Metallurgical and corrosion characterization of structural materials for S-I cycle

Radhakrishnan Santhanakrishnan
University of Nevada, Las Vegas

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METALLURGICAL AND CORROSION CHARACTERIZATION OF STRUCTURAL
MATERIALS FOR S-I CYCLE

by

Radhakrishnan Santhanakrishnan
Bachelor of Engineering in Mechanical Engineering
University of Madras, India
May 2003

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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Thesis Approval
The Graduate College
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November 16, 2005

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Radhakrishnan Santhanakrishnan

Entitled
Metallurgical and Corrosion Characterization of Structural Materials
for S-I Cycle.

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

Examination Committee Member

Dean of the Graduate College

Examination Committee Member

Graduate College Faculty Representative
ABSTRACT

Metallurgical and Corrosion Characterization of Structural Materials for S-I Cycle

by

Radhakrishnan Santhanakrishnan

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

Tensile testing involving Alloy C-22 and Nb1Zr exhibited reduced strength with increasing temperature within a range relevant to the H1x decomposition process. A reduction in failure strain was however, noted, at 100°C possibly due to dynamic strain ageing effect. Even though the ductility parameters were not influenced by the change in temperature in stress-corrosion-cracking (SCC) testing in an acidic solution the true failure stress in this alloy was reduced appreciably. Nb1Zr did not exhibit any conventional SCC pattern. The critical potentials for localized corrosion in both alloys became more active at higher temperatures. No cracking was observed with C-ring and U-bend specimens of Alloy C-22 in a similar environment at 150°C. The corrosion rate of Alloy C-22 was gradually reduced for exposure up to 28 days followed by an enhancement at a longer duration. The characterization of primary fracture surface of cylindrical specimens used in tensile and SCC testing exhibited dimpled microstructure, indicating ductile failures.
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CHAPTER 1

INTRODUCTION

The energy consumption in developing and developed nations is increasing at an alarming rate. Energy derived from the fossil fuels such as oil and gas have been extensively used for the past 100 years \cite{1}. However, there is a significant disparity between the supply and demand of such type of fossil fuels. In addition, the combustion products from fossil fuels are also leading to the greenhouse effect causing global warming. In order to circumvent the problems associated with the tight fuel supply, rising cost and the environmental degradations, the United States Department of Energy (USDOE) is considering the development of an alternate source of energy, which would be environment-friendly and cost effective for commercial applications. One such energy is hydrogen that may be commercially generated in a cost effective manner, thus eliminating the dependence of energy requirements on foreign oil and gas while still maintaining the environmental ecology.

Hydrogen can be generated by many different techniques. A common method of hydrogen generation is steam reforming that involves the reaction of steam with a hydrocarbon over a catalyst at around 750-800\degree C to form hydrogen and substantial amount of carbon dioxide. A different technique based on electrolysis involves the dissociation and separation of hydrogen and oxygen from water molecules. However, the
cost of electricity needed to produce hydrogen by this method may be not high, thus, rendering this process unrealistic. Biological production of hydrogen by algae and bacteria has also been explored, resulting in hydrogen production by fermentation. However, this method is not feasible in view of its slow production rate and the necessity of larger areas for cultivation of bacteria. Apart from looking into all these methods, the USDOE has been proposing an innovative method of hydrogen generation using heat from the existing nuclear power plants.

The nuclear hydrogen generation, envisioned by the USDOE, will be based on thermochemical water splitting cycles using high temperature from nuclear reactors and consisting of a series of chemical reactions. An illustration of hydrogen generation using nuclear power is shown in Figure 1.1. The heat generated from nuclear power plant will be transferred to the hydrogen generating plant through an intermediate heat exchanger, as shown in this figure. The chemicals to be used in these cycles will be chosen to create a closed loop, where water can be fed to the process, oxygen and hydrogen gases are collected and all other reactants are regenerated and recycled. Even though numerous thermochemical water splitting cycles have been identified by the Nuclear Energy Research Institute (NERI), two most promising cycles have been selected for further research and development due to the simplicity of these cycles, their efficiency and the ability to separate hydrogen in the most viable manner. These two thermochemical processes for hydrogen generation are the sulfur iodine (S-I) and calcium bromine (Ca-Br). Even though the high temperature electrolysis (HTE) may be considered in future by the USDOE, a major emphasis is currently being placed on the thermochemical processes alone, instead of HTE. This investigation is primarily focused on the applicability of the
S-I cycle for nuclear hydrogen generation. While some discussions on the Ca-Br cycle and HTE are attempted in the following sections, a detailed discussion on the S-I cycle will be given next.

The SI process, which involves a water-splitting cycle, was originally developed by the General Atomics Corporation (GA). This process consists of three chemical reactions that sum to the dissociation of water using iodine (I\textsubscript{2}) and sulfur dioxide (SO\textsubscript{2}) as chemical catalysts. Initially water reacts with I\textsubscript{2} and SO\textsubscript{2} at approximately 120°C to form hydrogen iodide (HI) and sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) according to the reaction shown in Equation 1.1. This reaction is known as the “Bunsen Reaction”. HI and H\textsubscript{2}SO\textsubscript{4} are subsequently separated from each other. I\textsubscript{2} and SO\textsubscript{2} are then recovered from HI and H\textsubscript{2}SO\textsubscript{4} and recycled. Hydrogen and Oxygen gases are then collected separately as shown in Figure 1.2.

![Figure 1.1 Typical Nuclear Hydrogen Generation Concept.](image-url)
The reaction that involves the highest heat input is the thermal decomposition of sulfuric acid occurring at approximately 850°C, as shown in reaction 1.2. The utilization of such a high temperature is necessary to ensure the production of larger quantity of hydrogen in a cost-effective manner since the efficiency of hydrogen generation may be reduced drastically at lower temperatures. Finally the reaction 1.3 occurs at a temperature of approximately 400°C resulting in the production of hydrogen and iodine from hydrogen iodide. The reactions involved in SI cycle are shown in the Figure 1.2.

Figure 1.2 SI cycle
The decomposition of HI can be accomplished by two methods, namely reactive distillation and extractive distillation. The former process involves heating of HI, I₂ and H₂O (HIₓ) at temperatures of approximately 400°C leading to the boiling of HI gas and spontaneous decomposition into H₂ and I₂ at the top of the reactive column. The reactive distillation process has been preferred to the second process due to its simplicity and efficiency, thus, requiring relatively less complex processing hardware. However, this reaction occurs at high temperature and pressure (400°C and 50 bar respectively), which can produce a very hostile corrosive environment. Thus, the selection of the suitable containment material is a major challenge.

The second process used in HI decomposition involves phosphoric acid extraction in which phosphoric acid is added to HIₓ to extract H₂O from it. The HI gas is then separated from the mixture of HI and I₂. This method involves numerous steps including phosphoric acid separation and concentration that makes this process relatively expensive. However the extractive process needs much lower temperature, thus, placing significantly less emphasis on the materials requirements in successful production of hydrogen.

While this investigation is primarily focused on the applicability of the SI cycle for hydrogen generation using nuclear power, another thermochemical method based on Ca-Br cycle has also been investigated by researchers at Japan Atomic Energy Research Institute (JAERI). This cycle consists of several sets of reactions at much lower temperature leading to the formation of hydrobromic acid and reduction of water by bromide. However, the efficiency of hydrogen production by this method is limited to only 40%. Compared to the thermochemical processes, hydrogen generation by high
temperature electrolysis of steam occurs at a much higher temperature. This process however, is beyond the scope of the current investigation.

