Comparison of Nitronic 50 and Stainless Steel 316 for use in Supercritical Water Environments

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Abstract

Increased efficiency can greatly benefit any mode of power production. Many proposed coal, natural gas, and nuclear reactors attempt to realize this goal through the use of increased operating temperatures and pressures, and as such require materials capable of withstanding extreme conditions. One such design employs supercritical water, which in addition to high temperatures and pressures is also highly oxidizing. A critical understanding of both mechanical and oxidation characteristics of candidate materials are required to determine the viability of materials for these reactors. This work investigates two potential materials, austenitic stainless steels, namely, Nitronic-50 and stainless steel 316, for use in these conditions.

The supercritical water loop at the University of Nevada, Reno allowed for the study of materials at both subcritical and supercritical conditions. The materials were investigated mechanically using slow strain rate tests under conditions ranging from an inert nitrogen atmosphere, to both subcritical and supercritical water, with the failed samples surface characterized by optical microscopy, scanning electron microscopy, and Raman spectroscopy. Electrochemical studies were performed via potentiodynamic polarization in subcritical water only, and characterized using Raman spectroscopy. The samples were also exposed to supercritical water, and characterized using Raman spectroscopy. Nitronic-50 was found to have superior mechanical characteristics to stainless steel 316. SS-316 was found to have a surface film consisting of iron oxides, while the surface film of N-50 consisted predominantly of nickel-iron spinel. The crack interior of the sample was different from the exterior, indicating that the time and
temperature of the exposure might play a defining role in determining the chemistry of the film
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The opportunities I am afforded were paid for dearly by those that came before me; through bravery and sacrifice that I cannot fathom. It is in respect for the courage of my grandparents, the patience of my mother and father, and in earnest hope that I will be of the same benefit to my nieces, to whom I dedicate this thesis.
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Chapter 1. Introduction.

1.1 Nuclear Energy

The growing demand for energy requires immediate attention. Energy needs have been met almost exclusively with traditional fossil fuels, and the U.S. Energy Information Administration predicts, in a 2013 report, that almost 80% of global energy demand will continue to be met by fossil fuels through 2040 [1]. Considering global energy demand is expected to rise ~33% by 2035, it is imperative to develop and employ more stable long-term energy production systems [2, 3]. Nuclear energy can meet the demands of growing energy consumption, the International Atomic Energy Agency (IAEA) predicts up to a 100% increase in nuclear generating capacity by 2030 [4]. This can be achieved economically, as nuclear energy is currently economically competitive with only a fraction of the production cost stemming from fuel supply cost. Per unit energy produced, the fuel cost of nuclear power generation is approximately 15-40% of that using coal [4, 5]. While alternative energy sources have been proposed, their ability to function as the primary base-load power source in the immediate future has yet to be confirmed. A 2012 perspective piece written by Dr. Steven Chu, Secretary of the Department of Energy at the time, and Dr. Arun Majumdar, Department of Energy’s Advanced Research Projects Agency-Energy, characterized biofuel and solar power generation for both stationary and transportation systems as, “…largely at the research and development stage, and are not yet ready to displace more mature sources of energy” [3]. Nuclear energy has proven capable of providing immense base load through well-established technologies. Future nuclear systems will become
increasingly attractive as developing technologies will increase economic competitiveness and overall safety. Comprising nearly 20% of U.S. electricity production in 2012, nuclear energy is a vital part of the energy infrastructure, and will continue to be for the foreseeable future [4].

A modern trend has been the uprating, a term used to describe an increase in the maximum power output of a facility, of existing nuclear power plants. This is done to both avoid the immense capital cost associated with new plant constructions, and to increase profitability from existing plants. In the U.S., this had led to an increase of the capacity factor (energy produced over total energy possible) from roughly 60% in the 1970’s to 90% today [6]. The U.S. Nuclear Regulatory Commission (NRC) currently has 14 such uprates under review, representing 1,568 MWe, and another 35 are anticipated, representing an additional 1,854 MWe [7]. This is equivalent to the addition of three new AP1000, nuclear power plants [8]. Thus, nuclear energy forms an important part in meeting our energy requirements, and removing this vital component of energy production has serious consequences. Prior to shutting down half of their nuclear reactors in 2011, Germany produced a similar percentage of their power, 25%, from nuclear energy [9]. The drastic decision to eliminate nuclear power production in 2011 was the result of a long standing political alliance, and an increasingly strong anti-nuclear sentiment in the aftermath of the nuclear accident at the Fukushima Daiichi nuclear power station [9]. Prior to 2011, Germany’s initial moratorium on nuclear power plants, as part of the “Energiewende” which relied heavily on an increase in renewables, was postponed by 14 years to 2036 in the wake of a series of reports detailing the corresponding rise in the price of energy, increased CO₂ emissions, and instability of
the German energy infrastructure that a nuclear phase-out would entail [9, 10]. However, the events surrounding Fukushima Daiichi resulted in a public and political backlash, leading to an increased timetable of 2020 for a complete cessation of nuclear power. Expediting their departure from nuclear power is expected to lead to an increase of net annual energy imports of 9.9 TWh in 2015, and 26.3 TWh in 2020, even with the significant construction of gas-fired power plants that is currently underway [11, 12]. Furthermore, the post-Fukushima policies are expected to result in a projected increase of up to 20% in electrical prices by 2025 [9]. It, in the opinion of the author, is inadvisable that the US embark on a similar path towards increased carbon emissions, decreased energy independence, and increased energy prices by reducing nuclear power generation.

1.2 Reactor Designs & Material Concerns

As of 2009 there were 104 operating nuclear power plants in the United states [4]. This fleet of Light Water Reactors (LWRs) consist of Pressurized Water Reactors (PWRs) and Boiling Water Reactors (BWRs). Though significant differences between the two exist, most notably the isolation of the primary water loop in BWRs, the material challenges facing both are similar. However, the proposed next generation of nuclear reactors represents a vast array of designs, presenting unique challenges. Notably, the lowest outlet temperature of one of the designs, the SuperCritical Water Reactor (SCWR), is 510°C, or more than 150°C above LWR peak temperatures [13]. The desire to increase temperature comes from the relationship between efficiency and the
temperature difference across a heat engine, known as the Carnot efficiency [14]. The relationship is shown below in Figure 1.

\[ \eta = \frac{W}{Q_H} = 1 - \frac{T_C}{T_H} \]  \hspace{1cm} (Equation 1)

Despite the advantages of higher operating temperatures, it is not easy to operate power plants at high temperatures as all materials become increasingly susceptible to degradation and failure at higher temperatures. A clear example is the behavior of fire-resistant structural steels, which have demonstrated a loss of half their room temperature tensile strength when exposed to higher temperatures as shown in Figure 2.
Figure 2: Different low-alloy structural steels demonstrating the reduction in yield tensile stress with temperature. Arrows indicate lower strength. Figure adapted from Kelly et al., Journal of Constructional Steel Research 50 (1999) [15].

The drastic decrease in mechanical strength due to temperature is not the only concern, as nuclear reactors present the additional problems in that the structural material must be capable of withstanding the effects of irradiation. Notably, metals undergo irradiation hardening, which while increasing the yield strength, decreases the ductility of the metal, making it susceptible to brittle failure [16]. There are also significant corrosion concerns, which are specific to the environment presented by different reactor types. Identifying or developing materials that are able to withstand these harsh conditions is necessary for the development of advanced nuclear reactors.

The 2002 Generation IV International Forum (GIF) on advanced reactor development consisted of ten nations, Argentina, Brazil, Canada, France, Japan, Republic of Korea, Republic of South Africa, Switzerland, the United Kingdom, and the United States. The GIF listed the following as goals for the fourth generation of nuclear reactors, sustainability, economics, safety and reliability, proliferation resistance and physical protection [13]. Using these as guidelines, six potential reactor systems were
selected as capable of meeting these goals. They are the Gas-Cooled Fast Reactor (GCFR), Lead-Cooled Fast Reactor (LFR), Molten Salt Reactor (MSR), Sodium-Cooled Fast Reactor (SFR), Very-High-Temperature Reactor (VHTR), and the aforementioned supercritical water reactor (SCWR) [13]. The systems are presented and contrasted based on their respective differences in Figure 3.

![Figure 3](image)

**Figure 3:** A comparison of the six reactor designs selected at the GIF. (A) Mission focus of electricity production and or hydrogen production (B) potential fuel cycle capabilities and (C) size of the installation. Figure from A Technology Roadmap for Generation IV Nuclear Energy Systems, 2008 [13].

Gas cooled reactor technology is not completely novel. The first operational gas cooled system was Britain’s Dragon reactor in 1965 [17]. Historically, research on GCFR systems had mainly focused on directly evolutionarily designs; however after official selection as one of the six GIF reactors, the European Commission (EC) Gas Cooled Fast Reactor expanded the scope of the project to fully realize the potential of the technology [18]. A highly attractive aspect of the GCFR is the flexibility of this
technology. Utilizing a broader neutron spectrum, including “fast” neutrons above 1 MeV, allows GCFR to both fission minor actinides, such as $^{237}$Np, $^{241}$Am, $^{243}$Am, and $^{242}$Cm, and transmute $^{238}$U to $^{239}$Pu. Fissioning actinides greatly reduces their long term contribution to the toxicity and activity of used nuclear fuel [19]. The production of Pu from GCFR is also relatively diluted, allaying proliferation concerns [20]. South Africa considered the construction of the Eskom direct cycle 115 MWe Pebble Bed Modular Reactor (PBMR) for both nuclear power generation, and hydrogen production; the high temperature of the He coolant, 850˚C, making them suitable for the latter [6, 20]. Advanced features of this design were the incorporation of the Brayton cycle, directly powering a gas turbine with the heated gas, as well as their modular construction of up to eight units per site [21]. Though the multipurpose proposal is enticing, the extremely high temperatures of operation presents serious challenges to both fuel materials and structural components [20]. The use of CO$_2$ as coolant would decrease the operating temperature to roughly 650˚C, however employing this coolant introduces potential negative consequences due to its interaction with the fuel if the cladding were to fail [20]. Helium coolant also poses a specific problem, as coolant contamination of the proposed metallic fuel and Silicon Carbide (SiC) would cause separation between the two [22]. Despite considerable investment, the South African project was abandoned in 2010 [21].

The initial interest in LFR systems stemmed from their use as part of a closed fuel cycle, increasing the power output of a given uranium supply by a factor of 100, while also aiding in the reduction of minor actinides through fission [23]. In addition to meeting sustainability goals, LFR systems employ long-lived cores, making them
inherently proliferation resistant [13]. 2004 saw the establishment of the GIF LFR Provisional System Steering Committee, which selected the United States supported Small Secure Transportable Autonomous Reactor (SSTAR); and the European Lead-cooled System (ELSY) as the two LFR reactor designs for further development [23]. The SSTAR is expected to achieve 44% efficiency, employing a CO$_2$ driven Brayton cycle, with 20 MWe, while the European led ELSY is a larger model, designed for 42 % efficiency from a superheated steam cycle at 1000 MWe [23, 24]. Both reactors are pool-type, meaning the primary power cycle components are housed in the reactor vessel, which itself is enclosed in a guard vessel. This design takes advantage of the low pressure of the system, due to the high boiling point of liquid metals, therefore these reactors do not require pressurization to maintain the state of their coolant [23]. These benefits are balanced by the highly corrosive nature of liquid lead. The only practical solution possible with current technology is the periodic replacement of all components in contact with liquid lead [23]. Considering the goal of long-lived cores, for proliferation resistance, the need for relatively frequent replacement of primary systems is highly undesirable. The technology gap presented by exposing core internals to liquid lead, as well as requiring refueling machinery in such a corrosive environment, are of primary concern [13].

