Characterization of structural materials for applications in Hi(x) decomposition

Ancila V Kaiparambil

University of Nevada, Las Vegas

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CHARACTERIZATION OF STRUCTURAL MATERIALS FOR APPLICATIONS IN H1x DECOMPOSITION

by

Ancila V. Kaiparambil

Bachelor of Engineering in Mechanical Engineering
University of Mysore, Mysore, India
August 2001

A thesis submitted in partial fulfillment of the requirements for the

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

Graduate College
University of Nevada, Las Vegas
December 2005

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Ancila V. Kaiparambil

Entitled

Characterization of Structural Materials for
Applications in HIx Decomposition

is approved in partial fulfillment of the requirements for the degree of

Master of Science in Mechanical Engineering

Cyril K. Loy
Examination Committee Chair

Dean of the Graduate College

Examination Committee Member

Examination Committee Member

Graduate College Faculty Representative

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ABSTRACT

Characterization Of Structural Materials For Applications In HI\textsubscript{x} Decomposition

by

Ancila V. Kaiparambil

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

Zr705 and Nb7.5Ta have been tested for evaluation of their metallurgical and corrosion properties for applications in nuclear hydrogen generation using an S-I cycle based on the HI\textsubscript{x} decomposition process. The results of tensile testing involving both alloys indicate that the tensile strength was gradually reduced with increasing temperature, as expected. Further, the ductility for both alloys was reduced at some critical temperatures, possibly due to the dynamic strain-aging effect. Zr705 did not exhibit cracking in acidic aqueous solutions, both under constant-load and self-loaded conditions. The stress-corrosion-cracking (SCC) tests of Zr705 in an acidic solution showed reduced true failure stress but enhanced ductility at elevated temperatures. With respect to the SCC susceptibility of Nb7.5Ta in an identical environment, slight change in failure strain was noted at different temperatures. The critical potentials determined in localized corrosion study became more active with increasing temperature. The application of anodic and cathodic potentials enhanced the cracking susceptibility of Zr705. Dimpled microstructures, characteristic of ductile failure, were observed in both materials.
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CHAPTER 1

INTRODUCTION

Fossil fuels have been the primary source of energy in the world for an extended period. They currently provide about 66% of the world’s electricity and about 90% of the world’s energy demands. At this growing rate, the demand for energy is expected to exceed the supply by the year 2010. The United States of America alone is spending about 500 billion dollars a year to meet her energy requirements. The gradual enhancement in the dependence on fossil fuels has created a significant interest worldwide to explore alternate sources of energy, thus, reducing the cost associated with the currently available energy sources.

The alternate source of energy to be developed in the future must be clean, environment-friendly and cost-effective. Hydrogen (H\textsubscript{2}) is considered to be one such source, yet to be developed by the United States Department of Energy (USDOE) for commercial production. H\textsubscript{2} is one of the most abundant elements available in the earth’s atmosphere. It can combine with other elements such as oxygen and carbon, forming compounds. Numerous methods have been identified to produce pure H\textsubscript{2} in a cost-effective manner. However, a majority of these methods involve high temperatures and hence, need high heat energy.

An innovative method to generate H\textsubscript{2} is to utilize the heat energy from a nuclear power plant, resulting in reduced or almost no emission of carbon-dioxide (CO\textsubscript{2}) and thus, producing no greenhouse effect. The primary reason for
the production of H$_2$ using nuclear heat includes its cleanliness and capability of generation on a continuous basis. One of the existing methods to produce H$_2$ in small quantities is steam reforming of natural gas, which can generate a major portion of H$_2$ currently being used.$^{[3]}$ Hydrocarbons and fossil fuels are the two primary sources of heat utilized in H$_2$ production by this method. However, this method is not efficient for large scale generation of H$_2$ due to the possibility of emitting CO$_2$, which can result in greenhouse effect.

Currently, the USDOE is considering the use of both electrolysis and thermochemical processes involving nuclear power as a potential source of heat. Both approaches, however, need the utilization of significant amount of heat to generate H$_2$. The thermochemical processes currently being envisioned include two primary cycles known as sulfur-iodine (S-I) and calcium-bromine (Ca-Br). The USDOE is emphasizing the use of S-I cycle at the initial stage due to the fact that some feasibility of H$_2$ generation using this process has already been demonstrated by the national laboratories and corporate research organizations.

Even though the electrolytic process is a viable option to generate H$_2$, it may necessitate the use of unusually high temperature, and can thus, result in reduced efficiency.$^{[4]}$ Since electricity has to be used to generate high temperature for H$_2$ production, it is appropriate to achieve a better efficiency from power sources such as the nuclear power plants.

Thermochemical cycles based on both S-I and Ca-Br processes are associated with the decomposition of water into H$_2$ and oxygen (O$_2$) through a series of chemical reactions, also at relatively high temperatures. However, these processes do not result in CO$_2$ emission. The reactants used in these
processes can be recycled for repeated generation of H$_2$, rendering them to be more efficient than the high-temperature electrolysis process. The efficiency of the thermochemical water-splitting cycles may be estimated to be around 50%.$^{[5, 6]}$ Further, significant amount of knowledge already exists on the S-I cycle. In view of these rationales, the USDOE is considering this process as the primary method of generating H$_2$ through utilization of nuclear power. The maximum temperature to be used in the S-I cycle is in the vicinity of 950°C. Conversely, the Ca-Br process can operate at relatively lower temperature (~760°C). However, the efficiency of this cycle is estimated to be relatively lower, (approximately 40%) compared to that of the S-I cycle.$^{[7]}

A schematic view of the nuclear hydrogen generation process is illustrated in Figure 1.1, showing the transfer of heat from a gas-cooled nuclear reactor through an intermediate heat exchanger into the H$_2$ generation plant, which will involve the chemical reactions associated with the S-I process. The S-I cycle, developed by the General Atomics Corporation (GA), consists of three chemical reactions that can sum to the dissociation of H$_2$O using iodine (I$_2$) and sulfur-dioxide (SO$_2$) as chemical catalysts, as shown in Figure 1.2. A cursory evaluation of this figure clearly identifies three chemical reactions, in steps. These reactions include the acid (sulfuric acid - H$_2$SO$_4$, and hydrogen-iodide - HI) formation and separation, H$_2$SO$_4$ concentration and decomposition, and HI concentration and decomposition.
The chemical reactions involved in the S-I process are given below. A detailed description of each chemical reaction and the associated phenomenon related to each of these reactions are also presented.
\[
\begin{align*}
I_2 + SO_2 + 2H_2O &\rightarrow 2HI + H_2SO_4 \quad @ \sim 120^\circ C \quad \text{Reaction (1)} \\
H_2SO_4 &\rightarrow H_2O + SO_2 + \frac{1}{2}O_2 \quad @ \sim 800^\circ C \quad \text{Reaction (2)} \\
2HI &\rightarrow H_2 + I_2 \quad @ \sim 360^\circ C \quad \text{Reaction (3)} \\
H_2O &\rightarrow H_2 + \frac{1}{2}O_2
\end{align*}
\]

Reaction 1:- Acid formation and separation: This reaction involves I₂, SO₂ and H₂O leading to the formation of HI and H₂SO₄. Since H₂SO₄ and HI are immiscible, they can be separated by gravitation and individually be collected. HI is relatively heavier than H₂SO₄. Therefore, HI will settle below the H₂SO₄ phase. This reaction occurs at approximately 120°C, which is slightly above the melting point of I₂.

Reaction 2:- H₂SO₄ concentration and decomposition: The concentration of H₂SO₄ generated from reaction (1) can occur at a minimum temperature of 800°C. The reaction products including H₂O, SO₂ and O₂ are then allowed to flow through a vertical decomposition chamber where the vaporization of H₂SO₄ occurs.

Reaction 3:- HI concentration and decomposition: HI formed during reaction (1) is separated from the acidic solution containing HI, I₂ and H₂O, known as hydroiodic acid (HIₓ), by treating it with concentrated phosphoric acid (H₃PO₄), at a temperature of 360°C. The decomposition of HI into H₂ and I₂ occurs by extractive distillation that involves heating of HIₓ at a temperature, at which, HIₓ gas boils off and decomposes to H₂ and I₂ at the top of the reactive column. Although this method is relatively simple involving less processing equipment, it can create a highly corrosive environment at relatively high temperature and pressure. Thus, the structural material to be used for this application must be
highly corrosion-resistant. \( \text{H}_2 \) generation can also be achieved by use of extractive decomposition of \( \text{H}_3\text{PO}_4 \) at a lower temperature of 120°C. However, this process may involve additional reaction steps, thus, making it less viable for \( \text{H}_2 \) generation from \( \text{HI}_x \) decomposition.

Based on the preceding discussion, it is obvious that the structural material to be used for heat exchanger applications in the S-I cycle must withstand appreciably high-temperature and deleterious chemical species associated with the three chemical reactions, shown earlier. While different organizations including the United States national laboratories and, national and international private corporations are currently involved in nuclear \( \text{H}_2 \) generation using the S-I process, the researchers at the University of Nevada, Las Vegas (UNLV) have been concentrating on the identification and characterization of suitable structural materials for such applications. Depending on the severity of the environmental conditions associated with the three chemical reactions, different types of structural materials are being investigated at Materials Performance Laboratory (MPL), UNLV, for characterization of both the metallurgical and the corrosion behavior under prototypic conditions. This thesis is aimed at presenting the results of materials characterization only for \( \text{HI}_x \) decomposition process. This work is being performed in collaboration with GA of San Diego, CA.

Based on the recommendation of a materials advisory board formed by the USDOE, it was decided that refractory materials including zirconium (Zr) and niobium (Nb) alloys may provide the optimum corrosion resistance and the desired metallurgical properties to sustain the hostile operating conditions relevant to the \( \text{HI}_x \) decomposition process. These materials include Zr702,
Zr705, Nb1Zr and Nb7.5Ta. However, the data presented in this thesis are strictly related to the corrosion and metallurgical studies performed on two primary materials, namely Zr705 and Nb7.5Ta. Limited data on Zr702 are also included.

Both Zr and Nb alloys are known to possess excellent corrosion resistance in many chemical environments.\textsuperscript{[9-11]} Due to its superior corrosion resistance, Zr705 has been extensively used in many chemical industries. It is also used as a cladding material for nuclear fuels. In addition, this alloy has been known to possess moderate corrosion resistance in aqueous environments even at elevated temperatures up to 300°C.\textsuperscript{[12]} Zr alloys have been used in surgical appliances, lamp filaments, crucibles, linings and heat-exchangers due to their resistance to heat and corrosion. The use of Zr alloy as a heat-exchanger material for over 40 years has been documented in the literature. Heat-exchangers made of Zr alloys have been extensively used in the production of hydrogen peroxide from boiling 65% $\text{H}_2\text{SO}_4$ solution.\textsuperscript{[13]} Most chemical industries use Zr heat exchangers, due to the fact that they offer longer life, reduced maintenance, and higher efficiency.