Based on the preceding discussion it is obvious that the structural materials to be used in the SI system must withstand elevated temperatures (120°C - 800°C), presence of damaging chemical species and acidic solution having a pH of 1 or less. Under such hostile operating conditions, the structural materials may become susceptible to environment assisted degradations including general corrosion, localized corrosion, stress corrosion cracking (SCC) and/or hydrogen embrittlement (HE). Further they can undergo plastic deformation at elevated temperatures. Therefore, the identification and selection of candidate structural materials should be based on their capabilities to sustain the operating conditions and maintain structural stability at elevated temperature without any undesirable plastic deformation.

This investigation is primarily focused on the identification and characterization of structural materials for nuclear hydrogen generation by the Hlx decomposition process. Nickel-based alloy C-22 and refractory materials such as Zr705, Nb1Zr, and Nb7.5Ta have been recommended by the materials advisory board for such an application. Corrosion studies involving these alloys are in progress in a Hlx environment at the GA research facility. Since, corrosion studies involving these alloys could not be performed in the presence of Hlx environment at UNLV, extensive corrosion studies have been performed at the material performance laboratory (MPL) of UNLV in simulated aqueous environments. Further, metallurgical characterization including tensile properties evaluation at different temperatures relevant to the Nuclear Hydrogen Initiative (NHI) has been performed.
This thesis presents the results of tensile testing of Ni-based alloy C-22 and refractory material Nb1Zr at temperatures ranging from ambient to 400°C, which is relevant to the hydrogen generation process using HIx decomposition. The susceptibility of both materials to SCC has also been determined in a simulated acidic solution at ambient and elevated temperatures. The role of applied potential on the cracking susceptibility has also been investigated. In addition, the susceptibility of both alloys to localized attack such as pitting and crevice corrosion has been determined by an electrochemical polarization technique. The general corrosion behavior and the cracking susceptibility using self-loaded specimens have been studied at elevated temperature using an autoclave. The characterization of metallurgical microstructure has been conducted by optical microscopy. Further, the extent and morphology of failure in specimens used in the tensile and corrosion testing have been determined by scanning electron microscopy. The comprehensive test results based on metallurgical and corrosion testing are presented in this thesis.
2.1 Test Material

The structural materials for the construction of HTHX will be identified and selected based on their ability to meet service and design requirements, and be fabricated and assembled according to the industry standard. The material's ability to meet the desired requirements will be determined by mechanical, physical and corrosion properties, as well as their forming, shaping and bonding capabilities, as determined by applicable methods.

The materials identified for this investigation were an austenitic nickel (Ni) base Alloy C-22 and a refractory material containing Niobium and Zirconium (Nb1Zr). Hastelloy C-22 was originally developed by the Hayne’s International Inc. The Ni-base alloys have been extensively used in numerous industrial applications such as petrochemical, power generation and pharmaceutical due to their exceptional capabilities to withstand severe operating conditions including highly corrosive environment, elevated temperatures, high stresses and a combination of all these factors. The presence of Ni and the resultant face-centered-cubic (FCC) structure of this alloy provide enhanced ductility and toughness at significantly high temperatures. Further, the presence of chromium (Cr), and molybdenum (Mo) can render this alloy highly resistant to corrosion in many hostile environments \[^2\]. Alloy C-22 can also prevent sensitization and
intergranular corrosion due to the presence of very low carbon content. This alloy is also readily weldable and can be used in the as-welded condition without post-weld-thermal-treatment. The physical properties of Alloy C-22 are given in Table 2.1.

Table 2.1 Physical Properties of Hastelloy C-22

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>Temperature, °C</th>
<th>Metric Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>24</td>
<td>8.69 g/cm³</td>
</tr>
<tr>
<td>Melting Range</td>
<td>1357-1399</td>
<td>--</td>
</tr>
<tr>
<td>Electrical Resistivity</td>
<td>24</td>
<td>1.14 microhm-m</td>
</tr>
<tr>
<td>Mean Coefficient of Thermal Expansion</td>
<td>24-93</td>
<td>12.4 x 10⁻⁶ m/m.K</td>
</tr>
<tr>
<td>Thermal Diffusivity</td>
<td>21</td>
<td>2.7 x 10⁻⁶ m²/s</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>48</td>
<td>10.1 W/m.K</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>52</td>
<td>414 J/Kg.K</td>
</tr>
</tbody>
</table>

Cylindrical and round bars of alloy C-22 was procured from the Haynes International Inc. in a thermally-treated condition. The thermal treatment for this alloy consisted of solution annealing at temperatures ranging between 2000 and 2100 F (1093 to 1148 °C) followed by quenching. The chemical composition and the vendor-certified ambient temperature tensile properties of the test material are given in Tables 2.2 and 2.3 respectively.
Table 2.2 Chemical Composition of Alloy C-22 Tested (wt.%)

<table>
<thead>
<tr>
<th>Heat No.</th>
<th>Element</th>
<th>Ni</th>
<th>C</th>
<th>Co</th>
<th>Cr</th>
<th>Fe</th>
<th>Mn</th>
<th>Mo</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>V</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>2277</td>
<td>Bal</td>
<td>0.004</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3280</td>
<td>Bal</td>
<td>1.43</td>
<td>21.46</td>
<td>3.76</td>
<td>0.25</td>
<td>13.32</td>
<td>0.010</td>
<td>0.004</td>
<td>0.03</td>
<td>0.11</td>
<td>3.13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Bal: Balance

Table 2.3 Ambient Temperature Tensile Properties of Alloy C-22

<table>
<thead>
<tr>
<th>Heat #</th>
<th>Yield Strength, ksi (MPa)</th>
<th>Ultimate Tensile Strength, ksi (MPa)</th>
<th>%El</th>
<th>%RA</th>
</tr>
</thead>
<tbody>
<tr>
<td>2277</td>
<td>49.1 (339)</td>
<td>113 (779)</td>
<td>62</td>
<td>83</td>
</tr>
<tr>
<td>3280</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Nb1Zr is a low strength niobium alloy used at temperatures ranging from 1800-2200°F, where ease of manufacture and low cost are critical or in reactor applications, where the properties of the alloy are useful. Nb is a highly ductile and soft metal, which is highly corrosion resistant due to the formation of adherent and passive oxide film. In addition to being stable, the anodic niobium oxide film has a high dielectric constant and nobler breakdown potential. The typical physical properties of this alloy are given in Table 2.4.\(^5\)

Nb1Zr was procured from Wah Chang in a thermally treated and solution annealed condition. The chemical composition and the vendor-certified room temperature tensile properties of this alloy are given in Tables 2.5 and 2.6, respectively.
Table 2.4 Physical Properties of Nb1Zr

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>Temperature, °C</th>
<th>Metric Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>24</td>
<td>8.57 g/cm³</td>
</tr>
<tr>
<td>Melting Range</td>
<td>2468</td>
<td>--</td>
</tr>
<tr>
<td>Electrical Resistivity</td>
<td>24</td>
<td>15 microhm-m</td>
</tr>
<tr>
<td>Mean Coefficient of Thermal Expansion</td>
<td>20</td>
<td>7.1 x 10⁻⁶ /°C</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>1600</td>
<td>0.691 W/m.K</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>1227</td>
<td>.320 J/g</td>
</tr>
</tbody>
</table>