Similar to the LFR, the GenIV SFR is an intermediate to larger scale system [13]. At the GIF in 2002, a major advantage for the SFR was considered to be the timescale for its deployment, with the possible operating date of 2015. It was by far the earliest projection for any reactor design [13]. This was due to the robust research and the operation of Russian BR-5 for 43 years, the United States’ successful operation of EBR-
II for 30 years, and the nearly 50 years operation of the French Rapsodie, Phenix and Superphenix SFR reactors [25-28]. Passive safety systems in these reactors were successful as well, making the SFR a truly attractive option [29]. A notable drawback is SFR’s lower thermal efficiency compared to the previously discussed designs [30]. This is owed to these reactor’s lower operating temperature, limited by sodium’s relatively low boiling point [30]. There is a correlating safety issue as well. Though SFRs demonstrate some areas of superiority to LFRs in terms of Pu breeding and minor actinide burn-up, they do so at temperatures far closer to sodium’s boiling point. Compared to lead, sodium has a 30% lower volumetric heat capacity, as well as a boiling point that is 860˚C lower. Simulations show that SFRs could suffer catastrophically from unprotected Loss-of-Flow (ULOF), and unprotected Loss-of-Heat Sink (ULOHS) accidents as a result of these properties [31]. Sodium also carries an inherent risk of flammability when it comes into contact with water, requiring intermediate loops to isolate any steam elements. With LFRs seemingly void of this concern, they could provide lower construction costs. While actinide management and Pu breeding for long term sustainability are among the GIF goals, immediate plant safety and economic concerns cannot be overlooked.

MSR technology can be traced back to Oak Ridge National Laboratories (ORNL), with the first operational reactor in 1954 [32]. Consistent with other modern reactor designs, current MSR designs aim for high operating temperatures and a closed fuel cycle with breeder and burner reaction capabilities. The unique property of MSRs is that the fissile and fertile material also serves as the heat transfer fluid [32]. Three major design lineages exist, namely, the ORNL Molten Salt Breeder Reactor MSBR, Russian
efforts that began in the 1970s and evolved into the modern MOlten Salt Actinide Recycler & Transmuter (MOSART) system, and the French efforts at CNRS that have led to the Molten Salt Fast Reactor MSFR [33]. These designs represent a combination of single stream, where fertile and fissile material are dissolved in the same flowing molten salt, and the two stream, where fertile isotopes are separated in a “blanket” stream that breeds new fuel and serves as a reflector [32, 33]. In order to avoid hazardous precipitates of the fuel, temperatures at all points in the primary loop must exceed the melting salt point of the salt. Salts containing flourides of uranium and thorium have melting points upwards of 500°C but naturally these systems have to operate below the temperature limits of the structural material. Metal oxides are soluble in molten fluoride salts, making traditional corrosion protection, attributed to the formation of stable oxide surface films, inconsequential. Consequently, traditional high temperature alloys that rely on high chromium contents for oxidation protection cannot be employed. Furthermore, chromium has a chemical potential for oxidation as well as high solubility in fluoride salts [33]. Hastelloy N, as a nickel based super alloy, represents the most successful core material to date, demonstrating efficacy in the molten salt systems up to 704°C [34]. While providing excellent corrosion resistance, the main drawback of Hastelloy N is significant irradiation embrittlement, due to the resulting helium buildup from the (n, α) reaction with $^{58}$Ni [33, 35]. Additional material concerns involve irradiation induced structural issues with the graphite moderator in the core, where swelling up to 8% occurs at the high operating temperatures of MSRs [36]. Due to these drawbacks, the French MSFR program abandoned the use of graphite as a core material [33]. Fully realizing the advantage inherent to using molten salt
synergistically as fuel and heat transfer medium requires a structural material capable of resisting the highly corrosive environment, as well as withstanding the high irradiation damage imposed by having the fuel immediately in contact with the containment.

VHTRs operate at up to 700°C higher than current LWRs, making them ideal for high temperature electrolysis for hydrogen production [37, 38]. Current work on these reactors is being headed by Japan Atomic Energy Agency (JAEA), PBMR/Westinghouse, General Atomic, and AREVA NP/CEA/EDF [38]. These designs all have their foundation in the work done by INTERATOM in the 1970s [37]. The AREVA design features a combined Brayton cycle, where a nitrogen/helium working fluid is used to allow for already developed air-based gas turbine technology, and Rankine cycle. Such a system requires a minimum operating temperature of 925°C for hydrogen production [37]. A goal of this reactor mission is to provide a simpler and faster path to commercial viability by reducing the amount of new research and development necessary. The combined cycle does have a higher efficiency than possible by either of the Brayton or Rankine cycles allow, but it does require the development of an Intermediate Heat eXchanger (IHX) [38, 39]. The IHX has, as of yet, unmet materials problems, specifically caused by the presence of CO, CO₂, H₂, N₂, methane, and water vapor, contaminants that helium cooled reactors have demonstrated [39, 40]. Two materials have been selected as the leading candidates for the IHX, Haynes 230® and Inconel 617, and both demonstrate sufficient chromium oxide formation to protect the IHX up to 900°C [39]. However, the system requires narrow control over temperature and chemistry parameters to maintain stability, outside
of which oxidation, carburization, and decarburization can occur and have severe
detrimental effects on mechanical aspects of the IHX [39].

SCWRs represent an evolution of current PWR and BWR systems, by combining
the high pressures of the former and single loop of the latter [41, 42]. The technology
can accommodate both thermal neutron reactors, and fast neutron breeder or burner
reactors [13]. In a supercritical state, water only has one tenth its normal density, which
does not thermalize neutrons nearly as effectively as water in its liquid state and
therefore allows the SCWR to be a breeder reactor, due to the faster neutron spectra
that results from the lack of moderation [41, 43]. The removal of steam generators,
which are found in PWRs, significantly reduces the high capital cost of a nuclear
reactor’s power generating system, where steam generators can be as great as 70% of
all equipment and construction costs [44]. An additional advantage of the SCWR is the
use of already available commercial fuels, uranium oxide and depleted uranium. The
increased energy of the neutrons would expose the pressure vessel to extreme
irradiation, thus the core’s fuel rod configuration incorporates zirconium hydride, which
has been extensively investigated by NASA for its Systems Nuclear Auxiliary Power
(SNAP) program in the 1960s, to act as a moderator [45]. SCWRs are mainly attractive
due to the efficiencies possible, calculated to be 44% with an inlet temperature of 280°C
and on outlet temperature of 550°C [42]. The high temperatures necessitate high
operating pressures, upwards of 25MPa, to maintain the supercritical state. This
presents a formidable materials problem, as the pressure vessel will be exposed to not
only irradiation, but the highly oxidizing environment of supercritical water, high
temperatures, in addition to considerable mechanical stress. The resultant concerns are
corrosion, stress corrosion cracking (SCC), creep resistance, and dimensional stability [13].

1.3 Reactor Material Selection

Each of the previously discussed design presents unique materials problems. A variety of materials options are available, and their preferential use in each reactor system is shown in Table I [13]. Every material presents both advantages and disadvantages that must be matched with the specific environment of the reactor in question. Certain static internals, such as housing for fuel, can employ non-metals, whereas as structural materials requiring greater mechanical strengths necessitate the use of metals.

Table I: A summation of the proposed materials for each Gen IV reactor design [13].

<table>
<thead>
<tr>
<th>System</th>
<th>Fuel Materials</th>
<th>Structural Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxide</td>
<td>Metal</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GFR</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>MSK</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td>SFR</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>LFR</td>
<td>S</td>
<td>P</td>
</tr>
<tr>
<td>SCWR-Thermal</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td>SCWR-Pass</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>VHTR</td>
<td>P</td>
<td></td>
</tr>
</tbody>
</table>

P: Primary Option
S: Secondary Option
Austenitic stainless steels are used in a wide array of industries due to their high strength and general corrosion resistance [46]. However, they undergo significant irradiation induced swelling, which render even advanced materials containing stabilizing elements and having underwent cold work, unsuitable beyond 160dpa [47]. Ferritic/Martensitic (F/M) steels have demonstrated superior resistance to irradiation assisted swelling, a saturation at 10dpa of 10% swelling, but have poor creep properties and represent a significant challenge in manufacturing and assembly [47, 48]. Attempts to increase the high temperature mechanical characteristics of F/M steels has led to the use of oxide dispersion strengthened (ODS) steels, which have marked strength increases. ODS steels demonstrate creep strength exceeding 65MPa at 700°C [48]. They do however suffer from fabrication issues, particularly due to the lack of uniform oxide dispersion after joining [49]. Nickel based alloys, as previously discussed, suffer from swelling due to helium buildup, making these materials a poor choice for any component exposed to high neutron fluence [35]. Refractory metals have sufficient temperature resistance, but suffer from severe fabrication difficulties and radiation embrittlement [50].

The SCWR design benefits from the experience gained in supercritical systems used in other industry. The iterative work for materials development is concisely expressed in a 2000 publication by the Institute of Materials, Minerals and Mining, "The development of materials is therefore focused primarily on the improvement of creep strength and on the resistance to high temperature corrosion and, as will be shown later, this has led to the evolution from low alloy steels, through martensitic steels to 'super' austenitic steels and will eventually arrive at nickel-base alloys for these high
temperature components” [51]. A SCWR must balance these mechanical material concerns with irradiation effects, primarily of nickel. However, helium production can be mitigated by conservative fuel rod placement and neutron shielding in the manner addressed by currently operating LWRs [52]. Materials employed in other industries supercritical water plants are free from the constraints imposed by irradiation, allowing for the use of copper as an alloying element [53]. Copper produces both helium and hydrogen, from the $^{63}\text{Cu} (n,a)$ reaction and $^{63}\text{Cu}$ and $^{65}\text{Cu}$ by $(n,p)$ reactions, respectively, making it unfit for use in a SCWR [54]. Structural material concerns are of greater importance for the SCWR, due to the high pressures and temperatures of the encountered coolant. In addition to the mechanical strength constraints, supercritical water is extremely oxidizing, leading to corrosion of key components. Though not trivial, these are perhaps simpler material challenges when compared to other nuclear reactor designs.

The supercritical water loop (SCWL) at the University of Nevada, Reno (UNR) presents an opportunity for studying material behavior and performance through the use of mechanical and electrochemical testing for materials in the environment of a SCWR. The strength requirement led to the selection of nitronic-50 (N-50), an austenitic stainless steel which is also known as UNS S20910 and XM-19, as a candidate material. In this study, a comparison between N-50 and the more widely used stainless steel 316 (SS-316) will be used to demonstrate the suitability of N-50 to meet the challenges posed by the SCWR.

The composition of austenitic stainless steels N-50 and SS-316 are shown, with significant differences highlighted, in Table II. The addition of nitrogen, from which N-50
draws its name, provides many benefits over conventional stainless steels. The most beneficial traits are the increases in strength, toughness, and corrosion resistance, while repressing carbide formation at grain boundaries [55]. Increased nitrogen concentrations result in increased yield strength, and can be stabilized by increased chromium and manganese content [55, 56]. Niobium serves the dual purpose of suppressing chromium carbide formation, and increasing weldability [46]. The passive behavior of stainless steel alloys is attributed to the formation of a chromium rich protective oxide film on the metals surface. This chromium is further stabilized by the addition of the nitrogen [46].

**Table II**: The elemental composition of N-50 and SS-316. The primary alloying additions in N-50, highlighted in red, are of nitrogen and niobium, and the increase of chromium and manganese [57].

