AN INVESTIGATION OF THE ELEVATED TEMPERATURE CRACKING SUSCEPTIBILITY OF ALLOY C-22 WELD-METAL

DISSERTATION

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Adviso,
The use of nickel-base alloys has increased in recent years as the demand for high-temperature corrosion resistant alloys increases. However, the introduction of new alloys can present challenges in materials joining. During fabrication involving welding, both solidification cracking and ductility-dip cracking (DDC) cracking may occur in these alloys if proper precautions are not followed. One such nickel-base alloy is Alloy C-22, which has limited weldability data to date. Alloy C-22 is one of the most corrosion resistant Ni-Cr-Mo alloys available today, and is particularly versatile. As a result, Alloy C-22 is being considered for use in the construction of storage canisters for permanent disposal of radioactive waste in the Yucca Mountain Project. However, in such a critical application, weld related defects (such as these two forms of cracking) are simply unacceptable.

Solidification cracking occurs when weld shrinkage strains are applied to liquid films that result from microsegregation during solidification. Many nickel-base alloys are susceptible to solidification cracking since they solidify as austenite and many of their alloying additions partition during solidification and form low melting eutectic constituents. The transvarestraint test was used to quantify the susceptibility of Alloy C-22 to solidification cracking. The solidification cracking temperature range (SCTR) was found to be approximately 50°C (90°F); this SCTR predicts that Alloy-C-22 will have only slightly higher susceptibility than known crack-resistant alloys, such as duplex stainless-steel 2205 and austenitic stainless-steel Type 304 (FN6).

DDC is a solid-state cracking phenomenon that occurs below the effective solidus temperature in highly restrained austenitic alloys. Although this type of cracking is relatively uncommon, it can be costly in critical applications where there is a low
tolerance for defects. This investigation used two separate tests to quantify the susceptibility of the alloy to DDC: the hot-ductility test and the strain-to-fracture (STF) test.

The hot-ductility test revealed that Alloy C-22 weld-metal exhibits an intermediate temperature ductility-dip, with ductility recovery at the upper end of the testing temperature range. The ductility minimum in the hot-ductility tests occurred around 950°C (1742°F) in both the on-heating and on-cooling tests. The strain-to-fracture test also revealed Alloy C-22 to be susceptible to ductility-dip cracking. Alloy C-22 displayed a low threshold strain necessary to initiate cracking, a wide temperature range over which cracking occurred, and no recovery of ductility at the upper end of the testing temperature range.

The recovery of ductility at the upper end of the testing temperature range in the hot-ductility test, and the absence of this recovery in the STF test, is explained by the recrystallization behavior of the metal. Alloy C-22 has a low stacking-fault-energy, as compared to other DDC susceptible nickel-base alloys, and accordingly requires higher levels of deformation before recrystallization begins. With the relatively low strains experienced by the samples in the STF test (less than ten-percent), cracking will occur before enough strain is accumulated to cause recrystallization. In the hot-ductility test, where the sample is pulled to failure, sufficient strain (forty-percent or greater) is applied such that recrystallization occurs. This recrystallization is responsible for the recovery of ductility at the high end of the testing temperature range in the hot-ductility test.

The low threshold strain that is observed in the STF test is in part explained by the behavior of the metal during the thermal cycle of the test. Experimental observations indicate that tortuous (wavy) solidification grain boundaries (SGB) migrate, or straighten, during the temperature upslope and hold period of the STF test. This migration of the grain boundaries reduces the mechanical locking effect that tortuous grain boundaries provide, allowing cracking to occur at lower applied strains.

Button-melting experiments were conducted to examine the effect of compositional variation on both solidification cracking and ductility-dip cracking susceptibility of the
alloy. Molybdenum, tungsten, and iron were selected for variation, as previous research has shown these three elements to be significantly enriched or depleted in the terminal solidification products of Alloy C-22 weld-metal. The solidification temperature range and volume fraction of secondary phases were used as indicators of the susceptibility of the experimental alloys to solidification cracking and ductility-dip cracking, respectively.

Previous research on nickel-base alloys has demonstrated that the solidification temperature range of an alloy is directly proportional to the susceptibility of the alloy to solidification cracking. Experiments conducted within this investigation indicate that increasing the volume fraction of secondary phases in Alloy C-22 acts to increase the elevated temperature cracking-resistance and ductility of the alloy.

The solidification temperature ranges of the Alloy C-22 variants examined within the button-melting experiments did not significantly widen or narrow with increases in composition. These same compositional variations demonstrated that increasing amounts of molybdenum, tungsten, and iron increased the volume fraction of secondary phases, with each element having relatively the same potency. Based on the button melting experiments and thermodynamic simulations, it is expected that Alloy C-22 will have good resistance to weld solidification cracking over its entire composition range.
Für meine Eltern und meine Großeltern.
Ohne Ihre Opfer, wäre dies nicht möglich gewesen.
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# LIST OF ABBREVIATIONS

<table>
<thead>
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<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>BCC</td>
<td>Body Centered Cubic (crystal structure)</td>
</tr>
<tr>
<td>CEOF</td>
<td>Campus Electron Optics Facility</td>
</tr>
<tr>
<td>DDC</td>
<td>Ductility-Dip Cracking</td>
</tr>
<tr>
<td>DSS</td>
<td>Duplex Stainless Steel</td>
</tr>
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<td>DRT</td>
<td>Ductility Recovery Temperature</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron Backscattered Diffraction</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive X-Ray Spectroscopy</td>
</tr>
<tr>
<td>EWI</td>
<td>Edison Welding Institute</td>
</tr>
<tr>
<td>FCC</td>
<td>Face Centered Cubic (crystal structure)</td>
</tr>
<tr>
<td>GMAW</td>
<td>Gas-Metal Arc Welding</td>
</tr>
<tr>
<td>GTAW</td>
<td>Gas-Tungsten Arc Welding</td>
</tr>
<tr>
<td>HAZ</td>
<td>Heat Affected Zone</td>
</tr>
<tr>
<td>HCP</td>
<td>Hexagonal Close Packed (crystal structure)</td>
</tr>
<tr>
<td>LCTR</td>
<td>Liquation Cracking Temperature Range</td>
</tr>
<tr>
<td>MGB</td>
<td>Migrated Grain Boundary</td>
</tr>
<tr>
<td>NDT</td>
<td>Nil-Ductility Temperature</td>
</tr>
<tr>
<td>NST</td>
<td>Nil-Strength Temperature</td>
</tr>
<tr>
<td>OIM</td>
<td>Orientation Imaging Microscopy</td>
</tr>
<tr>
<td>PSN</td>
<td>Particle Stimulated Nucleation</td>
</tr>
<tr>
<td>RSM</td>
<td>Response Surface Method (experimental design)</td>
</tr>
<tr>
<td>SAW</td>
<td>Submerged Arc Welding</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SGB</td>
<td>Solidification Grain Boundary</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>SMAW</td>
<td>Shielded-Metal Arc Welding</td>
</tr>
<tr>
<td>SS</td>
<td>Stainless Steel</td>
</tr>
<tr>
<td>SS-DTA</td>
<td>Single-Sensor Differential Thermal Analysis</td>
</tr>
<tr>
<td>STF</td>
<td>Strain to Fracture (test)</td>
</tr>
<tr>
<td>TV</td>
<td>Transvarestraint (test)</td>
</tr>
<tr>
<td>UCC</td>
<td>Union Carbide Corporation</td>
</tr>
<tr>
<td>WJMG</td>
<td>Welding and Joining Metallurgy Group</td>
</tr>
<tr>
<td>YMP</td>
<td>Yucca Mountain Project</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

