Effect of Material and Environmental Variables on SCC Initiation in Slow-Strain-Rate Tests on Type 304 Stainless Steel


ABSTRACT: The effects of low-level environmental impurities, test temperature, sensitization heat treatment, and surface condition on crack initiation have been examined in Type 304 stainless steel in constant extension rate stress corrosion cracking tests. Tests were conducted at 288, 200 and 125°C in pure water environments containing 0.2, 0.2, and 1.8 ppm of dissolved oxygen, respectively. At 288°C in highly sensitized specimens, cracks initiated at less than 20% of life in pure water, with impurities accelerating initiation. The bulk pH affected initiation and failure strains, while increasing conductivity at neutral pH affected only strain to failure. At lower temperatures or lesser degrees of sensitization, crack initiation occurred later in life and impurity additions had a stronger impact. Shot-peening reduced the strain to initiation in constant extension rate tests, most noticeably at 125°C. The minimal data available for comparison support the findings of this study.

KEY WORDS: constant extension rate tests, high-temperature water, environmental impurities, surface condition, stainless steel, crack initiation, sensitization, strain rate

Constant extension rate tests (CERT) have been extensively used as an accelerated measure of stress corrosion cracking (SCC) susceptibility [1], particularly in the sensitized stainless steel/pure water system. Such testing promotes both the initiation and growth stages while maintaining a high degree of consistency and correlation with other types of tests. Previous studies have employed CERT as a measure of overall susceptibility to stress corrosion

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cracking, although this study shows that CERT is equally sensitize to test parameters which influence initiation. Since the initiation stage can be the controlling process in the incidence of SCC, increased research on the effects of initiation is required. The present investigation seeks to provide improved understanding of the initiation process in constant extension rate tests, particularly as it relates to the effects of environmental impurities (such as sulfate and chloride containing solutions of varying pH), temperature, and material variables (heat treatment and surface condition).

Experimental Procedure

Constant extension rate tests (CERT) were conducted primarily on Instron Model 1131 ball screw tension machines, which exhibit minimal stiction at low extension rates. Water was directed past the specimen, which was loaded in a compression tube, and egressed at the top of the compression tube into the remaining volume of the autoclave [2]. The dissolved oxygen concentration at the specimen was thus maintained very close to the inlet value. A flow rate of 20 cm³/min at 10.3 MPa (1500 psi) was maintained, with the solution preheated by a coaxial heat exchanger. The dissolved oxygen concentration was regularly checked by using a colorimetric technique.

Tests were also performed in a miniature autoclave which accommodates influent, effluent, reference electrode, and electrically insulated high-pressure sliding seals, and requires a somewhat different specimen design. Its advantages include inexpensive fabrication using corrosion-resistant materials, fast thermal and environmental response, high-pressure rating, and ease of test assembly. The seals can machined integral to the autoclave body and the inside diameter can be reduced to simplify machining. The autoclave wall thickness can be sized to the pressure/temperature requirements of the investigation; see Rules for Construction of Pressure Vessels (Section VIII, Division 1 of the American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code). A stainless steel autoclave (5 cm diameter) such as shown in Fig. 1 has an ASME code rating of about 34.5 MPa (5000 psi) at 350°C. Additionally, the small internal volume (of superheated water) greatly reduces the danger resulting from major leaks.

The specimen extends through the autoclave (Fig. 1), eliminating the problem of galvanic coupling to loading linkage. High-pressure sliding seals ride on the shoulders of the specimen and employ a constant-force, “trapped” Teflon design to maintain good performance at high temperatures and during thermal cycling. Figure 2 shows the Teflon seal sandwiched between pieces of Vespel SP-211 machined to ±0.05 mm tolerance to minimize extrusion of the Teflon. Thermal expansion and contraction are accommodated by using stainless steel Belleville spring washers stacked in series to provide approximately 0.5 mm compliance for a ±10% change in applied pressure on the seal.
An external, 0.1N Ag/AgCl reference electrode (Fig. 3) was used to monitor electrochemical potentials. The performance of the external reference electrode is excellent because the high-pressure, electrically insulated Teflon seal on the electrode performs well since it remains cool and very little space in the autoclave is required. The electrode also exhibits excellent stability and resistance to thermal cycling and gas bubble formation because only a small portion of the electrolyte is at a high temperature. Good agreement was observed among studies that have determined the calibration of the electrode [3-5]. Its fabrication and rejuvenation are simple, since it employs standard Swagelok fittings and stainless steel and heat-shrinkable Teflon tubing. An insulating cap is used to ensure that the silver rod is not ejected when the system is pressurized.

