Cracking of zirconium alloys at constant load with and without applied potentials

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CRACKING OF ZIRCONIUM ALLOYS AT
CONSTANT LOAD WITH AND WITHOUT
APPLIED POTENTIALS

by

Heidi T. Aquino
Bachelor of Science
University of Rochester
2001

A thesis submitted in partial fulfillment
of the requirements for the

Master of Science Degree in Engineering
Department of Mechanical Engineering
Howard R. Hughes College of Engineering

Graduate College
University of Nevada, Las Vegas
December 2003
The Thesis prepared by
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Entitled
Cracking of Zirconium Alloys at Constant Load with and without Applied Potentials

is approved in partial fulfillment of the requirements for the degree of
Master of Science in Mechanical Engineering

Examination Committee Chair

Dean of the Graduate College
ABSTRACT

Cracking of Zirconium Alloys at Constant Load with and without Applied Potentials

by

Heidi Aquino

Dr. Ajit K. Roy, Examination Committee Chair
Associate Professor of Mechanical Engineering
University of Nevada, Las Vegas

Cladding materials, namely Zircaloy-2 (Zr-2) and Zircaloy-4 (Zr-4), were tested for evaluation of their resistance to stress corrosion cracking (SCC), delayed hydride cracking (DHC), and localized corrosion (pitting and crevice) in neutral and acidic environments at ambient temperature and 90°C. For SCC testing, constant load and slow-strain-rate techniques were used. Some SCC testing were also performed under controlled electrochemical potentials ($E_{\text{cont}}$). The localized corrosion behavior was studied by cyclic potentiodynamic polarization technique. Metallurgical microstructures and fractography were analyzed by optical microscopy and scanning electron microscopy (SEM), respectively. The results obtained from this study indicate that no failures were observed under constant loading with smooth specimens. However, the notched specimens showed failures at reduced applied loads. The application of $E_{\text{cont}}$ to the smooth specimens showed some signs of hydrogen damage that might be the precursor to the development of DHC. Fractographic evaluations by SEM revealed dimpled microstructures indicating ductile failures.
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CHAPTER 1

INTRODUCTION

The disposal of nuclear waste poses a severe challenge to all nuclear power-generating nations in view of its toxicity and long radioactive life. Thus, it had been recommended in the United States (US) that these nuclear wastes be isolated from the natural environment for at least 10,000 years.\(^1\) In order to develop a feasible federal policy, the US Congress enacted the Nuclear Waste Policy Act of 1982 (NWPA) that was aimed at establishing a comprehensive national program for the safe management, storage, and permanent geologic disposal of highly radioactive waste in excess of 70,000 metric tons.\(^2\) Based on the field and laboratory studies performed among nine candidate sites, Yucca Mountain, located 90 miles northwest of Las Vegas, Nevada, consistently ranked as the most suitable site possessing the most desirable technical and scientific characteristics as a proposed geologic repository to contain high-level radioactive waste (HLW).\(^3\) The US Senate and the House approved the recommendation as well, and currently the Office of Civilian Radioactive Waste Management (OCRWM) is in the process of applying for the licensing of this potential underground repository by


the US Nuclear Regulatory Commission (NRC). If approved by the NRC, this repository may become operational in the year 2010.

One major criterion in proposing the Yucca Mountain site as a potential repository was the fact that the rocks surrounding this site are composed of vitrified tuff. Tuff is rock formed from volcanic fragments. This region is located in a dry and unsaturated zone well above the water table. Although the long-term storage of the spent nuclear fuel (SNF) inside the engineered barrier will be in a dry atmosphere, there is a possibility of moisture contact with the metallic waste package causing them to breach during the proposed disposal period. Also, there are evidences that water can move rapidly to these dry and unsaturated zones.\(^1\) In addition, in course of time, the temperature inside the repository may be reduced to below the boiling point of water. As a result, very little evaporation may occur, and the waste package container materials may become susceptible to different types of environment-induced degradation, including general corrosion, localized corrosion, and stress corrosion cracking (SCC).

As a part of the site characterization, researchers from the Lawrence Livermore National Laboratory (LLNL) have performed a series of tests including the Large Block Test (LBT) to develop a better understanding of the thermal loading effect on the resultant thermal-mechanical-hydrological-chemical (TMHC) processes occurring at this site. Based on this study, a sulfate-reducing bacteria (SRB) was discovered, that can survive at temperatures up to 200°C.\(^2\) The presence of these microbes can result in


microbiologically-induced corrosion (MIC) of container materials due to the formation of acidic species and their subsequent chemical reactions.

Figure 1.1. Waste Package Design

The current waste package design consists of a metallic, multi-barrier concept, as shown in Figure 1.1. The proposed emplacement of waste package includes the drip shield inside the repository are illustrated in Figure 1.2. This design is broken up into four parts that each serves a different purpose. They are the drip-shield, outer barrier, inner barrier, and cladding. The titanium drip-shield acts as an umbrella overlaying the entire waste package that can prevent contact between water dripping from the rocks and the containers. The outer barrier is a thin layer (2 cm) of corrosion-resistant, nickel-base Alloy 22 that will provide the necessary corrosion protection from the potential...
repository environments. Next, the inner barrier, made of Type 316 NG stainless steel, will be thicker (6 cm) and will serve as a structural support. The cladding tubes, as shown in Figure 1.3, act as the primary barrier that prevents the release of radionuclides contained in the SNF. The structural integrity of the SNF cladding plays a major role in preventing or minimizing the potential for degradation resulting from the combined effect of the repository environment and the products resulting from the radiolysis of the SNF.

Figure 1.2. Waste Package Emplacement
Zirconium alloys, namely Zircaloy-2 (Zr-2) and Zircaloy-4 (Zr-4), are commonly used as cladding materials in most commercial light-water and boiling-water reactors. Both Zr-2 and Zr-4 are highly desirable for cladding and other reactor internal structures due to their excellent corrosion resistance in elevated temperature water and steam, and their superior neutron absorption capability. Oxide layers can be readily formed on the

Figure 1.3. Cladding Tube Design
surface of clean and unirradiated zirconium and its alloys, thus protecting them from potential corrosion attack.\(^3\)

The waste package containers were designed to take into consideration disruptive natural events, such as faulting and seismic/igneous activities, that may be expected at the Yucca Mountain Site. Such events can damage the waste package container, but may still keep the inside cladding intact.\(^4\) However, these types of events can cause breaching of the waste package, and may lead to environment-induced degradation, such as SCC and localized corrosion of the container materials. Initially, the surface films will be ruptured due to interaction of the oxide layer with different types of condensed phases resulting from the evaporation of aqueous environments inside the repository, followed by perforations through the container wall thickness. This phenomenon is associated with the formation of pits, which is one type of localized corrosion that can be encountered by susceptible container metals and alloys in the presence of aggressive chemical species. Presence of residual stresses in these materials due to plastic deformation and welding, and their interaction with the aqueous repository environments can also result in SCC. In essence, numerous factors, such as surface condition, material type, residual stresses, and irradiation products, can influence the susceptibility of the prospective container materials to SCC.\(^5\)

The release of radionuclides from the SNF is the result of breaching of the cladding barrier contained inside the waste package inner container. As long as the

---


cladding remains intact, the release of these radionuclides may not occur. On the other hand, if the cladding materials sustain some damage, radionuclides will be slowly released into the surrounding repository atmosphere through these perforations. As the waste package containers undergo breaching, the liquid phases from the repository environments and the radiolytic products will interact with the cladding materials, thus causing some minor environment-induced damage. Since these damages are not that detrimental at the beginning, the cladding bundles can still prevent dissolution of the SNF. Perforated cladding made of zirconium alloys has been found to undergo cracking due to the lack of oxide film formation, and reactor power fluctuations leading to the development of cladding stresses due to the expansion of the fuel pellets. After long-term exposure, this oxide layer breaks down and becomes brittle and porous, thus exposing the cladding barrier to the adverse effects of corrosion damage.