<table>
<thead>
<tr>
<th></th>
<th>N-50</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Cr</td>
<td>Mo</td>
<td>N</td>
<td>Mn</td>
<td>C</td>
<td>V</td>
<td>Nb</td>
<td>Si</td>
<td>S</td>
<td>P</td>
</tr>
<tr>
<td>Max</td>
<td>12.18</td>
<td><strong>21.26</strong></td>
<td>2.14</td>
<td><strong>0.277</strong></td>
<td>4.86</td>
<td>0.034</td>
<td>0.14</td>
<td><strong>0.18</strong></td>
<td>0.49</td>
<td>0.001</td>
<td>0.022</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>SS-316</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Cr</td>
<td>Mo</td>
<td>N</td>
<td>Mn</td>
<td>C</td>
<td>V</td>
<td>Cu</td>
<td>Si</td>
<td>S</td>
<td>P</td>
</tr>
<tr>
<td>Max</td>
<td>14</td>
<td>18</td>
<td>3</td>
<td>X</td>
<td>2</td>
<td>0.08</td>
<td>1</td>
<td>1</td>
<td>0.04</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>Min</td>
<td>10</td>
<td>16</td>
<td>2</td>
<td>X</td>
<td>1.25</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

N-50 also possesses very low magnetic permeability, leading to consideration as a potential hull material by the German and United States Navy [58, 59]. These studies included mechanical and corrosion testing, where a molybdenum content of 3%, was found preferable to provide adequate pitting corrosion resistance, while lower manganese levels aided in protection against crevice corrosion [58, 59]. Mechanically, the superiority of N-50 can be observed from the tabulated results from several slow strain rate tests (SSRT) shown in Table III. Additional SSRT in a chloride containing
media comparing three different stainless steels yielded the following Force vs. Time
graph displayed in Figure 4. While the alloy 17-4PH displayed superior mechanical
characteristics, it had the most active pitting potential, rendering it unfit for use in the
chloride environment. Alternatively, these tests found N-50 to be the most noble,
ranking it superior in both mechanical strength and oxidation resistance to SS-316 [60].
N-50 has also been considered a candidate for high level waste (HLW) storage casks,
where it again outperforms SS-316L, as is demonstrated in Table IV, with the
composition of the test environment in Table V [61]. In both Brine and seawater, N-50
had a lower corrosion rate than SS-316.

**Table III**: A compilation of experimentally observed properties of N-50 and SS-316,
demonstrating the relative superiority of N-50 to SS-316 [46, 58, 59, 62].

<table>
<thead>
<tr>
<th>Steel</th>
<th>SS-316</th>
<th>N-50</th>
<th>N-50#</th>
<th>Sintered N-50</th>
<th>N-50$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate Tensile Stress, (MPa)</td>
<td>579</td>
<td>717-827</td>
<td>827</td>
<td>597</td>
<td>662-673</td>
</tr>
<tr>
<td>Yield Stress. (MPa)</td>
<td>290</td>
<td>393-413</td>
<td>427*</td>
<td>398*</td>
<td>X</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>50</td>
<td>50-60</td>
<td>45</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

# = 0.002 in./in./min strain rate, 289°C air-saturated water environment
$ = 0.0008 mm/min strain rate, -100°F
* = 0.2% offset
Figure 4: Reported slow strain rate test results obtained in a 30 wt% MgCl$_2$ solution at 155°C at a strain rate of $3.7 \times 10^{-7}$ mm/s from Ziaei et al., Stress Corrosion Cracking: The Slow Strain-Rate Technique, 1979 [60].

Table IV: Reported corrosion rates of N-50 and SS-316L in deoxygenated solutions were composed of ten different dissolved ions in varying concentrations, at 250°C [61].

<table>
<thead>
<tr>
<th>Steel</th>
<th>Brine A (mm/year)</th>
<th>Seawater (mm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-316L</td>
<td>0.015</td>
<td>0.005</td>
</tr>
<tr>
<td>N-50</td>
<td>0.008</td>
<td>0.003</td>
</tr>
</tbody>
</table>
Table V: Concentration of major ions in solution [61].

<table>
<thead>
<tr>
<th>Ion</th>
<th>Brine A, (ppm) ppm</th>
<th>Seawater, (ppm) ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>42,000</td>
<td>10,651</td>
</tr>
<tr>
<td>K⁺</td>
<td>30,000</td>
<td>380</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>35,000</td>
<td>1,272</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>600</td>
<td>400</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>5</td>
<td>13</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>190,000</td>
<td>18,980</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>3,500</td>
<td>884</td>
</tr>
<tr>
<td>I⁻</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>700</td>
<td>146</td>
</tr>
<tr>
<td>Br⁻</td>
<td>400</td>
<td>65</td>
</tr>
<tr>
<td>BO₃⁻</td>
<td>1200</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>6.5</td>
<td>8.1</td>
</tr>
<tr>
<td>Total Dissolved Solids:</td>
<td>306g/L</td>
<td>35g/L</td>
</tr>
</tbody>
</table>

The corrosion studies, including characterization of the oxides, chlorides, or sulfides formed on the surface, are only valid for the specific environment to which the samples were exposed. Therefore, despite significant knowledge regarding N-50’s performance in certain environments, extensive testing during exposure to SCW is required before it can be considered for use in the SCWR.

This study explores the characteristics of N-50 when exposed to supercritical water through SSRTs, electrochemical polarizations, and surface analysis. Mechanical and electrochemical properties are presented across the temperatures required for SCWRs, assessing the viability of N-50 as a structural material. The SCWR must employ structural materials which maintain integrity across a wide range of temperatures, spanning both sub and supercritical conditions. Thus, in order to evaluate the ability of materials to function in a SCWR, samples must be tested over a range of parameters to replicate the conditions. In order to establish a baseline for the
mechanical properties for both steels, slow strain rate testing was executed in an inert atmosphere of nitrogen, as well as water at ambient temperature and pressure. The 200°C and 8MPa conditions were chosen to represent a condition between ambient conditions and the 300°C and 15MPa testing conditions, which is within the operating conditions of current pressurized water reactors [63]. The final conditions of 425°C and 27MPa was selected to expose the samples to a supercritical environment within the operating conditions of proposed SCWR [13].
Chapter 2. Experimental

2.1 Materials

SS-316 was obtained from McMaster-Carr, and N-50 was obtained from HP Alloys. All samples within each material were from the same batch. Samples were cut using CO₂ laser. Sample geometry adheres to modified ASTM E8/E8M – 13a for pin-loaded tension test specimen. Computer-Aided Design (CAD) file for sample provided by MSM is shown in Figure 5. All samples underwent testing in their as-received conditions, only being rinsed with ethanol and D.I. water, to remove surface contaminants, prior to experimentation.

![Figure 5: CAD drawing used for CO₂ laser cutter. Prior to testing in the SCWL, all samples were washed with ethanol and D.I. to remove any contaminants from the surface. No further preparation was done.](image-url)
2.2 Testing Equipment

Both polarization and slow strain rate tests of SS-316 and N-50 were performed in the SCWL at the University of Nevada, Reno. The SCWL is composed of the flow loop, shown in Figure 6, and the autoclave, shown in Figure 7. The SCWL is capable of maintaining a temperature of up to 600°C and pressures up to 30MPa. The autoclave is constructed using Inconel 625, as is any tubing that contains heated water. This was done to minimize corrosion of the SCWL.

**Figure 6.** Supercritical water flow loop showing A) Front panel, including temperature and pressure readings, and high pressure pump. B) Automated control system for slow strain rate testing, as well as temperature and pressure.
2.3 SCWL Operation

Specimens were secured using either a ¼ in. SS-304 pin for slow strain rate tests, or a ¼ in. alumina rod for electrochemical polarization. A fresh pair of pins and rods was used for each test. The alumina rods were used to electrically insulate the sample from the holder. The sample holders and experimental setups are shown in Figure 8. The autoclave was sealed and purged with nitrogen once the samples were secured, and then it was then filled with 18 MΩ D.I. water, hereafter referred to as the solution. It was then pressurized prior to heating.

Figure 7: Autoclave, including stand, pull-rod, and electrical connections. A) Full stand, with autoclave lid suspended above chamber. B) Interior of autoclave, with sample in center.
Figure 8: Sample holder for specimen A) Configuration for mechanical testing and B) Electrochemical test.

The SCWL system control software allows for programming parameters designed to reach different temperatures. Due to undesirable transients encountered through the phase change, supercritical operations require preliminary heating to 350°C, allowing for the maximum solution supply temperature, before increasing temperature again into the supercritical region. Figure 9 displays a typical heating curve observed for the SCWL testing conditions at 425°C.
Figure 9: The temperature of the water inside the autoclave. The delay at roughly 350°C is to allow the supply solution to reach the maximum temperature before increasing heater temperatures.

In agreement with prior studies, dissolved oxygen in the solution was maintained below 10 ppb during testing in order to avoid oxidation of the SCWL flow loop [64-66]. The high pressure pump was maintained at 30 mL/min during all heating and cooling. After the desired experiment was completed, all heating was ceased, and the solution was allowed to cool until it was below 70°C. The high pressure pump was then shut off and pressure returned to ambient conditions. The autoclave was then drained and purged with nitrogen.
2.3.1 Slow Strain Rate Test Operation

A slow strain rate test continuously varies the load in order to achieve a constant strain rate. \(3.5 \times 10^{-4}\) mm/s was selected as the strain rate for all mechanical tests in this study. A stress transducer recorded the load in Newtons, while two linear variable differential transformers (LVDTs) recorded the extension in micrometers. These values were plotted as a stress vs. strain curve to identify material characteristics such as the regions of elastic and plastic deformation, as well as the ultimate tensile stress (UTS) and total elongation. The parameters for the SSRTs in this study are shown in Table VI. SS-316 and N-50 were independently subjected to these conditions. All experiments were conducted in duplicates to ensure repeatability and validate experimental observations. All tests were conducted until sample failure, followed by cooling the manner described above.

**Table VI**: Conditions for the slow strain rate tests are listed. Extension rate was kept constant at \(3.5 \times 10^{-4}\) mm/s in all experiments.

<table>
<thead>
<tr>
<th>SSRT</th>
<th>Temperature</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Room Temperature, (N_2)</td>
<td>Ambient</td>
</tr>
<tr>
<td></td>
<td>Room Temperature, (H_2O)</td>
<td>Ambient</td>
</tr>
<tr>
<td></td>
<td>200°C, (H_2O)</td>
<td>8MPa</td>
</tr>
<tr>
<td></td>
<td>300°C, (H_2O)</td>
<td>15MPa</td>
</tr>
<tr>
<td></td>
<td>425°C, (H_2O)</td>
<td>27MPa</td>
</tr>
</tbody>
</table>

2.3.2 Electrochemical Polarization

A Gamry™ PCI4/300 Potentiostat/Galvanostat/ZRA in conjunction with EChem Analyst software version 6.03 was employed to conduct and analyze all electrochemical testing. Potentiodynamic polarization facilitated evaluating the
electrochemical activity, and study the polarization behavior of each material at a given set of experimental conditions. A Nichrome mesh was used as the counter electrode, and the reference electrode was a 0.5 mm diameter platinum wire of greater than 99.99 wt% purity. Electrical connections were made using a 0.5 mm diameter SS-316 that was spot-welded to the sample. Open Circuit potential, $E_{OCP}$, was monitored and the samples were polarized from -500mV vs $E_{OCP}$ to +500mV vs $E_{OCP}$ at a rate of 1mV/s. The experimental conditions for polarization are displayed in Table VII

**Table VII**: Electrochemical polarization conditions for all samples that underwent potentiodynamic polarization testing.

<table>
<thead>
<tr>
<th>Polarization</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial $E$ vs $E_{OCP}$, (V)</td>
<td>-0.5</td>
</tr>
<tr>
<td>Final $E$ vs $E_{OCP}$, (V)</td>
<td>0.5</td>
</tr>
<tr>
<td>Scan Rate, (mV/s)</td>
<td>1</td>
</tr>
</tbody>
</table>

2.4 Characterization Methods

Post experiment, all samples were placed in plastic bags and removed to an inert atmosphere glovebox, where they were dried under vacuum. Traditional optical microscopy was performed at 80 x magnification using an OLYMPUS PMG 3 microscope, shown in Figure 10. This allowed for characterization of both the failed section of the sample, as well as, the bulk features such as surface cracks. A Hitachi S-4700 Field Emission Scanning Electron Microscope, shown in Figure 11, was used to study the surface morphology of samples. This SEM allowed for up to 500,000-x magnification, permitting detailed morphological analysis of the sample's failure morphology, as well as the formation of oxides.
Figure 10: The OLYMPUS PMG 3 microscope allowed for a clearer demonstration of bulk features.

Figure 11: Hitachi S-4700 Field Emission Scanning Electron Microscope. High magnification allowed for better morphological characterization of sample.