The characterization of candidate refractory materials, such as, Zr705 and Nb7.5Ta in the HI\textsubscript{x} environment could not be performed at UNLV due to the lack of proper testing facilities. Therefore, corrosion studies involving both alloys were performed in a simulated aqueous solution containing $\text{H}_2\text{SO}_4$ and sodium iodide (NaI) using numerous state-of-the-art experimental techniques. Simultaneously, the metallurgical characterizations including the tensile properties evaluation of both alloys were performed at temperatures relevant to the HI\textsubscript{x} decomposition process. With respect to the corrosion studies, the
susceptibility of both alloys to environment-induced cracking was determined under constant-load and slow-strain-rate conditions. The localized corrosion behavior was also studied by electrochemical polarization technique. Since the electrochemical potential can influence the cracking susceptibility of structural materials in aqueous environments, both anodic and cathodic potentials were applied to the test specimens while subjected to tensile loading in the simulated acidic solution. In addition, self-loaded specimens and coupons were tested at elevated temperatures to determine the cracking susceptibility and the corrosion rate, respectively. Optical microscopy and scanning electron microscopy were used to perform metallurgical and fractographic evaluations of the tested specimens. The comprehensive test results are presented in this thesis, elucidating the metallurgical and corrosion characteristics of both alloys for prospective applications in H₂ generation by the HI₅ decomposition process.
CHAPTER 2

TEST MATERIAL, SPECIMEN AND ENVIRONMENT

As mentioned in the previous chapter, the structural material for the heat-exchanger applications using the sulfur-iodine (S-I) cycle must withstand relatively high operating temperatures and aggressive chemical environments. Even though the temperature associated with hydrogen (H\textsubscript{2}) generation from the HI\textsubscript{x} decomposition process is relatively lower (360°C), care must be taken to ensure that the structural material is capable of sustaining the operating conditions related to this process. Based on this rationale, two refractory materials, namely Zr705 and Nb7.5Ta have been identified and selected for evaluation of their metallurgical and corrosion properties.

2.1. Test Materials

Refractory materials such as Zr705 and Nb7.5Ta are generally characterized by high melting points, which make them suitable for applications that require optimum strength at elevated temperatures. Zirconium (Zr) and its alloys are known for their superior corrosion resistance in many acidic environments. They have been used as heat-exchanger materials for producing hydrogen peroxide, resulting in enhanced efficiency of up to 90% with a service life of the heat-exchanger over 10 years.\(^{(14)}\) These alloys are also known to possess excellent corrosion resistance in hydrochloric acid and sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) solution, even at
temperatures above their boiling points. The addition of niobium (Nb) to Zr, as in the case of Zr705 (Zr2.5%Nb), is beneficial to enhance its corrosion resistance. The enhanced corrosion resistance of Zr705 due to the addition of Nb can be attributed to the rapid and spontaneous formation of passive oxide film on its surface. The presence of Nb can also resist attack by gases up to 300°C.\(^{(14)}\) The physical properties of Zr705 are given in Tables 2.1. The chemical compositions and the vendor-provided tensile properties at ambient temperature are given in Table 2.2 and Table 2.3, respectively. Both Zr705 and Nb7.5Ta were tested in a solution-annealed condition. No additional thermal treatments were given to them prior to the machining of the test specimens.

Table 2.1. Physical Properties of Zr705\(^{(15)}\)

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>Temperature, °C</th>
<th>Metric Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>20</td>
<td>6.64 g/cm(^3)</td>
</tr>
<tr>
<td>Melting Point</td>
<td>1840</td>
<td>--</td>
</tr>
<tr>
<td>Electrical Resistivity</td>
<td>20</td>
<td>44 x 10(^{-4})/°C</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion</td>
<td>149</td>
<td>4.9 x 10(^{-6}) mm/mm/°C</td>
</tr>
<tr>
<td>Modulus of Elasticity</td>
<td>25</td>
<td>13.7 x 10(^3) ksi</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>25</td>
<td>0.33</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>25-525</td>
<td>17.1 W/m-K</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>0-100</td>
<td>280.5 J/Kg-K</td>
</tr>
</tbody>
</table>
Table 2.2. Chemical Composition of Materials Tested (wt%)

<table>
<thead>
<tr>
<th>Element</th>
<th>Material/Heat #</th>
<th>Zr705/845558 Zr</th>
<th>Zr702/845992</th>
<th>Nb7.5Ta/580286</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr + Hf</td>
<td>(min)</td>
<td>95.5</td>
<td>99.2</td>
<td>0.005</td>
</tr>
<tr>
<td>Hf</td>
<td>0.90</td>
<td>1.1</td>
<td></td>
<td>0.003</td>
</tr>
<tr>
<td>Fe + Cr</td>
<td>0.10</td>
<td>0.10</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>H</td>
<td>0.0003</td>
<td>0.0006</td>
<td></td>
<td>0.0003</td>
</tr>
<tr>
<td>N</td>
<td>0.006</td>
<td>0.005</td>
<td></td>
<td>0.002</td>
</tr>
<tr>
<td>C</td>
<td>0.009</td>
<td>0.01</td>
<td></td>
<td>0.002</td>
</tr>
<tr>
<td>Nb</td>
<td>2.60</td>
<td>-</td>
<td></td>
<td>Bal.</td>
</tr>
<tr>
<td>O</td>
<td>0.12</td>
<td>0.14</td>
<td></td>
<td>0.005</td>
</tr>
<tr>
<td>Ta</td>
<td>-</td>
<td>-</td>
<td></td>
<td>7.6</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
<td>-</td>
<td></td>
<td>0.004</td>
</tr>
<tr>
<td>Si</td>
<td>-</td>
<td>-</td>
<td></td>
<td>0.005</td>
</tr>
<tr>
<td>W</td>
<td>-</td>
<td>-</td>
<td></td>
<td>0.003</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>-</td>
<td></td>
<td>0.002</td>
</tr>
<tr>
<td>Mo</td>
<td>-</td>
<td>-</td>
<td></td>
<td>0.003</td>
</tr>
</tbody>
</table>

Table 2.3. Ambient-Temperature Tensile Properties of Materials Tested

<table>
<thead>
<tr>
<th>Material/Heat No.</th>
<th>Yield Strength, ksi (MPa)</th>
<th>Ultimate Tensile Strength, ksi (MPa)</th>
<th>Percentage Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr705/845558 Zr</td>
<td>61.1 (421)</td>
<td>92.6 (638)</td>
<td>24</td>
</tr>
<tr>
<td>Nb7.5Ta/580286</td>
<td>16.8 (116)</td>
<td>34.6 (239)</td>
<td>50</td>
</tr>
</tbody>
</table>

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2.2. Test Specimens

Smooth cylindrical specimens having 4.00-inch (101.6 mm) overall length, 1.00-inch (25.4 mm) gage length and 0.25-inch (6.35 mm) gage diameter were machined from round bars of Zr705 and Nb7.5Ta. These specimens were machined such that the gage section was parallel to the longitudinal rolling direction. The ratio of the gage length to the gage diameter of these specimens was maintained at 4. The cylindrical specimens were used in both tensile and stress-corrosion-cracking (SCC) tests. The tensile testing was performed at ambient and elevated temperatures according to the American Society for Testing and Materials (ASTM) standard E 08 (2004).\(^\text{[10]}\) The susceptibility of both alloys to SCC was performed in a simulated environment under constant-load and slow-strain-rate (SSR) conditions. The dimensions and a pictorial view of the smooth cylindrical specimen are illustrated in Figure 2.1.

![Figure 2.1. Smooth Cylindrical Specimen](image-url)
Small cylindrical specimens having 0.5-inch (12.7 mm) length and 0.375-inch (9.50 mm) diameter were used to evaluate the localized corrosion behavior of both alloys by an electrochemical method in a similar environment. Since the electrochemical potential, in the presence of an aqueous solution, can influence the cracking susceptibility of structural materials during the HIx decomposition process, anodic and cathodic potentials based on the critical potentials obtained in electrochemical polarization studies were applied to Zr705. The cylindrical specimens used in the controlled potential ($E_{\text{cont}}$) testing were spot welded with a conductive wire, to apply potentials during SCC testing performed under SSR condition. The polarization and the $E_{\text{cont}}$ specimens are shown in Figures 2.2 and 2.3, respectively.

Figure 2.2. Polarization Specimen

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In order to accommodate the aggressive chemical species, relevant to the HIₓ decomposition process, general corrosion and SCC evaluations were performed in an autoclave using coupons and self-loaded specimens (C-ring and U-bend). The coupons were machined from the plate material in the longitudinal direction. The configuration and the pictorial view of the coupon are shown in Figure 2.4.
The C-ring specimen used in this investigation had an outer diameter of 1.00-inch (25.4 mm) and an inner diameter of 0.75-inch (19.05 mm) with a width of 0.50-inch (12.7 mm), as illustrated in Figure 2.5. These specimens were machined from round bars according to the specification given in ASTM G 38 (2001). The U-bend specimens were machined using plate materials having a length of 3.93-inch (99.82 mm) length, 0.34-inch (8.64 mm) width and a thickness of 0.12-inch (3.05 mm). The configuration of the U-bend specimen, shown in Figure 2.6, was achieved by bending the plate material according to the procedure specified in ASTM designation G 30 (1997). The U-bend and the C-ring specimens were machined in such a way that, the resultant tensile stress on the convex surface was parallel to the longitudinal rolling direction.

(a). Dimensions

(b). Pictorial View

Figure 2.5. C-Ring Specimen
2.3. Test Environment

As indicated in the previous section, this investigation is primarily focused on the characterization of the metallurgical and corrosion behavior of the candidate structural materials for application in the HI\textsubscript{x} decomposition process. The corrosion studies involving coupons and self-loaded specimens have been performed in the HI\textsubscript{x} solution at the GA research facilities. However, due to the toxicity of the HI\textsubscript{x} solution and the lack of proper infrastructure (hood), corrosion studies using the HI\textsubscript{x} solution could not be performed at Materials
Performance Laboratory (MPL). Instead, an environment relevant to the S-I cycle was used to evaluate the environment-induced degradations of the tested materials. This simulated environment contained H\textsubscript{2}SO\textsubscript{4}, NaI and de-ionized water, having a pH of approximately 1. The composition of this test solution is given in Table 2.4. For corrosion studies, performed inside the autoclave, an aqueous solution containing 7ml of H\textsubscript{2}SO\textsubscript{4} per 1000ml of solution was used. The pH of this solution was also in the vicinity of 1, as shown in Table 2.4.

Table 2.4. Chemical Composition of the Tested Solutions

<table>
<thead>
<tr>
<th>Test Solution</th>
<th>NaI</th>
<th>H\textsubscript{2}SO\textsubscript{4}</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulated acidic solution</td>
<td>10 gm/liter</td>
<td>Added to achieve the desired pH</td>
<td>~1.0</td>
</tr>
<tr>
<td>Acidic solution</td>
<td>None</td>
<td>7 ml/liter</td>
<td>~1.0</td>
</tr>
</tbody>
</table>
CHAPTER 3

EXPERIMENTAL TECHNIQUES

The structural materials for hydrogen generation by the hydrogen iodide decomposition process must possess significant metallurgical stability at the operating temperatures, and superior corrosion resistance. While immersion testing involving two candidate structural materials (Zr705 and Nb7.5Ta) has been performed in the HI\textsubscript{x} environment at General Atomics (GA), corrosion studies have been performed at the Materials Performance Laboratory (MPL) using a simulated environment containing sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) and sodium iodide (NaI). Testing has also been performed in a solution containing H\textsubscript{2}SO\textsubscript{4} alone. The susceptibility of both alloys to stress-corrosion-cracking (SCC) has been evaluated under both constant-load (CL) and slow-strain-rate (SSR) conditions. Further, localized corrosion behavior has been studied by cyclic potentiodynamic polarization (CPP) technique. The SCC susceptibility under SSR condition has been determined through the application of anodic and cathodic potentials. Limited testing has been performed using C-ring and coupons using an autoclave at 150°C for variable time period.

The tensile properties of both alloys have been determined at temperatures ranging between ambient and 400°C. Metallographic evaluations have been performed by optical microscopy (OM). The morphology of failure of the tested
specimens has been determined by scanning electron microscopy (SEM). The detailed experimental techniques are described below.