Table 2.5 Chemical Composition of Nb1Zr Tested (wt.%)

<table>
<thead>
<tr>
<th>Heat #</th>
<th>531137</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>Bal</td>
</tr>
<tr>
<td>C</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe</td>
<td>0.01</td>
</tr>
<tr>
<td>H</td>
<td>0.0015</td>
</tr>
<tr>
<td>Hf</td>
<td>0.02</td>
</tr>
<tr>
<td>Mo</td>
<td>0.05</td>
</tr>
<tr>
<td>N</td>
<td>0.01</td>
</tr>
<tr>
<td>Ni</td>
<td>0.005</td>
</tr>
<tr>
<td>O</td>
<td>0.025</td>
</tr>
<tr>
<td>Si</td>
<td>0.005</td>
</tr>
<tr>
<td>Ta</td>
<td>0.5</td>
</tr>
<tr>
<td>Ti</td>
<td>0.03</td>
</tr>
<tr>
<td>W</td>
<td>0.05</td>
</tr>
<tr>
<td>Zr</td>
<td>0.8-1.2</td>
</tr>
</tbody>
</table>

Bal: Balance

Table 2.6 Ambient Temperature Tensile Properties of Nb1Zr

<table>
<thead>
<tr>
<th>Heat #</th>
<th>Yield Strength, ksi (MPa)</th>
<th>Ultimate Tensile Strength, ksi (MPa)</th>
<th>%El</th>
<th>%RA</th>
</tr>
</thead>
<tbody>
<tr>
<td>531137</td>
<td>21.3 (147)</td>
<td>38 (262)</td>
<td>60</td>
<td>NA</td>
</tr>
</tbody>
</table>

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2.2 Test Specimens

The structural material to be used in heat exchangers for hydrogen generation must possess superior high temperature tensile properties and excellent corrosion resistance [6]. In view of these requirements specimens of different configurations were used to evaluate tensile and corrosion properties under conditions relevant to the nuclear hydrogen generation process. The tensile properties of both candidate materials were determined by using smooth cylindrical specimens having 4-inch (mm) overall length, 1-inch (mm) gage length and 0.25-inch (mm) gage diameter, maintaining the l/d ratio at 4, as prescribed by the ASTM Designation E 8 [7]. These specimens were machined from heat-treated round bars in such a way that the gage section was parallel to the longitudinal rolling direction. The geometric configuration and a pictorial view of smooth cylindrical specimens are shown in Figure 2.1 (a) & (b).

![Figure 2.1 (a) Pictorial view of the Tensile Specimen](image)
The susceptibility of both alloys to SCC in a simulated aqueous environment was also determined using smooth cylindrical specimen with a configuration shown in Figure 2.1. The susceptibility of both candidate structural materials to localized corrosion (pitting & crevice) was determined by using cylindrical specimen having smaller length and diameter with a central blind hole for holding with a stainless steel rod, as shown if Figure 2.2.

In addition to the cylindrical specimens mentioned above, self-loaded specimens such as C-ring and U-bend were used in this investigation, as illustrated in Figures 2.3 and 2.4, respectively. The C-ring is a versatile and economic type of specimen for quantitatively determining the susceptibility of a material to SCC of all types of alloys in a wide variety of product forms. It is particularly suitable for making transverse tests of tubing and rod
Figure 2.2 Schematic view of Polarization Specimen

and for making short-transverse tests of various products. The U-bend specimens were made by bending a rectangular strip at 180° around a pre-determined radius \[8\]. The U-bend and C-ring specimens were tested in the presence of an aqueous solution containing H\(_2\)SO\(_4\) inside an autoclave. The plastic strain imparted to the U-bend specimens during fabrication was maintained constant during SCC testing. The C-ring specimens were loaded to a desired applied stress level using an equation \[9\] shown below.

\[
\text{OD}_f = \text{OD} - \Delta, \text{ and} \\
\Delta = f \pi D^2 / 4 \pi E t Z
\]

Where,

\[
\begin{align*}
\text{OD} &= \text{outside diameter of C-ring before stressing, in (or mm),} \\
\text{OD}_f &= \text{outside diameter of stressed C-ring, in (or mm),} \\
f &= \text{desired stress, MPa (or psi) (within the proportional limit),}
\end{align*}
\]
Δ = change in OD giving desired stress, mm (or in.),

\( D = \) mean diameter (OD – t), mm (or in.),

t = wall thickness, mm (or in.),

E = modulus of elasticity, MPa (or psi), and

Z = a correction factor for curved beams.

Figure 2.3 C-ring Specimen

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Figure 2.4 U-bend Specimen
Attempts were also made to determine the weight loss of coupons made of Alloy C-22 in an identical aqueous solution containing sulfuric acid. The coupons were machined from the as-received plate materials. A circular hole of 0.25 in. diameter was machined near the top edge of the coupon to insert a glass rod having grooves to hold it in a glass sample holder while immersing it in the test solution contained in an autoclave. The configuration of coupons are shown in Figure 2.5

Figure 2.5 Configuration of the Coupon

2.3 Test Environment

As mentioned earlier, this investigation was primarily focused on the corrosion characterization of candidate structural materials for applications in the HIX environment. The experimental facility used at MPL is not capable of evaluation corrosion behavior in the presence of highly toxic HIX solution. However, GA is well-equipped to perform
corrosion testing in the presence of Hlx environment. While immersion testing involving different types of specimens are on going at GA, parallel testing involving Alloy C-22 and Nb\textit{Ir} was performed in two simulated aqueous environments. SCC testing using smooth cylindrical specimens was performed in an aqueous solution containing H$_2$SO$_4$ and sodium iodide (NaI) at 30 and 90° C. Simultaneously, localized corrosion studies by a polarization technique were performed in a similar environment 30, 60 and 90° C. However, autoclave testing involving C-ring, U-bend and coupons were performed in an aqueous solution containing H$_2$SO$_4$ only at 150° C. The chemical composition of both test solutions are given in Table 2.7

Table 2-7 Chemical Composition of Test Solutions (gram/liter)

<table>
<thead>
<tr>
<th>Solution (pH)</th>
<th>NaI</th>
<th>H$_2$SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic (1.0)</td>
<td>10.0</td>
<td>Added to adjust the desired pH</td>
</tr>
<tr>
<td>Acidic (1.0)</td>
<td>-</td>
<td>Added to adjust the desired pH</td>
</tr>
</tbody>
</table>
CHAPTER 3

EXPERIMENTAL PROCEDURES

The tensile properties of Hastelloy C-22 and Nb1Zr were evaluated at ambient and elevated temperatures by using an axial/torsional material testing system (MTS). The susceptibility of these alloys to SCC in an acidic environment was evaluated by using constant-load and slow-strain-rate (SSR) testing techniques at ambient temperature and 90°C. The electrochemical cyclic potentiodynamic polarization (CPP) method was used to evaluate the localized corrosion (pitting/crevice) behavior using a Gamry Potentiostat. SCC testing using self-loaded specimens and immersion testing using coupons were performed in an autoclave at 150°C. The coupons were used to determine the corrosion rate based on the resultant weight loss. Further, fractographic and metallographic evaluations were performed by SEM and optical microscopy, respectively. The detailed experimental techniques are given in the following subsections.

