800 can be simplified and expressed in Eqs. (2), (3), (4). The reaction rate can be expressed by the $\text{S}_2\text{O}_3^{2-}$ consumption rate. The reaction rate in compressed air NC-2 is $1.042 \times 10^{-8}$ mol L$^{-1}$ min$^{-1}$, which is the highest in the 3 tested solutions.

The Alloy 800 samples were also weighed before and after experiments in order to obtain the weight loss in the experiments and the results are listed in Table 5. It is clear that the weight loss in compressed air NC-2 is more obvious and higher than the weight loss in the sample exposed to air or immersed in the deaerated solution. However, the weight loss is similar in air-saturated NC-2 and aerated NC-2. This conclusion can match the results of $\text{S}_2\text{O}_3^{2-}$ consumption data.

The surfaces of the 3 samples were further investigated by using SEM and EDX and the results are shown in Fig. 12. Figure 12a shows a typical SEM image observed on the sample which was immersed in the aerated solution, and has a smaller corroded area than those found on the samples either immersed in the aerated NC-2 (Fig. 12b) or compressed air bubbled NC-2 (Fig. 12c). The corroded area is the biggest on the sample treated with compressed air bubbled NC-2. It implies that the corroded area is proportional to the oxygen concentration in NC-2.

The compositions of the corroded areas were investigated using EDX. The results are shown in Table 6. These 3 solutions were further investigated in order to determine the concentrations of Cr, Fe, Ni, Co and Cu in the solutions. The results are shown in Table 7. All the concentrations of 5 cations have been deducted in the background solution. At the end of the experimental period, the concentration of Ni is higher than that of Cr or Fe. On EDX results, the corroded regions are found to have a lower content of Ni, which agrees well with the ICP analysis results. No Co is found in all the

![Figure 11](image1.png)

**Figure 11.** (Color online) Thiosulfate decay due to a reaction with Alloy 800 samples in NC-2.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Initial mass (g)</th>
<th>Final mass (g)</th>
<th>Mass loss (g)</th>
<th>Corroded region (#)</th>
<th>Reaction rate (mol L$^{-1}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purging with N$_2$</td>
<td>12.3591</td>
<td>12.3591</td>
<td>0.0000</td>
<td>3</td>
<td>$5 \times 10^{-9}$</td>
</tr>
<tr>
<td>Exposed to air</td>
<td>12.3204</td>
<td>12.3203</td>
<td>0.0001</td>
<td>3</td>
<td>$6.667 \times 10^{-9}$</td>
</tr>
<tr>
<td>Purging with compressed air</td>
<td>11.9882</td>
<td>11.9871</td>
<td>0.0011</td>
<td>5</td>
<td>$1.042 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

![Figure 12](image2.png)

**Figure 12.** (Color online) SEM images of three samples immersed in different solutions. a: in deaerated NC-2, b: in aerated NC-2, and c: in compressed air bubbled NC-2.
solutions. Copper is found in the 14th day solutions, and its concentration is a little higher than in background solution. The copper content in this material is very low (see Table 2) and its concentration in all 3 NC-2 is higher than in background solution, indicating the highly selective dissolution of Cu with assistance of \( \text{S}_2\text{O}_3^{2-} \). A mechanism of \( \text{S}_2\text{O}_3^{2-} \)-induced corrosion is proposed that is consistent with the experimental results. The experimental evidence shows that \( \text{S}_2\text{O}_3^{2-} \) has a strong ability to coordinate with Cu(II) which can decrease the oxidation potential of copper and increase Cu(II) dissolution rate into a \( \text{S}_2\text{O}_3^{2-} \) solution, as illustrated in Reactions 3 and 4. As there is low copper content in the present alloy, the corroded areas should be very limited, as found in our experiments using cyclic polarization (Fig. 2) and potentiostatic measurements. Therefore, interaction of Cu with \( \text{S}_2\text{O}_3^{2-} \) is considered as the main means by which there was initiation of corrosion on Alloy 800 in \( \text{S}_2\text{O}_3^{2-} \) containing solutions.

Table 6. The EDX results observed on three alloy samples (at%).