As the demand for materials with increased corrosion resistance and elevated temperature strength increases, the use nickel-based alloys also increases. However, new materials can pose challenges in joining, especially in welding. Alloys are often created without sufficient consideration given to the weldability of the material. In many cases, these alloys are produced using complex thermal-mechanical processing steps that optimize the mechanical properties and/or corrosion resistance of the alloy. When such an alloy is welded, the properties of the weld-metal and the surrounding heat-affected zone (HAZ) may be degraded as compared to those of the base-metal. Additionally, it is often impractical or impossible to subject a full-scale weldment to the same thermal-mechanical processing that gave the base-metal its properties. As a result, welds are often the ‘weak-link’ in a structure with respect to mechanical properties or corrosion resistance.

Aside from the effect of welding on the properties of a weldment, discontinuities (including the various types of weld cracking) can become problematic. These discontinuities are especially problematic in critical applications where they can not only be costly and difficult to repair, but can also pose significant health and safety risks. The mechanisms behind the creation of these discontinuities must be well understood in order to avoid their formation, allowing these new materials to be used to their full potential.

One such critical application, in which Alloy C-22 is to be used, is the Yucca Mountain Project (YMP). Yucca Mountain is the proposed site for the first long-term geological repository of radioactive waste within the United States. This waste, from
both energy and defense applications, will be stored using a system of engineered and natural barriers; these barriers will ensure that waste does not escape into the environment. The engineered barriers will be the highly corrosion resistant canisters, into which the radioactive waste will be sealed; the outer portion of these canisters will be constructed of Alloy C-22. These canisters will be stored in tunnels (natural barrier) well below the surface of the mountain and well above the nearest water table.

These storage canisters will require a 10,000 year compliance period, and will initially be exposed to high temperatures and levels of radiation [6]. In such a critical application, welds must be free of defects and have a minimum number of discontinuities. The prospect of weld-cracking during the fabrication of these storage canisters is simply unacceptable, and would eliminate Alloy C-22 from consideration in the YMP. It is therefore necessary to obtain a metallurgical understanding of the mechanisms that cause elevated temperature cracking within Alloy C-22.

Aside from the YMP, Alloy C-22 is used in a variety of demanding environments, which are highly corrosive. Discontinuities or defects caused by weld-cracking are also highly undesirable in these applications, where (as previously mentioned) failure may not only be costly but also very dangerous.

This project was conducted to assess the susceptibility of Alloy C-22 to two types of weld cracking (solidification cracking and ductility-dip cracking). This assessment of cracking susceptibility was divided into two phases: initial testing and compositional variation. In the initial testing phase, established weldability tests were used to assess the cracking susceptibility of the alloy. The transvarestraint test was used to assess the solidification cracking susceptibility; both the strain-to-fracture and hot-ductility tests were used to assess the ductility-dip cracking susceptibility.

In the compositional variation phase, both thermodynamic simulations and the button-melting technique were used to develop an understanding of the effect of composition on these two cracking mechanisms. Thermodynamic software was used to conduct Scheil solidification simulations, and to create other diagrams of interest (pseudo-binary phase diagrams, continuous cooling diagrams, etc…). A number of
hypothetical Alloy C-22 variants were created using the button-melting technique. These variants were subsequently tested, using single-sensor differential thermal analysis and standard metallographic techniques, to experimentally evaluate the effect of composition on solidification cracking and ductility-dip cracking.

The initial testing of Alloy C-22 was useful in developing an understanding of the baseline susceptibility of the alloy to weld cracking. If the alloy were found to be particularly susceptible to either solidification cracking or ductility-dip cracking, use in highly critical applications might be discouraged. Understanding how variations in composition effects the cracking susceptibility is important with regards to heat-to-heat compositional variations. Every alloy is defined by a range of composition; as such, confidence in the weldability of the alloy requires confidence over the entire compositional range. Small heat-to-heat variations in composition must not lead to significant increases in the cracking susceptibility of Alloy C-22.

The combination of both these factors (baseline susceptibility and susceptibility versus composition) allows for an overall assessment of the susceptibility of Alloy C-22 to solidification cracking and ductility-dip cracking. If both of these factors are promising, further confidence is gained regarding the weldability of the alloy. Such confidence would allow the alloy to be used in highly critical applications such as the Yucca Mountain Project, or other aspects of the US Nuclear Waste Disposal program. Aside from the assessment of Alloy C-22, these findings may also be cautiously extrapolated to newer similar corrosion resistant alloys such as Alloy-59 and Inconel-686.
CHAPTER 2

BACKGROUND

2.1. Solid-Solution Strengthened Ni-Alloys

The following sections draw heavily from F. Galen Hodges [1] article entitled “The History of Solid-Solution-Strengthened Ni Alloys for Aqueous Corrosion Service”. Figure 2.1 illustrates schematically how solid-solution-strengthened nickel-based alloys are related. The following sections chronologically explain how these groups of alloys were developed, and the reasons behind their development.

![Corrosion alloy tree](image)

Figure 2.1: Corrosion alloy tree [1]
2.1.1. The Usage of Nickel Alloys

Nickel is an ideal base for corrosion-resistant alloys for a number of reasons. It is relatively abundant, it may form passive films, and it is tough and ductile. However, the most important property that nickel possesses in this respect is the ability to keep in solution large quantities of other major alloying elements (i.e., Cr, Mo, Fe, and W) that improve corrosion resistance. Chromium and molybdenum are the most important alloying elements, contributing to corrosion resistance in oxidizing and reducing environments respectively. However, chromium and molybdenum seem to exert a synergistic effect together, especially on localized corrosion.