In order to evaluate the long-term performance of the waste package container materials without appreciable damage, corrosion testing has been performed at the Southwest Research Institute (SwRI) in aqueous environments containing various concentrations of chloride. These tests were intended to establish the minimum temperature and chloride concentration needed to initiate localized corrosion in these materials. In general, zirconium alloys may not suffer from localized corrosion in

---

chloride and sea water environments. However, the susceptibility of these alloys to localized attack may depend on the chloride ion concentration and the temperature.\(^9\)

\[\text{Figure 1.4. Residual Stress Development Processes}\]

Figure 1.4 illustrates the mechanism by which oxidation-induced residual stresses are introduced in zircaloy cladding. The outermost layer of the zirconium alloy creates a protective, waterside oxide layer that is subjected to a large residual stress resulting from the large volume expansion of the zirconium oxide. The oxide layer contracts to form a rigid bond with the zircaloy cladding, and, consequently, develops tensile residual stresses that may produce cracks in this oxide layer. This event results in developing conditions by which hydrogen can be introduced into the zirconium alloys leading to the development of DHC.

Corrosion is a result of electrochemical reactions that may occur between metals and the environments to which they are exposed. Extensive work has been performed during the past forty years to evaluate the aqueous corrosion behavior of numerous materials in high-temperature, nuclear environments using conventional and electrochemical techniques. Also, there are indications in the open literature that application of cathodic electrochemical potential can induce DHC in zirconium alloys.

In light of the preceding discussion, this project was focused on the evaluation of the effect of environmental and metallurgical parameters on the cracking susceptibility and localized corrosion behavior of two zirconium alloys. Conventional and electrochemical testing techniques were used to perform these evaluations. Further,

---

state-of-the-art surface analytical techniques were used to analyze the metallurgical microstructures, fractography, and elemental characteristics in all tested specimens. Materials and detailed experimental techniques used in this investigation are presented in the next section.
CHAPTER 2

MATERIALS AND ENVIRONMENTS

Materials

The chemical compositions of Zircaloy-2 (Zr-2) and Zircaloy-4 (Zr-4), two cladding materials tested in this investigation, are shown in Table 2.1. These materials were tested in solution-annealed condition. Solution annealing is a full annealing operation forming a recrystallized structure in a vacuum or air furnace heated within the temperature range of 650-800°C. Their ambient temperature mechanical properties are shown in Table 2.2. Zr-2 and Zr-4 are highly desirable for nuclear fuel cladding and other reactor internal structures primarily due to their excellent corrosion resistance in high-temperature water, and their transparency to thermal energy neutrons. These two alloys are commonly used in water-cooled nuclear reactors. Other properties that make them suitable for nuclear applications are moderate strength, excellent ductility after prolonged irradiation in reactor coolant, absence of interactions with fuels and fission products, and superior resistance to creep deformation.

---

1 Zircaloy-2 and Zircaloy-4, Wah Chang Certified Test Reports, September 2001.
Table 2.1. Chemical Composition of Zirconium Alloys

<table>
<thead>
<tr>
<th>Material / Heat No.</th>
<th>Elemental Analysis (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td>Zircaloy-2 / 242831</td>
<td>0.10</td>
</tr>
<tr>
<td>Zircaloy-2 / 243528</td>
<td>0.10</td>
</tr>
<tr>
<td>Zircaloy-4 / 242731</td>
<td>0.12</td>
</tr>
<tr>
<td>Zircaloy-4 / 243195</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Table 2.2. Mechanical Properties of Zirconium Alloys at Ambient Temperature

<table>
<thead>
<tr>
<th>Material / Heat No.</th>
<th>Vendor Certification: Wah Chang</th>
<th>Lab-Generated Data: UNLV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yield Strength (ksi)</td>
<td>Ultimate Tensile Strength (ksi)</td>
</tr>
<tr>
<td>Zircaloy-2 / 242831</td>
<td>53.25</td>
<td>78.7</td>
</tr>
<tr>
<td>Zircaloy-2 / 243528</td>
<td>53.38</td>
<td>79.12</td>
</tr>
<tr>
<td>Zircaloy-4 / 243195</td>
<td>55.10</td>
<td>79.6</td>
</tr>
<tr>
<td>Zircaloy-4 / 242731</td>
<td>49.80</td>
<td>78.1</td>
</tr>
</tbody>
</table>

NA: Not Available

Zirconium (Zr) alloys exhibit strong anisotropic characteristics. Zr has a hexagonal close-packed (hcp) crystal structure, but undergoes an allotropic transformation at about 870 °C (1590 °F) when it changes to a body-centered cubic (bcc) structure, as shown in Table 2.3. The alpha-stabilizing elements can raise the temperature of allotropic transformation from α to β. These elements include tin (Sn), nitrogen (N), and oxygen (O). On the other hand, the beta-stabilizing elements such as

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iron (Fe), chromium (Cr) and nickel (Ni) can lower this transition temperature, thus showing an opposite effect.

During welding, Zr and its alloys can react with the surrounding gases (oxygen, hydrogen, and nitrogen) at the operating temperatures. Due to their high reactivity, these materials need to be shielded with inert gases such as helium and argon during welding. Zr alloys are commonly welded by using the gas tungsten arc welding (GTAW) technique. Both Zr-2 and Zr-4 have low coefficient of thermal expansion (Table 2.3), so the base metal experiences very little distortion during the welding process. The presence of inclusions does not pose a problem during the welding process because zirconium has a high solubility for its own oxide. Since no flux is used in this type of welding, the possibility of flux entrapment is eliminated. Residual stresses are quite low in a finished weld due to the low modulus of elasticity of zirconium. The welded area has a tendency of being weak, so the weld puddle, the bead behind the weld puddle, and the backside of the weld puddle can be better protected by using an additional secondary shielding technique.