3.1. Mechanical Properties Evaluation

A model 319.25 Materials Testing System (MTS) was used to evaluate the tensile properties of smooth cylindrical specimens including yield strength (YS), ultimate tensile strength (UTS), percent elongation (%El) and percent reduction in area (%RA). This machine had a maximum axial load capability of 250 KN (55 kip) and a torsional load transducer with a maximum capacity of 2200 N-m (20,000 lbf-in). The test specimen was loaded using a heavy-duty load-frame connected to an adjustable cross-head on the upper part. A movable hydraulic actuator connected to a wedge grip enabled the fixing of the specimen at the lower end. The specimen fixed between the two wedge grips was pulled by this actuator. The cross-head movement enabled the application of load to the specimen. The magnitude of load was measured by a load cell contained in the cross-head. A conventional MTS unit is shown in Figure 3.1.

In addition, the MTS was operated with an 8-channel signal-conditioning box. The strain gauges, extensometer and temperature sensors were controlled by the signal-conditioning box. The software interface managed all the corresponding signals during the testing. The test data was acquired at the rate of 100 points/sec. In order to accommodate high-temperature tensile testing, the MTS unit contained a ceramic-lined chamber with a thermocouple, which held a constant temperature during testing. The MTS unit had the capability of testing specimens up to a maximum temperature of 600°C. The heating time to achieve the required temperature was established as a part of calibration of the
furnace. The corresponding times to achieve the different temperatures are given in Table 3.1. Nitrogen was flown through the ceramic chamber while testing the specimen at elevated temperatures to avoid contamination or oxidation. Duplicate tests were performed to ensure the accuracy of the data and to determine an average value.

Figure 3.1. MTS Test Setup
Table 3.1. Calibration Data for the Furnace

<table>
<thead>
<tr>
<th>Target temperature (°C)</th>
<th>Chamber set point temperature (°C)</th>
<th>Time to reach target temperature (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>143</td>
<td>60</td>
</tr>
<tr>
<td>200</td>
<td>253</td>
<td>60</td>
</tr>
<tr>
<td>300</td>
<td>363</td>
<td>60</td>
</tr>
<tr>
<td>400</td>
<td>467</td>
<td>55</td>
</tr>
</tbody>
</table>

The evaluation of the tensile properties of the test materials was also performed involving smooth cylindrical specimens in a newly-installed model 8862 Instron equipment having a much higher testing temperature capability (up to 1250°C). The strain rate used in tensile testing, involving both the MTS and Instron equipment was maintained at $10^{-3}$ inch/inch/sec according to the ASTM designation E 08 (2004).\(^{16}\) The tensile properties were determined based on the engineering stress vs. strain (s-e) diagram and the specimen dimensions as a function of the testing temperature. The magnitude of YS was determined by drawing a line parallel to the linear portion of the s-e diagram at an offset value corresponding to 0.2% strain. The magnitude of %El and %RA were determined according to the equations 3.1 through 3.4.
\% \text{El} = \left( \frac{L_f - L_i}{L_i} \right) \times 100 \quad L_i > L_o \quad (3.1)

\% \text{RA} = \left( \frac{A_i - A_f}{A_i} \right) \times 100 \quad A_i > A_f \quad (3.2)

A_i = \left( \frac{\pi \times D_i^2}{4} \right) \quad (3.3)
A_f = \left( \frac{\pi \times D_f^2}{4} \right)

Where,

\[ A_i = \text{Initial Cross Sectional Area} \]

\[ A_f = \text{Cross Sectional Area at Failure} \]

\[ L_i = \text{Initial Gage Length} \]

\[ L_f = \text{Final Gage Length} \]

\[ D_i = \text{Initial Gage Diameter} \]

\[ D_f = \text{Final Gage Diameter} \]

3.2. Stress-Corrosion-Cracking Evaluation

3.2.1. Constant-Load Testing

SCC testing involving smooth cylindrical specimens at CL was performed according to the National Association of Corrosion Engineers (NACE) standard TM-01-77.\(^{(19)}\) A calibrated proof ring was used to load the test specimens at the desired load levels. The magnitude of displacement needed to apply the desired load was determined from the load vs. deflection curve provided by the vendor for each proof ring. A typical calibration curve for the proof ring is illustrated in Figure 3.3. A test chamber made of corrosion resistant Alloy C-276 was used to contain the test specimen, immersed in a simulated acidic solution as indicated in the previous section. For elevated temperature testing, heating cartridges were inserted at the bottom cover of the cell, as shown in Figure 3.4. Further,
condensers were used at the top of the loading chamber to prevent liquid-loss due to the evaporation of the testing solution at elevated temperatures.

Figure 3.3. Proof Ring Calibration Curve

Figure 3.4. Constant-Load Test Setup
The magnitude of the applied stress was based on the room temperature YS value of the test material. The specimen was loaded at stress values corresponding to the different percentages of the material's YS value and the corresponding time-to-failure (TTF) was recorded. A timer attached to the top of the proof ring was used to record the TTF. The testing was performed for a maximum duration of 720 hours. The SCC testing using this technique enabled the determination of a threshold stress ($\sigma_{th}$), below which no failure occurred in 720 hours (30 days) due to the synergistic effect of the applied stress and the testing environment.

3.2.2. Slow-Strain-Rate Testing

In order to circumvent the problems associated with the prolonged testing duration at a CL, many times an alternate method known as constant extension rate testing (CERT) is used to promote failure in a cylindrical specimen at a shorter duration. This method, also known as the SSR testing technique, consists of pulling a specimen at a constant strain rate according to the ASTM Designation G 129.\textsuperscript{[21]} It is well known that the straining of a cylindrical specimen at a faster rate can cause only mechanical failure due to the instability of the testing material at a reasonably faster rate. On the other hand, a cylindrical specimen loaded in tension at a CL in the presence of an aqueous solution may undergo corrosion damage and may require unusually long duration to cause failure. Therefore, it is necessary to optimize the strain rate so that the contribution from both the mechanical constraint and the environment can be maximized.\textsuperscript{[22]} In view of this rationale, SSR testing involving smooth specimen were performed at a strain rate of $3.3 \times 10^{-6}$ inch/inch/sec using a similar environment inside a corrosion-resistant
chamber made of Alloy C-276. This strain rate was selected based upon prior research work performed at the Lawrence Livermore National Laboratory (LLNL). \(^{(23-25)}\)

The SSR test setup used in this investigation, (Figure 3.5) consisted of a top-loaded actuator with a maximum loading capacity of 7500 lbs. The top-loaded actuator was used to prevent any damage resulting from the spilled solution during straining of the specimen. A hand-wheel was provided at the bottom end of the test frame to preload the test specimen. A linear-voltage-displacement-transducer (LVDT) was used to monitor the displacement of the gage section during straining. For elevated temperature testing, prewired heating cartridges were inserted onto the bottom cover of the test chamber. A thermocouple inserted into this chamber measured the solution temperature.

![Figure 3.5. Slow-Strain-Rate Test Setup](image)

A - LVDT  
B - Top Actuator  
C - Environmental Chamber  
D - Bottom Actuator
The computer interface recorded the load values and the corresponding displacement of the LVDT. The load frames were subjected to load compliance test prior to the actual test to determine the load-frame-compliance-factor (error function). Threaded specimens made of ferritic Type 430 stainless steel was used for the load compliance test. The typical graphs for the three load frames used in this study was obtained during the load compliance test, which are shown in Figure 3.6. The cracking susceptibility of the test material under SSR condition could not be expressed in terms of $\sigma_{th}$ in a specific environment since the magnitude of the stress gradually changes due to the reduction in gage diameter, while being strained at constant rate. Instead, the cracking tendency of the test material was characterized by the TTF, %EI, %RA and true failure stress ($\sigma_f$).

![Figure 3.6. Load Frame Compliance Test Graphs](image)
3.3. Electrochemical Testing

The degradations experienced by structural materials while exposed to an aggressive electrolyte may be significantly influenced by electrochemical factors. Under an equilibrium condition, the extent of anodic reaction is balanced by the cathodic reaction. The potential at which this equilibrium condition exists is known as corrosion or open-circuit potential ($E_{corr}$). However, this equilibrium condition is very difficult to maintain in a real life situation. This equilibrium condition may be disturbed by the application of an external potential or current resulting from environmental conditions existing during the operation of a structure/component. This deviation from the equilibrium to a non-equilibrium condition is referred to as the polarization concept. Thus, the performance of polarization experiments by electrochemical techniques involving a structural material can provide important information on the corrosion rate, the susceptibility of the material to environment-induced degradations and corrosion mechanisms as a function of metallurgical and environmental variables.

The difference in potential resulting from polarization is commonly measured by an over voltage ($\eta$), which is a measure of the polarized potential ($E_p$) with respect to the $E_{corr}$. The magnitude of $\eta$ can be either positive or negative depending on the applied electrochemical potential during the polarization of the test specimen. $\eta$ is given by the following equation.

$$\eta = E_p - E_{corr}$$

(3.5)
Polarization can be performed either potentiodynamically or galvanostatically. The basic difference lies in applying potential or current at a specified rate and recording the resultant current and potential, respectively. Polarization experiments were performed in this investigation using a technique known as the cyclic potentiodynamic polarization (CPP). Both anodic and cathodic polarization can be performed by this technique in a cyclic manner. This technique is primarily used to determine the localized corrosion behavior, identifying the different critical potentials namely $E_{\text{corr}}$, pitting potential ($E_{\text{pit}}$), and repassivation or protection potential ($E_{\text{prot}}$). The potentiostat used in the CPP testing was calibrated according to the ASTM Designation G 05. The calibration experiment involving a ferritic Type 430 stainless steel was performed in a 1N H$_2$SO$_4$ solution at 30°C using a potential scan rate of 0.17 mV/sec. A typical calibration curve generated by CPP technique is shown in Figure 3.7.

![Figure 3.7. ASTM G 05 Standard Calibration Curve](image-url)
A three electrode polarization system consisting of the test specimen as an anode, two graphite rods as cathode and silver/silver chloride (Ag/AgCl) as the reference electrode was used during the CPP testing. The experimental setup is shown in Figure 3.8. The reference electrode was contained in a luggin probe placed within 2-3 mm of the cylindrical test specimen that also acted as a salt bridge, as shown in Figure 3.9. An initial delay of 30 minutes was given prior to the performance of the forward potential scanning to attain a stable $E_{\text{corr}}$ value. The determination of $E_{\text{pit}}$ was achieved by the change in slope during the forward potential scan from the passive region to the transpassive region. At this potential, the material may undergo localized breakdown of the protective surface film causing the initiation of pits. A material which is capable of repassivation by the formation of a protective film during the reverse potential scan can be characterized by the development of $E_{\text{prot}}$, as shown in Figure 3.10.

![Figure 3.8. CPP Test Setup](image-url)
3.4. SCC Testing under Applied Potential

It is well known that the cracking susceptibility of a structural material may be influenced by the application of an external potential or current. In view of
this rationale, Zr705 was subjected to SCC testing under an SSR condition using both anodic and cathodic controlled electrochemical potential ($E_{\text{cont}}$). The SCC testing performed in a similar solution at ambient temperature under anodic and cathodic $E_{\text{cont}}$ was based on the $E_{\text{corr}}$. For anodic $E_{\text{cont}}$ testing, the magnitude of the applied potential was substantially noble (positive) with respect to the $E_{\text{corr}}$ value. On the other hand, SCC testing under cathodic $E_{\text{cont}}$ was performed at potentials more active (negative) to the $E_{\text{corr}}$ value.