Carbon is a strengthening agent in nickel, having a maximum solid solubility of 0.6 weight-percent at 1325°C (2417°F); however, as low a carbon level as possible is desired with nickel-base alloys. With stainless steels, a carbon level of 0.03 weight-percent produces an ‘L-grade’ stainless steel; that is, carbon levels are so low that carbides will not precipitate during welding. However, the level required for a Ni-Cr-Mo alloy to obtain L-grade status is 0.003 weight-percent. Aside from reducing the level of carbon within the alloy, carbide precipitation can be controlled by using stabilizing elements such as niobium or tantalum.

2.1.2. First-Generation Alloys

Table 2.1 chronologically lists the trade-name and composition of the first-generation of nickel-based alloys. These alloys appear to have been developed for general use within the chemical industry. That is, they were developed and introduced before specific applications were determined. For example, the first application for Alloy-C was as a search-light reflector for ships during World War II; the material could be polished to a reflectivity similar to glass and did not corrode in seawater [1].
Table 2.1: First-generation nickel-based alloys [1]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monel</td>
<td>Ni-Cu</td>
<td>1906</td>
</tr>
<tr>
<td>Hastelloy Alloy B</td>
<td>Ni-26.5Mo-5Fe</td>
<td>1921</td>
</tr>
<tr>
<td>A-Nickel (Ni-200)</td>
<td>Ni</td>
<td>1924</td>
</tr>
<tr>
<td>Hastelloy Alloy A</td>
<td>Ni-20Mo-20Fe</td>
<td>1929</td>
</tr>
<tr>
<td>Hastelloy Alloy D</td>
<td>Ni-10.5Si-2.5Cu</td>
<td>1930</td>
</tr>
<tr>
<td>Hastelloy Alloy C</td>
<td>Ni-16Cr-16Mo-4W-7Fe</td>
<td>1931</td>
</tr>
<tr>
<td>Inconel Alloy 600</td>
<td>Ni-15Cr-8Fe</td>
<td>1931</td>
</tr>
<tr>
<td>Incoloy Alloy 800</td>
<td>Fe-32Ni-20Cr</td>
<td>1949</td>
</tr>
<tr>
<td>Hastelloy Alloy F</td>
<td>Ni-22Cr-18Fe-6Mo-2Nb</td>
<td>1950</td>
</tr>
<tr>
<td>Incoloy Alloy 825</td>
<td>Ni-22Cr-32Fe-2Cu-2Mo</td>
<td>1952</td>
</tr>
<tr>
<td>Hastelloy Alloy G</td>
<td>Ni-22Cr-18Fe-6.5Mo-2Nb-2Cu</td>
<td>1952</td>
</tr>
<tr>
<td>Inconel Alloy 625</td>
<td>Ni-21.5Cr-9Mo-3.6Nb</td>
<td>1964</td>
</tr>
</tbody>
</table>

The International Nickel Company (Inco) was formed in 1902. At this new company, Robert Stanley produced a Ni-Cu alloy in 1904 that would come to be known as Monel. A.L. Marsh, also working for Inco, developed and filed patent in 1906 for a Ni-Cr alloy. At the same time another inventor, Elwood Haynes, was working on nickel and cobalt alloys with chromium; he also filed a patent. In 1912 Haynes created the Haynes Stellite Company and continued working on nickel and cobalt alloys.

Inco produced what was originally called ‘A-Nickel’, which would later become known as Nickel-200 or commercially pure nickel. Nickel-200 and Nickel-201 (the low-carbon version) are still the most widely used alloys for caustic solutions. Inconel® Alloy-600 was developed by Inco in 1931 and is still in production today.

The Union Carbide Corporation (UCC) laboratories, Haynes parent company at the time, developed Hastelloy® Alloy-B, Alloy-A, Alloy-D, and finally Alloy-C. All of these alloys were originally cast products because the carbon control was insufficient to allow wrought alloy production; typical values for carbon were 0.10-0.12 weight-percent.

Because nickel was considered a strategic material during the Korean War, companies developed alloys with lower nickel contents, replacing nickel with iron in most cases; Incoloy Alloy-800 is an example of this trend. The composition of Alloy-
800 was very useful and exhibited corrosion properties in both aqueous and high-temperature environments. This composition was the starting point for several other alloys including Incoloy Alloy-825 (1952), where copper additions increased the corrosion resistance in sulfuric acid. Also created during this time period were Hastelloy Alloy-F and Hastelloy Alloy-G for similar applications.

Inco developed Inconel Alloy-625 in 1964, primarily for high-temperature applications, but discovered that the alloy had excellent corrosion resistance in a number of environments. This alloy marks the end of the first generation of nickel alloy development; virtually every alloy from this point forward is based on a previously developed alloy.

2.1.3. Second Generation Alloys

Metallurgical melting advances made the second-generation alloys possible. These alloys were generally used for the same applications as their predecessors, with new applications being continuously developed. Table 2.2 chronologically lists the trade-name and composition of the second-generation of nickel-based alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hastelloy Alloy C-276</td>
<td>Ni-16Cr-16Mo-4W-5Fe</td>
<td>1966</td>
</tr>
<tr>
<td>Inconel Alloy 690</td>
<td>Ni-29Cr-8Fe</td>
<td>1967</td>
</tr>
<tr>
<td>Hastelloy Alloy C-4</td>
<td>Ni-16Cr-16Mo</td>
<td>1973</td>
</tr>
<tr>
<td>Hastelloy Alloy B-2</td>
<td>Ni-27Mo-1Fe-1Cr</td>
<td>1976</td>
</tr>
<tr>
<td>Hastelloy Alloy G-3</td>
<td>Ni-22Cr-18Fe-7Mo-0.5Nb-2Cu</td>
<td>1977</td>
</tr>
<tr>
<td>Hastelloy Alloy G-30</td>
<td>Ni-30Cr-15Fe-5.5Mo-0.8Nb-2.5W</td>
<td>1983</td>
</tr>
<tr>
<td>Hastelloy Alloy C-22</td>
<td>Ni-22Cr-13Mo-3W</td>
<td>1985</td>
</tr>
<tr>
<td>Alcor</td>
<td>Ni-31Cr-10Mo-2W-0.4Nb</td>
<td>1985</td>
</tr>
</tbody>
</table>

Table 2.2: Second-generation alloys [1]

In 1966, metallurgical melting improvements allowed Haynes to lower the carbon and silicon contents on Hastelloy Alloy-C, creating Alloy C-276. In 1973, another Alloy-C
modification, Alloy C-4, was developed to lessen the precipitation of intermetallic phases during high-temperature heat-treatments. However, this alloy lacked the localized corrosion resistance of Alloy-C276 and had limited use. In 1976, the low carbon and silicon melting practices were applied to Alloy-B, creating Alloy B-2. The development of Alloy C-276 and Alloy B-2 now allowed these alloys to be used in the as-welded condition in most chemical environments. The Alloy-C family was modified again in 1985 with the introduction of Alloy C-22. This version had higher chromium than Alloy C-276, and provided better corrosion resistance in oxidizing environments.