---

Table 2.3. Typical Physical and Mechanical Properties of Zr-2 and Zr-4

<table>
<thead>
<tr>
<th>Property</th>
<th>Zircaloy-2</th>
<th>Zircaloy-4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density at 20 °C (70 °F), g/cm³</td>
<td>6.56</td>
<td></td>
</tr>
<tr>
<td>Crystal Structure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-phase</td>
<td>hcp (&lt;865 °C or 1590 °F)</td>
<td></td>
</tr>
<tr>
<td>β-phase</td>
<td>bcc (&gt;865 °C or 1590 °F)</td>
<td></td>
</tr>
<tr>
<td>(α+β) phase</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Melting Point, °C (°F)</td>
<td>1850 (3362)</td>
<td></td>
</tr>
<tr>
<td>Boiling Point, °C (°F)</td>
<td>4375 (7907)</td>
<td></td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion per °C (°F)x10⁻⁶ at 25 °C (75 °F)</td>
<td>6.0 (10.8)</td>
<td></td>
</tr>
<tr>
<td>Thermal Conductivity at 300-800 K, W/m*K</td>
<td>21.5 (12.7)</td>
<td></td>
</tr>
<tr>
<td>(Btu<em>ft/ft²</em>°F)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific Heat, J/kg<em>K (cal/m</em>/g*K)</td>
<td>285 (0.068)</td>
<td></td>
</tr>
<tr>
<td>Vapor Pressure, kPa (mm Hg)</td>
<td></td>
<td>---</td>
</tr>
<tr>
<td>At 2000 °C (3630 °F)</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>At 3600 °C (6510 °F)</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Electrical Resistivity, μΩ*cm at 20 °C (70 °F)</td>
<td>74.0</td>
<td></td>
</tr>
<tr>
<td>Temperature Coefficient of Resistivity per °C at 20 °C (68 °F)</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Latent Heat of Fusion, kJ/kg (cal/m*/g)</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Latent Heat of Vaporization, kJ/kg (cal/m*/g)</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td><strong>Mechanical</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modulus of Elasticity, GPa (10⁶ psi)</td>
<td>99.3 (14.4)</td>
<td></td>
</tr>
<tr>
<td>Shear Modulus, GPa (10⁶ psi)</td>
<td>36.2 (5.25)</td>
<td></td>
</tr>
<tr>
<td>Poisson's Ratio at Ambient Temperature</td>
<td>0.37</td>
<td></td>
</tr>
</tbody>
</table>
Environments

Based on laboratory experiments, three possible repository environments relevant to the Yucca Mountain Site have been identified. They are: simulated dilute water (SDW, well J-13 type water), simulated concentrated water (SCW, 10-100x concentrations of well J-13 water), and simulated acidic water (SAW, 1000x concentrations of well J-13 water). The environments used in the current investigation are SAW and modified SAW (SAWM). Modification of SAW by adding hydrochloric acid (HCl) was intended to produce a more acidic pH. The compositions of these two environments are given in Table 2.4. It is well-known that environments with very low pH values can be produced inside the potential geologic repository due to the presence of microbes such as sulfate-reducing bacteria (SRB), and formulation of acidic species such as nitric acid (HNO₃) and hydrogen peroxide (H₂O₂) resulting from the radiolysis of SNF. It is envisioned that the use of SAWM environment may simulate the pH values resulting from the presence of SRB and the radiolytic effect. Both environments were used in an aerated condition to enhance the beneficial effect of oxygen in producing a protective oxide layer on Zr-2 and Zr-4.

---

Considerable efforts were made to eliminate the amount of oxygen content during melting and processing of Zr alloys. Zr alloys can react with oxygen in air at temperatures above 540 °C (1000 °F), thus forming a white zirconium oxide film that is brittle and porous. After prolonged exposure, the formation of these oxides may degrade the integrity of these alloys. Initially, it was thought that oxygen may act as an impurity that should be minimized since it may cause the metal to become more brittle. It has, however, been found that reducing the oxygen content to below 1000 ppm can reduce the strength levels in Zr alloys. An oxide film can form on the surface of Zr alloys providing the supplemental form of protection during the corrosion process. It can act as an effective barrier to prevent hydrogen absorption. Although the formation of an oxide film has its advantages, the films become ineffective at elevated temperatures.

---

CHAPTER 3

EXPERIMENTAL PROCEDURE

As indicated earlier, this investigation is aimed at evaluating the susceptibility of Zr-2 and Zr-4 to SCC, DHC, and localized corrosion including pitting and crevice corrosion in two environments of different pH values. The susceptibility to SCC and DHC was evaluated by using a constant-load technique incorporating both smooth and notched cylindrical specimens. For DHC testing, an electrochemical controlled potential ($E_{cont}$) was applied during testing under constant loading. The magnitude of $E_{cont}$ was based on the measured open-circuit potential ($E_{corr}$) in a similar environment. Since DHC is a result of hydrogen diffusion into the metal lattice during SCC testing, the tensile specimens were cathodically polarized under a potentiostatic condition at different negative potentials with respect to $E_{corr}$. The susceptibility to localized corrosion was determined by cyclic potentiodynamic polarization (CPP) method under similar environmental conditions. A limited number of slow-strain-rate (SSR) tests was also performed to evaluate SCC behavior of Zr-2 and Zr-4. The individual testing technique has been described later in this section.

Prior to the evaluation of the SCC/DHC behavior of the zirconium alloys, their ambient-temperature mechanical properties were determined by using a Materials Testing System (MTS) machine in air according to the ASTM Designation E 8.¹ Tensile

¹ ASTM Designation: E 8 – 89b, Standard Methods of Tension Testing of Metallic Materials.
specimens, received from a qualified supplier, were used in the solution-annealed condition. The resultant tensile data enabled a comparison of supplier-provided mechanical properties to those determined at the UNLV's Materials Testing Laboratory. Configurations of both smooth and notched tensile specimens, and a pictorial view of the MTS equipment are shown in Figures 3.1 through 3.3.

Figure 3.1. Smooth Tensile Specimen
Figure 3.2. Notched Tensile Specimen
Constant Load Testing Technique

Constant-load testing was performed by using calibrated proof rings. In addition to the calibration curves received from the manufacturer, calibration of these rings was performed by an independent laboratory selected by the United States Department of Energy (USDOE). Some of the tensile specimens were randomly checked by the same laboratory for verification of dimensions. The cylindrical specimens were loaded to the desired applied load by use of these calibration curves. By knowing the ambient-

Figure 3.3. MTS Testing Machine
temperature yield strength of the material, the desired applied load was calculated by multiplying the cross-sectional area of the specimen at the gage section with the percent applied stress to be applied. For example, if the yield strength of the material was 100 ksi and a stress level of 90% of the yield strength was desired, the applied stress would be 90 ksi. Since a gage diameter (d) of 0.25-inch was used, the cross-sectional area (A) was calculated using the Equation 3.1.

\[ A = \frac{\pi d^2}{4} \]  

(Equation 3.1)

Thus, the desired load (in pounds) would be 90 times A. By knowing the desired load, the deflection needed was determined from the calibration curve, as shown in Figure 3.4. The amount of this deflection was achieved by using of a dial gage attached to the proof ring, as shown in Figure 3.5.

![Figure 3.4. Calibration Curve for a Proof Ring](image-url)
Prior to loading, the test specimen was thoroughly cleaned with deionized water, acetone and alcohol followed by air-drying. The specimen was then inserted into the test chamber and the loading was performed as discussed in the previous paragraph. For elevated temperature testing, a condenser was attached to the test vessel to compensate for the water loss due to evaporation. A test vessel made of highly corrosion-resistant nickel-base Hasteloy C-276 was used for elevated temperature testing. The heating of this vessel containing the test solution was accomplished by using two heating cartridges inserted into the bottom slots of this vessel, and the temperature was monitored by a thermocouple connected to a temperature controller. A timer was attached to the upper inner diameter of the proof ring to record the time-to-failure (TTF). Thus, the precise TTF was automatically recorded by use of this timer as the sample failed. The maximum duration of tests under constant-loading was 30 days. If the sample did not fail in 30 days, it was construed that the material may not fail at that applied load in a specific
environment. The magnitude of threshold stress (σth), below which no failure may occur, was determined from these tests as functions of solution pH and temperature.