3.1. Tensile Testing

The tensile properties including the yield strength (YS), ultimate tensile strength (UTS), and the ductility in terms of percent elongation (%El) and reduction in area (%RA) were determined at ambient temperature, 100, 200, 300 and 400°C using an MTS model 319.25 unit. The smooth cylindrical specimens were strained in tension at a strain rate of $10^{-3}$/sec according to the ASTM Designation E8. [7] A minimum of two specimens were tested under each condition and the average value was recorded. The experimental
data such as the load, time, and extensometer reading were recorded in the data file at the rate of 100/sec. The engineering stress versus engineering strain diagrams were developed from these data. The magnitude of the YS at each temperature was determined by the point of intersection of a line drawn parallel to the linear portion of this curve at a strain offset value of 0.2% of strain. UTS and %El were also determined from this plot, and the dimensions of the cylindrical specimen before and after testing.

The MTS unit, shown in Figure 3.1, had an axial load transducer of 55 kip (250 kN) and a torsional load transducer of 20,000 lbf-in (2200 N-m) capacity. It had a hydraulically-controlled actuator with 5.5” stroke and approximately 55° angular rotation. It consisted of a large heavy-duty load frame with an adjustable crosshead attached to the wedge grip at the top, and a movable actuator with another wedge grip at the bottom to enable loading and unloading of the test specimen. The axial motion was controlled by force, displacement, or an external signal from the strain gage. The specimen was mounted between two wedge grips and was pulled by a movable actuator. The load cell, contained in the crosshead, measured the applied force on the tensile specimen. The movement of the crosshead relative to the locked crosshead generated the strain within the specimen and consequently, the corresponding load.

The MTS machine was equipped with an 8-channel signal-conditioning box for monitoring the strain gages, extensometers, and temperature sensors. Signals from this box were processed directly by the MTS control software programs (Test Star 790.00 v 4.0E and Test Ware SX v 4.0D) that automatically controlled all signals during testing. A laser extensometer having a scan rate of 100 scans/sec was added to this MTS unit to
measure the elongation of the gage section of test specimen during plastic deformation under tensile loading.

![Figure 3.1 Tensile Testing Setup](image)

The MTS unit was modified to accommodate high-temperature testing in the presence of nitrogen using a ceramic-lined custom-made chamber. The testing temperature inside this chamber was monitored by two K-type thermocouples. A pair of custom-built water-cooled specimen grips made of maraging steel (M250) was attached to the MTS machine to prevent these grips from being heated during testing at elevated temperatures. Temperature profiles were developed to determine the times needed to achieve the
desired test temperatures as a part of the furnace calibration process. The resultant times and the environment chamber set point temperatures for different target temperatures in the presence of nitrogen gas at 20 bar on Argon scale are shown in Table 3-1. It should, however, be noted that testing was performed at 100, 200, 300 and 400°C in the presence of nitrogen.

Table 3.1 Minimum Time to Reach the Desired Temperature

<table>
<thead>
<tr>
<th>Material</th>
<th>Target temperature (°C)</th>
<th>Environmental chamber set point temperature (°C)</th>
<th>Minimum time to reach the target temperature (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy C-22</td>
<td>100</td>
<td>143</td>
<td>60</td>
</tr>
<tr>
<td>Nb1Zr</td>
<td>300</td>
<td>363</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>467</td>
<td>55</td>
</tr>
</tbody>
</table>

3.2. Constant-load Testing

A calibrated proof ring made by Cortest Inc. was used for constant-load (CL) testing. The proof rings were specifically-designed to meet the National Association of Corrosion Engineers (NACE) standard TM-01-77. Each proof ring was accompanied by a calibration curve showing the load versus deflection of the ring. The test specimens were loaded under a stress state of uniaxial tension. The ring deflection was measured with a 8-9" diameter micrometer, with the supplied dial indicator providing a check. The proof rings were fabricated from precision-machined alloy steel. Tension on the proof ring was quickly and easily adjusted using a standard wrench on the tension-adjusting screw and lock nut. A thrust bearing distributed the load and prevented seizure. Specimen grips in
these proof rings were made of stainless steel, fully-resistant to the desired testing environments. The environmental test chamber was secured with O-ring seals that prevented any leakage during testing. The environmental chambers made of highly corrosion-resistant Hastelloy C-276 were used for testing at elevated temperatures. The experimental setup is shown in Figure 3.2.

![Figure 3.2 Constant-load Test Setup](image)

The amount of deflection needed to apply the desired load in the CL testing was determined by use of the calibration curve of each proof ring, as shown in Figure 3.3. The magnitude of the applied stress was based on the ambient temperature tensile YS of the test material. The specimens were loaded at stress values equivalent to different percentages of the test material’s YS value, and the corresponding time-to-failure (TTF) was recorded. The determination of the SCC tendency using this technique was based on the TTF for the maximum test duration of 30 days. An automatic timer attached to the
test specimen recorded the TTF. The cracking susceptibility was expressed in terms of a threshold stress ($\sigma_{th}$) below which cracking did not occur during the maximum test duration of 30 days.\textsuperscript{[11]}

\[ y = 54171x - 257.54 \]

\[ R^2 = 0.9964 \]

Figure 3.3 A Typical Calibration Curve of a Proof Ring

3.3. Slow-Strain-Rate Testing

Slow-strain-rate (SSR) testing was performed using a specially-designed system known as a constant-extension-rate-testing (CERT) machine, as shown in Figure 3.4. The CERT machines enabled testing to simulate a broad range of load, temperature, strain-rate and environmental conditions using both mechanical and electrochemical corrosion testing techniques. These machines, designed and manufactured by the Cortest Inc.,
offered accuracy and flexibility in testing the effect of strain rate, providing up to 7500 lbs of load capacity with linear extension rates ranging from $10^5$ to $10^8$ in/sec. To ensure the maximum accuracy in test results, this apparatus was comprised of a heavy duty load-frame that minimized the system compliance while maintaining precise axial alignment of the load train. An all-gear drive system provided consistent extension rate. Added features included a quick-hand wheel to apply a pre-load prior to the operation.

![CERT Machine for SSR Testing](image)

**Figure 3.4 CERT Machine for SSR Testing**

The SSR test setup used in this investigation consisted of a top-loaded actuator, testing chamber, linear variable differential transducer (LVDT) and load cell as shown in Figure 3.5. The top-loaded actuator was intended to pull the specimen at a specified strain rate so that the spilled solution, if any, would not damage the actuator. A heating coil was connected to the bottom cover of the environmental chamber for elevated-temperature testing. A thermocouple was connected through the top cover of this chamber to monitor
the testing temperature. The load cell was intended to measure load through an interface with the front panel. The LVDT was used to record the displacement of the gage section during testing.

![Figure 3.5 SSR Test Setup](image)

Prior to the performance of SCC testing by the SSR technique, the load-frame-compliance factor (LFCF), which indicates the deflection in the frame per unit load, was determined by using a ferritic Type 430 stainless steel specimens. The generated LFCF data are shown in Figure 3.6. These LFCF values were given to the load frame acquisition system prior to the SCC testing.

The SCC phenomenon is a consequence of two major factors including the applied or residual stress and a potent environment. If the stress is applied to the specimen at a very fast rate while it is exposed to the aqueous environment, the resultant failure may not be different from the typical mechanical deformation produced without an environment. Conversely, if the strain rate is too slow, the resultant failure may simply be attributed to
the corrosion damage due to the breakdown of the protective surface film by interaction of the test material with the susceptible environment.