Because Alloy-G exhibited hot short conditions during welding with 2 weight-percent copper and niobium, Alloy G-3 was developed with 0.5 weight-percent niobium. In some applications involving nitric acid, the corrosion resistance of Alloy G-3 was insufficient, so the chromium level was increased to 30 weight-percent in Alloy G-30. Later, Allvac (now ATI) developed a similar alloy named Allcorr.

Inconel Alloy-600 had become widely used in the nuclear industry for the primary water circuit in the pressurized water reactor process. Problems were detected in the steam generator heat exchangers after several years of use. As a result, Inco created Inconel Alloy-690 with significantly higher chromium content.

2.1.4. New Generation Alloys

Table 2.3 chronologically lists the trade-name and composition of the third-generation of nickel-base alloys. The third-generation alloys were generally developed with specific applications in mind, although new applications were often developed in industry by the customer.
Table 2.3: New-generation alloys [1]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>VDM Alloy 59</td>
<td>Ni-23Cr-16Mo</td>
<td>1990</td>
</tr>
<tr>
<td>Inconel Alloy 686</td>
<td>Ni-21Cr-16Mo-4W</td>
<td>1992</td>
</tr>
<tr>
<td>Hastelloy Alloy B-3</td>
<td>Ni-28Mo-1.5Fe-1.5Cr</td>
<td>1993</td>
</tr>
<tr>
<td>VDM Alloy B-4</td>
<td>Ni-28Mo-3Fe-1.3Cr</td>
<td>1993</td>
</tr>
<tr>
<td>MAT 21</td>
<td>Ni-19Cr-19Mo-1.8Ta</td>
<td>1995</td>
</tr>
<tr>
<td>Hastelloy Alloy C-2000</td>
<td>Ni-23Cr-16Mo-1.6Cu</td>
<td>2001</td>
</tr>
<tr>
<td>Hastelloy Alloy G-35</td>
<td>Ni-31Cr-10Mo-0.4Nb-2W</td>
<td>2004</td>
</tr>
</tbody>
</table>

In the late 1980’s, environmental concerns led to the world-wide implementation of wet scrubbing systems for flue gasses from coal-fired power stations. Originally alloys 625, C-276, and C-22 were used for these applications; while these alloys were sufficient for the majority of applications, some problem areas led to the modification of these alloys for superior corrosion resistance. In 1990 ThyssenKrupp VDM introduced Alloy-59; in 1992 Inco introduced Alloy-686; and in 1995 Mitsubishi Alloys introduced MAT21®. Copper additions in Alloy C-2000 (as compared to Alloy C-22) produced an alloy with the inherent corrosion resistance of previous alloys and improved resistance in reducing environments.

Haynes altered the composition of Alloys G-3 and G-30 to create Alloy G-35, with significantly improved corrosion resistance. Alloy G-35 is used in evaporators that concentrate phosphoric acid in phosphoric acid production, where the previously developed alloys were not quite corrosion resistant enough. Because a long range ordering reaction could occur rapidly in Alloy B-2, possibly leading to cracking during heat treatment, Haynes created Alloy B-3.

2.1.5. Hastelloy ‘C-Series’ Alloys

The following paragraphs provide a more detailed explanation of the development of the Hastelloy ‘C-Series’ alloys. Additionally, the fabricability and uses of Alloy C-22 are discussed.
Hastelloy alloys are high-temperature, nickel-based alloys known throughout the chemical processing industry as premier corrosion resistant alloys [1,2]. The ‘C-series’ of Hastelloy alloys are derived from the Ni-Cr-Mo ternary system. Hastelloy-C was the first alloy within this family. Although a premier corrosion resistant alloy, Hastelloy-C required post-weld annealing in order to avoid HAZ knife-line attack caused mainly by the formation of μ (Ni7Mo6) and Mo6C precipitates [3]. Additionally, the formation of M23C6, M2C, and Ni2Cr within this alloy was problematic. Hastelloy C-276 was later developed having lower levels of carbon and silicon, which considerably slowed the aforementioned precipitation reactions. Although Hastelloy C-276 could be used in the as-welded condition, the μ-precipitate could still form at longer aging times.

Consequently, Hastelloy C-4 was developed with lower Fe, Co, and W levels. These compositional changes eliminated the formation of the μ-phase at long aging times. Unfortunately, the lower level of tungsten within the alloy decreased the alloys resistance to pitting and crevice corrosion. Hastelloy C-22 was developed as a remedy for this issue. The lower carbon levels of the C-22 alloy retard carbide formation, while the levels of W and Mo were selected as a balance such that μ-formation was retarded yet pitting and crevice corrosion resistance were not appreciably sacrificed. More recently, Hastelloy C-2000, containing a copper addition, has been developed to provide improved corrosion resistance in reducing acids.

Hastelloy C-22 (also known as Alloy C-22) is readily welded by GTAW, GMAW, and SMAW [2]. Alloy C-22 welding products include matching composition filler metal for the joining of Alloy C-22, as ‘over-alloyed’ filler metal for joining of stainless steel and nickel alloys, for welding of dissimilar corrosion resistant alloys, and for weld overlay cladding [4]. Additionally, Alloy C-22 is suitable for most applications in the as-welded condition, resists the formation of grain-boundary precipitates, and is resistant to intergranular attack [4,2]. Haynes discourages postweld stress relief Alloy C-22 in the 650°C (1200°F) temperature range [4]. If required, solution heat-treatment of Alloy C-22 (to dissolve secondary phases formed during welding), may be accomplished at
1121°C (2050°F) for an appropriate amount of time, followed by a water quench or a rapid air cool [4].