For constant-load SCC testing under controlled electrochemical potential (Econt), the tensile specimen was potentiostatically polarized using a three-electrode polarization concept. The tensile specimen was used as an anode, a graphite electrode was used as a cathode, with silver/silver chloride (Ag/AgCl) being used as a reference electrode. The detailed experimental setup for electrochemical testing is shown in Figure 3.6. Both smooth and notched tensile specimens were tested under selected Econt values. An 8-channel multipotentiostat, manufactured by Princeton Applied Research (PAR), was used to apply Econt to the test specimens while loaded in tension.

![Figure 3.6. Potentiostatic Polarization Test Setup](image-url)
Upon completion of testing, the test specimens were cleaned with deionized water followed by rinsing with acetone and alcohol. If the sample failed, the two broken halves were visually examined for the primary fracture and the secondary cracking, along the gage section, if any. Finally, a part of the broken specimen was metallographically mounted, polished, etched, and examined by optical microscopy for microstructural evaluation and detection of secondary cracks, if any. SEM was also used to analyze the fractographic characteristics of the primary failure experienced by these specimens. The pH of the test solution was measured before and after testing. The ductility parameters in terms of percent elongation (%E1) and percent reduction in area (%RA) were also determined from the changes in the total length and the gage diameter of the tested specimen. Thus, the SCC susceptibility of both Zr alloys was evaluated by analyzing all these resultant parameters.

Slow-Strain-Rate Testing Technique

While this investigation was primarily focused on the evaluation of SCC and DHC behavior of Zr-2 and Zr-4, under constant loading a limited number of SSR tests were also performed. Since no failure was observed with the smooth tensile specimens under constant load, SSR tests were performed at a strain rate of 3.3e-6 sec⁻¹ to optimize the effect of mechanical constraint and environmental conditions to promote failure in these specimens. The experimental setup used in the SSR testing was identical to that of the constant-load testing, with an exception that the specimen was continuously strained at the desired strain rate using a calibrated load cell until the sample failed. The extent
and morphology of failure in the tested specimen were analyzed by optical microscopy and SEM, as discussed earlier. The SSR test setup is shown in Figure 3.7.

Figure 3.7. Slow-Strain-Rate Test Setup

Cyclic Potentiodynamic Polarization

The cyclic potentiodynamic polarization (CPP) tests were performed to evaluate the localized corrosion behavior of Zr-2 and Zr-4 in similar environments using a three-electrode polarization technique in which the test specimen was used as a working electrode, two graphite electrodes were used as counter electrodes, and a Ag/AgCl reference electrode contained in a Luggin probe acted as a reference electrode. Tests were performed at ambient and elevated temperatures. The experimental setup is shown in Figure 3.8. Prior to the performance of the CPP tests, a model 273A potentiostat
manufactured by PAR, was calibrated according to the ASTM Designation G 5.¹ Calibration of this potentiostat was performed to generate a characteristic potentiodynamic polarization curve for ferritic Type 430 stainless steel in 1N (1 Normal) H₂SO₄ solution at 30°C. Small cylindrical specimens of Type 430 stainless steel, shown in Figure 3.9, were polished with 600 grit silicon carbide paper and cleaned with deionized water, acetone, and alcohol, respectively, prior to the performance of testing.

Figure 3.8. Electrochemical Test Setup

The resultant potentiodynamic polarization curve was compared to the plot shown in Figure 3.10, taken from ASTM Designation G 5. Ideally, the average $E_{\text{corr}}$ value should be about $-0.52$ V with respect to a saturated calomel electrode (SCE). The measured $E_{\text{corr}}$ value can have an acceptance variance of $\pm0.075$ V from this value. The shape of the curve should match with that of Figure 3.10 with an exception of noise signals that may result during the generation of this potentiodynamic plot. The magnitudes of two noses ($N_1$ and $N_2$) should by approximately $-0.07$ V and $+0.43$ V, respectively, with respect to SCE. Acceptability of the calibration data was based on the technical judgment of the measured values of $N_1$ and $N_2$. If the data were considered unacceptable, the equipment was sent back to the manufacturer for repair. The frequency
of performance of the calibration test was based on the quality and reproducibility of the generated data. Calibration tests were performed following every 20 experiments.

![Potentiodynamic Polarization Plot](image)

**Figure 3.10. Potentiodynamic Polarization Plot Shown in ASTM Designation G 5**

For CPP testing, the specimens were polished with 600 grit silicon carbide paper and cleaned with deionized water, acetone, and alcohol, respectively. The counter electrodes, salt-bridge probe, and other components were placed appropriately into the test cell. 800 mL of the desired test solution was poured into the clean polarization glass cell. The polarization cell was immersed inside the water bath heated to different temperatures (30°C, 60°C, and 90°C). Prior to the scanning of electrochemical potential, nitrogen was bubbled through the test solution for one hour to remove oxygen. The cylindrical test specimen was then inserted into the central hole of the polarization cell by
use of a specimen holder. The salt-bridge probe tip was adjusted to within approximately 2 mm from the surface of the working electrode. The probe was filled with the deaerated test solution, and subsequently the reference electrode was inserted into it.

Once the cell was assembled, $E_{\text{corr}}$ of the specimen was recorded with respect to the Ag/AgCl reference electrode. For cyclic polarization, forward and reverse potential scans were used at the ASTM-suggested\textsuperscript{2} rate of 0.17 mV/sec. The magnitude of the critical pitting potential ($E_{\text{pa}}$) and the protection potential ($E_{\text{prot}}$), if any, were determined from the resultant CPP diagram.

\textsuperscript{2} ASTM Designation: G 61 – 78, Standard Practice for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion.
RESULTS AND DISCUSSION

Results

Constant Load

Neither Zr-2 nor Zr-4 smooth tensile specimens exhibited any SCC failure in constant-load tests in either environment at applied stresses up to 95 percent of the materials’ YS values. The overall results of constant-load SCC testing are shown in Table 4.1. Since no failures were observed with the smooth specimens, SCC tests were performed using notched specimens. Calculation of the stress concentration factor (K) due to this notch was determined using a computerized finite-element technique.\(^1\) The theoretical stress concentration factor (K\(_t\)) was determined using dimensionless ratios based on the size and shape of the notch. Figure 4.1 shows the dimensions used for this calculation. The calculations in Equations 4.1 and 4.2 show the geometric ratios for notched specimens with gage diameter and notch diameter of 0.250 in and 0.156 in, respectively.