A Thermo-Scientific DXR dispersive Raman microscope, shown in Figure 12, with OMNIC 9 software was utilized to characterize the oxide formations on the sample.
surfaces. This instrument allowed for both point analysis and 2D spectral mapping of the samples. Raman scattering is a form of inelastic scattering which allows for identification of the vibrational and rotational modes of a molecular system. The resulting spectra were then compared to both values found in literature, as well as, with standards collected on the specific instrument to accurately characterize surface chemistry of the sample. Using a 10mW 532nm laser, 64 exposures of 10 seconds each was collected at 100 x magnification for analysis from all samples. The Omnic software allows for the removal of artifacts, an example of which is shown in Figure 13. The removed peaks were consistent across samples, and did not interfere with the identification of oxides.

Figure 12: Thermo-Scientific DXR dispersive Raman microscope used for identification of oxide formations.
**Figure 13:** Raman spectra of SS-316, having undergone slow strain rate testing in liquid water at 300°C, 15MPa, showing both original spectrum and spectrum with artifacts removed.
Chapter 3. Initial Sample Characteristics

Samples of both materials, N-50 and SS-316, were characterized in their as-received state to establish their initial properties. All of the following analyses techniques were performed on the same samples after rinsing in ethanol and D.I. water with no additional surface treatment prior to or in between analysis.

3.1 Optical Microscopy

Samples of as-received N-50 and SS-316 were imaged with optical microscopy to establish a baseline to determine changes in morphology that would occur as a result of experimentation. Figure 14 shows images of both materials without any surface treatment. There is an observable difference in the two surfaces. N-50 bears linear markings with a rough surface and contains macroscopic surface features. SS-316 has no such markings, and significantly lesser amount of macroscopic defects.

![Figure 14: Optical micrograph of as-received samples: A) N-50 and B) SS-316. The surfaces differ greatly, with N-50 having larger amount of surface features.](image)
3.2 Scanning Electron Microscopy

Following optical microscopy, samples were imaged using SEM. Micrographs of each material in their as-received conditions are displayed in Figure 15. The features of SS-316 are consistent with the optical images, whereas the micrograph of N-50 is of a smooth section, not corrosion pit. Thus, the discolorations observed in optical microscopy images are due to surface roughness.

![Figure 15: SEM micrographs of as-received A) N-50 and B) SS-316. The surface of N-50 is much more uniform than that of SS-316, which bears a venetian surface morphology indicating the SS-316 underwent acid roughening [67]. SEM was operated at 20kV and 10k magnification for A, and 10kV and 10k magnification for B.](image)

3.3 Raman Spectroscopy

Raman spectroscopy was used to characterize the vibrational and rotational modes of the oxide films present on the surface of samples that underwent either slow strain rate testing or electrochemical polarization. Figure 16 shows the Raman spectra of the two steels in their as-received state. Magnetite (Fe$_3$O$_4$) and hematite (Fe$_2$O$_3$) standards were obtained from Alfa Aesar, and a NiFe$_2$O$_4$ standard was obtained from
US Research and Nanomaterials Inc. The spectra from the standards are shown in Figure 17. There is considerable overlap between the magnetite and hematite standards, due to the common vibrational modes of iron oxide bonds. They are distinguishable from one another by the feature at 539 wavenumbers for magnetite, and the feature at 603 wavenumbers for hematite.

It is known that austenitic stainless steels form a bi-layer in de-oxygenated water, with an inner layer predominantly comprised of a chromium rich spinel, and an outer layer of magnetite or iron-nickel spinel [68]. A correlation has been reported between the iron content of spinels in the form NiFe$_{2-x}$Cr$_x$O$_4$; the Raman feature shifts to higher wavenumbers as the amount of iron increases [69]. Table VIII shows the Raman peak positions obtained from standards alongside values from various literature references. A range of values exists for each compound, demonstrating the minor inconsistencies in Raman analyses. To avoid these systematic errors, the standards analyzed in this study were used as the primary means of identification of oxides.

![Figure 16](Figure 16: Raman spectra from as-received samples of N-50 and SS-316. The samples display nearly identical spectra indicating a native oxide film consisting of chromium and magnetite [70].)
Figure 17: Raman spectra obtained from standards of A) magnetite B) hematite C) NiFe$_2$O$_4$. 
Table VIII: Comparison of features observed in Raman spectra collected in this study with literature values for A) magnetite, B) hematite, and C) NiFe$_2$O$_4$ [69, 71-76].

(A) **Magnetite**

<table>
<thead>
<tr>
<th>This Study</th>
<th>Hosterman [69]</th>
<th>McCarty et al. [71]</th>
<th>de Faria et al. [76]</th>
<th>Shebanova et al. [72]</th>
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</thead>
<tbody>
<tr>
<td>665</td>
<td>667</td>
<td>671</td>
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<tr>
<td>539</td>
<td>531</td>
<td>542</td>
<td>533.6</td>
<td>538</td>
</tr>
<tr>
<td>482</td>
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<td>513</td>
<td></td>
</tr>
<tr>
<td>401</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>294</td>
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<td></td>
<td>301.6</td>
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<td>219</td>
<td></td>
<td></td>
<td></td>
<td>193</td>
</tr>
</tbody>
</table>

(B) **Hematite**

<table>
<thead>
<tr>
<th>This Study</th>
<th>Hosterman [69]</th>
<th>de Faria et al. [76]</th>
<th>Hanesch [73]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1305</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>603</td>
<td>612.8</td>
<td>611.9</td>
<td></td>
</tr>
<tr>
<td>498</td>
<td>498.5</td>
<td>497.1</td>
<td></td>
</tr>
<tr>
<td>402</td>
<td>410.8</td>
<td>410.9</td>
<td>412</td>
</tr>
<tr>
<td>289</td>
<td>298.6</td>
<td>292.5, 299.3</td>
<td>290-300</td>
</tr>
<tr>
<td></td>
<td>245.4</td>
<td>245.7</td>
<td>245</td>
</tr>
<tr>
<td>222</td>
<td>226</td>
<td>226.7</td>
<td>225</td>
</tr>
</tbody>
</table>

(C) **NiFe$_2$O$_4$**

<table>
<thead>
<tr>
<th>This Study</th>
<th>Hosterman [69]</th>
<th>Kim et al. [74]</th>
<th>Graves et al. [75]</th>
</tr>
</thead>
<tbody>
<tr>
<td>695</td>
<td>704</td>
<td>702</td>
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<td>339</td>
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<td></td>
<td>211</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chapter 4. Results

4.1 Slow Strain Rate Test Characteristics

4.1.1 Experiments Conducted in an Inert Atmosphere

The engineering stress-strain curves for inert conditions are displayed in Figure 18. Equation 2 was used to determine stress from the area across which force is applied, and Equation 3 was used to determine strain by the amount of deformation and original dimension [77].

\[ \sigma = \frac{F}{A} \]  \hspace{1cm} (Equation 2)

\[ \varepsilon = \frac{\Delta l}{L} \]  \hspace{1cm} (Equation 3)

These baseline values allow for a comparison of degradation of mechanical properties under subsequent testing conditions. The engineering stress-strain graphs are the result of individual slow strain rate tests, however the characteristic values presented in discussion will refer to averaged values for the two slow strain rate tests for each steel at each condition, along with a table showing the percent change in values from the previous SSRT. For the duplicate samples, N-50 averaged an UTS of 830MPa, while SS-316 had an average UTS of 614MPa. A similar variation was observed in 0.5% YS, with N-50 averaging 458MPa, and SS-316 having an average of 357MPa. SS-316 did however experience a greater total elongation, 75% compared to the 60% elongation experienced by N-50. Thus, at these inert conditions, N-50 demonstrated greater tensile
strength, but less ductility. Table IX shows the values for each SSRT at these conditions.

\[
\begin{array}{|c|c|c|}
\hline
& \text{N-50, Inert} & \text{SS-316, Inert} \\
\hline
0.5\% \text{YS} & 489 \text{ MPa} & 362 \text{ MPa} \\
\text{UTS} & 832 \text{ MPa} & 615 \text{ MPa} \\
\text{Elongation} & 60 \% & 75 \% \\
\hline
\end{array}
\]

**Figure 18:** Engineering stress-strain curves for A) N-50 and B) SS-316 under inert conditions. N-50 displays significantly higher UTS, while SS-316 possesses greater ductility.

Failed samples were characterized by sample region, which are demonstrated in Figure 19. These region designations will be used for all samples. The unstrained region is off-
axis from the applied uniaxial tension, the fillet is area of circular reduction leading to the gauge, which is the section that undergoes deformation. Until the UTS is attained, the gauge undergoes uniform deformation. The area on the gauge which undergoes necking deformation after UTS will be referred to as the neck region.

![Image](image-url)

**Figure 19:** Demonstrates the A) original sample and B) different regions of the failed samples, using an N-50 sample from a slow strain rate test under nitrogen atmosphere. All regions are defined as the surface along the length of the sample.

**Table IX:** All values for slow strain rate tests for both N-50 and SS-316.

<table>
<thead>
<tr>
<th>Specimen/Inert</th>
<th>UTS, MPa</th>
<th>0.5% YS, MPa</th>
<th>Time till failure, h</th>
<th>Specimen/Inert TTF, %</th>
<th>Elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-50</td>
<td>832</td>
<td>489</td>
<td>7.9</td>
<td>X</td>
<td>60</td>
</tr>
<tr>
<td>N-50</td>
<td>828</td>
<td>427</td>
<td>8.1</td>
<td>X</td>
<td>61</td>
</tr>
<tr>
<td>SS-316</td>
<td>613</td>
<td>351</td>
<td>10.4</td>
<td>X</td>
<td>74</td>
</tr>
<tr>
<td>SS-316</td>
<td>615</td>
<td>362</td>
<td>10.1</td>
<td>X</td>
<td>75</td>
</tr>
</tbody>
</table>
4.1.2 Experiments Conducted in Ambient Water

The first experiment in solution was conducted under ambient conditions (room temperature and pressure). The engineering stress-strain curves, and salient mechanical characteristics, are presented in Figure 20. The mechanical properties for both steels remain near or at those from the slow strain rate tests under inert conditions discussed previously. The UTS for N-50 was 822MPa, while SS-316 was considerably lower at 609MPa. Similarly, N-50 demonstrated a greater yield stress, 529MPa, than SS-316, which had a yield stress of 359MPa. The only observed characteristic where SS-316 was superior was in elongation, 73% compared to the 62% experienced by N-50. Table X shows all values for both N-50 and SS-316 at these conditions. Table XI shows the percentage change of these characteristics, along with the change in the specimen’s time till failure (TTF) compared to inert conditions.
Figure 20: Engineering stress-strain curves for A) N-50 and B) SS-316 in the test solution at ambient temperature and pressure. In agreement with the testing under inert conditions, N-50 displays significantly higher UTS, while SS-316 possesses greater ductility.
Table X: Characteristics observed from slow strain rate tests for both N-50 and SS-316 samples. N-50 has higher UTS and 0.5% YS, while SS-316 is more ductile.

<table>
<thead>
<tr>
<th></th>
<th>UTS, MPa</th>
<th>0.5% YS, MPa</th>
<th>Time till failure, h</th>
<th>Specimen/Inert TTF, %</th>
<th>Elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-50</td>
<td>822</td>
<td>545</td>
<td>8.3</td>
<td>100</td>
<td>63</td>
</tr>
<tr>
<td>N-50</td>
<td>821</td>
<td>513</td>
<td>8.1</td>
<td>100</td>
<td>60</td>
</tr>
<tr>
<td>SS-316</td>
<td>607</td>
<td>373</td>
<td>9.9</td>
<td>96</td>
<td>72</td>
</tr>
<tr>
<td>SS-316</td>
<td>611</td>
<td>345</td>
<td>10.3</td>
<td>100</td>
<td>73</td>
</tr>
</tbody>
</table>

Table XI: The percentage change for both steels from inert atmospheric conditions to ambient water conditions. The averaged values are relatively stable values, particularly for UTS, elongation, and TTF.