The smooth cylindrical specimens were spot welded with a conductive wire for $E_{\text{cont}}$ testing, as described in the previous chapter. The wire was coated with lacquer in order to avoid contamination of the test solution. The control potential was applied through the spot welded wire using a similar three electrode polarization technique consisting of the test specimen as an anode, graphite rod as cathode and an Ag/AgCl electrode contained in a Luggin probe as the reference electrode. The desired potential was applied to the test specimen throughout the testing period under an SSR condition and the corresponding current was recorded with time. The cracking susceptibility vs. the magnitude of applied potential was determined in terms of ductility parameters, TTF and $\sigma_l$ in a similar manner, as in the conventional SSR testing. The experimental setup used in SSR testing under $E_{\text{cont}}$ is shown in Figure 3.11.
3.5 Corrosion Studies at elevated Temperature

Corrosion studies at CL and under SSR condition could be performed up to a maximum temperature of 90°C only, due to the limitation of the experimental setup in such testing. Therefore efforts were made to evaluate the corrosion behavior of Zr705 in an autoclave (Figure 3.12) made of Alloy C-276 in an acidic solution (H₂SO₄ only) at 150°C using both C-ring specimen and coupons. The C-ring specimens were loaded at a stress corresponding to 98% of the material’s room temperature YS value according to the ASTM Designation G 38. The displacement (Δ) of the outer diameter of the C-ring specimen was determined using the equation 3.6. A correction factor (Z) for curved beam was determined from Figure 3.13 based on the ratio of the mean diameter to the wall thickness of the C-ring specimen.
Figure 3.12. High-Temperature, High-Pressure Autoclave

\[ OD_f = OD - \Delta, \]  

(3.6)

and,

\[ \Delta = \frac{f \pi D^2}{4EiZ} \]

Where,

- \( OD \) = outside diameter of C-ring before stressing, in.
- \( OD_f \) = outside diameter of stressed C-ring, in.
- \( f \) = desired stress, psi
- \( \Delta \) = change of OD giving desired stress, in.
- \( D \) = mean diameter (OD-t), in.
- \( t \) = wall thickness, in.
- \( E \) = modulus of elasticity, psi.
- \( Z \) = a correction factor for curved beams.
In case of corrosion testing using coupons, the initial weight was measured prior to the exposure to the test solution. Duplicate specimens of both C-ring and coupons were tested for variable time period (7, 14, 28 and 56 days). The C-ring specimens were visually examined for the initiation of cracking at the convex surface which is expected to undergo sustained tensile loading. The weights of the coupons were measured at the end of each test duration, and the corresponding corrosion rate was determined from the weight loss in terms of mils per year (mpy).

The U-bend specimens, fabricated for SCC testing was not tested at the MPL. However these specimens are currently undergoing corrosion testing in the HI_x environment at the GA testing facility. The results of these testing are not yet available. The experimental setup used at GA testing facility is illustrated in Figure 3.14. The test specimens were immersed in the HI_x solution contained in a glass chamber placed in a mullite container. A constant temperature and pressure was maintained during the test period. The test
specimens were immersed for 4, 20 and 100 hours, respectively followed by their visual examination.

Figure 3.14. Immersion Test Setup at GA

3.6 Metallographic Evaluation

A Leica inverted OM, with a maximum resolution of 1000X was used to characterize the metallurgical microstructure of the tested materials. The optical microscopic evaluation is based on the impingement of high energy light rays onto the specimen surface and transmitting them through a number of condensing lenses and shutters into a half-penetrating mirror. The transmitted
light then passes through an objective lens forming a primary image which is magnified through the eyepiece. A digital camera with a resolution of 1 mega pixel and the software interface enabled the development of the microstructure on a computer screen. The different components of the microscopic evaluation setup are shown in Figure 3.15.

![Leica Optical Microscope](image)

Figure 3.15. Leica Optical Microscope

The sectioned specimen was mounted in an epoxy resin followed by polishing and etching according to the conventional technique. The etchants used for microstructural evaluations of both the test materials are given in Table 3.2.
Table 3.2. Composition of Etchants and Procedures

<table>
<thead>
<tr>
<th>Material</th>
<th>Constituents</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr705</td>
<td>HF (48%)</td>
<td>Etched 10-15 min, air dry.</td>
</tr>
<tr>
<td></td>
<td>HNO₃ (70%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Glycerol</td>
<td></td>
</tr>
<tr>
<td>Nb7.5Ta</td>
<td>4-5%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30-35%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Balance</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20%</td>
<td>Etched for 10 sec</td>
</tr>
</tbody>
</table>

3.7. Fractographic Evaluation

The extent and morphology of failure at the primary fracture surfaces of cylindrical specimens of both Zr705 and Nb7.5Ta were determined using a JEOL model 5600 SEM (Figure 3.16). A magnification of up to 100,000X may be achieved by this technique. The sectioned tensile specimens cut to a specified length, was placed on a sample holder to accommodate multiple specimens for fractographic evaluations. Rectangular coupons of Zr702 and Zr705, tested at GA were also evaluated for verification of localized attack and general dissolution using SEM. The energy dispersive spectroscopy (EDS) was also used to analyze the elements present on the surface of the coupons.

Figure 3.16. Scanning Electron Microscopy
CHAPTER 4

RESULTS

The results of tensile testing using smooth cylindrical specimens of Zr705 and Nb7.5Ta as a function of the testing temperature are presented in this chapter. The comprehensive results of stress-corrosion-cracking (SCC), localized corrosion and autoclave testing of Zr705 are also included. Further the results of slow-strain-rate (SSR) and localized corrosion testing involving Nb7.5Ta are provided in this section. Additionally, the results of optical microscopic (OM) and scanning electron microscopic (SEM) evaluations are given in detail. The individual test results corresponding to the specific types of testing are discussed in the following subsections.

4.1. Optical Microscopy

The metallurgical microstructures of Zr705 and Nb7.5Ta in the etched condition are shown in Figures 4.1 and 4.2, respectively. The etchants used for Zr705 consisted of 4-5 volume percent of hydrogen fluoride (HF) and 30-40 volume percent of nitric acid (HNO₃) contained in deionized water. For Nb7.5Ta, an etchant consisting of 60 volume percent of HF, 20 volume percent of HNO₃ and 20 volume percent of glycerol was used. An examination of the Zr705 microstructure, shown in Figure 4.1, clearly reveals the presence of fine-grained microstructure, which is consistent with the microstructure reported in
the open literature.\textsuperscript{26} Comparatively, Nb7.5Ta showed much larger grains, as illustrated in Figure 4.2.

![Figure 4.1. Optical Micrograph of Zr705, Etched, 200X](image1)

![Figure 4.2. Optical Micrograph of Nb7.5Ta, Etched, 200X](image2)

4.2. Tensile Properties Evaluations at Different Temperatures

The results of tensile testing involving smooth cylindrical specimens of Zr705 and Nb7.5Ta at temperatures ranging from ambient to 400°C are
illustrated in Figures 4.3 and 4.4, respectively. Both figures compare the engineering stress vs. strain (s-e) diagram as a function of the testing temperature. An examination of these s-e diagrams indicate that the magnitude of yield strength (YS) and ultimate tensile strength (UTS) was gradually reduced with increasing temperature due to enhanced plasticity, as expected. However, an interesting observation was made, in that, the failure strain ($e_f$) was gradually reduced at temperatures above 200°C, while showing increased $e_f$ values at temperatures ranging between ambient and 200°C, as commonly expected.$^{27-30}$ For some engineering alloys, such reduction in $e_f$ value has been attributed to dynamic strain ageing associated with reduced plastic flow resulting from the pinning of dislocations at the grain boundaries.$^{31}$ A similar explanation may also be provided to account for such a phenomenon, observed with Zr705.

![Figure 4.3. s-e Diagram vs. Temperature for Zr705](image)

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With respect to the s-e diagrams for Nb7.5Ta a consistent pattern on the variation of $e_t$ with temperature was not observed. The cause of such an irrational behavior is yet to be determined. The data shown in Figures 4.3 and 4.4 are reproduced in Tables 4.1 and 4.2, respectively, showing the magnitude of YS, UTS, %E1 and %RA at different temperatures tested in this investigation. An examination of Table 4.2 reveals that the ductility of Nb7.5Ta, in terms of %RA, was not influenced by the changes in temperature due to unusual softness, as determined by visual examination of the fractured surface upon completion of the tensile testing. Simultaneously, an inconsistent variation of %E1 at different temperatures was also noted in this table.
Table 4.1. Tensile Properties of Zr705 vs. Temperature

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>YS, ksi</th>
<th>UTS, ksi</th>
<th>%EI</th>
<th>%RA</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>64.65</td>
<td>84.76</td>
<td>29.87</td>
<td>58.16</td>
</tr>
<tr>
<td>100</td>
<td>55.74</td>
<td>75.78</td>
<td>32.74</td>
<td>68.13</td>
</tr>
<tr>
<td>200</td>
<td>43.80</td>
<td>63.52</td>
<td>36.35</td>
<td>68.90</td>
</tr>
<tr>
<td>300</td>
<td>35.08</td>
<td>55.94</td>
<td>35.10</td>
<td>76.32</td>
</tr>
<tr>
<td>400</td>
<td>29.03</td>
<td>53.74</td>
<td>32.54</td>
<td>77.38</td>
</tr>
</tbody>
</table>

RT: Room Temperature

Table 4.2. Tensile Properties of Nb7.5Ta vs. Temperature

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>YS, ksi</th>
<th>UTS, ksi</th>
<th>%EI</th>
<th>%RA</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>17.41</td>
<td>29.55</td>
<td>52.13</td>
<td>97.48</td>
</tr>
<tr>
<td>100</td>
<td>14.59</td>
<td>24.05</td>
<td>58.08</td>
<td>98.34</td>
</tr>
<tr>
<td>200</td>
<td>14.36</td>
<td>23.15</td>
<td>47.58</td>
<td>98.61</td>
</tr>
<tr>
<td>300</td>
<td>13.79</td>
<td>21.66</td>
<td>44.06</td>
<td>98.45</td>
</tr>
<tr>
<td>400</td>
<td>12.64</td>
<td>19.14</td>
<td>51.20</td>
<td>99.07</td>
</tr>
</tbody>
</table>

RT: Room Temperature

The variations of YS and UTS with temperatures for both Zr705 and Nb7.5Ta are illustrated in Figures 4.5 and 4.6, respectively. A comparative analysis of these data reveals that Zr705 was capable of sustaining much higher tensile strength even at a temperature of 400°C. These results may suggest that, in terms of the metallurgical stability, Zr705 would be a better-suited structural material for application in hydrogen generation, resulting from the HI\textsubscript{x} decomposition process, that may also occur at comparable temperature regime. With respect to the variation of %RA of Zr705 at different temperatures,
its magnitude was gradually enhanced at elevated temperatures due to enhanced plastic flow, as shown in Figure 4.7. However, the ductility of this alloy in terms of %El was enhanced at temperature up to 200°C followed by gradual reduction beyond this temperature (Figure 4.8), possibly due to the strain ageing effect. As to the ductility of Nb7.5Ta, in terms of %El, an inconsistent pattern was noted, as indicated earlier.

Figure 4.5. Variation of YS vs. Temperature

Figure 4.6. Variation of UTS vs. Temperature
4.3. SCC Testing Under Constant-Load

The results of SCC testing at CL involving smooth cylindrical specimens of Zr705, in a simulated aqueous solution containing H$_2$SO$_4$ and NaI, at ambient temperature and 90°C are shown in Table 4.3. These results, based on duplicate testing, indicate that Zr705 may not undergo SCC under a constant loading condition, while exposed to an acidic solution even at an applied stress...
corresponding to 98% of the material's room temperature YS value. Thus, suggesting that the magnitude of threshold stress ($\sigma_{th}$) for cracking, in this environment may lie in the vicinity of 0.98YS. The cracking susceptibility of Nb7.5Ta could not be performed in an identical environment at CL due to the non-availability of the cylindrical specimens at a proper time.