### Table 4.1. Results of Constant-Load SCC Tests Using Smooth Specimens

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Material / Heat No.</th>
<th>Environment Tested</th>
<th>Applied Stress</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temperature (°C)</td>
<td>pH</td>
<td>% YS</td>
</tr>
<tr>
<td>CL-1</td>
<td>Zr-2 / 242831</td>
<td>27</td>
<td>7.22</td>
<td>95</td>
</tr>
<tr>
<td>CL-2</td>
<td>Zr-2 / 242831</td>
<td>27</td>
<td>2.22</td>
<td>95</td>
</tr>
<tr>
<td>CL-9</td>
<td>Zr-2 / 242831</td>
<td>27</td>
<td>7.22</td>
<td>90</td>
</tr>
<tr>
<td>CL-10</td>
<td>Zr-2 / 242831</td>
<td>27</td>
<td>2.22</td>
<td>90</td>
</tr>
<tr>
<td>CL-17</td>
<td>Zr-2 / 242831</td>
<td>90</td>
<td>7.25</td>
<td>95</td>
</tr>
<tr>
<td>CL-18</td>
<td>Zr-2 / 242831</td>
<td>90</td>
<td>2.22</td>
<td>95</td>
</tr>
<tr>
<td>CL-25</td>
<td>Zr-2 / 242831</td>
<td>90</td>
<td>7.25</td>
<td>90</td>
</tr>
<tr>
<td>CL-26</td>
<td>Zr-2 / 242831</td>
<td>90</td>
<td>2.22</td>
<td>90</td>
</tr>
<tr>
<td>CL-33</td>
<td>Zr-4 / 243195</td>
<td>90</td>
<td>6.23</td>
<td>95</td>
</tr>
<tr>
<td>CL-34</td>
<td>Zr-4 / 243195</td>
<td>90</td>
<td>2.09</td>
<td>95</td>
</tr>
<tr>
<td>CL-41</td>
<td>Zr-4 / 243195</td>
<td>27</td>
<td>6.23</td>
<td>90</td>
</tr>
<tr>
<td>CL-42</td>
<td>Zr-4 / 243195</td>
<td>27</td>
<td>2.53</td>
<td>90</td>
</tr>
<tr>
<td>CL-49</td>
<td>Zr-4 / 243195</td>
<td>27</td>
<td>6.23</td>
<td>95</td>
</tr>
<tr>
<td>CL-50</td>
<td>Zr-4 / 243195</td>
<td>27</td>
<td>2.09</td>
<td>95</td>
</tr>
<tr>
<td>CL-57</td>
<td>Zr-4 / 243195</td>
<td>90</td>
<td>6.46</td>
<td>90</td>
</tr>
<tr>
<td>CL-58</td>
<td>Zr-4 / 243195</td>
<td>90</td>
<td>2.53</td>
<td>90</td>
</tr>
</tbody>
</table>

YS: Yield Strength  
NF: No Failure
Based on the ratio shown in the chart contained in Figure 4.1, the value of $K_t$ was approximately 2.9. The chart displays results for shafts with a grooved notch, but the notch machined in the tested tensile specimens had different geometry. The circular notch had a 60° angle at its root having a maximum radius of 0.005 in. Estimation of the $K_t$ value was based on this specimen configuration.

![Figure 4.1. Stress Concentration Factors for Grooved Shafts with Axial Loading](image)

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\[
\frac{D}{d} = \frac{0.250\text{in}}{0.156\text{in}} = 1.60 \quad \text{(Equation 4.1)}
\]

where \(D\) = gage diameter, \(d\) = notch diameter

\[
\frac{r}{d} = \frac{0.005\text{in}}{0.156\text{in}} = 0.032 \quad \text{(Equation 4.2)}
\]

where \(r\) = radius of curvature at the root of the notch, \(d\) = notch diameter

Results indicate that the presence of this notch in the center of the gage section of the tested specimen, however, produced failure in acidic solution at ambient temperature in Zr-2 specimen at applied loads corresponding to 80% and 85% of its yielding load (YL) value, as shown in Table 4.2. It is interesting to note that failure was also observed in Zr-4 at ambient temperature at an applied load of 80% of the material's yielding load. Further, failure was observed with Zr-2 in the 90°C acidic solution at an applied load equivalent to 80% of this material's yield load value. No failures were observed at reduced applied loads. Data presented in Table 4.2 are reproduced in Figures 4.2 through 4.5 showing the threshold load values below which failure may not occur in specific environments using notched specimens. Based on the data, it appears that the threshold load for SCC in Zr alloys may lie in the vicinity of 75 to 80% of their yielding loads in the environments tested. The arrows indicate that no failure occurred at these applied loads.
loads. However, it should be noted that this range may be valid for the notch configuration used in this investigation.

Table 4.2. Results of Constant-Load SCC Tests using Notched Specimens

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Material / Heat No.</th>
<th>Environment Tested</th>
<th>Applied Load</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temperature (°C)</td>
<td>pH</td>
<td>%YL</td>
</tr>
<tr>
<td>CL-1Na</td>
<td>Zr-2/242831</td>
<td>27</td>
<td>6.93</td>
<td>85</td>
</tr>
<tr>
<td>CL-1N</td>
<td>Zr-2/242831</td>
<td>27</td>
<td>6.51</td>
<td>80</td>
</tr>
<tr>
<td>CL-2N</td>
<td>Zr-2/242831</td>
<td>27</td>
<td>2.36</td>
<td>80</td>
</tr>
<tr>
<td>CL-9N</td>
<td>Zr-2/242831</td>
<td>27</td>
<td>8.01</td>
<td>75</td>
</tr>
<tr>
<td>CL-10N</td>
<td>Zr-2/242831</td>
<td>27</td>
<td>2.00</td>
<td>75</td>
</tr>
<tr>
<td>CL-17N</td>
<td>Zr-2/242831</td>
<td>90</td>
<td>1.98</td>
<td>80</td>
</tr>
<tr>
<td>CL-18N</td>
<td>Zr-2/242831</td>
<td>90</td>
<td>1.99</td>
<td>80</td>
</tr>
<tr>
<td>CL-26N</td>
<td>Zr-2/242831</td>
<td>90</td>
<td>2.00</td>
<td>75</td>
</tr>
<tr>
<td>CL-33N</td>
<td>Zr-4/243195</td>
<td>27</td>
<td>6.51</td>
<td>80</td>
</tr>
<tr>
<td>CL-34N</td>
<td>Zr-4/243195</td>
<td>27</td>
<td>2.36</td>
<td>80</td>
</tr>
<tr>
<td>CL-41N</td>
<td>Zr-4/243195</td>
<td>27</td>
<td>5.99</td>
<td>75</td>
</tr>
<tr>
<td>CL-42N</td>
<td>Zr-4/243195</td>
<td>27</td>
<td>2.00</td>
<td>75</td>
</tr>
<tr>
<td>CL-49N</td>
<td>Zr-4/243195</td>
<td>90</td>
<td>5.99</td>
<td>80</td>
</tr>
<tr>
<td>CL-50N</td>
<td>Zr-4/243195</td>
<td>90</td>
<td>1.99</td>
<td>80</td>
</tr>
<tr>
<td>CL-65N</td>
<td>Zr-2/242831</td>
<td>90</td>
<td>2.76</td>
<td>65</td>
</tr>
<tr>
<td>CL-66N</td>
<td>Zr-2/242831</td>
<td>90</td>
<td>2.76</td>
<td>60</td>
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<tr>
<td>CL-67N</td>
<td>Zr-2/242831</td>
<td>90</td>
<td>2.00</td>
<td>70</td>
</tr>
</tbody>
</table>

Pf: Failure Load
%YL: Percent Yield Load
NF: No Failure
TTF: Time-to-Failure
%EI: Percent Elongation
Figure 4.2. Applied Load vs. TTF for Notched Zr-2 in Acidic Solution

Figure 4.3. Applied Load vs. TTF for Notched Zr-2 in Neutral Solution
Figure 4.4. Applied Load vs. TTF for Notched Zr-4 in Acidic Solution

Figure 4.5. Applied Load vs. TTF for Notched Zr-4 in Neutral Solution

Metallographic evaluation of the tested tensile specimens (smooth and notched) by optical microscopy did not indicate any secondary cracking along their gage sections. Figure 4.6 shows a micrograph of the primary failure of a notched Zr-2 specimen tested in SAWM environment at ambient temperature at an applied load of 80% of this material’s yielding load under constant loading condition. Fractographic evaluation of
broken specimens by SEM revealed dimpled microstructure (Figure 4.7) indicating ductile failure.