![Graph showing compliance test data](image)

Figure 3.6 Load Frame Compliance Test

A strain rate of $3.3 \times 10^{-6}$ sec$^{-1}$ was used to evaluate the combined effect of the applied load and the environment, during the SCC testing. The selection of this optimum strain rate was based on the results of SSR testing obtained at the Lawrence Livermore National Laboratory (LLNL). The specimen was continuously strained in tension until fracture, according to the ASTM Designation G 129, in contrast to more conventional SCC test conducted under a sustained loading condition. The application of a slow dynamic straining during the SSR testing to the specimen caused failure that probably might not occur under a constant load or might have taken a prohibitively longer duration to initiate cracks in producing failures in the tested cylindrical specimens.
Load versus displacement and stress versus strain curves were plotted during these tests. Dimensions (length and diameter) of the test specimens were measured before and after testing. The cracking tendency of the test specimen was expressed by the time-to-failure (TTF), and a number of ductility parameters such as %El and %RA. Further, the true failure stress ($\sigma_f$) determined from the stress-strain diagram and the final dimensions were taken into consideration to characterize the cracking tendency. The magnitudes of %El, %RA and $\sigma_f$ were calculated using the following equations:

\[
\% El = \left( \frac{L_f - L_o}{L_o} \right) \times 100 \tag{Equation 3.1}
\]

\[
\% RA = \left( \frac{A_o - A_f}{A_o} \right) \times 100 \tag{Equation 3.2}
\]

\[
\sigma_f = \frac{P_f}{A_f} \tag{Equation 3.3}
\]

\[
A_o = \frac{\pi \times D_o^2}{4} \tag{Equation 3.4}
\]

\[
A_f = \frac{\pi \times D_f^2}{4} \tag{Equation 3.5}
\]

Where,

$A_0$ = Initial cross sectional area

$A_f$ = Final cross sectional area at failure

$P_f$ = Failure load

$\sigma_f$ = True Failure Stress

$L_o$ = Initial length
L_f = Final length
D_o = Initial diameter
D_f = Final diameter

3.4. Cyclic Potentiodynamic Polarization Testing

The susceptibility of Hastelloy C-22 and Nb1Zr to localized (pitting and crevice) corrosion was determined by performing CPP experiments in the acidic solution using a Model PCI4 GAMRY potentiostat. The CPP testing was based on a three-electrode-polarization concept, in which the working electrode (specimen) acted as an anode and two graphite electrodes (counter electrodes) acted as cathodes as shown in Figure 3.7. The reference electrode was made of Ag/AgCl solution contained inside a Luggin probe having the test solution that acted as a salt-bridge. The tip of the Luggin probe was placed within a distance of 2 to 3 mm from the test specimen as shown in Figure 3.8.

Figure 3.7 Electrochemical Testing Setup
At the onset of the CPP testing, the corrosion or the open circuit potential ($E_{corr}$) of the specimen was determined with respect to the Ag/AgCl reference electrode, followed by forward and reverse potential scans at the ASTM specified \cite{17} rate of 0.17 mV/sec. An initial delay time of 50 minutes was given for attaining a stable $E_{corr}$ value. The magnitudes of the critical pitting potential ($E_{pin}$) and protection potential ($E_{prot}$), if any, were obtained from the CPP diagram. Prior to the CPP testing, the potentiostat was calibrated according to the ASTM Designation G 5. \cite{18} Calibration of the potentiostat was performed to generate a characteristic potentiodynamic polarization curve (Figure 3.9) using small cylindrical test specimens of ferritic Type 430 stainless steel in 1 Normal (1N) sulfuric acid ($H_2SO_4$) solution at 30°C.
3.5 Corrosion Testing in Autoclave

Efforts were made to determine the weight-loss of test coupons in a 150°C aqueous solution containing sulfuric acid. The test setup is shown in Figure 3.10. Duplicate coupons were exposed to the test solution for periods of 7, 14 and 28 days. Further, C-ring and U-bend were immersed for 28 days. The weights of the coupons, C-ring and U-bend before and after testing were measured, and weight loss was calculated as a function of exposure period. The corrosion rate of alloy C-22 was subsequently determined in terms of mils per year (mpy) according to Equation 3.6 [19]. Upon completion of exposure, the coupons were visually examined followed by microscopic examination to characterize the extent of corrosion damage.
Where, $W =$ weight loss in mg

$D =$ density in gm/cm$^3$ (for alloy C-22, $D= 8.18$)

$A =$ area in sq.in.

$T =$ time of immersion in hours

3.6 Metallography by Optical Microscope

The metallographic technique using an optical microscope enables the characterization of phases present, their distributions within grains and their sizes which depend on the typical chemical composition and thermal treatments performed on a
material of interest. Characterization of metallurgical microstructures of the test specimens before and after testing by optical microscopy is of paramount importance. The principle of an optical microscope is based on the impingement of a light source perpendicular to the test specimen. The contrast observed under the microscope results from either an inherent difference in intensity or wavelength of the light absorption characteristics of the phases present. It may also be induced by preferential staining or attack of the surface by etching with a chemical reagent.

The test specimens were sectioned and mounted using the standard metallographic technique, followed by polishing and etching to reveal the microstructures including the grain boundaries. The etchant composition for alloy C-22 is: 5% of 70% concentrated HNO₃ and 95% of Methanol. The polished and etched specimens were rinsed in deionized water, and dried with acetone and alcohol prior to their evaluation by a Leica optical microscope, shown in Figure 3.11. This microscope is capable of resolution of up to 1000X.

Figure 3.11 Leica Optical Microscope

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3.7 Fractographic Evaluation by SEM

The extent and morphology of failure in the tested specimens were determined by Scanning Electron Microscope (SEM). Analysis of failure in metals and alloys involves identification of the type of failure. The test specimens were sectioned into 1/2 to 3/4 of an inch in length to accommodate them in the vacuum chamber of the SEM. Usually, failure can occur by one or more of several mechanisms, including surface damage, such as corrosion or wear, elastic or plastic deformation and fracture. Failures can be classified as ductile or brittle. Dimpled microstructure is a characteristic of ductile failure. Brittle failure can be of two types, intergranular and transgranular. An intergranular brittle failure is characterized by crack propagation along the grain boundaries while a transgranular failure is characterized by crack propagation across the grains.

In a SEM, electrons from a metal filament are collected and focused, just like light waves, into a narrow beam. The beam scans across the subject, synchronized with a spot on a computer screen. Electrons scattered from the subject are detected and create a current, the strength of which makes the spot on the computer brighter or darker. This creates a photograph-like image with an exceptional depth of field. Magnifications of several thousand times are possible. Normally, SEM provides black and white micrographs. A JEOL-5600 scanning electron microscope, shown in Figure 3.12, capable of resolution of up to 50 nm at magnifications of up to 100,000 times, was used in this study. The manual stage of this SEM can accommodate four 1 cm diameter samples or one sample with up to 3.2 cm diameter.
Figure 3.12 Scanning Electron Microscope
CHAPTER 4

RESULTS

This Chapter presents the results of both the metallurgical and corrosion studies performed on Alloy C-22 and Nb1Zr. Austenitic Alloy C-22 has been evaluated both at UNLV and GA for sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) decomposition and hydroiodic acid (HI\textsubscript{x}) decomposition, respectively. While, the GA results are unavailable on both the alloys, extensive work has been performed on Alloy C-22 to characterize its high temperature properties and corrosion resistance. In addition, a refractory alloy known as Nb1Zr has been included in this investigation for application in the HI\textsubscript{x} decomposition process.