<table>
<thead>
<tr>
<th></th>
<th>UTS</th>
<th>0.5% YS</th>
<th>Elongation</th>
<th>Specimen/Inert TTF</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-50</td>
<td>-1</td>
<td>16</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>SS-316</td>
<td>-1</td>
<td>1</td>
<td>-3</td>
<td>-2</td>
</tr>
</tbody>
</table>

4.1.3 Experiments Conducted at 200°C

The first elevated temperature point was liquid water at 200°C, with a pressure of 8MPa. These parameters were chosen to provide a consistent incremental increase in both temperature and pressure from ambient conditions through to the higher temperatures and pressures discussed in subsequent sections. The engineering stress-strain curves obtained under these conditions are presented in Figure 21. The most noticeable effect of these conditions was the reduction of the ductility in SS-316. Under inert and ambient conditions, SS-316 had superior ductility over N-50, and experienced elongations of 70% for both the inert atmosphere and ambient water slow strain rate tests. This value was greatly reduced to 44.5% ductility experiments at 200°C for SS-
316, and to 46% ductility for N-50 under this elevated temperature. N-50 again had higher UTS than SS-316, as it averaged 639MPa compared to 412MPa observed in SS-316. Likewise, N-50 had an average 0.5% offset yield stress of 314MPa, whereas SS-316 had an average 0.5% offset yield stress of 249MPa. The modulus of elasticity showed similar trends; modulus of elasticity for SS-316 decreased from 123GPa to 109GPa for an 11% reduction from inert conditions, and that N-50 decreased from 148GPa to 141GPa, a 5% reduction in the modulus of elasticity from inert conditions. Table XII shows all values for both N-50 and SS-316 at 200°C, 8MPa. Table XIII shows the percentage change of these characteristics compared to ambient water conditions.
Figure 21: Engineering stress-strain curves for A) N-50 and B) SS-316 in solution at 200°C and 8MPa. Both samples showed marked decrease in tensile strength. The ductility of SS-316 was dramatically lower at 200°C compared to ductility in inert conditions and ambient water.
Table XII: Observed values for slow strain rate tests for both N-50 and SS-316. N-50 maintains its superior strength, while SS-316 has a decrease in ductility. N-50 shows greater elongation at these conditions as well, though not considerably so.

<table>
<thead>
<tr>
<th></th>
<th>UTS, MPa</th>
<th>0.5% YS, MPa</th>
<th>Time till failure, h</th>
<th>Specimen/Inert TTF, %</th>
<th>Elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-50</td>
<td>643</td>
<td>324</td>
<td>7.1</td>
<td>89</td>
<td>48</td>
</tr>
<tr>
<td>N-50</td>
<td>634</td>
<td>303</td>
<td>7.1</td>
<td>88</td>
<td>47</td>
</tr>
<tr>
<td>SS-316</td>
<td>408</td>
<td>238</td>
<td>6.3</td>
<td>61</td>
<td>44</td>
</tr>
<tr>
<td>SS-316</td>
<td>415</td>
<td>240</td>
<td>6</td>
<td>58</td>
<td>45</td>
</tr>
</tbody>
</table>

Table XIII: Percentage change of slow strain rate test (SSRT) characteristics from ambient conditions to 200°C, 8MPa conditions.

<table>
<thead>
<tr>
<th>Specimen/Inert TTF</th>
<th>UTS</th>
<th>0.5% YS</th>
<th>Elongation</th>
<th>Specimen/Inert TTF</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-50</td>
<td>-23</td>
<td>-32</td>
<td>-21</td>
<td>-11</td>
</tr>
<tr>
<td>SS-316</td>
<td>-33</td>
<td>-33</td>
<td>-40</td>
<td>-40</td>
</tr>
</tbody>
</table>

4.1.4 Experiments Conducted at 300°C

The second elevated temperature point was liquid water at 300°C, and 15MPa pressure. These are within the operating parameters of current PWRs [63]. Figure 22 shows the engineering stress-strain curves for both steels under these conditions. SS-316 displays locking serrations, where the sharp increases in stress are the result of forming new dislocation bands, and the drop in stress is the result of new dislocation creation [78]. This is a form of work hardening, as the newly formed dislocations become locked, increased stress is needed to form and propagate a dislocation band [78]. N-50 does not show serrations, indicating uniform deformation until UTS, after which necking occurs. An average UTS of 363MPa was observed for SS-316, while the average UTS for N-50 was found to be 588MPa. N-50 also has a 0.5% YS of 258MPa,
which is higher than 0.5% YS of SS-316, which was found to be 160MPa. The total elongation is similar for both steels with N-50 experiencing 48% and SS-316 experiencing 44% elongation. Table XIV shows all values for SSRTs at these conditions. Table XV shows the percentage change of these characteristics from 200°C to 300°C. The most drastic alteration is the 33% decrease in 0.5% YS SS-316 exhibits.

![Engineering stress-strain curves](image)

**Figure 22:** Engineering stress-strain curves for A) N-50 and B) SS-316 in solution at 300°C and 15MPa. Both samples tensile strength continue to decrease from the previous slow strain rate tests. Only SS-316 displays locking serrations.
Table XIV: Various characteristics as observed and calculated from slow strain rate tests at these conditions. N-50 actually shows greater elongation than SS-316, while maintaining overall superiority of tensile strength.

SSRT Conducted at 300°C, 15MPa

<table>
<thead>
<tr>
<th>Specimen/Inert</th>
<th>UTS, MPa</th>
<th>0.5% YS, MPa</th>
<th>Time till failure, h</th>
<th>Specimen/Inert TTF, %</th>
<th>Elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-50</td>
<td>595</td>
<td>267</td>
<td>7.0</td>
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</tr>
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<td>N-50</td>
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<td>249</td>
<td>6.2</td>
<td>78</td>
<td>46</td>
</tr>
<tr>
<td>SS-316</td>
<td>361</td>
<td>154</td>
<td>6.2</td>
<td>67</td>
<td>45</td>
</tr>
<tr>
<td>SS-316</td>
<td>365</td>
<td>165</td>
<td>5.7</td>
<td>56</td>
<td>43</td>
</tr>
</tbody>
</table>

Table XV: The greatest change for both N-50 and SS-316 was in 0.5% YS, indicating an earlier transition from elastic to plastic deformation for both. The reduction of strength was apparent in both, as they decreased in terms of UTS as well.

Percent Change from 200°C, 8MPa to 300°C, 15MPa

<table>
<thead>
<tr>
<th>Specimen/Inert</th>
<th>UTS</th>
<th>0.5% YS</th>
<th>Elongation</th>
<th>Specimen/Inert TTF</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-50</td>
<td>-8</td>
<td>-18</td>
<td>0</td>
<td>-7</td>
</tr>
<tr>
<td>SS-316</td>
<td>-12</td>
<td>-33</td>
<td>0</td>
<td>-6</td>
</tr>
</tbody>
</table>

4.1.5 Experiments Conducted at 425°C

At 425°C and 27MPa, the samples were exposed to supercritical water, and the conditions were within the operating regime of SCWRs [42]. Figure 23 shows the engineering stress-strain graphs for the slow strain rate tests for both steels under these conditions. Both N-50 and SS-316 display locking serrations, with two other serration modes observed in SS-316. Figure 24 shows the two additional serrations observed in SS-316. The serrations shown in Figure 24 A are known to occur as a result of the same mechanism previously described for locking serrations, but with a reduction in strain hardening [79]. The rapid serrations shown in Figure 24 B shows are known as the Portevin-Le Chatelier effect (PLC), having first been reported in 1909 by Le Chatelier, and they are the result of dynamic strain aging [80]. This phenomena has
been described as arising from solute atoms becoming segregated at mobile dislocations [78, 81]. N-50 does not exhibit these additional effects, and is therefore less altered under these conditions. These results are in agreement with other work, as dynamic strain aging has been observed in austenitic steels for use in pressure vessels at strain rates and temperatures comparable to this study [82]. Table XVI shows all values for SSRT at these conditions. Table XVII shows the average calculated values averaged for SSRTs conducted on both N-50 and SS-316. N-50 maintains its superiority in mechanical strength to SS-316, with an UTS roughly 200MPa greater than SS-316. Both steels display significant degradation of mechanical properties at supercritical conditions as compared to the simulated PWR temperature and pressure of 300°C. However, N-50 suffered relatively less deterioration in both UTS and 0.5% YS. N-50 displayed a 20% reduction in UTS, compared to 24% reduction in UTS seen for SS-316. The difference in 0.5% YS is more drastic, with N-50 experiencing a 47% reduction in 0.5% YS, while SS-316 experienced a 69% reduction in 0.5%. In contrast to all other previous trends, the elongation and time till failure of the sample as compared to inert conditions were less severe for SS-316 than N-50; the N-50 experienced a 13% reduction in elongation compared to the relatively stable 2% reduction in elongation observed for SS-316. N-50% demonstrated a 6% reduction in failure time compared to inert conditions than at 300°C, while SS-316 underwent a 4% increase in time till failure compared to inert conditions.
Figure 23: Engineering stress-strain curves for A) N-50 and B) SS-316 in solution at 425°C and 27MPa. Both samples were observed to have lower strength from the previous slow strain rate test, and both display locking serrations. However, SS-316 also displays Portevin-Le Chatelier (PLC) effect serrations, indicating dynamic strain aging [83].
Table XVI: Observed and calculated characteristic values from SSRTs at these conditions. N-50 again displayed higher UTS and 0.5% YS than SS-316, though their elongation was nearly identical at supercritical conditions.

<table>
<thead>
<tr>
<th></th>
<th>UTS, MPa</th>
<th>0.5% YS, MPa</th>
<th>Time till failure, h</th>
<th>Specimen/Inert TTF, %</th>
<th>Elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-50</td>
<td>472</td>
<td>137</td>
<td>6</td>
<td>75</td>
<td>41</td>
</tr>
<tr>
<td>N-50</td>
<td>466</td>
<td>138</td>
<td>6.4</td>
<td>80</td>
<td>42</td>
</tr>
<tr>
<td>SS-316</td>
<td>277</td>
<td>57</td>
<td>6.1</td>
<td>75</td>
<td>42</td>
</tr>
<tr>
<td>SS-316</td>
<td>277</td>
<td>44</td>
<td>6.6</td>
<td>72</td>
<td>44</td>
</tr>
</tbody>
</table>

Table XVII: Calculated characteristics from SSRT tests. SS-316 demonstrated a greater reduction in strength than N-50 as shown by the greater percentage decrease in UTS and 0.5% YS. However, SS-316 was found to be more ductile than N-50 as seen from % elongation when compared to slow strain rate testing at 300°C conditions.

Percent Change from 300°C, 15MPa to 425°C, 27MPa

<table>
<thead>
<tr>
<th></th>
<th>UTS</th>
<th>0.5% YS</th>
<th>Elongation</th>
<th>Specimen/Inert TTF</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-50</td>
<td>-20</td>
<td>-47</td>
<td>-13</td>
<td>-6</td>
</tr>
<tr>
<td>SS-316</td>
<td>-24</td>
<td>-68</td>
<td>-2</td>
<td>4</td>
</tr>
</tbody>
</table>
Figure 24: Engineering stress-strain curves for SS-316 in solution at 425°C and 27MPa demonstrating A) serrations with reduced work hardening and the B) Portevin-Le Chatelier effect.
4.1.6 Summary of Slow Strain Rate Tests

A compilation of the results obtained from the slow strain rate tests is displayed in Table XVIII for N-50, and Table XIX for SS-316. N-50 demonstrates higher mechanical strength, as indicated by greater UTS and 0.5% YS at all conditions. The average values of the two slow strain rate tests is displayed in Figures 25 and 26, along with light blue bars indicating the maximum and minimum values recorded for each testing parameter. Figure 25 compares the UTS and 0.5% YS of both steels from SSRT at each condition, with N-50 demonstrating a clear difference over SS-316. Figure 26 shows the elongation and specimen/inert time till failure across all conditions. At all elevated temperature testing conditions, N-50 and SS-316 demonstrated similar elongation. However, N-50 exhibited a 33% lower in elongation at supercritical conditions compared to inert conditions, whereas SS-316 was observed to be 42% lower.