Figure 4.6. Optical Micrograph of a Failed Notched Zr-2 Specimen

Figure 4.7. SEM Micrograph of a Notched Zr-2 Specimen in SAWM Environment at 90°C under CL Conditions
The results of SSR testing using smooth tensile specimens of Zr-2 and Zr-4 are shown in Table 4.3. These data indicate that the magnitude of $\sigma_f$ was gradually reduced for both alloys at 60°C and 90°C, compared to those at ambient temperature, as expected. However, the TTF and the ductility in terms of %El and %RA were enhanced to some extent at the elevated temperatures, possibly due to the increased ductility at these temperatures. The synergistic effect of pH and temperature on %El and TTF for smooth specimens of Zr-2 is shown in Figures 4.8 and 4.9. The effect of temperature on the resultant stress-strain diagrams for Zr-4 in air and SAWM environment is illustrated in Figure 4.10 showing enhanced %El and TTF, but reduced $\sigma_f$ at higher testing temperatures. A similar effect of temperature on ductility parameters for zirconium alloys has also been reported in the open literature.\(^1\) The data in Curve 1 (in blue) shows that there is a reduction in strain at the bend of the curve. It is an unusual occurrence, that may be the result of compliance fluctuations. Other curves show consistent signs of noise which is possibly attributed to the heating cartridges that supply the test setup with elevated temperature conditions.

Table 4.3. Results of Slow-Strain-Rate SCC Tests using Smooth Specimen

<table>
<thead>
<tr>
<th>Material/Heat No</th>
<th>Environment</th>
<th>Temperature (°C)</th>
<th>$\sigma_f$ (ksi)</th>
<th>% El</th>
<th>% RA</th>
<th>TTF (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-2 / 242831</td>
<td>SAW</td>
<td>30</td>
<td>89.50</td>
<td>26.07</td>
<td>47.47</td>
<td>24.97</td>
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<td></td>
<td>SAW</td>
<td>90</td>
<td>83.81</td>
<td>32.55</td>
<td>54.53</td>
<td>28.87</td>
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<tr>
<td></td>
<td>SAWM</td>
<td>30</td>
<td>92.38</td>
<td>25.38</td>
<td>48.78</td>
<td>24.86</td>
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<tr>
<td></td>
<td>SAWM</td>
<td>90</td>
<td>67.97</td>
<td>30.98</td>
<td>50.43</td>
<td>28.93</td>
</tr>
<tr>
<td>Zr-4 / 242731</td>
<td>SAW</td>
<td>30</td>
<td>89.24</td>
<td>31.26</td>
<td>49.62</td>
<td>28.59</td>
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<tr>
<td></td>
<td>SAW</td>
<td>90</td>
<td>87.56</td>
<td>36.75</td>
<td>52.48</td>
<td>32.76</td>
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<tr>
<td></td>
<td>SAWM</td>
<td>30</td>
<td>95.78</td>
<td>30.10</td>
<td>51.76</td>
<td>28.10</td>
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<tr>
<td></td>
<td>SAWM</td>
<td>90</td>
<td>65.00</td>
<td>38.65</td>
<td>50.52</td>
<td>33.07</td>
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</table>

Figure 4.8. %El as a Function of pH for Smooth Zr-2 Specimen
Figure 4.9. TTF as a Function of pH for Smooth Zr-2 Specimens

Figure 4.10. Effect of Temperature on the Stress–Strain Diagram for Zr-4 in SAWM Environment
Metallographic evaluation of broken specimens by SEM revealed dimpled microstructure indicating ductile failure at the primary fracture face of the failed specimen, as shown in Figures 4.11 through 4.14.

**Cyclic Potentiodynamic Polarization**

The results of CPP tests are shown in Table 4.4. Analyses of these data indicate that no consistent pattern can be established on the effects of temperature (30°C, 60°C and 90°C) and pH (neutral versus acidic) on either the corrosion potential ($E_{\text{cor}}$) or the critical pitting potential ($E_{\text{pit}}$). Typical ambient temperature polarization diagrams for Zr-
2 in neutral and acidic solutions are superimposed in Figure 4.15 showing $E_{\text{corr}}$, $E_{\text{pit}}$, and $E_{\text{pro}}$. These data, however, exhibit some consistency in that both $E_{\text{corr}}$ and $E_{\text{pit}}$ became more noble (positive) in the neutral solution compared to those in the acidic solution, as expected. No localized attack was observed in the polarized specimens. They only showed general dissolution.

Table 4.4. Results of Cyclic Potentiodynamic Polarization Tests

<table>
<thead>
<tr>
<th>Material/Heat No</th>
<th>Environment</th>
<th>Temperature (°C)</th>
<th>Scan Rate (mV/sec)</th>
<th>$E_{\text{corr}}$, mV (Ag/AgCl)</th>
<th>$E_{\text{pit}}$, mV (Ag/AgCl)</th>
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<tbody>
<tr>
<td>Zr-2 / 242831</td>
<td>SAWM</td>
<td>30</td>
<td>0.166</td>
<td>-571</td>
<td>282</td>
</tr>
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<td></td>
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<td>60</td>
<td>0.166</td>
<td>-417</td>
<td>704</td>
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<td>-390</td>
<td>550</td>
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<td>SAW</td>
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<td>0.166</td>
<td>-332</td>
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<td>0.166</td>
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<td>175</td>
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<td>Zr-4 / 242731</td>
<td>SAWM</td>
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<td>0.166</td>
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<td>360</td>
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<td>0.166</td>
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<td></td>
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<tr>
<td></td>
<td></td>
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<td>0.166</td>
<td>-481</td>
<td>322</td>
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<tr>
<td></td>
<td></td>
<td>90</td>
<td>0.166</td>
<td>-365</td>
<td>99</td>
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</table>
Potentiostatic Potential

A limited number of SCC tests was performed in the 90°C acidic solution under controlled cathodic potential ($E_{\text{cont}}$). In essence, these tests were potentiostatic polarization of tensile specimens of Zr-2 and Zr-4 under constant loading. The magnitude of $E_{\text{cont}}$ was based on the measured $E_{\text{corr}}$ value obtained in a similar environment. Initially, experiments were performed for seven days at $E_{\text{cont}}$ values of -100, -200, -300, and -500 mV with respect to the $E_{\text{corr}}$ value. Later, these tests were extended to periods more than seven days. However, the test solution contained in the Luggin probe started to evaporate beyond seven days, thus losing contact with the tip of the Ag/AgCl reference electrode. Therefore, all potentiostatic SCC tests were performed for seven days only. No failures were observed in smooth tensile specimens loaded up to 95% of the materials’ YS value under the desired $E_{\text{cont}}$ values. Therefore, efforts were...
made to visually examine the specimen surface at the gage region, followed by evaluations by optical microscopy and SEM.

Figure 4.16. SEM Micrograph of Zr-4 Specimen under Applied Cathodic Potential

Even though no failure occurred during the application of cathodic (negative) controlled potential, surface damages were observed in the gage sections of the tested specimens. SEM analyses were performed on the damaged surfaces, as shown in Figure 4.16. Analyses of these micrographs revealed significant localized dissolution showing rupture of surface oxide film along the gage section. In addition, optical microscopy was used to verify the presence of secondary cracking that might have incurred on the surface of the specimen due to the application of the controlled potential. The results of optical analysis indicated no signs of secondary cracking, as expected. In addition to the SEM and optical microscopy analyses, elemental analysis was performed by the energy dispersive spectroscopy (EDS) technique at some selected locations. The EDS data
showing the primary elements such as zirconium (Zr), chromium (Cr), iron (Fe), and nickel (Ni) are illustrated in Figure 4.17. Because zirconium is the major element in the Zr-2 and Zr-4 chemical composition, the EDS analysis resulted in the greatest element count of zirconium.