The tensile properties of Alloy C-22 and Nb1Zr performed at temperatures relevant to the HI\textsubscript{x} decomposition process are presented in this chapter. The results of stress corrosion cracking and localized corrosion studies performed by the state-of-the-art experimental techniques in aqueous solutions at ambient and elevated temperatures have also been presented. Further, metallographic and fractographic evaluations of the tested specimens are included in this chapter.

4.1 Metallographic Evaluations

The optical micrographs of Alloy C-22 and Nb1Zr are shown in Figures 4.1 and 4.2, respectively in the etched condition. The etchant used for Alloy C-22 was a mixture of nitric acid (HNO\textsubscript{3}) and Methanol (CH\textsubscript{3}OH) in the ratio of 5:95. For Nb1Zr, the etchant
consisted of 60 volume % of hydrofloric acid (HF), 20 volume % of nitric acid (HNO₃) and 20 volume % of glycerol. An evaluation of these micrographs verified austenitic grains and annealing twins in nickel-based Alloy C-22 [20] while showing fully recrystallized structure resulting from annealing of Nb1Zr. [21]

Figure 4.1 Optical Micrograph of Alloy C-22, 5% HNO₃+95% Methanol, 50X

4.2 Optical Micrograph of Nb1Zr, 60% HF+20%HNO₃+20% glycerol, 200X.
4.2 Tensile Properties Evaluations

A maximum operating temperature of 400°C has been suggested for the HIx decomposition process. Accordingly, the tensile properties of both candidate alloys were determined at temperatures ranging between ambient and 400°C. For elevated temperature testing, the test chamber was filled with nitrogen to prevent contamination or formation of oxide layer on the specimen surface. The results of duplicate tensile testing of Alloy C-22 at each temperature are shown in Figure 4.3 in the form of engineering stress vs. strain (s-e) diagram, superimposed as a function of the testing temperature. An evaluation of these s-e diagrams reveals that the magnitude of yield strength (YS) and ultimate tensile strength (UTS) was gradually reduced with increasing temperature, as expected. However an interesting observation was made in that, the failure strain ($\varepsilon_f$) was reduced at 100°C, followed by gradual enhancement at temperatures up to 400°C. Such reduction in $\varepsilon_f$ may be attributed to the dynamic strain ageing of Ni-based alloys due to its resistance to dislocation motion, which might have eventually been enhanced at temperatures above 100°C.

The s-e diagrams for Nb1Zr as a function of the testing temperature are illustrated in Figure 4.4. An evaluation of this diagram indicates that the magnitude of $\varepsilon_f$ was gradually reduced with increasing temperature. The failure stress, noted by the change in slope of the curve, was also reduced to some extent as the temperature was increased. It is well known that materials containing interstitial elements such as carbon (C) and nitrogen (N) can promote the yield point phenomenon, showing the presence of upper and lower yield points. An examination of the chemical composition of Nb1Zr, shown in Table 2.5, indicate the presence of 0.01 weight % of N that could possibly explain the occurrence of
yield point phenomenon in this alloy \cite{22}, as shown in Figure 4.4 This type of heterogeneous transition from elastic to plastic deformation has been reported for low carbon steel in the open literature.

![Figure 4.3 s-e Diagrams vs. Temperature for Alloy C-22](image)

Figure 4.3 s-e Diagrams vs. Temperature for Alloy C-22

The magnitudes of all four tensile parameters (YS, UTS, %El and %RA), determined from the s-e diagram and the specimen dimensions, are given in Tables 4.1 and 4.2, respectively for Alloy C-22 and Nb1Zr. The variations of YS and UTS with temperature for both Alloy C-22 and Nb1Zr are shown in Figures 4.5 and 4.6 respectively. A comparison of both parameters indicates that austenitic Ni-based Alloy C-22 can sustain significantly higher tensile strength compared to that of a refractory material namely Nb1Zr. Thus, from the structural stability point of view Alloy C-22 would undoubtedly
be a superior structural material for heat exchanger application involving the HIx decomposition process.

![Figure 4.4 s-e Diagrams vs. Temperature for Nb1Zr](image)

**Figure 4.4 s-e Diagrams vs. Temperature for Nb1Zr**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>YS, Ksi (MPa)</th>
<th>UTS, Ksi (MPa)</th>
<th>%El</th>
<th>%RA</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>59(407)</td>
<td>115.5(796)</td>
<td>85.17</td>
<td>82.26</td>
</tr>
<tr>
<td>100</td>
<td>52(359)</td>
<td>106(731)</td>
<td>83.62</td>
<td>80.80</td>
</tr>
<tr>
<td>200</td>
<td>44(303)</td>
<td>96(662)</td>
<td>84.39</td>
<td>78.00</td>
</tr>
<tr>
<td>300</td>
<td>41(283)</td>
<td>94.5(652)</td>
<td>84.90</td>
<td>75.52</td>
</tr>
<tr>
<td>400</td>
<td>37(255)</td>
<td>91(627)</td>
<td>85.07</td>
<td>73.66</td>
</tr>
</tbody>
</table>

Table 4.1 Tensile Properties of Alloy C-22 at Different Temperatures
Table 4.2 Tensile Properties of Nb1Zr at Different Temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>YS, Ksi (MPa)</th>
<th>UTS Ksi (MPa)</th>
<th>%El</th>
<th>%RA</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>24.5 (169)</td>
<td>39.5 (272)</td>
<td>46.81</td>
<td>92.46</td>
</tr>
<tr>
<td>100</td>
<td>24 (165)</td>
<td>34 (234)</td>
<td>44.68</td>
<td>93.53</td>
</tr>
<tr>
<td>200</td>
<td>20.5 (141)</td>
<td>30 (207)</td>
<td>44.03</td>
<td>94.00</td>
</tr>
<tr>
<td>300</td>
<td>17 (117)</td>
<td>28 (193)</td>
<td>42.90</td>
<td>94.07</td>
</tr>
<tr>
<td>400</td>
<td>15 (103)</td>
<td>27 (186)</td>
<td>37.10</td>
<td>94.43</td>
</tr>
</tbody>
</table>

Figure 4.5 Variations of YS
In terms of the ductility of Alloy C-22, this material exhibited unusually high percent elongation and percentage reduction in area at all tested temperature. It is well known that the enhanced ductility of Ni-based alloys can be attributed to increased plastic deformation in many slips planes oriented in random directions. With respect to the ductility of Nb1Zr at different temperatures, the magnitude of its %E1 was relatively lower compared to that of Alloy C-22. As to the % RA of this alloy, the hardness of this material was so low that the calculated reduction in area did not exhibit any temperature effect. The variations in % El and % RA with temperature for both alloys are compared in Figures 4.7 and 4.8 respectively.
Figure 4.7 Variations of %El

Figure 4.8 Variations of %RA

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4.3 SCC Evaluation at Constant Load

The results of SCC testing performed by a previous UNLV investigator \cite{23} at constant load indicate that Alloy C-22 may not undergo stress corrosion cracking (SCC) in an aqueous solution containing sulfuric acid and sodium iodide at ambient and elevated temperature. No failure of Alloy C-22 has been reported even at an applied stress corresponding to 95% of the material’s ambient temperature YS value.