The serrations observed at 300˚C for SS-316 and at 425˚C for N-50 are known as locking serrations, and indicate the creation of new vacancies as the mode of deformation [78]. The higher frequency serrations shown in Figure 24 B) are known as the Portevin-Le Chatelier (PLC) effect. PLC is the result of dynamic strain aging, where solute and dislocation interactions cause discontinuous deformation as dislocations move within the band [78]. Temperature dependence between locking serrations and PLC has been observed, in that PLC will occur at higher temperatures in materials that had previously exhibited locking serrations at lower temperatures [78]. The observations in this study are in agreement with these observations. The serrations shown in Figure 24 A) have been characterized as locking serrations with a reduction or absence of
work hardening [79]. This is supported by the observation that both the work hardening exponent and coefficient in steels reach a maximum in the dynamic strain aging region, but decrease with increasing temperature [84, 85]. N-50 does not display these features when exposed to supercritical water. Figure 27 shows the samples after failure from each set of testing conditions.

Figure 28 shows the Young’s modulus for both steels in each experimental environment as determined by a sum of least squares of the slope of the linear region of the engineering stress-strain curve, in accordance with ASTM E111-04. Figure 29 shows a comparison of the Young’s moduli for individual samples of SS-316 at different conditions. N-50 experienced relatively less variation in Young’s modulus, whereas SS-316 shows a drastic 77% increase under supercritical water environment compared to inert conditions. A study performed at Tufts University observed an increase in Young’s modulus of 22.7% by tensile tests after cathodic hydrogenation of 21-6-9 stainless steel [86]. An increase in Young’s modulus has recently been observed through acoustic measurements, where it was hypothesized to result from hydrogenation, and subsequent stress redistribution [87]. It has also been established that in austenitic stainless steels the $\gamma$(fcc) phase will become $\varepsilon$(hcp) hydride with the addition of hydrogen, which will then decompose with the removal of hydrogen into an $\alpha$(bcc) phase [88-91]. N-50 is well known to possess superior mechanical traits at subcritical water conditions [46, 58, 59, 62, 92]. This study demonstrates that N-50 maintains its mechanical superiority over SS-316 under supercritical water conditions, as well, showing that N-50 is less mechanically altered by supercritical conditions than SS-316.
Table XVIII: Observed and calculated mechanical characteristics of N-50 across the testing conditions.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Ultimate Tensile Stress, MPa</th>
<th>0.5% Yield Stress, MPa</th>
<th>Time till failure, h</th>
<th>Specimen / Inert TTF, %</th>
<th>Elongation, %</th>
<th>Young’s Modulus, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2, ambient</td>
<td>832</td>
<td>489</td>
<td>7.9</td>
<td>X</td>
<td>60</td>
<td>148</td>
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<tr>
<td>N2, ambient</td>
<td>828</td>
<td>427</td>
<td>8.1</td>
<td>X</td>
<td>61</td>
<td>147</td>
</tr>
<tr>
<td>H₂O, ambient</td>
<td>822</td>
<td>545</td>
<td>8.3</td>
<td>100</td>
<td>63</td>
<td>174</td>
</tr>
<tr>
<td>H₂O, ambient</td>
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<td>513</td>
<td>8.1</td>
<td>100</td>
<td>60</td>
<td>145</td>
</tr>
<tr>
<td>200°C, 8 MPa</td>
<td>643</td>
<td>324</td>
<td>7.1</td>
<td>89</td>
<td>48</td>
<td>135</td>
</tr>
<tr>
<td>200°C, 8 MPa</td>
<td>634</td>
<td>303</td>
<td>7.1</td>
<td>88</td>
<td>47</td>
<td>147</td>
</tr>
<tr>
<td>300°C, 15 MPa</td>
<td>595</td>
<td>267</td>
<td>7.0</td>
<td>88</td>
<td>50</td>
<td>146</td>
</tr>
<tr>
<td>300°C, 15 MPa</td>
<td>580</td>
<td>249</td>
<td>6.2</td>
<td>78</td>
<td>46</td>
<td>131</td>
</tr>
<tr>
<td>425°C, 27 MPa</td>
<td>472</td>
<td>137</td>
<td>6.0</td>
<td>75</td>
<td>41</td>
<td>135</td>
</tr>
<tr>
<td>425°C, 27 MPa</td>
<td>466</td>
<td>138</td>
<td>6.4</td>
<td>80</td>
<td>42</td>
<td>138</td>
</tr>
</tbody>
</table>
Table XIX: Observed and calculated mechanical characteristics of SS-316 across the testing conditions.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Ultimate Tensile Stress, MPa</th>
<th>0.5% Yield Stress, MPa</th>
<th>Time till failure, h</th>
<th>Specimen / Inert TTF, %</th>
<th>Elongation, %</th>
<th>Young's Modulus, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2, ambient</td>
<td>613</td>
<td>351</td>
<td>10.4</td>
<td>X</td>
<td>74</td>
<td>121</td>
</tr>
<tr>
<td>N2, ambient</td>
<td>615</td>
<td>362</td>
<td>10.1</td>
<td>X</td>
<td>75</td>
<td>125</td>
</tr>
<tr>
<td>H₂O, ambient</td>
<td>607</td>
<td>373</td>
<td>9.9</td>
<td>96</td>
<td>72</td>
<td>157</td>
</tr>
<tr>
<td>H₂O, ambient</td>
<td>611</td>
<td>345</td>
<td>10.3</td>
<td>100</td>
<td>73</td>
<td>131</td>
</tr>
<tr>
<td>200°C, 8 MPa</td>
<td>408</td>
<td>238</td>
<td>6.3</td>
<td>61</td>
<td>44</td>
<td>102</td>
</tr>
<tr>
<td>200°C, 8 MPa</td>
<td>415</td>
<td>240</td>
<td>6.0</td>
<td>58</td>
<td>45</td>
<td>115</td>
</tr>
<tr>
<td>300°C, 15 MPa</td>
<td>361</td>
<td>162</td>
<td>6.2</td>
<td>67</td>
<td>45</td>
<td>111</td>
</tr>
<tr>
<td>300°C, 15 MPa</td>
<td>365</td>
<td>166</td>
<td>5.7</td>
<td>56</td>
<td>43</td>
<td>101</td>
</tr>
<tr>
<td>425°C, 27 MPa</td>
<td>277</td>
<td>57</td>
<td>6.1</td>
<td>75</td>
<td>42</td>
<td>206</td>
</tr>
<tr>
<td>425°C, 27 MPa</td>
<td>277</td>
<td>44</td>
<td>6.6</td>
<td>72</td>
<td>44</td>
<td>246</td>
</tr>
</tbody>
</table>
Figure 25: Comparison of A) Ultimate Tensile Stress and B) 0.5% Yield Stress for N-50 and SS-316 conditions. N-50 demonstrates significantly greater tensile strength than SS-316 at all conditions. The light blue bars represent the maximum and minimum values recorded for the samples.
Figure 26: Comparison of A) Total elongation and B) The time till failure (TTF) as percent of TTF under inert conditions of N-50 and SS-316 across all conditions. N-50 experiences less variation in elongation than SS-316 across the testing regime, supporting the hypothesis that N-50 undergoes less deterioration. The light blue bars represent the maximum and minimum values calculated for the samples.
Figure 27: Slow strain rate test samples after failure. The missing gauges from the 300°C samples were removed for analysis. All samples show an increasingly darker surface coloration as temperature increases.

Figure 28: Comparison of Young’s modulus of N-50 and SS-316 comparison across all conditions. N-50 demonstrates relatively less variation in Young’s modulus across all conditions compared to SS-316. Young’s modulus for SS-316 was found to increase significantly under supercritical conditions. The light blue bars represent the maximum and minimum values calculated for the samples.
Figure 29: A comparison of the regions of linearity, representing the Young’s modulus, for SS-316 across all testing conditions. There is a relative increase in Young’s Modulus for samples under supercritical conditions over those that underwent testing at subcritical and inert conditions.

4.2 Optical Microscopy

4.2.1 Optical Micrographs from Samples tested in Inert Atmosphere

The samples were imaged using optical microscopy, and the results are shown in Figure 30. The surface morphology of the unstrained regions for both N-50 and SS-316 is consistent with the as-received samples. The highly deformed gauge and neck regions show metal that was unexposed prior to failure. However, due to the inert nature of the testing environment, this does not appear to change the amount of surface corrosion observed on either sample.
Figure 30: Optical micrographs of samples that underwent slow strain rate testing under inert N$_2$ atmosphere for N-50 (A,C,E,G) and SS-316 (B,D,F,H) for unstrained (A,B), fillet (C,D), gauge (E,F) and neck region (G,H). The unstrained and fillet regions display identical morphology to the as-received samples. The gauge, which undergoes deformation, appears to expose bare metal on the both samples. This is also evident at the neck region, where the dimensional change is significant to only allow a small area of effective focus.
4.2.2 Optical Micrographs from Samples Tested in Ambient Water

The morphological features that are present on samples that underwent SSRT under ambient conditions are shown in Figure 31. The unstrained and fillet regions are indistinguishable from the as-received samples for both steels. The ductility of both samples is apparent at the neck region, where the deformation allowed for effective focusing on only a small area.

4.2.3 Optical Micrographs from Samples Tested at 200°C

The micrographs obtained from samples that underwent SSRT at 200°C are displayed in Figure 32. There are distinct changes from mechanical properties discussed previously. Particularly, there is an increase in surface pits on the N-50 sample, and more general surface roughness is present on the SS-316 sample. Additionally, the surface of SS-316 appears to have defined cracks, where N-50 has maintained smoother deformation features.

4.2.4 Optical Micrographs from Samples Tested at 300°C

The optical micrographs of samples that underwent SSRT at 300°C are shown in Figure 33. Though signs of corrosion were present in both steels, N-50 did not appear to have an altered mode of deformation from the less extreme conditions presented earlier. Alternatively, SS-316 again shows surface cracks. The exposed fresh metal at SS-316’s neck region appears less corroded than the unstrained region. This indicates that the formation of oxides at the surface is dependent upon the temperature at which the alloy is exposed to the solution and the amount of time metal is exposed to the solution.
Figure 31: Optical micrographs of samples that underwent slow strain rate testing under ambient water for N-50 (A,C,E,G) and SS-316 (B,D,F,H) for unstrained (A,B), fillet (C,D), gauge (E,F) and neck region (G,H). The unstrained and fillet regions display identical morphology to the as-received samples. The gauge, which undergoes deformation, appears to expose bare metal on both samples. This is also evident at the neck region, where the dimensional change is significant to only allow a small area of effective focus. Both N-50 and SS-316 have an increase in surface defects in their respective gauge regions compared to the fillet and unstrained regions.
Figure 32: Optical micrographs of samples that underwent slow strain rate testing under 200°C, 8MPa conditions for N-50 (A,C,E,G) SS-316 (B,D,F,H) for unstrained (A,B), fillet (C,D), gauge (E,F) and neck region (G,H). The unstrained region of N-50 does not appear altered from the previous SSRTs, while there is a noticeable general surface roughness on the SS-316 unstrained region. For both N-50 and SS-316, the amount of surface defects increase from unstrained, to fillet, gauge, and neck regions.
Figure 33: Optical micrographs of samples that underwent slow strain rate testing under 300°C, 15MPa conditions for N-50 (A,C,E,G) and SS-316 (B,D,F,H) for unstrained (A,B), fillet (C,D), gauge (E,F) and neck region (G,H). All regions in both samples show increased degradation from the previous SSRTs. N-50 showed accelerated degradation along the edges of the linear surface marks in the unstrained and fillet regions, along with deeper defects. In the deformed gauge and neck regions, SS-316 shows surface cracks.
4.2.5 Optical Micrographs from Samples Tested at 425°C

The optical micrographs of the samples exposed to supercritical water, shown in Figure 34, are consistent with increased material degradation compared to the subcritical condition slow strain rate tests. N-50 shows signs of a new deformation mode on the surface as both gauge and neck regions. SS-316 again displays defined fractures on the surface.