Table 4.3. Constant-Load SCC Test Results

<table>
<thead>
<tr>
<th>Environment/ Temperature (°C)</th>
<th>% Yield Load/ Load Applied (ksi)</th>
<th>TTF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic / RT</td>
<td>98/63.36</td>
<td>NF</td>
</tr>
<tr>
<td>Acidic / 90°C</td>
<td>95/61.42</td>
<td>NF</td>
</tr>
<tr>
<td>Acidic / 90°C</td>
<td>98/63.36</td>
<td>NF</td>
</tr>
</tbody>
</table>

RT: Room Temperature, NF: No Failure, Acidic: $\text{H}_2\text{SO}_4 + \text{NaI} + \text{H}_2\text{O}$

4.4. SCC Testing Under SSR Condition

The results of SCC tests involving both Zr705 and Nb7.5Ta using the SSR technique are shown in Figures 4.9 and 4.10, respectively in the form of s-e diagram, superimposed as functions of testing environment and temperature. The magnitude of %El, %RA, time-to-failure (TTF) and true failure stress ($\sigma_t$) determined from the s-e diagrams of Zr705 and the specimen dimensions before and after testing are shown in Table 4.4. A cursory evaluation of these data indicates that, the average values of TTF, %El and %RA were gradually enhanced with increasing temperature, suggesting enhanced ductility. As reported in previous investigations,$^{32,33}$ performed at UNLV, zirconium (Zr) alloys may not be adversely effected by the testing environment until a critical
temperature (~200°C) is reached.[34] However, the magnitude of $\sigma_t$ was gradually reduced indicating increased cracking susceptibility at higher temperature, as expected.

Figure 4.9. s-e Diagram for Zr705 Under SSR Condition
Figure 4.10. s-e Diagram for Nb7.5Ta Under SSR Condition

Table 4.4. Slow-Strain-Rate Test Result of Zr705

<table>
<thead>
<tr>
<th>Environment / Temperature, °C</th>
<th>$\sigma_t$, ksi</th>
<th>%E1</th>
<th>%RA</th>
<th>TTF, hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air / RT</td>
<td>125.47</td>
<td>31.84</td>
<td>60.85</td>
<td>28.73</td>
</tr>
<tr>
<td>Acidic / RT</td>
<td>120.62</td>
<td>32.10</td>
<td>60.32</td>
<td>29.54</td>
</tr>
<tr>
<td>Acidic / 60</td>
<td>115.08</td>
<td>34.23</td>
<td>60.75</td>
<td>30.68</td>
</tr>
<tr>
<td>Acidic / 90</td>
<td>105.82</td>
<td>34.65</td>
<td>61.41</td>
<td>31.99</td>
</tr>
</tbody>
</table>

RT: Room Temperature, Acidic ($H_2SO_4 + NaI + H_2O$)

With respect to the SCC behavior of Nb7.5Ta, a totally different observation was made due to substantially lower strength and hardness of this alloy. An examination of the s-e diagrams of this alloy, indicate that very little changes in
6f occurred due to change in temperature from ambient to 90°C. The magnitude of %RA and \( \sigma_f \) could not be determined precisely due to the unusual appearance of the fracture surface of the cylindrical specimen upon completion of testing.

4.5. CPP Test Results

In order to ensure the accuracy of the polarization data, the Gamry potentiostat was calibrated according to the ASTM Designation G 5\(^{[20]} \). The calibration diagram showing the potential versus the current is illustrated in Figure 4.11. A comparison of this diagram to the standard calibration diagram (Figure 3.7) verifies the accuracy of the GAMRY potentiostat by displaying a similar shape.

![Figure 4.11. ASTM G 5 calibration curve](image)

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The results of localized corrosion studies involving Zr705 by cyclic potentiodynamic polarization (CPP), in an identical testing environment are illustrated in Figures 4.12, through 4.14, as a function of the testing temperatures. While active to passive transition was noted for this alloy at all three temperatures (30, 60 and 90°C), a negative hysteresis loop was observed indicating the formation of protective oxide film resulting from oxygen evolution due to electrolysis of water at high current densities. It should however, be noted that the critical pitting potential ($E_{pit}$) could not be determined from these diagrams due to the absence of well-defined change in slope. An interesting observation was that the magnitude of current was increased with increasing temperature, as identified by the point of intersection of the cathodic and anodic curves.

![CPP Diagram at 30°C](image)

Figure 4.12. CPP Diagram at 30°C
Zr705
Acidic: H₂SO₄ + NaI + H₂O

Figure 4.13. CPP Diagram at 60°C

Zr705
Acidic: H₂SO₄ + NaI + H₂O

E_{corr} = 238 mV

Figure 4.14. CPP Diagram at 90°C
The magnitudes of $E_{\text{corr}}$, determined from duplicate CPP testing under each experimental condition are given in Table 4.5. These data indicate that $E_{\text{corr}}$ became more active with increasing temperature, which is consistent with observations made by the other investigators\(^{32, 33}\) (Figure 4.18). A comparison of the CPP diagrams of Zr705 to those of Zircaloy-2 indicate that a positive hysteresis loop was observed with the later material possibly due to the absence of Nb, which is known to enhance corrosion resistance in Zr alloys. As to the localized corrosion behavior of Nb7.5Ta, both $E_{\text{corr}}$ and $E_{\text{pit}}$ were identified in the CPP diagrams (Figure 4.15 through 4.17) at three temperatures. A negative hysteresis loop was also observed with this alloy during reverse potential scan. The magnitude of the critical potentials ($E_{\text{corr}}$ and $E_{\text{pit}}$), determined from the CPP testing of this alloy are also given in Table 4.5. Once again, both potentials became more active with increasing temperature, as illustrated in Figure 4.19.

![Figure 4.15. CPP Diagram at 30°C](image)

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Figure 4.16. CPP Diagram at 60°C

Figure 4.17. CPP Diagram at 90°C
Table 4.5. Critical Potentials Obtained During CPP Tests

<table>
<thead>
<tr>
<th>Environment / Temperature, °C</th>
<th>Material</th>
<th>$E_{corr}$, mV</th>
<th>$E_{corr}$, mV</th>
<th>$E_{pit}$, mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic / 30</td>
<td>Zr705</td>
<td>282</td>
<td>130</td>
<td>521</td>
</tr>
<tr>
<td>Acidic / 60</td>
<td>Nb7.5Ta</td>
<td>238</td>
<td>92</td>
<td>418</td>
</tr>
<tr>
<td>Acidic / 90</td>
<td></td>
<td>195</td>
<td>45</td>
<td>396</td>
</tr>
</tbody>
</table>

RT: Room Temperature, Acidic ($\text{H}_2\text{SO}_4 + \text{NaI} + \text{H}_2\text{O}$)

Figure 4.18. Variation of $E_{corr}$ vs. Temperature

Figure 4.19. Variation of Critical Potentials vs. Temperature

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4.6. SSR Testing under Controlled Potentials

As indicated earlier in chapter 3, the cracking susceptibility of Zr705 was determined by SSR testing under controlled cathodic and anodic applied potentials ($E_{\text{cont}}$) with respect to the measured $E_{\text{corr}}$ value in an identical environment. The cathodic $E_{\text{cont}}$ testing was performed at potentials of -300 and -600 mV, with respect to the $E_{\text{corr}}$ value. On the other hand, SSR testing under anodic $E_{\text{cont}}$ was performed at potentials more noble (+600, +750 and +900 mV) to the $E_{\text{corr}}$ values. The s-e diagrams generated in SSR testing under cathodic and anodic $E_{\text{cont}}$ are shown in Figures 4.20 and 4.21, respectively. The magnitudes of $\%E_l$, $\%R_A$, TTF and $\sigma_t$, derived from these diagrams and specimen dimensions are given in Tables 4.6 and 4.7, for cathodic and anodic $E_{\text{cont}}$ testing, respectively. An evaluation of these data based on duplicate testing indicates that all four parameters were gradually reduced irrespective of the type of applied potential. No notable difference in their magnitudes was, however, observed with either type of applied potential.
Figure 4.20. s-e Diagram under Cathodic $E_{\text{cont}}$

Figure 4.21. s-e Diagram under Anodic $E_{\text{cont}}$

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Table 4.6. SSR Results under Cathodic $E_{cont}$

<table>
<thead>
<tr>
<th>Environment / Temperature, °C</th>
<th>$E_{cont}$</th>
<th>$\sigma_t$, ksi / MPa</th>
<th>%$E_1$</th>
<th>%$RA$</th>
<th>TTF, hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic / RT</td>
<td>No $E_{cont}$</td>
<td>124.01/855.05</td>
<td>32.30</td>
<td>61.26</td>
<td>29.85</td>
</tr>
<tr>
<td>Acidic / RT</td>
<td>-20 mV</td>
<td>113.60/783.27</td>
<td>28.45</td>
<td>54.25</td>
<td>27.28</td>
</tr>
<tr>
<td>Acidic / RT</td>
<td>-320 mV</td>
<td>109.43/754.52</td>
<td>24.70</td>
<td>53.86</td>
<td>23.52</td>
</tr>
</tbody>
</table>

RT: Room Temperature, Acidic ($\text{H}_2\text{SO}_4 + \text{NaI} + \text{H}_2\text{O}$)

Table 4.7. SSR Results under Anodic $E_{cont}$

<table>
<thead>
<tr>
<th>Environment / Temperature, °C</th>
<th>$E_{cont}$</th>
<th>$\sigma_t$, ksi / MPa</th>
<th>%$E_1$</th>
<th>%$RA$</th>
<th>TTF, hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic / RT</td>
<td>No $E_{cont}$</td>
<td>124.01/855.05</td>
<td>32.30</td>
<td>61.26</td>
<td>29.85</td>
</tr>
<tr>
<td>Acidic / RT</td>
<td>880 mV</td>
<td>114.82/791.68</td>
<td>28.29</td>
<td>54.90</td>
<td>27.20</td>
</tr>
<tr>
<td>Acidic / RT</td>
<td>1.03 V</td>
<td>113.41/781.96</td>
<td>27.69</td>
<td>54.32</td>
<td>26.88</td>
</tr>
<tr>
<td>Acidic / RT</td>
<td>1.18 V</td>
<td>110.07/758.82</td>
<td>26.73</td>
<td>51.88</td>
<td>25.33</td>
</tr>
</tbody>
</table>

RT: Room Temperature, Acidic ($\text{H}_2\text{SO}_4 + \text{NaI} + \text{H}_2\text{O}$)

4.7. Immersion Testing

The susceptibility of Zr705 to SCC was determined in an autoclave containing aqueous solution of $\text{H}_2\text{SO}_4$ at 150°C, involving C-ring specimens loaded to 98% of its room temperature YS value, as indicated in chapter 3. These specimens were periodically removed from the autoclave to examine the presence or absence of cracking. Visual examinations of the C-ring specimens indicate that Zr705 did not exhibit any cracking irrespective of the exposure period, which ranged from 7 to 56 days. Simultaneously, efforts were made to determine the general corrosion rate of Zr702 in an identical solution at 150°C using coupons. However a very little change in appearance and, no reduction in weight of these specimens was noted, even after exposure for 28 days. Pictorial
views of the tested C-ring and coupons are shown in Figures 4.22 and 4.23, respectively.