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Si</th>
<th>Ti</th>
<th>S</th>
<th>Cr/Fe/Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk</td>
<td>22.0</td>
<td>43.2</td>
<td>31.2</td>
<td>1.0</td>
<td>0.5</td>
<td>ND</td>
<td>0.51/1.072</td>
</tr>
<tr>
<td>pit</td>
<td>22.5</td>
<td>43.1</td>
<td>31.1</td>
<td>1.3</td>
<td>0.5</td>
<td>0.3</td>
<td>0.52/1.072</td>
</tr>
<tr>
<td>pit</td>
<td>22.5</td>
<td>44.4</td>
<td>31.1</td>
<td>1.0</td>
<td>0.5</td>
<td>ND</td>
<td>0.50/1.070</td>
</tr>
<tr>
<td>pit</td>
<td>22.5</td>
<td>61.4</td>
<td>14.9</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.37/1.024</td>
</tr>
<tr>
<td>pit</td>
<td>21.6</td>
<td>44.3</td>
<td>31.5</td>
<td>0.6</td>
<td>0.3</td>
<td>ND</td>
<td>0.49/1.071</td>
</tr>
<tr>
<td>pit</td>
<td>42.0</td>
<td>40.5</td>
<td>6.1</td>
<td>1.2</td>
<td>2.3</td>
<td>ND</td>
<td>1.04/1.015</td>
</tr>
<tr>
<td>pit</td>
<td>28.9</td>
<td>47.5</td>
<td>15.5</td>
<td>1.2</td>
<td>ND</td>
<td>0.9</td>
<td>0.61/1.033</td>
</tr>
<tr>
<td>Purging with N₂</td>
<td>bulk</td>
<td>21.9</td>
<td>42.9</td>
<td>30.9</td>
<td>0.9</td>
<td>0.6</td>
<td>ND</td>
</tr>
<tr>
<td>pit</td>
<td>42.2</td>
<td>45.2</td>
<td>1.6</td>
<td>0.9</td>
<td>0.4</td>
<td>2.3</td>
<td>0.93/1.004</td>
</tr>
<tr>
<td>pit</td>
<td>40.2</td>
<td>46.1</td>
<td>5.4</td>
<td>1.1</td>
<td>ND</td>
<td>1.2</td>
<td>0.87/1.012</td>
</tr>
<tr>
<td>pit</td>
<td>19.4</td>
<td>51.4</td>
<td>26.3</td>
<td>1.5</td>
<td>ND</td>
<td>ND</td>
<td>0.38/1.051</td>
</tr>
<tr>
<td>pit</td>
<td>24.5</td>
<td>64.9</td>
<td>1.9</td>
<td>1.0</td>
<td>2.8</td>
<td>ND</td>
<td>0.38/1.03</td>
</tr>
<tr>
<td>pit</td>
<td>46.5</td>
<td>43.9</td>
<td>1.2</td>
<td>0.6</td>
<td>ND</td>
<td>1.1</td>
<td>1.06/1.033</td>
</tr>
<tr>
<td>pit</td>
<td>27.7</td>
<td>58.9</td>
<td>1.6</td>
<td>1.4</td>
<td>ND</td>
<td>3.3</td>
<td>0.47/1.003</td>
</tr>
<tr>
<td>Exposed to air</td>
<td>bulk</td>
<td>22.1</td>
<td>42.8</td>
<td>31.1</td>
<td>1.0</td>
<td>0.6</td>
<td>ND</td>
</tr>
<tr>
<td>pit</td>
<td>21.7</td>
<td>56.1</td>
<td>13.8</td>
<td>1.4</td>
<td>0.8</td>
<td>0.8</td>
<td>0.39/1.025</td>
</tr>
<tr>
<td>pit</td>
<td>22.8</td>
<td>56.3</td>
<td>8.5</td>
<td>1.7</td>
<td>0.1</td>
<td>2.3</td>