4.2.6 Summary of Optical Microscopy Studies

In their as-received state, the surface of N-50 was less uniform and had more defects than that of SS-316. However, N-50 maintained this surface at conditions where SS-316 showed a notable increase in defects. The unstrained regions from the slow strain rate tests at 200°C shown in Figure 32 A) and B) for N-50 and SS-316, respectively, is the clearest example of this. However, it is also shown by the more prevalent surface cracks of SS-316, which are larger and more numerous than at corresponding regions of the N-50 samples. It cannot be determined by optical microscopy whether these cracks are in a surface film on the samples, or the base metal. However, at the neck region, an area which underwent rapid deformation, it is reasonable to assume that the deep fissures at least exposed base metal at the time of deformation.
Figure 34: Optical micrographs of samples that underwent slow strain rate testing under 425°C, 27MPa conditions for N-50 (A,C,E,G) and SS-316 (B,D,F,H) for unstrained (A,B), fillet (C,D), gauge (E,F) and neck region (G,H). All regions in both samples show increased degradation from the previous SSRTs. N-50 shows demonstrates enlarged nearly circular cracks in the deformed gauge and neck regions. The SS-316 appears more degraded at the neck region than N-50. The materials appear more degraded compared to the previous slow strain rate tests.
4.3 Scanning Electron Microscopy (SEM)

4.3.1 SEM Micrographs from Samples Tested in Inert Atmosphere

The failed surface was observed using SEM, and the results are presented in Figure 35. The fracture surface is identified as that of a ductile fracture, due to the cup and cone shape and characteristic spherical dimples.

Figure 35: SEM micrographs of failed surface of samples that underwent slow strain rate testing under inert N$_2$ atmosphere at 30 x magnification for A) N-50, B) SS-316, and at 1000 x magnification for C) N-50 and D) SS-316. Both samples display noticeable dimpling, which indicates areas of void formation during deformation. Both display a cup and cone fracture surface, indicative of ductile failure. SEM was operated at 20kV.
4.3.2 SEM Micrographs from Samples Tested in Ambient Water

SEM was used to characterize the ambient water samples. The micrographs that were obtained are shown in Figure 36. As with the optical micrographs, the SEM studies are consistent with the slow strain rate test samples from the inert atmosphere, in that the morphology indicates predominantly ductile failure. The spherical dimples of N-50 are smaller than those of SS-316.

4.3.3 SEM Micrographs from Samples Tested at 200°C

The SEM micrographs for both N-50 and SS-316 at 200°C and 8MPa are presented in Figure 37. A cup and cone fracture surface is apparent on both samples, which indicates a ductile failure, as was observed in the previous slow strain rate tests. Under greater magnification, surface features become apparent on the SS-316 sample, which are not present on the N-50 sample. These voids would have been exposed to the solution only as the sample failed, and not during the previous heating from ambient conditions to the test conditions of 200°C and 8MPa. However, they would have been exposed to the test solution as it was cooled to below 70°C.
Figure 36: SEM micrographs of the failed surface of samples that underwent slow strain rate testing under ambient water solution at 30 x magnification for A) N-50 and B) SS-316, and at 1000 x magnification for C) N-50 and D) SS-316. Both samples display noticeable dimpling, which indicates areas of void formation during deformation. As with the inert atmosphere, there is a cup and cone fracture surface, indicating ductile failure. The N-50 has smaller dimples along its failed surface. SEM operated at 20kV acceleration.

4.3.4 SEM Micrographs from Samples tested at 300°C

The differences noted in optical microscopy of samples that underwent SSRT at 300°C were further investigated using SEM, the results of which are shown in Figure 38. The fissures on the surface of SS-316 are larger and more frequent than those of N-50 along regions of deformation. Crystalline formations, assumed to be oxides, were found
across all surfaces on both samples, though the interior of cracks are less densely populated, and consist of particles smaller than on the surface. The difference in particle size could be attributed to the smaller amount of time exposed to the test solutions for the crack interior regions. The fracture surface of N-50 appears entirely ductile, with spherical dimples across the entire fracture surface. SS-316 appears to have maintained a cup and cone ductile failure, even though, SS-316 displayed larger dimples than N-50. Figure 39 shows the larger triangular formations found on SS-316.
**Figure 37**: SEM micrographs of samples that underwent slow strain rate testing under 200°C, 8MPa conditions at 30 x magnification for the failed surface of A) N-50 and B) SS-316 and 5000 x magnification of the interior of a void at the failed surface of C) N-50 and D) SS-316. There are noticeable surface features, possibly oxides, along the interior of the void in SS-316, whereas none are visible for N-50. SEM was operated at 20kV acceleration.
Figure 38: SEM micrographs of samples that underwent slow strain rate testing under 300°C, 15MPa conditions for the failed surface at 30 x magnification for A) N-50 and B) SS-316, and at 1000 x magnification for C) N-50 and D) SS-316. The spherical dimples of SS-316 are relatively larger than those of N-50. These images were obtained with the SEM operated at 20kV. SEM micrographs of these same samples were also taken at 10000 x magnification along the gauge region for E) N-50 and F) SS-316. The SS-316 gauge has larger cracks than N-50. These two micrographs were obtained with the SEM operating at 10kV.
Figure 39: SEM micrographs of samples that underwent slow strain rate testing 300°C, 15MPa conditions of the crack interior at 20000 x magnification for A) N-50 and B) SS-316. The features on the SS-316 crack interior are broader, larger, and distinctly triangular compared to those found on N-50. SEM was operated at 20kV.

4.3.5 SEM Micrographs from Samples Tested at 425°C

The SEM micrographs shown in Figure 40 show the fracture surface of N-50 and SS-316. Figure 41 shows the surface of the neck regions and the interior of a crack. The fracture surface of both appears entirely ductile at these conditions, as evidenced by the presence of spherical dimples across the surface. However, as observed in previous SEM micrographs, N-50 has smaller spherical dimples. Both steels have an increase in the amount of surface cracks observed at the neck regions. The interior surface that is exposed during failure display smaller and less clearly formed features than those formed on the exterior surface, which was exposed to the testing solution during both heating, and at the solution temperature prior to the formation of the crack.
Figure 40: SEM micrographs of samples that underwent slow strain rate testing at 425°C, 27MPa conditions at 30 x magnification for the failed surface of A) N-50 and B) SS-316 and C) 1000 x magnification C) N-50 and D) SS-316. Both steels show ductile failure, with the spherical dimples of N-50 being smaller than those of SS-316. SEM operated at 20kV.
Figure 41: SEM micrographs of samples that underwent slow strain rate testing at 425°C, 27MPa conditions at 30 x magnification for the failed surface of the neck region of A) N-50 and B) SS-316 and 50000 x magnification at the neck region of C) N-50 and 10000 x magnification for D) SS-316. N-50 again shows smaller dimples than SS-316, and less fractures at the neck region. Both show formations in the interior of cracks. SEM was operated at 20kV.

4.3.6 Scanning Electron Microscopy Summary

All samples showed a ductile mode of failure, which is consistent with these strain rates and temperatures. However, N-50 consistently had smaller spherical dimples than SS-316, which has been indicated as a sign of relatively greater resistance to void formation [93]. In agreement with observations made from optical micrographs,
the surface cracks of N-50 are less numerous and of smaller size than those seen on SS-316. The features observed inside these cracks also differ in shape, as N-50 presents more oblong formations than those of SS-316. Both N-50 and SS-316 have larger formations on their surface than in the interior of their cracks however, a likely indication that the length of time exposed to the temperatures of the test solution is a criterion in their formation.

4.4 Raman Spectra

4.4.1 Raman Spectra of Samples Tested at 200°C

The presence of oxides on 200°C slow strain rate test samples was confirmed using Raman spectroscopy and the results for the unstrained and fillet regions are shown in Figure 42. The primary feature for SS-316 at the unstrained region is -664 cm\(^{-1}\), indicating magnetite, just as the feature at -663 cm\(^{-1}\) for SS-316’s fillet region also indicates magnetite. At the unstrained and fillet regions, N-50 has a spectra which matches the spectra from the as-received N-50 sample. Figure 43 shows the spectra for the gauge and neck regions. At these regions there is evidence of the NiFe\(_2\)O\(_4\) spinel for N-50, having a main feature at 684 cm\(^{-1}\) for both regions. This feature increases in intensity from the gauge region, shown in Figure 44, to the neck region for N-50, shown in Figure 45. SS-316 displays the iron oxides hematite and magnetite on both regions, with a feature at -660 cm\(^{-1}\) at the gauge region and -663 cm\(^{-1}\) at the neck region both primarily indicating magnetite. This indicates that the native film of N-50 has withstood these conditions greater than SS-316, which had formed a film with newer composition.
Figure 42: Raman spectra for samples having undergone slow-strain rate testing at 200°C, 8MPa A) unstrained region of SS-316 and B) unstrained region of N-50. N-50 maintains a spectra similar to the as-received sample, while SS-316 developed iron oxide films. Spectra from the as-received SS-316 and N-50 are included for reference. All spectra were obtained from an average of 16 points 10µm apart in a 4 x 4 grid.
Figure 43: Raman spectra for samples having undergone slow-strain rate testing at 200°C, 8MPa A) fillet region of SS-316 and B) fillet region of N-50. The results are the same as for the unstrained regions, N-50 maintains a spectra similar to the as-received sample, while SS-316 developed iron oxide films. Spectra from the as-received SS-316 and N-50 are included for reference. All spectra were obtained from an average of 16 points 10µm apart in a 4 x 4 grid.
Figure 44: Raman spectra for samples having undergone slow-strain rate testing at 200°C, 8MPa. A) gauge region of SS-316 and B) gauge region of N-50. The results are the same as for the unstrained regions, N-50 shows evidence of nickel iron spinel, as well as retaining features of the as-received chromium oxide. SS-316 again shows iron oxide formation. Spectra from the as-received SS-316 and N-50 are included for reference. All spectra were obtained from an average of 16 points 10µm apart in a 4 x 4 grid.
**Figure 45**: Raman spectra for samples having undergone slow-strain rate testing at 200°C, 8MPa A) neck region of SS-316 and B) neck region of N-50. The results are the same as for the previous regions, N-50 shows evidence of nickel iron spinel, as well as retaining features of the as-received chromium oxide. SS-316 again shows iron oxide formation. Spectra from the as-received SS-316 and N-50 are included for reference. All spectra were obtained from an average of 16 points 10µm apart in a 4 x 4 grid.
4.4.2 Raman Spectra from Samples Tested at 300°C

The difference between surface oxide species formed on the surface and the crack interiors was effectively investigated by Raman spectroscopy. Figure 46 shows the results obtained from the unstrained regions of samples having undergone slow strain rate tests at 300°C and 15MPa. The unstrained region of N-50 has its primary feature at 692cm⁻¹, while SS-316 had its most intense feature at 684cm⁻¹. This indicates a spinel with relatively greater iron content in the case of N-50 compared to SS-316 [69]. Figure 47 shows the Raman spectra from the crack exterior and interior for N-50 and SS-316. The crack interior regions had been exposed to the test solution for a significantly less amount of time and the Raman spectra at these locations did appear to have contributions from multiple oxides, notably a nickel iron spinel. Hematite was present at the surface of the crack of the SS-316 sample. The resulting spectra from crack interior and exterior had no distinguishable differences for N-50, both displaying nickel iron spinel. Figure 39 A) shows the comparatively sparse and smaller formations present on the crack interior of N-50, while Figure 39 B) shows the larger triangular formations inside the surface crack fo SS-316. The Raman spectra for the interiors of both steels display features indicating nickel iron spinel, therefore the different morphology observed in the SEM micrographs may only be the result of orientation of the nickel iron spinel.
Figure 46: N-50 and SS-316 Raman spectra for the unstrained regions and as-received spectra for samples having undergone slow strain rate tests at 300°C for A) SS-316 and B) N-50. Both N-50 and SS-316 have features indicating nickel iron spinel. All spectra taken as an average of 16 points 10µm apart in a 4 x 4 grid.
Figure 47: Raman spectra for crack interior and exterior A) SS-316 and B) N-50. SS-316 shows a clear difference between the crack interior which had nickel iron spinel features, and the surface which had iron oxide features. N-50 shows broad features that can potentially be attributed to both magnetite and nickel iron spinel. All spectra taken represent a single point.