Figure 4.22. C-ring Specimen Tested in Autoclave

Figure 4.23. Coupon Tested in Autoclave

The susceptibility of Zr702 and Zr705 to general and localized corrosion was also evaluated in the HIx (HI + I₂ + H₂O) solution at 310°C using the testing facility at GA for variable time periods. A cursory examination of the tested coupons revealed that Zr705, tested for 100hrs, suffered some general
dissolution only, while Zr702, tested for 20hrs exhibited both general and localized attack as shown in Figures 4.24 and 4.25. The surface analysis of the tested Zr702 coupons by energy dispersive spectroscopy (EDS) showed predominantly the presence of zirconium and traces of oxygen, as illustrated in Figure 4.26.

Figure 4.24. SEM Micrograph for Zr702 coupon, 40X

Figure 4.25. SEM Micrograph for Zr705 coupon, 40X
4.8 Scanning Electron Microscopy

The morphology of failure at the primary fracture surface of cylindrical specimens of both Zr705 and Nb7.5Ta, used in both, tensile and SSR testing, determined by SEM is shown in Figures 4.27 through 4.30. An evaluation of these micrographs revealed the presence of dimpled microstructure, indicating ductile failure. It is interesting to note that the size of the dimples in the SEM micrographs of Zr705 was relatively larger at higher temperatures, as shown in Figure 4.27. Additionally, the dimple size for Nb7.5Ta was considerably larger compared to that of Zr705. This difference in dimple size may be attributed to the grain-size difference between these two alloys. No detrimental effect of applied potential, both cathodic and anodic, on the fracture morphology of Zr705 was noticed, as illustrated in Figure 4.31 and 4.32 respectively.
Figure 4.27. SEM Micrographs of Tensile Testing of Zr705, 400X
Figure 4.28. SEM Micrographs of Tensile Testing of Nb7.5Ta, 400X
Figure 4.29. SEM Micrographs of SSR Testing of Zr705, 400X

(a) Ambient Temperature, Air

(b) Ambient Temperature, Acidic

(c) 60°C, Acidic

(d) 90°C, Acidic
Figure 4.30. SEM Micrographs of SSR Testing of Nb7.5Ta, 400X

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Figure 4.31. SEM Micrographs of SSR Testing Under Cathodic $E_{\text{cont}}$, 400X

(a) $E_{\text{cont}} = -20 \text{ mV}$

(b) $E_{\text{cont}} = -320 \text{ mV}$

Figure 4.32. SEM Micrographs of SSR Testing Under Anodic $E_{\text{cont}}$, 400X

(a) $E_{\text{cont}} = +880 \text{ mV}$

(b) $E_{\text{cont}} = +1.03 \text{ V}$

(c) $E_{\text{cont}} = +1.18 \text{ V}$
CHAPTER 5

DISCUSSION

This investigation was primarily focused on the characterization of the metallurgical and corrosion behavior of two refractory materials including Zr705 and Nb7.5Ta for application as structural materials in hydrogen generation using the Hlx decomposition process. A majority of testing was performed at the Materials Performance Laboratory (MPL) while some selected type of testing was conducted at GA using its Hlx testing facility. The metallurgical characterization included microstructural, tensile properties, and fractographic evaluations. As to the corrosion studies, the susceptibility of both alloys to stress-corrosion-cracking (SCC) and localized corrosion was determined by slow-strain-rate (SSR) and cyclic potentiodynamic polarization (CPP) technique, respectively. SCC testing of Zr705 was also performed at constant-load (CL). The effect of control potential ($E_{\text{corr}}$) on the cracking susceptibility of Zr705 was also studied under both cathodic and anodic applied potentials. In addition, corrosion studies were performed in an autoclave at 150°C incorporating both C-ring and coupons.

Limited studies have been performed at GA to evaluate the general/localized corrosion, and SCC susceptibility in the Hlx environment. Some of these testing are still ongoing. Thus, the results of these testing are unavailable at this time. With respect to the surface characterization of all tested specimens,
scanning electron microscopy (SEM) has been extensively used to analyze the morphology of failure. Optical microscopy (OM) has also been used to analyze their metallurgical microstructures. The key results obtained from this investigation are discussed below.

A comparative analysis of the tensile data involving both Zr705 and Nb7.5Ta indicate that the magnitude of both the yield strength (YS) and the ultimate tensile strength (UTS) was gradually reduced with increasing temperature, due to the enhanced plasticity, as expected. However the structural stability in terms of tensile strength was appreciably superior for Zr705 compared to that of Nb7.5Ta. The variation of YS and UTS vs. temperature, shown in Figures 4.5 and 4.6, clearly demonstrated this phenomenon. As to the engineering stress-strain (s-e) diagram, it was interesting to note that for Nb7.5Ta, an unusual characteristic was observed, in that the cylindrical specimens exhibited higher plastic strain (Figure 4.14) due to unusually lower hardness (VHN ~80) of this material.

An evaluation of the measured ductility in terms of percentage elongation (%El) indicate that, in general, its value was enhanced up to certain temperatures for both alloys, followed by gradual decline above this temperature. The critical transition temperature for Zr705 and Nb7.5Ta was 200 and 100°C, respectively. As to the ductility in terms of percentage reduction in area (%RA), Zr705 exhibited a conventional pattern showing a gradually enhancement with increasing temperature. However, once again, Nb7.5Ta showed an unusual pattern showing unchanged %RA at elevated temperatures. It is interesting to note that this alloy exhibited notably larger grain size compared to that of Zr705.
As to the cracking susceptibility of Zr705, this alloy did not exhibit any failure at CL even at an applied stress approaching 0.98YS while exposed to a simulated acidic solution even at an elevated temperature (90°C). The SCC data obtained by the SSR technique revealed a gradual drop in true failure stress ($\sigma_f$) with increasing temperature, which is consistent with the observations made by other investigators.\(^3\) However, the other parameters including $\%$E\(_i\), $\%$RA and time-to-failure (TTF) were not appreciably influenced by the variation in the environmental condition (air vs. acidic solution). For Nb7.5Ta, the failure strain ($e_f$) was reduced due to a change in temperature from 30 to 90°C, when tested in a similar environment.

An evaluation of the localized corrosion behavior by the CPP technique indicates that both alloys exhibited active-passive transition with negative hysteresis loop during the reverse potential scan. This phenomenon is attributed to the formation of new protective oxide films on the specimen surface due to the generation of oxygen resulting from electrolysis at unusually high current densities, noted in the CPP diagram. While the magnitude of corrosion potential ($E_{corr}$) became more active with increasing temperature for both alloys, the pitting potential ($E_{pit}$) value could not be determined for Zr705 due to the absence of a well-defined passive region. For Nb7.5Ta, however, the magnitude of $E_{pit}$ also became more active (negative) at higher testing temperatures. The effect of temperature on the critical potentials ($E_{corr}$ and $E_{pit}$), as noted in this investigation, is similar to observations made by other investigators on engineering materials. It should, however, be noted that the magnitude of $E_{corr}$ of Zr705 was more noble at different temperatures compared to that of Nb7.5Ta. Thus, based on the overall results of tensile and corrosion

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testing, it can be concluded that Zr705 undoubtedly would be a superior structural material for heat-exchanger during hydrogen generation by the Hlx decomposition process.

The cracking susceptibility of structural materials under the combined effect of applied stress and environment can be influenced by the application of external potential or current. The electrochemical potential may be influenced by the variation of the environmental conditions. The results of SCC testing, performed under externally applied anodic and cathodic potentials, revealed enhanced cracking susceptibility, showing reduced $\sigma_t$, TTF, %EI and %RA. This observation is consistent with the results reported by other investigators,\textsuperscript{(32, 33)}

The results of autoclave testing involving Zr702 indicate that this alloy did not exhibit any weight-loss due to its exposure in a 150°C aqueous solution containing sulfuric acid ($\text{H}_2\text{SO}_4$). Simultaneously, the stressed C-ring specimens of Zr705 did not suffer from cracking even after an exposure of 56 days in a similar environment at 150°C. Eventhough, the tested environment is different from the Hlx solution used at GA, the resultant data at MPL suggest that either of the Zr alloy may provide the corrosion resistance needed for heat-exchangers in nuclear hydrogen generation. As to the corrosion resistance of these alloys in the Hlx solution, both materials suffered from general dissolution at 310°C. Further, Zr702 underwent localized attack in this environment.

With respect to the fractographic evaluation of Zr705 and Nb7.4Ta, used in tensile and SCC testing, both materials showed dimpled microstructure at the primary fracture surface, suggesting ductile failures with and without the presence of any aggressive testing environment.
Zr705 and Nb7.5Ta were tested for evaluation of their tensile properties and corrosion resistance for prospective applications in nuclear hydrogen generation. Tensile testing was performed at temperatures relevant to the $\text{H}_2\text{O}$ decomposition process. The cracking susceptibility of the candidate materials was determined by different state-of-the-art experimental techniques at ambient and elevated temperatures. The susceptibility to localized corrosion was determined by a polarization technique. The role of applied potential on the cracking susceptibility was also investigated. Microscopic evaluations were performed to determine the metallurgical microstructure and failure morphology of the tested specimens. The key results are summarized below.

- Zr705 exhibited higher strength at elevated temperatures (up to 400°C) compared to Nb7.5Ta, suggesting that Zr705 will be a better-suited structural material for application in $\text{H}_2\text{O}$ decomposition.
- The magnitude of $e_f$ for both alloys was enhanced up to a critical temperature above which reduction of this parameter was noted. The reduced $e_f$ may be the result of dynamic strain aging.
- Zr705 did not exhibit any failure at CL indicating a $\sigma_{\text{th}}$ approaching 0.98YS.
• The results of SSR testing involving Zr705 exhibited reduced $\sigma_f$ value with increasing temperature. However, TTF, %El and %RA was enhanced at 90°C indicating improved ductility at elevated temperatures. For Nb7.5Ta, both %El and TTF were reduced at 90°C, as expected.

• The critical potentials obtained in CPP testing became more active at higher temperatures, without showing any positive hysteresis loop.

• The effect of controlled potential on the cracking susceptibility of Zr705 was not appreciable. A slight reduction in $\sigma_f$, %El, %RA and TTF was, however, observed.

• No appreciable weight-loss of Zr702 specimens was observed in 150°C acidic solution. Also, C-ring specimen did not exhibit cracking in a similar environment.

• Both Zr702 and Zr705 showed general corrosion and/or localized attack in the Hlx solution at 310°C.

• Dimpled microstructure, characteristic of ductile failure, was observed at the fractured surface of cylindrical specimens, used in tensile and SCC testing.
CHAPTER 7

SUGGESTED FUTURE WORK

Some future work is suggested in order to derive more conclusive results as specified below.