Alloy C-22 is used in the fabrication of paper mill components, acid pumps, pickling systems, heat exchangers, in pesticide production, and the nuclear power industry [2]. Within the nuclear industry, strict requirements are made regarding the high temperature strength, corrosion resistance, and weldability of the materials used [5]. Due to its excellent corrosion resistance, Alloy C-22 is being investigated as one of the principal fabrication materials of storage canisters for permanent disposal of radioactive waste in the Yucca Mountain project.

2.2. Solidification Cracking

In early work with Hastelloy X, Savage and Krantz [1] observed hot cracking to occur exclusively in areas affected by microsegregation. Local areas with higher solute concentrations have lower melting temperatures. When these liquated areas are subjected to the shrinkage strains inherent to welding processes, cracks may form. Hot cracking may occur both within the weld metal and within the heat affected zone (HAZ).

The mechanism by which hot-cracking occurs is most often explained using the modified-generalized theory [9]. In this theory, solidification is subdivided into four stages corresponding to decreasing temperature ranges. Stage-one, known as the mushy-stage, occurs at the beginning of solidification. During this stage too much liquid is present in the microstructure for cracking to occur. Stage-two is known as the coherency-stage. Cracking may occur in this stage; however, enough liquid is present in the microstructure in this temperature range such that all cracks that form will be healed.

Stage-three is known as the critical-stage; in this stage, cracking occurs and there is insufficient residual liquid for crack healing. This stage is further subdivided into stages 3H and 3L, known as the film-stage and droplet-stage respectively. In the film-stage, cracks may both initiate and propagate; in the droplet-stage, cracks may only propagate from film-stage cracks. Stage-four corresponds to complete solidification, and hot-cracks neither initiate nor propagate in this temperature range.
Solidification cracking is the term that refers specifically to hot cracking within the weld metal, whereas HAZ liquation cracking refers specifically to hot cracking within the HAZ of the base metal. This investigation has been limited to solidification cracking, as a propensity for HAZ liquation cracking was not observed during testing.

Within the weld metal, hot cracking occurs at both grain boundaries and subgrain boundaries, which have high solute concentrations as a result of partitioning during solidification. This phenomenon has been reported by numerous researchers, including Savage and Lundin who, during the development of the Varestraint test, reported that hot cracking initiated exclusively at sites of segregation [9]. Solidification cracking usually appears along the weld centerline, i.e. the last portion of the weld to solidify, in thick or highly restrained welds [11].

Partitioning of solute occurs during solidification when solute that cannot be accommodated by the newly solidified matrix is rejected into the liquid directly ahead of the solid/liquid interface. As a result, solidification grain boundaries and subgrain boundaries, which are the last regions to solidify, have the highest solute concentrations within the matrix, the lowest melting temperatures, and therefore the highest tendency towards solidification cracking. Partitioning during solidification has been explained elsewhere in much greater detail [12].

The wetting characteristics of the solidification grain boundaries and sub-grain boundaries also play an important role in the solidification cracking behavior of the alloy [13]. When a low fraction of liquid (less than one percent) with a high ratio of solid/solid to solid/liquid interfacial energies is present at the end of solidification, the tendency for the alloy to experience solidification cracking is remote. The liquid will likely exist in isolated pockets, where sufficient solid-solid interface exists to resist cracking. A moderate fraction of liquid (one to ten percent) with a low ratio of solid/solid to solid/liquid interfacial energies at the end of solidification represents the worst case scenario for solidification cracking. This liquid will continuously wet the solidification boundaries, thereby creating a very susceptible structure for solidification cracking. If greater than ten-percent liquid is present at the end of solidification, the microstructure
becomes less susceptible to solidification cracking because the large quantity of liquid at the end of solidification is able to ‘back-fill’ any cracks that may form [12].

Although solidification cracking can in many cases be prevented by the proper selection of filler metal, Lippold [14] noted that cracking in autogenous welds cannot be remedied via this method. It has also been noted that inhomogeneity of the microstructure, \textit{i.e.} solute banding, may either increase or decrease the local susceptibility of the alloy to hot cracking [1].

2.2.1. HAZ Liquation Cracking

As previously mentioned, this investigation will focus primarily on solidification cracking. However, the following paragraphs briefly explain the mechanisms which cause HAZ liquation cracking. Explanations have been derived from an extensive literature search performed by Lippold \textit{et al.} [15]. HAZ liquation cracking occurs in the region immediately adjacent to the fusion boundary, known as the Partially Melted Zone (PMZ). HAZ liquation cracking is often studied in alloys used in applications where weld integrity is critical, and is most commonly observed within stabilized austenitic stainless steels and highly alloyed nickel-base superalloys.

The two major mechanisms responsible for HAZ liquation cracking are the Penetration Mechanism and the Segregation Mechanism. The penetration mechanism involves the intersection of migrating grain boundaries with liquated particles. These particles are liquated in the PMZ due to a non-equilibrium phenomenon known as constitutional liquation [16].

However, HAZ liquation cracking is often seen in alloys were constitutional liquation is not observed. Therefore, another mechanism causing HAZ liquation cracking must exist; this mechanism has been broadly termed as the segregation mechanism. In the segregation mechanism, solute is segregated to grain boundaries where it reduces the solidus temperature resulting in local melting. Many mechanisms have been proposed to explain how solute is segregated to the grain boundaries. These mechanisms include
equilibrium diffusion, grain boundary sweeping, and pipeline diffusion; all of which are explained elsewhere [15].

2.2.2. Previous Research on Alloy C-22 and Similar Alloys

Cieslak et al. [6] investigated the relative weldability of Hastelloy alloys C-4, C-22, and C-276. Although C-4 was found to have comparable weldability to the crack resistant stainless steel 304L, C-22 and C-276 were found to be more susceptible to hot cracking. It was discovered that C-22 and C-276 both formed non-equilibrium, low melting terminal solidification constituents. These terminal solidification constituents were seen to be significantly enriched in Mo and W, and depleted in Ni and Fe, see Figure 2.2. Chromium and cobalt were not observed to partition within these alloys.

![Figure 2.2: Elemental partitioning of an Alloy C-22 weldment [17]. Within the figure the dendrite core and interdendritic regions are labeled as DC and ID respectively.](image)

Differential Thermal Analysis (DTA) conducted on Alloy C-22 revealed a temperature range of approximately 1400-1360°C for primary austenitic solidification, while the σ-phase detected on the DTA curve did not solidify until approximately 1290°C, see Figure 2.3. With DTA, one must consider that the cooling rates observed, 10°C/min in this case, are extremely slow as compared to the cooling rates experienced by a weldment, which are a much faster non-equilibrium process.
Thin foil micrographs and EDS spectra revealed that Alloy C-22 contained three terminal solidification constituents: P-phase (orthorhombic), σ-phase (tetragonal), and μ-phase (hexagonal). As a whole, the terminal solidification constituent population consisted of approximately eighty percent P-phase, twenty percent σ-phase, and trace amounts of μ-phase.