4.4.3 Raman Spectra from 425°C Samples

Figure 48 shows the Raman spectra of surface films on both N-50 and SS-316 compared to their as-received conditions. The main feature for the unstrained region of
N-50 is at 674cm\(^{-1}\), indicating a potential mix of nickel iron spinel and/or magnetite. Raman spectra from the unstrained region of SS-316 shows an intense feature at 665cm\(^{-1}\) corresponding to magnetite. Similar to Raman spectra from previous SSRT samples, there is a difference between spectrum obtained from a freshly exposed metal on the crack interior and the spectrum from the surface, as shown in Figure 49. Spectrum from N-50 shows broad features on the unstrained region, indicating likely contributions from both magnetite and nickel iron spinel, with the main feature at 668cm\(^{-1}\) at the interior showing a noticeable shoulder at higher wavenumbers, and 662cm\(^{-1}\) for the exterior. Figure 41 C) shows the crack interior to display elongated formations, potentially indicating a different morphology for the nickel iron spinel than that of the iron oxides. SS-316 displays predominantly iron oxide features, with a possible nickel iron spinel feature as well. The surface of the cracks at the neck region have features indicating the presence of hematite and magnetite, as well as nickel iron spinel, with the main feature for the exterior at 674cm\(^{-1}\) and 219cm\(^{-1}\), indicating magnetite and hematite, respectively. The chemistry of the interior of these cracks more closely aligns with features of nickel iron spinel and magnetite, and is free of indications of hematite. However, Figure 41 D) shows that the interior of the cracks for SS-316 to be free of the elongated features that are apparent on N-50. Given the similarity in spectra, it may indicate a difference in oxide morphology but not composition. At the unstrained surface, Raman spectra for SS-316 indicates the presence of hematite, as well as the presence of nickel iron spinel and magnetite. As with N-50, the interior of the cracks of SS-316 do not have features indicating hematite. The significant difference between the crack interior regions and the surface is the amount of time to which the region was
exposed to the test solution and the starting temperature of that test solution. This indicates that hematite forms later in the process and is the surface oxide in agreement with other studies [65]. However, all exposed surfaces must be brought down from the testing temperature to below 70°C, so it is not possible to determine exactly when the hematite forms.
Figure 48: Raman spectra for the unstrained region of samples having undergone SSRTs at 425°C and their as-received spectra for A) SS-316 and B) N-50. N-50 has broad features, indicating possible contributions from both nickel iron spinel and magnetite. SS-316 has more defined iron oxide features, though nickel iron spinel is also indicated. All spectra taken as an average of 16 points 10µm apart in a 4 x 4 grid.
Figure 49: Raman spectra for crack interior and exterior of samples having undergone slow strain rate tests at 425°C A) SS-316 and B) N-50. The N-50 interior has a spectra indicating nickel iron oxide, while the surface indicates both iron oxides magnetite and hematite. SS-316 has more defined iron oxide features, though nickel iron spinel is also indicated. All spectra taken represent a single point.

4.4.4 Summary of Slow Strain Rate Test

At 200°C, 8MPa, N-50 only developed nickel-iron spinel on the regions which were deformed, the gauge and neck regions. The unstrained and fillet regions, which do
not undergo deformation, of N-50 did not develop a new surface film, as the Raman spectra indicated the presence of the passive chromium oxide film. At 200°C, 8MPa, SS-316 developed surface films of magnetite and hematite at both the dimensionally stable unstrained and fillet regions, as well as the deformed gauge and neck regions. At the subcritical 300°C, 8MPa conditions the Raman spectra of N-50 indicated a surface film composed of both nickel-iron spinel and magnetite. This was observed for the surface as well as for freshly exposed material at surface crack interiors. At the subcritical 300°C, 8MPa conditions the Raman spectra of SS-316 indicated a surface film composed of nickel-iron spinel at the unstrained region, with the development of magnetite and hematite along the gauge region. The crack interiors of SS-316 at these conditions developed a surface film of nickel-iron spinel. N-50 developed a surface film composed of both nickel-iron spinel and magnetite and the unstrained region and the interior of cracks of samples subjected to supercritical 425°C, 27MPa conditions. The gauge of N-50 samples at these conditions indicated the formation of both magnetite and hematite. At the supercritical conditions 425°C, 27MPa conditions, the surfaces of the unstrained region and the gauge region of SS-316 forms a surface composed of magnetite and hematite. The Raman spectra of the crack interiors of SS-316 at these conditions indicate only nickel-iron spinel. This is in agreement with previous observations for austenitic stainless steel oxidation in supercritical water [65]. However, Raman spectra of SS-316 consistently demonstrates features indicating greater contributions of iron oxides than N-50, the spectra from which predominantly indicates nickel iron spinel. At the higher temperatures in this study, N-50 did also have spectra of iron oxides, indicating perhaps a slower oxidation than SS-316. At supercritical
conditions, increased hematite fraction in the oxide is believed to reduce spallation [65]. Thus, neither N-50 nor SS-316 display clear oxidation pathways, as the slower oxidation of N-50 is offset by the development of the hematite surface film in SS-316.

4.5 Electrochemical Polarization

Figure 50 shows the polarization curves for both steels at ambient water conditions. Figures 51 and 52 show the polarization curves of samples subjected to 200°C and 8MPa, and 300°C and 15MPa, respectively. The difference in electrochemical potential can be supported by the observations in Figure 12, the optical microscopy for as-received samples, which shows N-50 having a different surface morphology than SS-316. It can be hypothesized that N-50 had a less complete native oxide film on its surface, resulting in the relatively more active behavior compared to SS-316 in ambient conditions. At subsequent exposure conditions N-50 and SS-316 have very similar polarization curves. This is in agreement with the Raman spectra of samples that underwent SSRT at elevated temperatures. The oxide formation was very similar, though the Raman spectra of SSRT samples at 200°C, 8MPa did indicate that SS-316 had a more fully formed oxide layer.
**Figure 50**: Polarization curves for N-50 and SS-316 at ambient water conditions. N-50 is more active than SS-316.
**Figure 51:** Polarization curves for both N-50 and SS-316 at 200°C and 8MPa. They display very similar characteristics and are nearly identical.

**Figure 52:** Polarization curves for both N-50 and SS-316 at 300°C and 15MPa. Similar to the results shown in Figure 46, the two steels have very similar activity, although N-50 is slightly more noble than SS-316.
4.5.1 Raman Spectra of Polarized Samples

The Raman spectra of the electrochemically polarized samples at ambient conditions is shown in Figure 53. At ambient conditions, polarized samples of SS-316 and N-50 have spectra that matches their as-received samples. Figure 54 shows the Raman spectra for N-50 and SS-316 samples that underwent polarization at the 200°C and 300°C conditions. Raman spectra obtained from N-50 is more similar to its spectra from as-received conditions than SS-316. Raman spectrum obtained from SS-316 shows a main feature at 676 cm\(^{-1}\), which is between the observed peak for magnetite and nickel iron spinel possibly indicating contributions from both. However, at 300°C the spectra is nearly identical for both steels. SS-316 shows a main feature at 682 cm\(^{-1}\) and N-50 shows a main feature at 687 cm\(^{-1}\). Both of these peaks more strongly indicate nickel iron spinel than the features observed at 200°C.
Figure 53: Raman spectra of samples after polarization under ambient conditions for A) SS-316 and B) N-50. These spectra are the same as their as-received counterparts.
Figure 54: Raman spectra of samples polarized at A) 200°C and and B) 300°C. Both samples have spectra matching their as received samples at ambient conditions. At 300°C and 15Mpa both samples are nearly identical and the surface chemistry is indicative of a nickel iron spinel and magnetite. At the intermediate 200°C, 8MPa conditions, the surface of SS-316 shows much more transformation to spinel than N-50, which still shows similar surface chemistry as ambient conditions.
4.5.2 Raman Spectra from Samples Exposed to Supercritical Conditions

Samples of N-50 and SS-316 were secured via alumina rods and exposed to 425°C conditions for 7 hours. The surface was then characterized using Raman spectroscopy, the results from which are shown in Figure 55. The main feature for N-50 is at 682 cm\(^{-1}\), with a broad feature that potentially indicates a mixture of nickel iron spinel and magnetite. The Raman spectra of SS-316 indicates the presence of iron oxides, with the most prominent feature at 277 cm\(^{-1}\) indicating the presence of hematite.

Figure 55: Raman spectra of N-50 and SS-316 for the surface of samples exposed to supercritical conditions for 7 hours. N-50 predominantly displays nickel iron spinel, and SS-316 displays features of the iron oxides hematite and magnetite.

4.5.3 Summary of Electrochemical Polarization and Exposure

N-50 and SS-316 behaved very similarly at elevated temperatures. However, the surface films formed were not the same, and closely matched those observed from the
slow strain rate tests. N-50 mostly developed a nickel iron spinel, as well as retaining features from its native oxide film. At the higher 300°C conditions, both N-50 and SS-316 had broad features that corresponded to a potential combination of nickel iron spinel and magnetite. As stated earlier, it appears that SS-316 oxides more rapidly than N-50. No hematite was observed on the electrochemically polarized samples, which supports the early statement that hematite forms at later stages as an outer film. At supercritical conditions, SS-316 displayed a surface of iron oxides, while N-50 again was characterized mainly by nickel iron spinel, though with features indicating iron oxides as well. The polarization experiments did not require as much time at testing conditions as the SSRTs, indicating that length of exposure may be a dominant factor in surface film development at the testing parameters in this study.
Chapter 5. Conclusions

5.1 Conclusions from this Work

N-50 demonstrated mechanical superiority under both subcritical and supercritical conditions. Not only was N-50 observed to have greater strength as measured by UTS and 0.5% YS, but also less deterioration of these measures as compared to SS-316. This is evidenced by the greater percentage drop in strength observed in SS-316 across the testing conditions compared to N-50. This change coincided with the demonstration of the Portevin-Le Chatelier (PLC) effect in SS-316, whereas N-50 did not display such behavior. PLC is the result of interactions between solute atoms and dislocations, which along with the larger voids along the crack tip exhibited by SS-316, allows to hypothesize that the mechanical superiority of N-50 is likely attributed to interactions at the microstructure scale. The inclusion of nitrogen as an interstitial atom in N-50, and its absence in SS-316, is the likely source of the difference.

Electrochemical polarization and surface characterization through Raman spectroscopy did not yield as clear of superiority for either steel. SS-316 formed iron oxides more rapidly, as evidenced by the Raman spectra of both the SSRTs and polarization at 200°C. SS-316 had Raman features indicating iron oxides at all regions and after polarization. Only at the deformed gauge and neck region did N-50 display features differing from its native oxide film. In instances where both N-50 and SS-316 displayed features of iron oxides, SS-316 had relatively more frequent and clearer
features indicating hematite. Thus, while N-50 appears to oxidize more slowly, the surface formed is not as preferable as the one developed on SS-316.

5.2 Future Work

The initial stage of future experimentation should be an incremental increase in the temperature of slow strain rate tests. This would determine if the Portevin-Le Chatelier effect observed in SS-316 could also affect N-50 at higher temperatures. Decreasing the strain rate would allow investigation of the stress corrosion cracking susceptibility of N-50 and SS-316. Stress corrosion cracking could also be studied via more sensitive surface characterization techniques such as X-ray photoelectron spectroscopy and electron backscattering diffraction. N-50 and SS-316 should also be investigated through creep strength testing, as creep strength plays a critical role in the design of the SCWR [13]. Crystallographic studies would allow for further characterization of the changes that result from mechanical testing, potentially elucidating further differences and explaining the observed differences in the behavior of SS-316. The effects of temperature could further be isolated by heating the samples in an inert atmosphere either prior to or during mechanical testing.
References.