• SCC evaluation using double cantilever beam (DCB) specimens at temperatures up to 400°C in prototypic environments.
• Characterization of defects (dislocations) by TEM to understand dynamic strain aging.
• Evaluation of fracture toughness and crack growth rates at different temperatures.
• Determination of crack growth rate of structural materials in corrosive environment.
APPENDIX A

TENSILE TEST DATA

A.1. Tensile Test Data of Zr705
A.1.1. Stress-Strain curves at ambient temperature
A.1.1.1. Tested in MTS

(A conversion factor of 6.895 can be used to convert ksi to MPa)
A.1.1.2. Tested in Instron
A.1.2. Stress-Strain curves at 100°C

A.1.2.1. Tested in MTS

Sample 1

Sample 2
A.1.2.2. Tested in Instron

A.1.3. Stress-Strain curves at 200°C

A.1.3.1. Tested in MTS
A.1.3.2. Tested in Instron
A.1.4. Stress-Strain curves at 300°C

A.1.4.1. Tested in MTS

Sample 1

Sample 2
A.1.4.2. Tested in Instron

![Stress-Strain curve for Sample 3 at 400°C](image1)

A.1.5. Stress-Strain curves at 400°C

A.1.5.1. Tested in MTS

![Stress-Strain curve for Sample 1 at 400°C](image2)
A.1.5.2. Tested in Instron
Table A.1. Combined Tensile Test Results for Zr705

<table>
<thead>
<tr>
<th>Test Temperature (°C)</th>
<th>Sample #</th>
<th>YS, ksi</th>
<th>UTS, ksi</th>
<th>% El</th>
<th>% RA</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>Sample 1</td>
<td>64.51</td>
<td>86.07</td>
<td>29.81</td>
<td>57.92</td>
</tr>
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<td></td>
<td>Sample 2</td>
<td>64.78</td>
<td>83.45</td>
<td>29.93</td>
<td>59.87</td>
</tr>
<tr>
<td></td>
<td>Sample 3</td>
<td>66.59</td>
<td>89.71</td>
<td>31.09</td>
<td>56.70</td>
</tr>
<tr>
<td>100</td>
<td>Sample 1</td>
<td>56.56</td>
<td>76.20</td>
<td>32.15</td>
<td>67.25</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>54.92</td>
<td>75.35</td>
<td>33.33</td>
<td>69.01</td>
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<td>Sample 3</td>
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<td>72.95</td>
<td>34.36</td>
<td>68.30</td>
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<td>63.49</td>
<td>34.17</td>
<td>68.70</td>
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<tr>
<td></td>
<td>Sample 2</td>
<td>43.74</td>
<td>63.55</td>
<td>38.52</td>
<td>69.10</td>
</tr>
<tr>
<td></td>
<td>Sample 3</td>
<td>44.76</td>
<td>68.32</td>
<td>35.03</td>
<td>69.80</td>
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<tr>
<td>300</td>
<td>Sample 1</td>
<td>34.30</td>
<td>55.57</td>
<td>35.35</td>
<td>76.92</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>35.86</td>
<td>56.30</td>
<td>34.85</td>
<td>75.72</td>
</tr>
<tr>
<td></td>
<td>Sample 3</td>
<td>34.85</td>
<td>56.51</td>
<td>33.58</td>
<td>72.25</td>
</tr>
<tr>
<td>400</td>
<td>Sample 1</td>
<td>28.81</td>
<td>53.10</td>
<td>33.32</td>
<td>76.23</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>29.26</td>
<td>54.38</td>
<td>31.75</td>
<td>78.53</td>
</tr>
<tr>
<td></td>
<td>Sample 3</td>
<td>30.67</td>
<td>54.01</td>
<td>30.57</td>
<td>76.61</td>
</tr>
</tbody>
</table>

RT: Room Temperature
A.2. Tensile Test Data of Nb7.5Ta

A.2.1. Stress-Strain curves at ambient temperature

Sample 1

Sample 2
A.2.2. Stress-Strain curves at 100°C

Sample 1

Sample 2
A. 2.3. Stress-Strain curves at 200°C

Sample 1

Sample 2
A. 2.4. Stress-Strain curves at 300°C

Sample 1

Sample 2
A. 2.5. Stress-Strain curves at 400°C

Sample 1

Sample 2
Table A.2. Combined Tensile Test Results for Nb7.5Ta

<table>
<thead>
<tr>
<th>Test Temperature (°C)</th>
<th>Sample #</th>
<th>YS, ksi</th>
<th>UTS, ksi</th>
<th>% EL</th>
<th>% RA</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>Sample 1</td>
<td>17.53</td>
<td>30.33</td>
<td>52.20</td>
<td>97.48</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>17.28</td>
<td>28.77</td>
<td>52.05</td>
<td>97.47</td>
</tr>
<tr>
<td>100</td>
<td>Sample 1</td>
<td>14.36</td>
<td>24.18</td>
<td>58.32</td>
<td>98.35</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>14.82</td>
<td>23.91</td>
<td>57.83</td>
<td>98.32</td>
</tr>
<tr>
<td>200</td>
<td>Sample 1</td>
<td>14.29</td>
<td>23.69</td>
<td>51.92</td>
<td>98.62</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>14.42</td>
<td>22.61</td>
<td>43.23</td>
<td>98.60</td>
</tr>
<tr>
<td>300</td>
<td>Sample 1</td>
<td>13.78</td>
<td>22.26</td>
<td>43.23</td>
<td>98.45</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>13.80</td>
<td>21.06</td>
<td>44.89</td>
<td>98.44</td>
</tr>
<tr>
<td>400</td>
<td>Sample 1</td>
<td>12.70</td>
<td>18.72</td>
<td>50.56</td>
<td>99.07</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>12.63</td>
<td>17.89</td>
<td>51.85</td>
<td>99.14</td>
</tr>
</tbody>
</table>

RT: Room Temperature
APPENDIX B

SLOW-STRAIN-RATE TEST DATA

B.1. SSR Testing on Zr705

B.1.1. SSR Testing in Air

![Sample 1](image-url)
B.1.2. SSR Testing in acidic Solution at ambient Temperature
B.1.3. SSR Testing in acidic Solution at 60°C
B.1.4. SSR Testing in acidic Solution at 90°C
Table. B.1. SSR Test Results for Zr705

<table>
<thead>
<tr>
<th>Environment / Temperature (°C)</th>
<th>Sample #</th>
<th>$\sigma_{th}$, ksi</th>
<th>% El</th>
<th>% RA</th>
<th>TTF, hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air / RT</td>
<td>Sample 1</td>
<td>125.96</td>
<td>30.78</td>
<td>60.97</td>
<td>28.42</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>124.97</td>
<td>32.90</td>
<td>60.73</td>
<td>29.04</td>
</tr>
<tr>
<td>Acidic / RT</td>
<td>Sample 1</td>
<td>117.23</td>
<td>31.90</td>
<td>59.38</td>
<td>29.22</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>124.01</td>
<td>32.30</td>
<td>61.26</td>
<td>29.85</td>
</tr>
<tr>
<td>Acidic / 60</td>
<td>Sample 1</td>
<td>113.17</td>
<td>33.93</td>
<td>60.29</td>
<td>30.19</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>116.99</td>
<td>34.52</td>
<td>61.21</td>
<td>31.17</td>
</tr>
<tr>
<td>Acidic / 90</td>
<td>Sample 1</td>
<td>107.04</td>
<td>34.10</td>
<td>61.39</td>
<td>31.88</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>104.59</td>
<td>35.19</td>
<td>61.43</td>
<td>32.10</td>
</tr>
</tbody>
</table>

RT: Room Temperature, Acidic (H$_2$SO$_4$ + NaI + H$_2$O)
B.2. SSR Testing on Nb7.5Ta

B.2.1. SSR Testing in Air

Sample 1

Sample 2
B.2.2. SSR Testing in acidic Solution at ambient Temperature

Sample 1

Sample 2
B.2.3. SSR Testing in acidic Solution at 90°C

Sample 1

Sample 2

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Table B.2. SSR Test Results for Nb7.5Ta

<table>
<thead>
<tr>
<th>Environment / Temperature (°C)</th>
<th>Sample #</th>
<th>% El</th>
<th>TTF, hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Air / RT</strong></td>
<td>Sample 1</td>
<td>48.90</td>
<td>42.81</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>48.92</td>
<td>42.55</td>
</tr>
<tr>
<td><strong>Acidic / RT</strong></td>
<td>Sample 1</td>
<td>46.01</td>
<td>41.12</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>45.95</td>
<td>39.98</td>
</tr>
<tr>
<td><strong>Acidic / 90</strong></td>
<td>Sample 1</td>
<td>45.4</td>
<td>40.31</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>44.7</td>
<td>39.79</td>
</tr>
</tbody>
</table>

RT: Room Temperature, Acidic (H₂SO₄ + NaI + H₂O)

96
C.1. CPP curves for Zr705

C.1.1. CPP diagrams at 30°C

Sample 1
Zr705
Acidic: $\text{H}_2\text{SO}_4 + \text{NaI} + \text{H}_2\text{O}$

$E_{\text{corr}} = 282 \text{ mV}$

Sample 2

C.1.2. CPP diagrams at 60°C

Zr705
Acidic: $\text{H}_2\text{SO}_4 + \text{NaI} + \text{H}_2\text{O}$

$E_{\text{corr}} = 237 \text{ mV}$

Sample 1
C.1.3. CPP diagrams at 90°C

Sample 2

Sample 1

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Zr705
Acidic: $\text{H}_2\text{SO}_4 + \text{NaI} + \text{H}_2\text{O}$

Table C.1. Open Circuit Voltage for Zr705

<table>
<thead>
<tr>
<th>Test Temperature, °C</th>
<th>Sample #</th>
<th>$E_{corr}$, mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>Sample 1</td>
<td>278</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>282</td>
</tr>
<tr>
<td>60</td>
<td>Sample 1</td>
<td>237</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>238</td>
</tr>
<tr>
<td>90</td>
<td>Sample 1</td>
<td>194</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>196</td>
</tr>
</tbody>
</table>
C.2. CPP curves for Nb7.5Ta

C.2.1. CPP diagrams at 30°C

Sample 1

Sample 2

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C.2.2. CPP diagrams at 60°C

Sample 1

Sample 2

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C.2.3. CPP diagrams at 90°C

**Sample 1**

- **Nb7.5Ta**
- Acidic: \( \text{H}_2\text{SO}_4 + \text{NaI} + \text{H}_2\text{O} \)
- \( E_{\text{pit}} = 401 \text{ mV} \)
- \( E_{\text{corr}} = 48 \text{ mV} \)

**Sample 2**

- **Nb7.5Ta**
- Acidic: \( \text{H}_2\text{SO}_4 + \text{NaI} + \text{H}_2\text{O} \)
- \( E_{\text{pit}} = 391 \text{ mV} \)
- \( E_{\text{corr}} = 43 \text{ mV} \)

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Table C.2. Critical Potentials for Nb7.5Ta

<table>
<thead>
<tr>
<th>Test Temperature, °C</th>
<th>Sample #</th>
<th>$E_{\text{corr}}, \text{mV}$</th>
<th>$E_{\text{pit}}, \text{mV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>Sample 1</td>
<td>133</td>
<td>525</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>127</td>
<td>517</td>
</tr>
<tr>
<td>60</td>
<td>Sample 1</td>
<td>93</td>
<td>420</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>91</td>
<td>415</td>
</tr>
<tr>
<td>90</td>
<td>Sample 1</td>
<td>48</td>
<td>401</td>
</tr>
<tr>
<td></td>
<td>Sample 2</td>
<td>43</td>
<td>391</td>
</tr>
</tbody>
</table>
Zr705 specimens were subjected to SSR testing under both cathodic and anodic control potential ($E_{\text{cont}}$) testing. All $E_{\text{cont}}$ tests were conducted at room temperature in an acidic solution (pH~1) containing sodium iodide, sulfuric acid and deionized water.