The compositions of the Type 304 stainless steel used in this investigation are presented in Table 1, along with an identification number. Specimens for Experiments 78 (Heat C-17882) and 114 (Heat 48898) were solution-annealed at 1100°C for 30 min and water-quenched. They were then centerless, wet ground (using a 100 grit wheel) to 6.35 mm diameter by 38 mm gage length, encapsulated and evacuated in quartz tubes, and furnace-sensitized at 600°C.
FIG. 2—Expanded view of the high-pressure seal showing the Teflon sealant sandwiched between Vespe SP-211, which is in turn supported by stainless steel “washers”. Belleville spring washers provide for expansion and contraction of the seal assembly while maintaining a moderately constant force on the Teflon seal.

FIG. 3—Schematic drawing of the external, pressure-balanced reference electrode.
for 24 h. The gage sections of specimens for Experiment 114 were then shot-peened with Size 550 ceramic shot at 0.012 Almen intensity to provide a hardened surface layer. This hardened layer fails mechanically at ~ 2% strain, resulting in shear cracks of ~ 50-μm depth. This approach has been used to diminish the time required for crack initiation [6], as well as to simulate conditions that occur when welds are ground severely.

Specimens for Experiment 116 (Heat TH6656) were machined from a 254-mm diameter pipe weld so that the weld was centered in the gage section. The final machining step involved wet, centerless grinding. Specimens were encapsulated, evacuated, and heat-treated either at 500°C for 24 h or 400°C for 10 days.

Table 2 summarizes the test variables. Specimens were tested under three oxygen/temperature conditions: 1.8 ppm oxygen and 125°C, 0.2 ppm oxygen and 200°C, and 0.2 ppm oxygen and 288°C. The primary environmental im-

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**TABLE 1**—Chemical composition of 304 stainless steel, weight percent.

<table>
<thead>
<tr>
<th>Test</th>
<th>Carbon</th>
<th>Cobalt</th>
<th>Chromium</th>
<th>Copper</th>
<th>Manganese</th>
<th>Molybdenum</th>
<th>Nickel</th>
<th>Phosphorus</th>
<th>Sulfur</th>
<th>Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>0.076</td>
<td>0.13</td>
<td>18.62</td>
<td>0.20</td>
<td>1.75</td>
<td>0.24</td>
<td>8.32</td>
<td>0.021</td>
<td>0.025</td>
<td>0.58</td>
</tr>
<tr>
<td>114</td>
<td>0.07</td>
<td>0.12</td>
<td>18.38</td>
<td>0.18</td>
<td>1.68</td>
<td>0.22</td>
<td>8.6</td>
<td>0.025</td>
<td>0.017</td>
<td>0.60</td>
</tr>
<tr>
<td>116</td>
<td>0.051</td>
<td>0.26</td>
<td>18.8</td>
<td>0.25</td>
<td>1.7</td>
<td>0.23</td>
<td>9.5</td>
<td>0.028</td>
<td>0.013</td>
<td>0.48</td>
</tr>
</tbody>
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**TABLE 2**—Crack initiation test variables.

<table>
<thead>
<tr>
<th>Water Purity</th>
</tr>
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<tbody>
<tr>
<td>Anion and concentration</td>
</tr>
<tr>
<td>pH versus conductivity</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature/Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>288°C, 0.2 ppm oxygen</td>
</tr>
<tr>
<td>200°C, 0.2 ppm oxygen</td>
</tr>
<tr>
<td>125°C, 1.8 ppm oxygen</td>
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<table>
<thead>
<tr>
<th>Sensitization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution-annealed + 600°C/24 h</td>
</tr>
<tr>
<td>As-welded + 500°C/24 h</td>
</tr>
<tr>
<td>As-welded + 400°C/ten days</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Surface Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet ground</td>
</tr>
<tr>
<td>Shot-peened</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Strain Rate</th>
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</thead>
<tbody>
<tr>
<td>$0.5 \times 10^{-7}$ to $3.3 \times 10^{-7}$ s$^{-1}$</td>
</tr>
</tbody>
</table>
purity was $\text{H}_2\text{SO}_4$, employed because it accurately simulates the decomposition of demineralizer resins in nuclear reactors [7]. In some instances NaHSO$_4$ and mixtures of $\text{H}_2\text{SO}_4$ and HCl were employed. Most of the tests were conducted at a nominal strain rate of $3.3 \times 10^{-7}$ s$^{-1}$, although some were conducted at 0.5 and $2.2 \times 10^{-7}$ s$^{-1}$.