![Figure 4.17. EDS Data on a Tested Zr-2 Specimen](image)

**Figure 4.17. EDS Data on a Tested Zr-2 Specimen**

**Discussion**

As discussed earlier, this research project is focused on the evaluation of SCC, DHC, and localized corrosion of Zr alloys in neutral and acidic environments at ambient
and elevated temperatures. The susceptibility to SCC was determined by using both CL and SSR techniques. The effect of hydrogen on the cracking susceptibility (DHC) was determined by applying a controlled cathodic potential ($E_{cont}$) to the specimen loaded in tension. The susceptibility to localized attack was evaluated by electrochemical cyclic potentiodynamic polarization (CPP) method. The results of constant-load SCC testing using smooth tensile specimens, as discussed earlier, indicate that no failures occurred with either Zr-2 or Zr-4 even at applied stresses approaching 95 percent of the YS value of these two alloys. These results are not surprising in view of the fact that Zr alloys are known to be highly corrosion-resistant under operating conditions even inside the nuclear reactors.  

It is well-known that zirconium and its alloys are resistant to SCC in pure water, moist air, steam, and many solutions of sulfates and nitrates. Further, these alloys are known to be corrosion-resistant in environments containing alkalies, acids, and salts. However, these materials may have a tendency to corrode in hydrofluoric and hot concentrated sulfuric acids. Even though the Zr alloys have high level of corrosion resistance, SCC does become a problem in ferric chloride and cupric chloride solutions with these alloys. In addition, these materials may exhibit cracking in water containing halides, such as halogen vapors, carbon tetrachloride, and fused salts at high temperatures. Exposure to these environments can also cause pitting in zirconium alloys.

**Stress Corrosion Cracking**

As indicated earlier, no failure was observed with either alloy under constant loading condition using smooth specimens. However, an introduction of a notch at the

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gage section of the smooth specimen produced failures in both neutral and acidic solutions at applied loads corresponding to 75, 80, and 85% of the materials' yielding load values. Obviously, the cracking susceptibility of zirconium alloys was influenced by the presence of a notch. The effect of notch on the mechanical and corrosion properties of cladding materials has been studied by other researchers in boiling-water reactors.

Their study indicated that the primary failure made was due to the pre-fabricated notch, but not due to the secondary hydride damage observed on the test specimens. An evaluation of the cracking morphology suggested that it was a Mode I type of failure which is usually characterized by a crack growth in a direction perpendicular to the load-application line.

The results of constant-load SCC testing performed in the current investigation under controlled electrochemical potential (E_{cont}) indicate that both Zr-2 and Zr-4 experienced localized damage at different locations within the gage section that could be attributed to the generation of hydrogen due to cathodic charging. Even though no cracking was observed in these short-term tests, it is possible that cracks could have been initiated from this localized damage if the specimens were subjected to E_{cont} for a prolonged exposure period. SCC behavior of zirconium and its alloys have been studied by other investigators in methanol-hydrochloric solution using electrochemical techniques. The mechanical and electrochemical properties of stressed and unstressed Zr were compared in their study. Surprisingly, the application of cathodic potentials to Zr

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alloys increased their time-to-failure indicating enhanced ductility. Therefore, it was suggested by these investigators that the presence of hydrogen may not be the controlling failure mechanism in the cracking of Zr, but anodic dissolution might be responsible for SCC. The ductility parameters obtained in this study were not influenced by the application of the cathodic controlled potential, suggesting that the presence of hydrogen may not cause any detrimental effect on the cracking susceptibility of Zr alloys. However, the observation made by these investigators was in contrast to the results obtained in the current investigation that showed damage in the test specimen due to cathodic charging. In light of the results obtained from the present study, it is suggested that additional SCC testing be performed under $E_{\text{cont}}$ for a longer duration.

**Delayed Hydride Cracking**

Although no efforts were made in this program to evaluate the cracking susceptibility and crack growth behavior by any other techniques, efforts have been made by other investigators\(^7\) to characterize the cracking susceptibility of Zr alloys by other available methods. The concept of fracture mechanics has been applied to the characterization of DHC, where the crack velocity ($V$) has been estimated as a function of stress intensity factor ($K_i$), as illustrated in Figure 4.18. Based on this study, it appears that the threshold stress intensity factor ($K_{th}$) can be established for DHC below which cracks may not grow, and a stable crack velocity can be determined that is independent of $K_1$ before it reaches the plane strain fracture toughness ($K_{IC}$).\(^8\) A repetitious cycle is incurred in this time-dependent process under sustained-loading conditions.\(^9\) It has been

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postulated that the diffusion of hydrogen resulting from the reactors at the operating temperatures can lead to the formation and accumulation of hydrides at the crack tip. This phenomenon can produce residual stresses at the hydride crack tip with eventual propagation into a macroscopic failure.

![Figure 4.18. Crack Growth vs. Stress Intensity](image)

It is well-known that zirconium alloys can undergo hydrogen embrittlement by hydride precipitation due to its tendency to pick up hydrogen resulting from the corrosion reactions. There are indications in the literature that some elements, such as tin (Sn), iron (Fe), chromium (Cr), and nickel (Ni) can influence the corrosion behavior of Zr

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alloys, in particular, their hydrogen absorption capability in aqueous environments. An examination of the chemical composition of Zr-2 and Zr-4 tested in this program (Table 2.2) indicate that Zr-4 contains no nickel, but possesses a slightly higher iron content than that of Zr-2. This difference in composition did not exhibit any consistent pattern on the role of elements on the corrosion behavior, with or without the application of $E_{\text{con}}$ in the current study. However, it is important to note that the corrosion behavior of Zr alloys may also be related to the environmental factors, which were somewhat different in this investigation compared to those cited in the open literature. In general, the occurrence of hydrogen embrittlement by hydride formation is characterized by loss of ductility and fracture strength. An analysis of constant-load SCC test data under $E_{\text{con}}$ indicate that there was no consistent pattern on the effect of hydrogen produced by potentiostatic polarization on the resultant ductility of the tested specimens. Even though no attempt has been made in this investigation to analyze the concentration of hydrogen produced by different $E_{\text{con}}$ values, it is obvious that the concentration of hydrogen would be gradually increased with more negative applied potentials.

It has been been suggested\(^\text{13}\) that the tendency to embrittlement may decrease at elevated temperatures due to the high solubility of hydrogen at higher testing temperatures. In general, the formation of hydride can initiate cracking, and can render the metal to become more susceptible to fracture. A research group\(^\text{14}\) has suggested the formation of nitric acid during radiolysis due to the moisture contamination under radioactive environment associated with SNF. These radiolytic effects have been


investigated by them using both slow-strain-rate and constant-strain testing techniques. Their results suggest that SCC can occur in solutions containing high concentrations of nitric acid (20 wt% or greater) at 25°C due to the formation of hydrogen in these environments.