4.4 SCC Evaluation under SSR Condition

The results of SCC testing involving Alloy C-22 in an aqueous solution containing H$_2$SO$_4$, NaI and H$_2$O at ambient temperature and 90°C are shown in Figure 4.9 in the form of s-e diagram. The s-e diagram without this environment is also superimposed in this figure for comparison purpose. An evaluation of this figure indicates that the magnitude of failure strain was almost identical with and without the presence of the

![Figure 4.9 Comparisons of s-e Diagrams at Different Temperatures](image-url)
aqueous testing environment. The magnitude of %E1, %RA, time-to-failure (TTF) and $\sigma_f$ derived from these plots and the specimen dimensions, before and after testing are shown in Table 4.3. A cursory examination of these parameters indicates that the cracking susceptibility in terms of %E1, %RA and time to failure was not significantly influenced either by the environment or the temperature. However, the magnitude of $\sigma_f$ was reduced by an appreciable amount due to the change in temperature from ambient to 90°C in an identical testing environment. Since, the detrimental effect of stress concentration factor on the cracking susceptibility in terms of $\sigma_f$ has been investigated earlier by another UNLV researcher, no attempt has been made in this study to perform SCC testing involving notched cylindrical specimens. Similarly, SCC testing under controlled electrochemical potential using the SSR technique has also been performed involving Alloy C-22 by a previous investigator. Therefore, no attempts have been made in this investigation to study the role of applied potential on the cracking susceptibility of this alloy.

Table 4.3 SSR Test Results for Alloy C-22

<table>
<thead>
<tr>
<th>Environment/Specimen Type</th>
<th>Temperature ($^\circ$C)</th>
<th>%E1</th>
<th>%RA</th>
<th>$\sigma_f$ ksi (MPa)</th>
<th>TTF (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air/Smooth Tensile</td>
<td>RT</td>
<td>21.6</td>
<td>81.2</td>
<td>277 (1910)</td>
<td>74.4</td>
</tr>
<tr>
<td>Acidic Sol./Smooth Tensile</td>
<td>RT</td>
<td>21.4</td>
<td>80.9</td>
<td>272 (1875)</td>
<td>73.9</td>
</tr>
<tr>
<td>Acidic Sol./Smooth Tensile</td>
<td>90</td>
<td>20.9</td>
<td>80.6</td>
<td>250 (1724)</td>
<td>72.8</td>
</tr>
</tbody>
</table>

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4.5 Localized Corrosion Evaluation by CPP

The results of localized corrosion studies by the cyclic potentiodynamic polarization (CPP) technique involving Alloy C-22 and Nb1Zr in a solution containing H$_2$SO$_4$ and NaI at ambient and elevated temperatures are illustrated in Figures 4.11 and 4.12, respectively. An evaluation of these CPP diagrams indicates that no positive hysteresis loop was seen during the reverse potential scan. A negative hysteresis loop signifies the formation of protective oxide film on the specimen surface due to the generation of oxygen resulting from the electrolysis at high current densities.
The magnitude of the corrosion potential ($E_{\text{corr}}$) and the critical pitting potential ($E_{\text{pit}}$) determined from this CPP diagram are reproduced in Tables 4.4 for Alloy C-22 and Nb1Zr. An evaluation of both tables indicates that the magnitude of $E_{\text{corr}}$ and $E_{\text{pit}}$ became

\[ E_{\text{corr}} = 301 \text{ mV} \]

\[ E_{\text{pit}} = 623 \text{ mV} \]

Acidic Sol. Na1 + H2SO4 + H2O

Figure 4.11(a) CPP Diagram in Room Temperature Acidic Solution for Alloy C-22

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Figure 4.11(b) CPP Diagram in 60 °C Acidic Solution for Alloy C-22

$E_{\text{corr}} = 274 \text{ mV}$

$E_{\text{pit}} = 575 \text{ mV}$

Acidic Sol. NaI + H$_2$SO$_4$ + H$_2$O

Figure 4.11(c) CPP Diagram in 90 °C Acidic Solution for Alloy C-22

$E_{\text{corr}} = 245 \text{ mV}$

$E_{\text{pit}} = 470 \text{ mV}$

Acidic Sol. NaI + H$_2$SO$_4$ + H$_2$O
Figure 4.12(a) CPP Diagram in Room Temperature Acidic Solution for Nb1Zr

$E_{corr} = 152 \text{ mV}$

$E_{pit} = 585 \text{ mV}$

Acidic Sol. NaI + H$_2$SO$_4$ + H$_2$O

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Figure 4.12(b) CPP Diagram in 60 °C Acidic Solution for Nb1Zr

$E_{corr} = 106 \text{ mV}$

$E_{pit} = 468 \text{ mV}$

Acidic Sol. NaI + H$_2$SO$_4$ + H$_2$O

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more active (negative) with increasing temperature. This observation is consistent with the data reported in the open literature\cite{24}. The variations of $E_{\text{corr}}$ and $E_{\text{pit}}$ as a function of the testing temperature are illustrated in Figures 4.13 and 4.14 respectively, once again demonstrating an identical observation.

Table 4.4 Results of CPP testing

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Alloy C-22</th>
<th>Nb1Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average $E_{\text{corr}}$ (mV)</td>
<td>Average $E_{\text{pit}}$ (mV)</td>
</tr>
<tr>
<td>30°C</td>
<td>301</td>
<td>623</td>
</tr>
<tr>
<td>60°C</td>
<td>274</td>
<td>575</td>
</tr>
<tr>
<td>90°C</td>
<td>245</td>
<td>470</td>
</tr>
</tbody>
</table>
Figure 4.13 Variations of $E_{\text{corr}}$ with temperature for both alloys

Figure 4.14 Variations of $E_{\text{pit}}$ with temperature for both alloys
4.6 Weight-Loss and SCC Evaluation at 150°C

A major limitation to the SCC evaluation using the constant load and SSR techniques is that the testing could be performed only up to a maximum temperature of 100°C using the current experimental facilities at MPL. Therefore SCC testing involving self-loaded specimens (C-ring and U-bend) was performed in an acidic aqueous solution containing H₂SO₄ at 150°C inside an autoclave. The results of autoclave testing indicate that no failures were observed in either type of specimen even after 28 days of exposure. A slight reduction in weight was observed in both the specimens, as shown in Table 4.5. The appearances of the C-ring and U-bend specimens of Alloy C-22 following exposure are illustrated in Figure 4.15 (a) & (b).

Efforts were also made to evaluate the weight loss of Alloy C-22 coupons exposed to an identical environment at 150°C for variable time period (7-56 days). The corrosion rates determined from the weight loss of these coupons at different exposure time up to 28 days followed by its enhancement at the end of 56 days. The variations of the weight loss with time are illustrated in Figure 4.16.