D.1. CATHODIC CONTROL POTENTIAL DATA

D.1.1. $E_{\text{cont}}$ at -20mV
D.1.2. $E_{\text{cont}}$ at -320mV
Table D.1. SCC Parameters under Cathodic E$_{cont}$

<table>
<thead>
<tr>
<th>Sample #</th>
<th>$E_{cont}$, mV</th>
<th>$\sigma_t$, ksi</th>
<th>%El</th>
<th>%RA</th>
<th>TTF, hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>-20</td>
<td>113.60</td>
<td>28.45</td>
<td>54.25</td>
<td>27.28</td>
</tr>
<tr>
<td>Sample 2</td>
<td>-20</td>
<td>113.09</td>
<td>29.43</td>
<td>52.32</td>
<td>26.47</td>
</tr>
<tr>
<td>Sample 1</td>
<td>-320</td>
<td>109.43</td>
<td>24.70</td>
<td>53.86</td>
<td>23.52</td>
</tr>
<tr>
<td>Sample 2</td>
<td>-320</td>
<td>110.61</td>
<td>25.95</td>
<td>54.82</td>
<td>24.28</td>
</tr>
</tbody>
</table>
D.2. ANODIC CONTROL POTENTIAL DATA

D.2.1. $E_{\text{cont}}$ at +880mV

![Graph showing stress vs. strain for Sample 1 at $E_{\text{cont}}$ of +880mV.]

D.2.2. $E_{\text{cont}}$ at +1.03 V

![Graph showing stress vs. strain for Sample 1 at $E_{\text{cont}}$ of +1.03 V.]

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D.2.3. $E_{\text{cont}}$ at +1.18 V
Sample 2

Table D.2. SCC Parameters under Anodic $E_{cont}$

<table>
<thead>
<tr>
<th>Sample #</th>
<th>$E_{cont}$, mV</th>
<th>$\sigma_t$, ksi</th>
<th>%EI</th>
<th>%RA</th>
<th>TTF, hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>+880</td>
<td>114.82</td>
<td>28.29</td>
<td>54.90</td>
<td>27.20</td>
</tr>
<tr>
<td>Sample 1</td>
<td>+1030</td>
<td>113.63</td>
<td>28.08</td>
<td>55.47</td>
<td>27.65</td>
</tr>
<tr>
<td>Sample 2</td>
<td>+1030</td>
<td>113.18</td>
<td>27.30</td>
<td>53.16</td>
<td>26.12</td>
</tr>
<tr>
<td>Sample 1</td>
<td>+1180</td>
<td>109.19</td>
<td>26.68</td>
<td>53.07</td>
<td>25.01</td>
</tr>
<tr>
<td>Sample 2</td>
<td>+1180</td>
<td>110.95</td>
<td>26.77</td>
<td>50.68</td>
<td>25.65</td>
</tr>
</tbody>
</table>
APPENDIX E

UNCERTAINTY ANALYSES

Every experiment in this investigation was performed with utter care in order to generate accurate results. Efforts were made to conduct duplicate tests, thus, the final results were the average to the number of tests conducted. However, each experimental technique may have a level of uncertainty related to the setup itself. This uncertainty may be due to the errors in the machine, human errors and/or environmental factors. Thus, the results generated may also have a certain degree of uncertainty. In order to reduce this amount of uncertainty, from the machine itself, all the experimental setups at Materials Performance Laboratory was calibrated on a timely basis, thus establishing standards. However, the uncertainties from human error and environmental effects can be minimized, not avoided. Hence, efforts were made to determine the uncertainty levels of results derived from different experimental techniques.

A model described by Kline and McClintock \(^{37}\) is being used to calculate the uncertainties of different parameters in this section. This method is known to be one of the precise methods to estimate uncertainties in experimental results since it requires careful specifications of the uncertainties in the various primary experimental measurements.\(^{37}\)
The slow-strain-rate experimental setup used in this investigation had a maximum load-cell reading of 7500 lbs ± 0.3% lbs. The reading on the load scale is thus uncertain to some extent which is expressed as a deviation either in the positive side or the negative side from the standard maximum value. Periodical and frequent calibration of the instrument may reduce this uncertainty. It should however be noted that the level of uncertainty is also dependent on the calibration standard. Calibration of instruments using high precision standards will lead to lower level of uncertainty compared to that performed using gages or instruments of unknown calibration.

Since, all the test units at MPL were recently calibrated as indicated before, the results derived for these experiments are expected to have low uncertainties. The equation suggested by Kline and McClintock for uncertainty analysis is shown below. The uncertainty levels calculated are based on this relationship.

\[ W_R = \left[ \left( \frac{\partial R}{\partial x_1} w_1 \right)^2 + \left( \frac{\partial R}{\partial x_2} w_2 \right)^2 + \cdots + \left( \frac{\partial R}{\partial x_n} w_n \right)^2 \right]^{1/2} \]  

(E.1)

Where, \( W_R \) = Uncertainty in the results

\( R \ = \) Given function of the independent variables \( x_1, x_2, \ldots x_n \)

\( R = R(x_1, x_2, \ldots x_n) \)

\( w_1, w_2, \ldots w_n = \) Uncertainty in the independent variables
E.1. Uncertainty Calculation for Parameters Derived from MTS Results

The different parameters calculated using the data generated by the MTS units includes, stress ($\sigma$), percentage elongation (%$E_1$), and percentage reduction in area (%$RA$). Stress $\sigma$ is calculated using the equation E.2. %$E_1$ is based on the change in length ($\Delta l$) of the specimen, which is calculated using equation 3.1. Similarly %$RA$ is calculated based on the initial and final cross-sectional areas ($A_i$ and $A_f$) of the tested specimen according to the equation 3.2.

$$\sigma = \frac{P}{A_i}$$ (E.2)

Where P = load

$A_i$ = initial Area

The magnitude of P was directly obtained from the load-cell of the MTS unit. However, the values for $\Delta l$, $A_i$, and $A_f$ were calculated based on the final and initial dimensions of the tested specimens measured by a caliper. The uncertainties in load-cell and caliper were ± 0.03% lbs and ± 0.001 in, respectively. These values were obtained from the calibration.

E.1.1. Calculation of Uncertainty in Stress ($U_\sigma$)

$$U_\sigma = U(P, A_i)$$

$$U_{A_i} = (U_{\Delta l})^2$$

Uncertainty in load-cell = ± 0.03% lb

Uncertainty in caliper = ± 0.001 in
Sample calculation:

For yield stress (YS) \(= 64.51 \text{ ksi}\)

The measured load (P) \(= 3131.26\)

Uncertainty in load \((U_p)\) \(= 3131.26 \times 0.0003\)

\(= \pm 0.939\)

Uncertainty in cross-sectional area \((U_{ai})\) for the smooth specimen:

Measured initial Diameter \((D_i)\) \(= 0.2486 \text{ in}\)

Uncertainty in diameter \((U_{Di})\) \(= \pm 0.001 \text{ in}\)

\[
\frac{\pi D_i^2}{4} \quad \text{Area (A)} = 0.0485
\]

\[
\frac{dA_i}{dD_i} = \frac{\pi D_i}{2}
\]

\(= 0.39\)

\[
U_{ai} = \left[ \left( \frac{dA_i}{dD_i} \cdot U_{Di} \right)^2 \right]^{\frac{1}{2}}
\]

Uncertainty in area,

\(= 0.393 \times 0.001\)

\(= \pm 0.00039\)

\[
U_{\sigma} = \left[ \left( \frac{\partial \sigma}{\partial P} \cdot P \right)^2 + \left( \frac{\partial \sigma}{\partial A_i} \cdot A_i \right)^2 \right]^{\frac{1}{2}}
\]

(E.2)

Uncertainty in stress,

\[
\frac{\partial \sigma}{\partial P} = \frac{1}{A_i}
\]

\(= 20.62\)
\[ \frac{\partial \sigma}{\partial A_i} = \frac{P}{A_i^2} \]

= -1331176.53

Substituting these values in equation E.1,

\[ U_\sigma = \left[ \left( 20.62 \times 0.939 \right)^2 + \left( 1331176.53 \times 0.00039 \right)^2 \right]^{\frac{1}{2}} \]

= 519.52 psi

= ± 0.52 ksi

E.1.2. Calculation of Uncertainty in Percentage Elongation (U\%El)

Sample calculation:

Change in length (\(\Delta l\)) = 0.3233 in

Gage length (l) = 1.00 in

\%

\%El = \frac{\Delta l}{l} \times 100

Uncertainty in \(\Delta l\) (U\(\Delta l\)) = ± 0.001

Uncertainty in \%El (U\%El),

\[ U_{\%El} = \left[ \left( \frac{d\%El}{d\Delta l} \times \Delta l \right)^2 \right]^{\frac{1}{2}} \]  

(E.3)

\[ \frac{d\%El}{d\Delta l} = \frac{100}{l} \]

= 100

Substituting the values in equation E.3,

\[ U_{\%El} = \left[ \left( 100 \times 0.001 \right)^2 \right]^{\frac{1}{2}} \]

\[ U_{\%El} = ± 0.1 \]
E.1.3. Calculation of Uncertainty in Percentage Reduction in Area ($U_{\%RA}$)

Sample calculation:

For $\%RA = 57.92\%$

From section E.1,

Uncertainty in initial cross-sectional area ($U_{A_i}$) = $\pm 0.00039$,

Uncertainty in final cross-sectional area ($U_{A_f}$):

Final Diameter ($D_f$) = 0.2045 in

Uncertainty in final diameter ($U_{D_f}$) = $\pm 0.001$ in

Uncertainty in final cross-sectional area, 

$$\frac{\pi D_f^2}{4}$$

$$A_i = 0.0328$$

$$\frac{dA_f}{dD_f} = \frac{\pi D_f}{2}$$

$$= 0.321$$

Uncertainty in final cross-sectional area, 

$$U_{A_f} = \left[\left(\frac{dA_f}{dD_f} * U_{D_f}\right)^2\right]^{1/2}$$

$$= 0.0328 * 0.001$$

$$= 0.000328$$

Uncertainty in $U_{\%RA}$,

$$U_{\%RA} = \left[\left(\frac{\partial \%RA}{\partial A_i} * U_{A_i}\right)^2 + \left(\frac{\partial \%RA}{\partial A_f} * U_{A_f}\right)^2\right]^{1/2}$$ (E.4)
\[
\%RA = \left( \frac{A_i - A_f}{A_i} \right) \times 100
\]

\[
= \left( 1 - \frac{A_f}{A_i} \right) \times 100
\]

\[
\frac{\partial \%RA}{\partial A_i} = \frac{100A_f}{A_i^2}
\]

\[
= 1394.095
\]

\[
\frac{\partial \%RA}{\partial A_f} = -\frac{100}{A_i}
\]

\[
= -2060.193
\]

Substituting the values in equation E.4,

\[
U_{\%RA} = \left[ (1394.095 \times 0.000393)^2 + (-2060.193 \times 0.0000328)^2 \right]^\frac{1}{2}
\]

\[
= 0.552
\]

E.2. Uncertainty Calculation for Parameters Derived from SSR Results

E.2.1. Calculation of Uncertainty in Time-to-failure (U_{TTF})

The TTF is obtained from the Field Point software of the SSR unit, which is accurate up to 1/100th of a second in finding the TTF. Therefore, the uncertainty of the TTF in the SSR testing is negligible.
E.3 Uncertainty Calculation for Parameters Derived from CPP Results

The uncertainty of the potentiostat provided by the manufacturer is ± 0.003 mV within a range of 1 mV.

Sample calculation:

For corrosion potential \( (E_{\text{corr}}) = 278 \text{ mV} \)

The uncertainty in \( E_{\text{corr}} = 278 \times 0.003 \)

\[ = \pm 0.834 \]
BIBLIOGRAPHY


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http://www.cortest.com


22. Slow-Strain-Rate Testing, Corrosion Source Website
http://www.corrosionsource.com/handbook/testing/ssrt.htm


VITA

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• Ancila Kaiparambil and et al., “Corrosion Behavior of Candidate Materials for Hydrogen Generation,” ANS Student Conference, April 14 - 16th, 2005, Columbus, Ohio, USA.


Thesis Title: “Characterization of Structural Materials for Applications in Hlx Decomposition.”

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