![Figure 2.3: DTA curve for Alloy C-22](image)

In this early work by Cieslak, he attempted to predict the solidification sequence of the alloys by examining isothermal sections of the Ni-Cr-Mo ternary diagram at 850°C and 1250°C. The ternary system simplification was justified by grouping the alloying elements into Ni, Cr, and Mo equivalents based upon their partitioning tendencies. From this model, Cieslak proposed the following solidification sequence for Hastelloy C-22:

\[
\{ L \rightarrow L + \gamma \rightarrow L + \gamma + \sigma \rightarrow \gamma + \sigma \rightarrow \gamma + \sigma + P \rightarrow \gamma + \sigma + P + \mu \}
\]

Note that this model predicts solid state transformation as the explanation for the presence of the P and μ-phases observed within the metallographic investigation.
Subsequent research on the solidification behavior of Hastelloy alloys was conducted by Perricone, Dupont, and Cieslak [18]. This investigation used computational thermodynamics to investigate the solidification sequences of Hastelloy alloys C-22 and C-276. The computational tools utilized were Thermo-calc Version N software and the ThermoTech Ni-Base database. The Mehrabian-Flemings model [19], used to describe macrosegregation, was used to for the purpose of solidification path calculations.

\[
C_{l,Mo} = C_{O,Mo} \left( \frac{C_{l,Cr}}{C_{O,Cr}} \right)^{k_{Mo} - 1} \left( \frac{k_{Cr} - 1}{k_{Cr}} \right)
\]

Where:
- \( C_{l,i} \) = composition in liquid of element \( i \)
- \( C_{o,i} \) = nominal composition of element \( i \)
- \( k_i \) = partition coefficient for element \( i \)

The most significant advantage of using the computational thermodynamic software was the ability to account for alloying additions other than Ni, Cr, and Mo as considered previously by Cieslak et al. [17]. Figure 2.4a through Figure 2.4c display the cumulative effect of additions of Fe and W on the fields of phase stability in the Ni-Cr-Mo ternary system.

In Figure 2.4a through Figure 2.4c, the nominal compositions of Alloy C-276 and Alloy C-22 are represented by the star-points that are superimposed on the diagram. The alloys begin to solidify from these points; arrows on the lines of two-phase saturation indicate the direction of solidification as temperature decreases. One can see from Figure 2.4c that the predicted solidification sequence of Alloy C-22 when Fe and W are considered is:

\{ L \rightarrow L + \gamma \rightarrow L + \gamma + P \rightarrow L + \gamma + P + \sigma \rightarrow \gamma + P + \sigma \}
The most significant deviation between this predicted solidification sequence and the previous sequence proposed by Cieslak et al. [17] is the formation of P-phase as a terminal solidification constituent, as opposed to formation through a solid-state transformation. The Mehrabian-Flemings model predicts a eutectic fraction of six-percent for the composition of Alloy C-22 used within the simulation. It must also be noted that the Mehrabian-Flemings model utilizes the same assumptions as the Scheil equation, namely that dendrite-tip undercooling and solid-state diffusion of each solute are negligible, that there is thermodynamic equilibrium at the solid/liquid interface, and that diffusion is infinitely fast in the liquid. The first two assumptions (the negligibility of dendrite-tip undercooling and back-diffusion), may actually have significant effects with the cooling rates experienced by a GTA weldments, and would lessen the fraction of terminal solidification constituents predicted by the model.

Rowe et. al [11] investigated the weldability of the Ni-Cr-Mo alloy Hastelloy C-2000, containing 1.6 weight-percent copper. The study revealed that copper did not have a strong tendency to partition into the solidifying liquid, and did not lead to increased cracking susceptibility over other Ni-Cr-Mo alloys. The relative weldability of Hastelloy C-22, C-276, and C-2000 ranked as follows (from least to most cracking susceptible): C-2000, C-22, and C-276. It should be noted however, that the separation between the cracking susceptibility of the three alloys was generally less than the standard deviation of the test results; this essentially indicates that C-22, C-276, and C-2000 have approximately the same solidification cracking susceptibility.
In work with nickel-based Alloy 625, Cieslak [20] found that intentional niobium additions greatly increased the solidification cracking temperature range of the alloy. Niobium promoted $\gamma$/MC (NbC) carbide, $\gamma$/Laves, and $\gamma$/M$_6$C carbide eutectic-type constituent. Carbon promoted $\gamma$/MC formation, while silicon promoted the formation of $\gamma$/Laves constituents. The study found that even in Ni-Cr-Mo alloys without Nb, which generally have greater cracking resistance, C and Si additions increased the susceptibility of the alloy to solidification cracking.
Dupont et al. [21] performed a similar study on the solidification cracking susceptibility of several Nb-bearing nickel-base alloys. DTA techniques were used to determine the sequence of solidification of the alloys; later metallographic investigation confirmed the DTA samples solidification sequence was the same as Varestraint weld samples. The solidification sequence of these alloys have three stages: primary austenite formation $L \rightarrow \gamma$, the $L \rightarrow \gamma + NbC$ reaction (taking place over a broad temperature range), and the $L \rightarrow \gamma + Laves$ reaction (taking place over a narrow temperature range).

Dupont et al. [21] differs from Cieslak [20] in that they found the solidification cracking susceptibility of the Nb-bearing alloys to decrease with increasing carbon content. The addition of C increased the start temperature of the $L \rightarrow (\gamma + NbC)$ reaction, through a corresponding decrease in the temperature range of primary austenite formation ($L \rightarrow \gamma$), resulting in an overall decrease of the SCTR. Additionally, high levels of C promote the formation of NbC, depleting the liquid of Nb until the $L \rightarrow (\gamma + Laves)$ reaction cannot take place. Dupont et al. [21] did however agree with Cieslak [20] in that Fe and Si additions increase the SCTR of the alloy, explaining that Fe and Si additions stabilize the Laves phase within these alloys.

Paterson and Milewski [22] investigated solidification cracking in dissimilar joints made between Alloy 625 and 304L. Auger Electron Spectroscopy (AES) revealed that S and P segregation increased the joint's tendency towards solidification cracking. Additionally, it was observed yet not explained, that pulsed current GTAW increased the susceptibility of the joint to solidification cracking as compared to constant current GTAW.