Figure 4.15 (a) C-ring  
Figure 4.15 (b) U-bend
Figure 4.16 Weight-loss Vs Time

Table 4.5 Weight loss and corrosion rate of Alloy C-22 coupons

<table>
<thead>
<tr>
<th>Test Duration (hrs.)</th>
<th>Specimen 1</th>
<th></th>
<th>Specimen 2</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight Loss (mg)</td>
<td>Corrosion Rate (mpy)</td>
<td>Weight Loss (mg)</td>
<td>Corrosion Rate (mpy)</td>
</tr>
<tr>
<td>168</td>
<td>73</td>
<td>12</td>
<td>68</td>
<td>11</td>
</tr>
<tr>
<td>336</td>
<td>102</td>
<td>8</td>
<td>101</td>
<td>8</td>
</tr>
<tr>
<td>672</td>
<td>129</td>
<td>5</td>
<td>120</td>
<td>5</td>
</tr>
<tr>
<td>1344</td>
<td>500</td>
<td>10</td>
<td>466</td>
<td>9.14</td>
</tr>
</tbody>
</table>

4.7 Fractographic Evaluations

As indicated earlier the extent and morphology of failures at the primary fractured surface of the cylindrical specimens of both alloys, tested for tensile properties and SCC
evaluation, were analyzed by scanning electron microscopy (SEM). The SEM micrographs for both alloys are illustrated in Figures 4.17 and 4.18, respectively. An evaluation of these micrographs indicates that both alloys showed dimpled microstructures, irrespective of the test type, indicating ductile failures.

Figure 4.17 SEM Micrograph of Smooth Cylindrical Specimen for Alloy C-22

(a) MTS, 400°C, 500X

(b) SSR, 90°C, Acidic solution, 500X

Figure 4.17 SEM Micrograph of Smooth Cylindrical Specimen for Alloy C-22
Figure 4.18 SEM Micrograph of Smooth Cylindrical Specimen for Nb1Zr
CHAPTER 5

DISCUSSION

Metallurgical and corrosion behavior of nickel-based Alloy C-22 and a refractory material known as Nb1Zr were evaluated for application in hydrogen generation using the HIx decomposition process. The tensile properties of both alloys were determined at temperatures relevant to the HIx decomposition process. The susceptibility of Alloy C-22 to stress-corrosion-cracking (SCC) was determined under slow-strain-rate (SSR) conditions in an acidic aqueous solution at ambient and elevated temperatures. For Nb1Zr, SCC susceptibility was determined in an identical environment by the SSR technique. The susceptibility of both alloys to localized attack was determined by cyclic potentiodynamic polarization (CPP) technique at ambient and elevated temperatures. The evaluations of weight loss in coupons, and SCC using self-loaded specimens (C-ring & U-bend) were performed in an acidic solution at an elevated temperature. Further, metallographic and fractographic evaluations of the tested materials were performed by optical microscopy and scanning electron microscopy respectively.

An interesting observation made from the results of tensile testing involving Alloy C-22 was that this alloy showed reduced ductility at 100°C followed by gradual enhancement in the failure strain at higher temperatures. This phenomenon may be attributed to the dynamic strain ageing effect of Ni-based alloys such as Alloy C-22 at a
critical temperature at which this material became hardened due to slow movement of dislocation past the grain boundary. A comparative analysis of the engineering stress vs. strain (s-e) diagrams of both alloys revealed that Alloy C-22 exhibited significantly higher strength and ductility at different temperatures. The ductility of Nb1Zr in terms of %RA was unrealistic due to significantly lower (90 VHN) hardness value of this alloy compared to that of Alloy C-22. As indicated earlier section, Nb1Zr also exhibited classical yield point phenomenon at all tested temperatures showing upper and lower yield point, possibly due to the presence of nitrogen$^{[22]}$.

The SCC test results, obtained by the SSR technique, indicate that the failure strain involving Alloy C-22 was not influenced by the presence of the aqueous environment. Further, the cracking susceptibility in terms of %EI, %RA, and TTF was not significantly influenced neither by the environment nor by the testing temperature. However, the magnitude of $\sigma_f$ was reduced by an appreciable amount due to the change in temperature from ambient to 90°C in the same testing environment. With respect to the SCC behavior of Nb1Zr, an inconsistent observation was noted in that the failure strain did not follow a conventional pattern as the temperature was changed from ambient to 90°C in the acidic solution. Transmission electron microscopy studies on the fractured specimens will throw light more on this inconsistent pattern, which is going to be one of the future works. Further, the true failure stress could not be determined due to the lack of significant variation in the final cross-section area of the specimen as a function of the environment and temperature.

With respect to the localized corrosion behavior in the same test environment, both alloys exhibited active-passive transition. However, the CPP diagram exhibited a
negative hysteresis loop during reverse potential scan, possibly due to the formation of protective oxide film on the materials' surface. It is also interesting to note that the magnitude of corrosion potential ($E_{cor}$) and critical pitting potential ($E_{pit}$) became more active with increasing temperature, as observed by other investigators [24]. The results of autoclave testing using coupons indicate that the corrosion rate was gradually reduced with exposure time up to 28 days followed by significant enhancement after 56 days of exposure. In addition, no cracking was observed in self-loaded specimens.

The optical micrographs revealed conventional metallurgical microstructures for both alloys. Further, dimpled microstructures, characteristic of ductile failure was observed at the primary fracture surface of all cylindrical specimens.
CHAPTER 6

SUMMARY AND CONCLUSION

Tensile properties evaluation of Alloy C-22 and Nb1Zr has been determined at different temperatures. The SCC susceptibility of both alloys has been determined by the SSR technique. Further their localized corrosion behavior has been determined by the CPP technique. Corrosion rate and SCC susceptibility have also been determined using coupon and C-ring/U-bend specimens, respectively, in an autoclave at 150°C. Metallographic and fractographic evaluations have been performed by optical microscopy and SEM, respectively. The key conclusions are given below.

- Alloy C-22 exhibited higher tensile strength at temperatures up to 400°C compared to Nb1Zr, suggesting that Alloy C-22 may be a better-suited structural material for application in the HI₅ decomposition process.
- The magnitude of failure strain (eₕ) for Alloy C-22 was reduced up to a critical temperature (100°C), above which an enhancement was noted. The reduced eₕ may be the result of dynamic strain aging.
- The tensile parameters for Nb1Zr including YS, UTS, and ductility were gradually reduced with increasing temperature.
- The true failure stress of Alloy C-22 was reduced by an appreciable amount in SSR testing at an elevated temperature. However, %El, %RA and TTF were
not significantly influenced by the testing temperature. An inconsistent SCC behavior was noted with Nb1Zr.

- Both \( E_{corr} \) and \( E_{pit} \) became more active with increasing temperature for each tested material.
- The corrosion rate of Alloy C-22 in terms of mpy was gradually reduced with exposure time up to 28 days followed by significant enhancement at a longer duration. No cracking was observed in self-loaded specimens.
- The fractographic evaluation of the specimens used in tensile and SCC testing revealed dimpled microstructure, indicating ductile failures.
CHAPTER 7

SUGGESTED FUTURE WORK

• SCC evaluation using self-loaded specimens and double cantilever beam specimens at temperatures (400°C) and pressures (50 bars) relevant to HIx decomposition.

• Corrosion rate evaluations using coupons in autoclave at elevated temperatures in HIx solution.

• Characterization of defects in tensile specimens by transmission electron microscopy to learn more about dynamic strain ageing.

• Fracture toughness and crack growth rate evaluations at different temperatures.

2. Lloyd, Amy C.; Noel, James J.; McIntyre, Stewart; Shoesmith, David W. “Cr, Mo and W alloying additions in Ni and their effect on passivity”. Electrochimica Acta (2004), 49(17-18), 3015-3027.


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

   (http://www.gamry.com/Homepage/index.html)


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