<td>0.40/1.015</td>
</tr>
<tr>
<td>pit</td>
<td>20.26</td>
<td>56.4</td>
<td>20.3</td>
<td>1.0</td>
<td>0.5</td>
<td>ND</td>
<td>0.36/1.036</td>
</tr>
<tr>
<td>pit</td>
<td>40.6</td>
<td>45.5</td>
<td>8.1</td>
<td>ND</td>
<td>0.1</td>
<td>0.5</td>
<td>0.89/1.018</td>
</tr>
<tr>
<td>pit</td>
<td>46.4</td>
<td>44.7</td>
<td>1.3</td>
<td>0.8</td>
<td>ND</td>
<td>0.8</td>
<td>1.04/1.03</td>
</tr>
<tr>
<td>bulk</td>
<td>20.9</td>
<td>44.8</td>
<td>30.0</td>
<td>1.0</td>
<td>0.5</td>
<td>ND</td>
<td>0.47/1.067</td>
</tr>
<tr>
<td>pit</td>
<td>33.3</td>
<td>30.7</td>
<td>0.7</td>
<td>2.8</td>
<td>ND</td>
<td>3.4</td>
<td>1.08/1.002</td>
</tr>
<tr>
<td>pit</td>
<td>35.7</td>
<td>47.4</td>
<td>6.9</td>
<td>1.1</td>
<td>ND</td>
<td>1.4</td>
<td>0.75/1.015</td>
</tr>
<tr>
<td>pit</td>
<td>8.3</td>
<td>9.1</td>
<td>3.8</td>
<td>ND</td>
<td>1.3</td>
<td>ND</td>
<td>0.91/1.042</td>
</tr>
<tr>
<td>pit</td>
<td>30.8</td>
<td>49.7</td>
<td>3.5</td>
<td>1.5</td>
<td>ND</td>
<td>5.0</td>
<td>0.62/1.007</td>
</tr>
<tr>
<td>pit</td>
<td>28.0</td>
<td>51.1</td>
<td>5.8</td>
<td>2.2</td>
<td>ND</td>
<td>4.3</td>
<td>0.55/1.011</td>
</tr>
<tr>
<td>Purging with compressed air</td>
<td>bulk</td>
<td>21.4</td>
<td>44.8</td>
<td>32.5</td>
<td>ND</td>
<td>0.3</td>
<td>ND</td>
</tr>
<tr>
<td>pit</td>
<td>20.1</td>
<td>41.3</td>
<td>29.9</td>
<td>0.7</td>
<td>ND</td>
<td>0.7</td>
<td>ND</td>
</tr>
<tr>
<td>pit</td>
<td>14.5</td>
<td>27.4</td>
<td>17.4</td>
<td>ND</td>
<td>0.7</td>
<td>ND</td>
<td>0.53/1.064</td>
</tr>
<tr>
<td>pit</td>
<td>3.73</td>
<td>34.7</td>
<td>2.7</td>
<td>2.1</td>
<td>ND</td>
<td>2.3</td>
<td>0.11/1.008</td>
</tr>
<tr>
<td>pit</td>
<td>3.0</td>
<td>12.6</td>
<td>2.8</td>
<td>ND</td>
<td>ND</td>
<td>1.2</td>
<td>0.24/1.022</td>
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<tr>
<td>pit</td>
<td>27.1</td>
<td>44.5</td>
<td>26.0</td>
<td>ND</td>
<td>0.9</td>
<td>ND</td>
<td>0.61/1.058</td>
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<tr>
<td>pit</td>
<td>22.7</td>
<td>40.9</td>
<td>30.5</td>
<td>1.5</td>
<td>1.8</td>
<td>ND</td>
<td>0.56/1.075</td>
</tr>
<tr>
<td>pit</td>
<td>22.4</td>
<td>41.55</td>
<td>29.3</td>
<td>1.5</td>
<td>1.7</td>
<td>ND</td>
<td>0.54/1.071</td>
</tr>
</tbody>
</table>