Baeslack et al. [23] investigated the effects of Ta additions to Nb-bearing nickel-based alloy Inconel 718. The investigation found that Ta additions to IN718 decreased the alloys susceptibility to both HAZ liquation cracking and solidification cracking. Examination of both the Ni-Ta and Ni-Nb binary phase diagrams reveals that Ni-Ta has a significantly narrower solidification temperature range than the Ni-Nb system.

Dupont, Michael, and Newbury [24] investigated the welding metallurgy of Alloy HR-160®, a high-temperature Ni-Co-Cr alloy. They found Alloy HR-160 to solidify in a
two step sequence: primary $L \rightarrow \gamma$ reaction followed by a eutectic-type $L \rightarrow [\gamma + (\text{Ni,Co})_{16}(\text{Ti,Cr})_6\text{Si}_7]$ reaction, with a broad SCTR of 225°C. Metallurgical investigation indicated that Ni, Si, and Ti segregated ($k_{\text{Ni}} = 0.96$, $k_{\text{Si}} = 0.71$, and $k_{\text{Ti}} = 0.44$) to the interdendritic regions, Co was depleted ($k_{\text{Co}} = 1.08$) in the interdendritic regions, and Cr was not partitioned ($k_{\text{Cr}} = 1.01$) during the solidification process.

2.3. Ductility-Dip Cracking

Collins, Lippold, and Ramirez [25] authored an extensive three part article on Ductility Dip Cracking (DDC) of nickel-based filler metals. DDC is an elevated temperature cracking phenomenon occurring below the effective solidus temperature of an alloy, see Figure 2.5. It is often observed in thick-section, multi-pass welds in austenitic materials. The large grain size and high restraint levels characteristic of these weldments contribute to the occurrence of DDC. Although DDC is relatively uncommon, it often occurs in applications (high-pressure steam, nuclear, and power generation) with low defect tolerances, where cracking can be very costly.
DDC occurs along migrated grain boundaries (MGB), and becomes increasingly favorable when these boundaries are straight as compared to tortuous. DDC has also been observed to initiate (and possibly terminate) at triple points, which have demonstrated to be microscopic stress concentrators. Unfortunately, the mechanisms behind DDC are currently not well understood and preventative methods are limited.

Collins et al. [25] specifically investigated two nickel-based filler metals: Filler Metal 52 and Filler Metal 82. The STF test was selected as the method to quantify the relative susceptibility of the filler metals. The STF test is a Gleeble based test for DDC susceptibility. The development of the test is discussed by Nissley and Lippold [26] and is explained in subsequent sections of this document.

FM-52 was found to be considerably more susceptible to DDC than FM-82. Of the two filler metals, only FM-82 contained intentional Nb-additions. As a result, FM-82 forms both NbC and Laves-phase during solidification; FM-52 only forms the Laves-
phase during solidification. The niobium-carbides within the FM-82 microstructure inhibit the migration of grain boundaries and produce tortuous migrated grain boundaries more effectively than the secondary constituents in FM-52. As a result, FM-82 possesses only tortuous migrated grain boundaries within its microstructure, whereas FM-52 exhibits a mixture of both straight and tortuous migrated grain boundaries. As mentioned previously, tortuous grain boundaries appear to inhibit DDC, especially at low strain levels.

Hydrogen and sulfur additions were observed to promote the occurrence of DDC, hydrogen having a much more pronounced effect. Although hydrogen is not normally problematic in austenitic materials, where it has high solubility, hydrogen additions have demonstrated a negative effect with respect to DDC. This negative effect is likely explained by the Decohesion Theory [27]. In the temperature range where DDC occurs, hydrogen becomes sufficiently mobile and migrates to grain boundaries and triple points, known as ‘traps’ within the Decohesion Theory. The atomic hydrogen within these traps is able to combine to form molecular hydrogen (H₂), which decreases the cohesion of the boundaries, allowing crack initiation and propagation to become more favorable.

At the upper end of the Ductility-dip Temperature Range (DTR), dynamic recrystallization is observed along the edges of ductility dip cracks. This dynamic recrystallization, a function of temperature and deformation, suppresses both crack initiation and propagation, signaling ductility recovery.

In the second portion of the investigation by Collins et. al [28], the fracture surfaces of DDC specimens were investigated; results were presented qualitatively. The nature of the fracture surface was most closely related to the temperature range that the specimens were tested at. Little difference was observed between the fracture surfaces of FM-52 and FM-82 samples that were tested at the same temperature. At the low and high ends of the DTR, where the ductility begins to recover, the fracture surface exhibited ductile dimpling with sharp features (i.e. necking on a micro-scale). At intermediate temperatures within the DTR, the fracture was also described as ductile dimpling, but with a more rounded appearance indicating less ductility.
Hydrogen, previously demonstrated to be detrimental with respect to DDC, produced a noticeably flatter fracture surface, with deep pore-like voids. These voids could be caused by: hydrogen decohesion occurring preferentially around grain boundary precipitates, atomic hydrogen combining to form molecular hydrogen in the form of pores, or the result of hydrogen-enhanced-local-plasticity (HELP; a condition where hydrogen concentration locally increases the plasticity of the material). These voids were not present in samples welded without the presence of hydrogen.

In the third part of the investigation by Collins et al. [29], the strain distribution along the grain boundaries was mapped using electron backscattered diffraction (EBSD), a technique that reveals crystallographic information on the sub-micron scale. The EBSD analysis revealed that strain concentrates along grain boundaries, and especially at triple point junctions. Essentially no strain was seen within the grain interiors.

The nature of the boundary also influences the susceptibility to of the alloy to cracking. Low angle grain boundaries, i.e. boundaries where the lattice mismatch to its nearest neighbor is small, are known to have a high resistance to crack propagation. These grain boundaries include solidification subgrain boundaries and solidification grain boundaries where the high-angle boundary has migrated away. Collins et al. [29] observed DDC almost exclusively along high angle grain boundaries, specifically migrated grain boundaries.

In multi-pass welding a higher degree of grain boundary migration occurs, due to the reheating of previously deposited passes. This boundary migration results in further segregation of impurity elements to the migrating boundaries, due to a grain boundary ‘sweeping’ effect. This impurity enrichment along the MGB may increase the susceptibility of an alloy to DDC.