Crack initiation was determined by periodic interruption of the test and stereoscopic inspection of the sample surface at $\times 20$ to $\times 50$. Cracks of surface length 0.5 mm and shorter were consistently detected. Evidence of cracking obtained by visual examination of the surface was often confirmed by metallographic examination. Tests were interrupted by slowly unloading the specimen and cooling the autoclave. Continuation of the test occurred in the reverse order, with specimens preloaded to approximately 90% of the load on interruption. Measurements of “machine strain” (crosshead speed times time) and specimen reduction in area and elongation were made at each interruption. Specimen elongation is predominantly used in this report.

Most samples were interrupted many times until initiation was observed. Additional tests were conducted by interrupting only once to confirm the previous results. The results of these latter tests always agreed closely with the previous data. Determination of the probable time to initiation between observations was based on experience and the size of the first cracks observed. Accuracy of the results is limited by the interruption interval employed, specimen and test variations, and the statistical nature of the initiation process. Nonetheless, agreement between duplicate experiments was generally within approximately $\pm 20\%$ of the strain to initiation.

Secondary ion mass spectrometry (SIMS) results were obtained on a Cameca IMS-3F by using a 14.5 keV cesium beam at 1 $\mu$A rastered over a 250-$\mu$m-square area. The analyzed area was 60 $\mu$m in diameter. While uncalibrated, a reasonable estimate for the sputtering rate in the oxide is about 1 nm/s. Tests were conducted in a 2-L titanium autoclave; following exposure the specimens were transferred in the test solution to the SIMS. Specimens were rinsed with distilled water to remove the salt solution before insertion into the vacuum chamber.

**Results and Discussion**

The results of crack initiation studies in pure water are summarized in Fig. 4. These data were determined by repeated interruption, and an example of the stress-strain behavior and associated surface appearance is shown in Fig. 5 (test interruption and stereoscopic examination often occurred at more frequent intervals than are indicated). Initial evidence of crack initiation was confirmed during subsequent interruptions to insure that it was correctly identified and that cracks continued to propagate. For example, with shot-peened samples, mechanical shear cracks formed in the shot-peened layer within the first several percent strain, but did not result in immediate inter-
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Effect of temperature on crack initiation, showing that initiation occurs at lower strains and percentages of life at higher temperatures. Note that the oxygen concentration changes from 0.2 ppm for the tests at 200 and 288°C to 1.8 ppm for the 125°C tests.

Stress-strain behavior of shot-peened, sensitized (600°C, 24 h) Type 304 stainless steel tested under CER conditions at 125°C at 1.8 ppm oxygen. Arrows and accompanying photographs show the initiation of cracking.
granular propagation. For nonpeened surfaces, however, incipient cracks immediately began to propagate.

Figure 4 shows the effect of temperature on initiation. Note the difference in oxygen concentration at 125°C (1.8 ppm) compared with 200°C and 288°C (0.2 ppm). For all samples, initiation occurred later in life as the temperature was decreased. The two closed points that represent initiation at approximately 100% of life failed by ductile rupture, although in both cases there were one or more small intergranular cracks outside of the necked region (Fig. 6). The strain to initiation parallels the percentage of life to initiation in all cases. Percentage of life to initiation was used as a basis for the curves, because variations in test severity are normalized.