ND means not detected, or the signal is lower than 2 fold noise background.

Table 7. Cation concentrations in 3 differently-treated NC-2s (unit: mg/kg).

<table>
<thead>
<tr>
<th>Time (d)</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Co</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purging with N₂</td>
<td>14</td>
<td>0.012</td>
<td>0.06</td>
<td>0.57</td>
<td>ND</td>
</tr>
<tr>
<td>Exposed to air</td>
<td>14</td>
<td>0.042</td>
<td>0.65</td>
<td>0.41</td>
<td>ND</td>
</tr>
<tr>
<td>Purging with compressed air</td>
<td>14</td>
<td>0.068</td>
<td>0.15</td>
<td>0.61</td>
<td>ND</td>
</tr>
</tbody>
</table>

ND means not detected, or the concentration is lower than it in background solution.
The possible mechanism of S\textsubscript{2}O\textsubscript{3}²⁻-induced corrosion of Alloy 800 is illustrated in Fig. 13. When the alloy was immersed in NC-2 thiosulfate and chloride absorbed onto the surface, the ratio of which depended on both concentrations in the solution and the interaction force between anions and oxide. The absorbance could be chemical or physical (Fig. 13a). As long as Cu(II) was present in the oxide film, S\textsubscript{2}O\textsubscript{3}²⁻ had a stronger affinity for Cu(II) and, as a result, S\textsubscript{2}O\textsubscript{3}²⁻ was more strongly absorbed on this region than did chloride ions (Fig. 13b). This was consistent with Lewis acid-base theory. Cu(II) can be considered as a soft acid. While S\textsubscript{2}O\textsubscript{3}²⁻ normally is considered to have structure A (\(\begin{array}{c}S \cdots O \cdots S\end{array}\)), it has another possible conjugated structure B (\(\begin{array}{c}S \cdots S \cdots O\end{array}\)),\textsuperscript{54} especially when the pH of a solution is so high that thiosulfate is fully ionized. The sulfur at the end of the structure B, which is softer than oxygen, can be considered as the basis center in this case. Therefore, the interaction between sulfur in S\textsubscript{2}O\textsubscript{3}²⁻ and Cu(II) is much stronger than that between Cu(II) and oxygen or harder basic species, e.g. chloride. S\textsubscript{2}O\textsubscript{3}²⁻ combines with Cu(II) and, as a result, a Cu(II)-S\textsubscript{2}O\textsubscript{3}²⁻ complex forms and dissolves into solution (Fig. 13b). Dissolution of Cu(II) from an oxide film locally degrades the oxide film. The exposed area can be further attacked by S\textsubscript{2}O\textsubscript{3}²⁻ and Cl⁻ (Reactions 3 and 4) to dissolve the other metal cations in the oxide layer. Hence, these regions are more readily subject to corrosion (Fig. 13c).

\[
\text{M}^{n+} + \text{S}_2\text{O}_3^{2-} \rightarrow [\text{M(S}_2\text{O}_3)_x]^{n-2} + \text{S}_2\text{O}_3^{2-} \rightarrow [\text{M(S}_2\text{O}_3)_x]^{n-2}\text{x} \quad (10)
\]

\[
\text{M}^{n+} + x\text{Cl}^- \rightarrow [\text{MCl}_x]^{n-x} \quad (11)
\]

Hisaoka et al. studied the stress corrosion cracking on alpha-brass in solutions of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} + NH\textsubscript{3} and NaCl + NH\textsubscript{3} and they found the time to failure decreases with increasing concentration in Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}, indicating the strong interaction between S\textsubscript{2}O\textsubscript{3}²⁻ and copper.\textsuperscript{49}

After the corrosion process begins the local compositions in both the oxide film and solution are changed and, as a result, a series of reactions occur in those regions (Figs. 13c and 13d). Metallic elements are oxidized to form either complexes of S\textsubscript{2}O\textsubscript{3}²⁻/Cl⁻ or oxide in the pits. The localized pH value decreases. Some hydrogen enters into the bulk material of the alloy and causes hydrogen embrittlement and, therefore, S\textsubscript{2}O\textsubscript{3}²⁻ also induces hydrogen embrittlement in some cases. S\textsubscript{2}O\textsubscript{3}²⁻ can be reduced to different sulfur species. On the oxide surface the oxygen in the solution can be protonated and form hydroxide, which causes a passivation on the intact oxide surface. The corrosion propagates on these active regions and causes the material failure. Detailed reactions in Fig. 13d are summarized below:

\[\text{Figure 13.} \quad \text{(Color online) Illustration of thiosulfate-induced corrosion mechanism. a: thiosulfate and chloride absorb on the general surface; b: thiosulfate initiates the corrosion at the Cu-enriched region; c: Cu and other cations left the oxide into solution due to coordination interaction; and d: massive reactions happened in the pit.}\]
Metal related reactions:

\[
\begin{align*}
M & \rightarrow M^{n+} + ne^- & \quad (12) \\
M^{n+} + nS_2O_3^{2-} & \rightarrow M(S_2O_3)_n & \quad (13) \\
2M^{n+} + nSO_4^{2-} & \rightarrow M_2(SO_4)_n & \quad (14) \\
4M(SO_3)_3 & \rightarrow 8M^{n+} + 3nSO_4^{2-} + nS_2^{2-} & \quad (15) \\
2M^{n+} + nS_2^{2-} & \rightarrow M_nS_2 & \quad (16)
\end{align*}
\]

Oxygen related reactions:

\[
\begin{align*}
H_2O & \rightarrow H^+ + OH^- & \quad (17) \\
H^+ + e^- & \rightarrow H_2 & \quad (18) \\
O_2 + 2H_2O + 2e^- & \rightarrow 4OH^- & \quad (19) \\
M^{n+} + nOH^- & \rightarrow M(OH)_n & \quad (20) \\
2M^{n+} + nH_2O & \rightarrow M_2O_n + 2nH^+ & \quad (21)
\end{align*}
\]