**Localized Corrosion**

The results of the CPP study involving Zr-2 indicate that at 30°C the measured $E_{\text{corr}}$ and $E_{\text{pit}}$ values were more active (negative) in the SAWM environment compared to that in the SAW environment, primarily due to a more acidic pH of the former solution. However, no consistent pattern was seen at elevated temperatures. As expected, the CPP diagram did not exhibit any active region, and was characterized by passive and transpassive regions. Even though the transpassive region is indicative of localized corrosion, such as pitting or crevice, no such damage was observed with either alloy indicating their resistance to localized attack. However, some localized dissolution was observed on the polarization specimens.

The more acidic pH values in SAWM environment were achieved by adding hydrochloric acid to the neutral solution (SAW). It was anticipated that the modification of the SAW environment by adding hydrochloric acid would increase the localized corrosion susceptibility of Zr alloys tested in the current investigation. However, no significant difference in localized corrosion tendency was observed in tested Zr alloys due to a change in pH from neutral to acidic by addition of hydrochloric acid (HCl). Zr alloys are known to be highly corrosion-resistant in many hostile environments due to the presence of 99% or higher Zr content. The effect of HCl of different concentrations on

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localized corrosion behavior of Zr alloys has been studied by other investigators, confirming similar observations made in the current investigation. The susceptibility to localized corrosion can, however, be enhanced by the presence of chloride ions (Cl\(^{-}\)), since zirconium alloys are known to undergo pitting in acidic oxidizing chloride solutions. The presence of Cl\(^{-}\) itself does not influence the corrosion behavior of zirconium alloys, but can produce a detrimental effect if cupric or ferric ions are also present with Cl\(^{-}\) ions.

Temperature and environment can play significant roles on the mechanical and electrochemical properties of zirconium alloys. The effect of elevated temperature on localized corrosion of zirconium alloys has been studied by other researchers. The results obtained from their investigations indicate that the oxygen content may be increased at elevated temperatures, thus producing thicker oxide films on the surface of zirconium alloys. The formation of thicker oxide films may lead to stable passivation of zirconium alloys at elevated temperatures in the presence of high oxygen content. Even though no protective oxide films were detected in specimens tested in this investigation, surfaces of some of the tested specimens were covered with loose dark films that were removed to some extent during the cleaning operations.

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Mitigation Techniques

Zr-2 and Zr-4 are two highly corrosion resistant alloys used in various industries. They are widely used in the nuclear reactor and chemical industries that require use of materials having excellent corrosion resistance. Even though these alloys possess suitable corrosion-resistance, high strength, and enhanced ductility properties, they can experience some service-related degradations. Different mitigation processes can be applied to prevent such damage. The application of these mitigation techniques and the inherent suitable physical and mechanical properties of zirconium alloys can lead to effective and multiple applications of these types of zirconium alloys in different industries.

There are several mitigation techniques that may protect zirconium alloys from corrosion. Obviously, the unique corrosion resistance of zirconium alloys may naturally provide protection from corrosion damages due to the formation of oxides on their surfaces. Although these oxide films may mechanically break or rupture, they have a tendency to regenerate very quickly if there are sufficient amounts of oxygen present. Oxide formation is possible using various methods that may include anodizing, autoclave film formation, and film formation in air. Anodizing forms a very thin layer of film. It is useful for special applications where protective films may form at room temperature. The nuclear reactor industry usually prefers autoclave film formation since this process can form a uniform film of high integrity. Another characteristic that makes this process is the fact that the film can be formed at lower temperatures. Finally, the most common type of film formation can be achieved in air that can produce thick oxide layers onto the surface of Zr alloys.

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As to the SCC susceptibility, it can be prevented by avoiding high sustained tensile stress, modifying the environment, achieving a crystallographic texture with the hexagonal basal planes perpendicular to the cracking path, maintaining a high-quality surface film, and using electrochemical protection techniques. The occurrence of fretting corrosion becomes a problem when the protective oxide coating is damaged or removed, but can be rectified mechanically. To prevent such damage, an oxide coating should be applied on the metal surface. This will reduce friction and prevent the removal of the passive protective oxide films. Since the presence of impurities may also initiate corrosion damage, use of inhibitors can minimize this type of problem. Use of inhibitors, such as zirconium nitrate or phosphorous pentoxide, can minimize or prevent the corrosion damage in nitric acid-fluoride solutions due to the conversion of corrosive F⁻ ions into non-corrosive complex ions.

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CHAPTER 5

SUMMARY AND CONCLUSIONS

Summary

Smooth and notched tensile specimens of Zircaloy-2 (Zr-2) and Zircaloy-4 (Zr-4) were tested to evaluate their stress corrosion cracking (SCC) susceptibility in neutral and acidic aqueous environments at ambient and elevated temperatures by using constant-load (CL) and slow-strain-rate (SSR) techniques. A limited number of SCC tests were also performed under CL condition at different controlled cathodic potentials (E\text{cont}). The localized corrosion susceptibility was evaluated by electrochemical cyclic potentiodynamic polarization (CPP) technique. The morphology of the primary failure in all broken tensile specimens was analyzed by scanning electron microscopy (SEM). Metallographic evaluations were performed by optical microscopy. At least duplicate experiments were performed under identical conditions showing repeatability with no significant variations.

Conclusions

The significant conclusions derived from this investigation are summarized below:

- No failures were observed with smooth Zr-2 and Zr-4 specimens in constant-load tests even at applied stresses approaching 95% of these materials' yield strength.
values. However, failures were observed at reduced applied loads in notched tensile specimens. The magnitude of the SCC due to the presence of a notch was in the vicinity of 75 to 80% of the materials' yielding load values. However, the threshold loads for SCC in Zr alloys may be true only for the configuration of the notch used in this study.

- Both the maximum stress ($\sigma_m$) and the failure stress ($\sigma_f$) were reduced with increasing temperature from ambient to 90°C in SSR tests. However, the time-to-failure (TTF), percent elongation (%EL), and percent reduction in area (%RA) were increased at the elevated test temperature, indicating enhanced ductility.

- The corrosion potential ($E_{corr}$) and critical pitting potential ($E_{crt}$) values for Zr-2 in 30°C acidic (SAWM) environment were more anodic (negative) due to the acidic pH. However, no consistent pattern on the effect of temperature on these critical potentials were observed with either alloy.

- The application of controlled cathodic potentials ($E_{cmt}$) showed a detrimental effect of hydrogen charging on the corrosion behavior of zirconium alloys under constant loading conditions. The extent of damage due to the cathodic charging was gradually increased with more negative applied potentials. These damages were characterized by either localized dissolution or formation of corrosion rings around the gage diameter. Additional testing for longer duration is recommended for future investigation.

- The primary failure mode of all broken specimens was ductile showing dimpled microstructures. No secondary cracks were observed by optical microscopy.
• All polarized specimens showed either general or localized dissolution, but no classical pits or crevices.
BIBLIOGRAPHY


“Problems with the Yucca Mountain Site.”


“Yucca Mountain Program: Near-Field Environment Characterization.”

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Effect of Stress Concentration on Cracking Behavior of Cladding Materials. 2003

Cracking of Zirconium Alloys in Neutral and Acidic Environments. 203rd
Meeting of the Electrochemical Society Technical Symposia. Paris, France. April
2003

Environment-Assisted-Cracking of Cladding Materials under Different Loading
Conditions. 10th International High-Level Radioactive Waste Management
Conference. Las Vegas, Nevada. March 2003

Casino Technology: Player Tracking and Slot Accounting Systems. UNLV

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