Staehle et al [8] reported only limited details of interrupted CER testing on sensitized Type 304 stainless steel at 10^{-6}s^{-7} in pure water with 8 ppm oxygen. At 250°C, no cracking was observed at 2% strain, whereas at 9% strain intergranular cracks of moderate (~ 1 mm surface length) were observed. Strain to failure was not reported, but is estimated at 20% based on the data of this and other studies [9]. Assuming that initiation occurred at approximately 7% strain, or 35% of life, reasonable agreement is obtained with the results of this investigation. At 121°C, initiation commenced between 12% (no cracks) and 23% (intergranular cracks). While they reported widely vary-

FIG. 6—Stress-strain behavior of as-machined, sensitized (600°C, 24 h) Type 304 stainless steel tested under CER conditions at 125°C at 1.8 ppm oxygen. Arrows and accompanying photographs show the initiation of cracking.
ing strain to failure values of 33% and 49%, the 33% value will be used since it agrees with the value observed in this study. Assuming initiation occurred at 20% strain, or 60% of life, general agreement is obtained with the current findings (although agreement is not as close as at 288°C). At this low test temperature, there is a high degree of sensitivity to surface condition, which may account for the greater difference at the lower test temperatures.

Figure 4 also shows the effect of surface condition. The two lower curves compare the as-machined (wet ground) surface with a similar specimen that was subsequently shot peened. At 288°C shot peening accelerates initiation only slightly. However, at 125°C, the difference in strain to initiation is very large, with the as-machined sample being highly resistant to crack initiation and the shot-peened sample exhibiting crack initiation at nearly the same point as was observed at 288°C. By contrast, Solomon \(^2\) observed that electro-polished specimens failed at higher strains and usually initiated only a single crack, compared to mechanically polished samples, where many cracks were observed. The acceleration by shot-peening of crack initiation at lower temperatures is presumably a result of surface shear cracks that form as the shot-peened layer is strained. At lower temperatures and at low constant stresses, shear cracking does not occur, resulting in the improved SCC properties that are generally associated with shot-peened surfaces. Small shear cracks appear at low strains on shot peened surfaces \([10]\), although growth of intergranular cracks was not observed in this study until later in life. Nonpropagating, or arresting, stress corrosion cracks have been discussed by Parkins \([11]\) and Ford \([12,13]\). Unlike the case for carbon steel \([12,14]\), Ford has shown that sensitized stainless steel exhibits consistent and stable crack growth under similar conditions to those used in this study.

The effect of the degree of sensitization on crack initiation is also shown in Fig. 4. The general trend in increasing degree of sensitization \([9]\) is from the 400°C (least sensitized) to the 600°C treatment. The strain to initiation increases monotonically with decreasing temperature of heat treatment. As with the surface condition results, variations in degree of sensitization are less significant at 288°C than at lower test temperatures. At lower heat treatment temperatures the concentration of chromium in thermodynamic equilibrium with the chromium in the M\(_{23}C_6\) carbide decreases. However, calculations shows that the width of the depleted region becomes narrower as a result of the steeper diffusion gradient \([9]\). Therefore, crack initiation seems to be more sensitive to the width of the chromium-depleted region (at, for example, a concentration of 12% chromium) than it is to the depth of the concentration trough. Apparently the depletion resulting from a 400°C ten-day heat treatment is too narrow to be readily “visible” to the pure water test environment.

The effect of environmental impurities on crack initiation was studied only for the lower temperature heat treatments (400°C and 500°C) in samples

machined from welded pipe. This simplifies the examination for cracks since intergranular (IG) SCC always occurs in a narrow region in the heat-affected zone of the weld. It also more closely represents the characteristics of sensitization which occur in many plant components. Figure 7 shows that acceleration in both initiation and strain to failure is observed in 6.5 ppm of sulfuric acid (55 μS/cm conductivity) relative to pure water. While a significant effect is observed in all cases, impurities strongly affect initiation in those cases where initiation occurs less readily, that is, at lower test and heat treatment temperatures. Particularly interesting is the specimen treated at 400°C and tested at 200°C, which failed by ductile rupture in pure water and exhibited severe IGSCC in the impure environment.