Staehle pointed out that SO_4^{2-} and S_2O_3^{2-} (Group 1) do not have a significant effect on corrosion. However, S_2O_3^{2-}, S_2O_5^{2-} and S_2\textsuperscript{2-} (Group 2) tend to accelerate the entry of hydrogen into metals and tend to speed up general and localized corrosion.\(^1\) The sulfur anions in Group 1 do not have Structure B ( \(\text{S-O-S}^2^-\) ) so that the interaction of these two species with oxide film is quite weak. However, the tetrahionate ions can be reduced readily to S_2O_3^{2-}, which has Structure B, and sulphide readily forms -S-M bonds. Due to the low solubility of sulphide and reduction reaction needed for conversion of tetrahionate to S_2O_3^{2-}, the effects of sulphide and tetrahionate are expected to be different from that of S_2O_3^{2-},\(^2\) and the detrimental effect of thiosulphate could be more serious than that of other sulfur-containing anions.

It has been reported that various kinds of sulphide species, such as FeS and FeS_2, were found on the surface of stainless steel,\(^3\) NiS and H_2S formed on Alloy 600 in S_2O_3^{2-} solution in high temperature environments,\(^4,5\) and Cr-Ni-S particles formed on Alloy 690,\(^6\) each indicating the possibility of reduction of S_2O_3^{2-} to sulfur in oxidation state −2 or 0 or between −2 and 0 (polysulfide).

The formation of either sulphides or oxides in corrosion products is really dependent on the thermodynamic properties of the respective sulphide or oxide, their solubility, and the pH value of the solutions. The reaction process may occur along the following steps:

\[
\begin{align*}
\text{S}^2- + \text{HO-M-O-M-} \rightarrow \text{M-S-M-O-M-} + \text{HO}^+ \\
\text{M-S-M-O-M-} \rightarrow \text{M-S-M-O-M-} + \text{M}_nS_2
\end{align*}
\]

On the other hand, coordination of S_2O_3^{2-} with cations in oxide film (Reaction 14) is the main reason for increase in the passive current. \([\text{M(S_2O_3)_n}]^{n+}\) is soluble in aqueous solution. As mentioned above, the coordination ability of S_2O_3^{2-} with Cu^{2+} is the highest among the major components of Alloy 800. Copper, one of impurities in Alloy 800, may be accumulated at the grain boundaries. As a result, the grain boundaries are the most easily attacked areas when in S_2O_3^{2-} solution, and also due to this interaction S_2O_3^{2-} may more readily induce the intergranular SCC observed by several groups on various materials.\(^6,7,8,16,18,20,21\)

5. Conclusions

The interaction of S_2O_3^{2-} with Alloy 800 was systematically investigated in order to obtain the kinetics of this interaction in simulated crevice solution. The pitting potential in a S_2O_3^{2-} solution (NC-2) was much lower than in a chloride-only solution (NC-0) or a sulfate-chloride solution (NC-1), and the pitting in S_2O_3^{2-} solution was more serious than that in either of a chloride solution or a sulfate-chloride solution, indicating that S_2O_3^{2-} could selectively and distinguishably degrade the oxide film on Alloy 800. AAS or ICP-MS results show that among the major alloy elements in Alloy 800, Fe dissolution is the easiest in a S_2O_3^{2-} solution. The donor density of the passive film formed in S_2O_3^{2-} solution was slightly higher than those formed in either the chloride-only solution or the sulphate and chloride solution. Even in the passivity range, the material degraded due to the interaction with S_2O_3^{2-}, especially when the applied potential was close to the pitting potential. The UV-Vis results revealed that the S_2O_3^{2-} formed a complex with Cu^{2+}, and the product was soluble in aqueous solutions. Thus S_2O_3^{2-} can assist Cu in dissolving from Alloy 800. Also, when the complex reaction occurred, the presence of S_2O_3^{2-} decreased the oxidation potential of Cu to Cu^{2+}. Because the Cu, an impurity in Alloy 800, normally accumulates at the grain boundary, triple points or inclusions, the S_2O_3^{2-}-induced corrosion should be pitting or intergranular attacks, which can match the results from massive references. Based on our experimental results, the reaction of S_2O_3^{2-} with Cu in Alloy 800 is proposed to be the main reason for the initiation of the S_2O_3^{2-}-induced corrosion. S_2O_3^{2-} has the conjugated structure of R-S-, which can strongly interact with Fe, Cr, and Ni and further degrades the material.

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