Figure 8 delineates the effect of conductivity (which is linearly related to pH in sulfuric acid) on the strain to initiation in sulfuric acid at a test temperature of 200°C. There is a monotonic decrease in strain to initiation with increasing pH, which is also observed at 288°C (Fig. 9). Initiation is not strongly influenced by increased conductivity at neutral pH with NaHSO₄ (Table 3). (NaHSO₄, while acidic at room temperature, is close to neutral pH at 288°C due to the weak second ionization constant of H₂SO₄, even at these low concentrations). While initiation does not seem to be strongly influenced by NaHSO₄, the strain to failure is greatly decreased in this environment compared to pure water. Clearly the strain to initiation does not influence the strain to failure in an additive fashion. This is due to the higher stresses present at cracks that initiate later in life in CER tests. Additionally, Fig. 10 shows that the dependence of initiation on pH is not strongly influenced by the type
Effect of Water Purity on Crack Initiation

$H_2SO_4$ Additive - 200°C - C.E.R.T.
Type 304 - Welded + 500°C/24 Hr.

FIG. 8—Effect of solution conductivity (resulting from additions of $H_2SO_4$) on crack initiation at 200°C in CERT.

Effect of Water Purity on Crack Initiation
$H_2SO_4$ Additive - 288°C - C.E.R.T.
Type 304 - Welded + 500°C/24 Hr.

FIG. 9—Effect of solution conductivity (resulting from additions of $H_2SO_4$) on crack initiation at 288°C in CERT.
TABLE 3—Effect of conductivity and pH on initiation solution.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Environment</th>
<th>Conductivity, (\mu S/cm)</th>
<th>pH, 25°C</th>
<th>Strain, %</th>
<th>Strain, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water</td>
<td>0.1</td>
<td>7</td>
<td>5</td>
<td>17</td>
</tr>
<tr>
<td>NaHSO(_4)</td>
<td>10</td>
<td>7\textsuperscript{b}</td>
<td>5</td>
<td>9.3</td>
</tr>
<tr>
<td>H(_2)SO(_4)</td>
<td>10</td>
<td>4.8</td>
<td>2.8</td>
<td>9.2</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Type 304 stainless steel, 288°C, 0.2 ppm oxygen.
\textsuperscript{b}Intended to represent neutral pH at 288°C. H\(_2\)SO\(_4\) dissociates at 25°C to form acid, but does not dissociate at 288°C.

of anion, since essentially identical strains to initiation were observed for sulfuric acid (10 \(\mu S/cm\)) as for a mixture of hydrochloric acid (6 \(\mu S/cm\)) and sulfuric acid (4 \(\mu S/cm\)).

Finally, the dependence of initiation on strain rate was examined over about an order of magnitude of strain rate in the mixed hydrochloric acid/sulfuric acid environment. Within the range of 0.5 to \(3.3 \times 10^{-7} \text{s}^{-1}\), no effect of strain to initiation was observed. Contrarily, however, the strain rate has a significant effect on the strain to failure, as has been shown previously for pure water [9].

Heat-to-heat variability for the three heats employed in this study was not examined. However, IGSCC susceptibility of 13 heats of Type 304 stainless

![FIG. 10—Effect of solution pH and anion mixtures on crack initiation at 288°C in CERT.](image)
steel, which ranged in carbon content from 0.040 to 0.070%, was examined [15] by using as-received (mill-annealed) specimens heat-treated at 500°C for 24 h. The wide variation that exists in the microstructure of “mill-annealed” samples can be magnified by this heat treatment. By contrast, in this investigation two of the alloys were very similar in composition and were heat-treated at 600°C for 24 h following a furnace solution anneal. The third alloy was sensitized by welding followed by a 500°C/24-h treatment that yields a far more consistent and predictable degree of sensitization than the mill-annealed condition. Any remaining effects of heat-to-heat variation were minimized by normalizing the observed behavior by using a percentage-of-life to initiation parameter.

The effect of impurities on crack initiation are due in part to structural and electronic changes that the passive film undergoes at temperatures in excess of about 200°C. Bianci et al [16] observed these changes in air-formed oxides on stainless steels, and Manning [17] demonstrated that similar phenomena are observed in the passive films formed in high-temperature aqueous environments. Using a straining electrode test and comparing the data with that of Manning [17], Andresen [18] showed there was very little effect of the passive film in preventing pitting in high-temperature chloride environments. Figure 11 shows that, for unstrained specimens, the pitting potential drops dramatically with temperature to a stable value. This value is very close to that observed in continuously strained specimens, where the passive film is contin-

![Figure 11](image_url)

**FIG. 11**—Pitting potentials of Type 304 stainless steel showing that, above 200°C, there is essentially no difference between tests in which the passive film is left intact and tests in which the bare surface is exposed by dynamic straining.
uously ruptured. Thus the pitting potential is controlled by the reaction at the metal-electrolyte interface. This is supported by the observation that at lower temperatures, where the pitting potential of unstrained specimens increases, continuously strained specimens exhibit the same pitting potential as at higher temperatures. A similar effect of temperature on the passive film properties has also been observed for the nickel-base alloys Hastelloy G and C-276.³

To further demonstrate that the passive film does not act as a physical barrier to impurities at the higher temperatures, secondary ion mass spectroscopy (SIMS) has been employed. Other investigators have shown that chloride ions do not significantly penetrate into the passive film at temperatures up to 100°C [19]. Figure 12 shows the results of a passive film profile taken from an electropolished 304 stainless steel specimen exposed sequentially to 288°C deaerated pure water for 24 h followed by deaerated 3N NaCl at 288°C for 24 h. In the initial stages, the iron, nickel, and chromium signals are higher because of enhanced sputtering yield in the oxide. Since over a 60-μm-diameter analyzed area the interface between the oxide and the substrate is not smooth (even on an electropolished surface), there is not a clearly defined transition between oxide and substrate (although a reasonable estimate would be between 150 and 200 s). Over the region where the oxide exists (0 to 150 s) it is clear that the chloride ion has fully penetrated the passive film. The chloride signal continues at significant levels beyond 200 s because of the surface unevenness and sputtering interactions with the heavier cesium ion (coupled with the very high sensitivity of SIMS for chloride). These data suggest that at elevated temperature it is the reaction with the metal substrate that controls pitting and perhaps also crack initiation.

Conclusions

1. Constant extension rate testing provides an accelerated, yet meaningful, measure of susceptibility to intergranular stress corrosion crack initiation, in addition to its common use as a measure of overall susceptibility. CER tests become initiation-limited as the severity of the environment (impurities, temperature) or material (degree of sensitization, surface condition) decreases.

2. Crack initiation is more strongly influenced by changes in solution pH than conductivity in the neutral to acid pH range. This contrasts with the effect of environmental impurities on crack propagation, which is accelerated by either acidic or neutral additions.

3. The effect on initiation of strain rate in the range of 0.5 to 3.3 × 10⁻⁷ s⁻¹ is minimal; its effect on overall susceptibility (propagation) is substantial, with the lower strain rates resulting in lower strains to failure.

4. Increasing temperature reduces the strain to initiation under all test con-

³P. L. Andresen, unpublished results.
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It is well known that sensitized metal can be passivated in high-purity water at elevated temperatures. The conditions, particularly for the more marginal conditions of lower degrees of sensitization and less susceptible surface conditions.

5. Shot-peening (and presumably any treatment that inflicts heavy cold work on the sample surface) promotes crack initiation in CER tests, unlike its usual beneficial effect under constant-load conditions.

6. Crack initiation becomes more difficult as the sensitization temperature is decreased from 600 to 400°C. Initiation is apparently influenced by the width (at a given concentration) of the chromium-deleted zone more than the minimum concentration of chromium at the carbide matrix interface.

7. The effect of temperature and environmental impurities on initiation may be related to changes in the electronic and structural properties of the passive film that forms on stainless steel and related iron and nickel base materials.

Acknowledgments

The author acknowledges Duane Broecker, who performed many of the experiments, and the Electric Power Research Institute, which, under the management of Dr. Michael Fox, provided support for much of this work under Contract T115-3.
References


DISCUSSION

Gustavo Cragnolino\(^1\) (written discussion)—Do you consider that the \(\text{SO}_4^{2-}\) anion should penetrate the oxide film as you have shown for \(\text{Cl}^-\), despite its larger size, in order to explain the aggressive effect of sulfate?

P. L. Andresen (author’s closure)—SIMS measurements in \(\text{SO}_4^{2-}\) solutions have not yet been performed, although it is certainly reasonable to hypothesize that, with a semiconducting oxide film, penetration would be a function of the characteristics of the sulfur ion and not the \(\text{SO}_4^{2-}\) ion. The change in the character of the passive film at higher temperatures is considered to be a contributing factor to early crack initiation, not a prerequisite.

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