Nissley et al. [30] performed work on the evaluation of DDC in austenitic stainless steels and nickel-base alloys. It was noted that the threshold strain ($\varepsilon_{th}$) and the DTR are the two primary quantitative measures of how susceptible an alloy is to DDC, see Figure 2.5. Additionally, it was noted that DDC is often observed in alloys free of second
phases or precipitates. Additionally, Nissley et al. [30] provide initial results on of the DDC susceptibility of Alloy C-22 in the STF test, see Figure 2.6.

Figure 2.6: Initial DDC evaluation of Alloy C-22 using the STF test [30]

Cola and Teter [31] investigated the DDC susceptibility of FM-52; they also found DDC to occur exclusively along high-angle migrated grain boundaries. Fractography revealed evidence of micro-ductility on the DDC fracture surfaces. The temperature range of the fractographic specimen cited falls onto the border of what Collins et al. [28] defined as the ‘intermediate’ and ‘high’ temperature ranges. Cola and Teter also noted that internal DDC occurred in in-situ fractured specimens. These internal cracks seemed to initiate at inclusions acting as stress concentrators.

2.4. Corrosion Considerations

Alloy C-22 and similar alloys are selected primarily for their ability to resist corrosion in aggressive environments. This fact must be taken into consideration when attempting to compositionally optimize such an alloy with respect to another performance criterion, such as weldability. In addition, corrosion considerations are especially
pertinent with respect to welding, as weldments are often the most susceptible portion of a structure to corrosion.

The performance of most corrosion resistant alloys is afforded through a phenomenon known as passivity. Passivity is the formation of a thin protective film on the surface of an alloy. This film is usually an oxide that is only nanometers thick. The film protects the underlying metal from the corrosive environment that the alloy is in contact with. Therefore, it is important to understand the effect of various alloying additions on the nature of the passive film protecting the alloy.

Shoesmith et al. [32] investigated the effects of Cr, Mo, and W on the passivity of Hastelloy alloys C-4, C-276, C-22, C-2000, and Inconel 625. Details of the electrochemical nature of corrosion processes, and test techniques to evaluate corrosion resistance are provided elsewhere [33]. Potentiostatic data was recorded at various potentials and temperatures. Temperature steps were spaced 10-12 hours apart in order to approach steady-state within the measurements. The electrolyte used for these experiments was a deaerated 1M NaCl + 0.1M H₂SO₄ solution.

Increasing temperature at a given applied potential increased the corrosion current density (i.e. corrosion rate) of the alloys investigated. At temperatures below 45°C, the passive current density was similar for all alloys. Above 45°C, the high-Cr alloys (C-22, C-2000, and 625) had significantly lower current densities. Above 85°C, a distinction between the tungsten-bearing alloys and the non tungsten-bearing alloys becomes evident. The tungsten-bearing alloys (C-276 and C-22) corroded slower than their corresponding low- and high-Cr alloys respectively.

Shoesmith et al. [32] used two metallographic techniques to characterize the surface oxides responsible for passivity of the alloys investigated: XPS surface analysis and TOF SIMS surface analysis. At low applied potentials, XPS indicates that Ni was present throughout the passive film thickness. At higher applied potentials it is revealed that Ni is depleted in the outer regions of the passive film but retained in the inner layer of the passive film. This indicates that Ni is retained in the bulk-alloy despite its rapid depletion.
from the surface of the passive film. Not surprising, Cr is the predominant component of all the passive films examined.

The TOF SIMS results presented in Figure 2.7 show the concentration of Mo- and W-oxides in the outer portion of the passive film, and the concentration of Cr-oxides in the inner portion of the passive film. The improved corrosion resistance of Mo- and W-bearing alloys is theorized to result from preferential migration of these elements to defect sites within the passive film that would otherwise become dissolution sites. Additionally, TOF SIMS results indicate that Alloy C-22 has the thickest passive film of all the alloys investigated.

Figure 2.7: TOF SIMS composition versus depth profile for Alloy C-22 at an applied potential of 500mV [32]

Rebak et al. [34-38] wrote a number of papers examining the effect of thermal aging on the corrosion resistance of Alloy C-22. These studies examined the effect of ageing temperatures between 260°C and 800°C and ageing times between 0.5 hrs and 40,000 hrs. This work was conducted to examine the effect of the long-term, low-temperature ageing that is expected within the Yucca Mountain repository environment.
The corrosion rates of the specimens studied in these investigations were primarily determined from mass loss immersion tests (ASTM G28A and G28B) of short duration. Examination of the aged microstructures reveals that significant microstructural changes occurred in the samples aged at or above 600°C. In this elevated temperature range, phases such as μ-phase and P-phase are able to form along grain boundaries, twin boundaries, and intra-granularly. These phases were seen to decrease the corrosion resistance of the alloy.

This finding is relevant to the current study in that many of the phases formed during thermal ageing, which are seen to be detrimental to corrosion resistance, also form as solidification constituents within weldments [17, 18]. This relationship highlights the importance of considering the metallurgical effects of welding within corrosion investigations.

2.5. Metallurgical Concepts

The following sections briefly outline metallurgical concepts that will help the reader to better understand discussions in subsequent sections.

2.5.1. Solidification

Solidification processes may be classified as three cases: equilibrium (case-one), microsegregation (case-two), and macrosegregation (case-three). Equilibrium solidification assumes complete back-diffusion of solute behind the advancing solid/liquid interface and complete mixing of the liquid ahead of the solid/liquid interface. This is an ideal situation, where a completely homogenous microstructure is produced during solidification. However, the times required for equilibrium, or near equilibrium, solidification are extremely long and certainly do not describe the solidification of welds.

In weldments, solute is partitioned during solidification. Solidification produces an inhomogeneous microstructure, where certain regions of the microstructure are richer in solute and certain regions are leaner in solute. The solidification experienced by welds is
more appropriately described as a combination of microsegregation and macrosegregation. Microsegregation (case-two) assumes complete mixing of the liquid ahead of the solid/liquid interface, and negligible back-diffusion into the solid behind the solid/liquid interface. This case best describes the segregation experienced by solidification subgrain-boundaries; this is illustrated in Figure 2.8.

![Solidification Subgrain Boundary](image)

Figure 2.8: Schematic illustrating microsegregation (case-two) along a solidification grain-boundary [52]

Macrosegregation (case-three) assumes incomplete mixing of the liquid ahead of the solid/liquid interface and negligible back-diffusion into the solid behind the solid/liquid interface. This case best describes the segregation experienced by solidification grain boundaries; this is illustrated in Figure 2.9.
Segregation during welding is often described by the Scheil equation, which is also known as the non-equilibrium lever-law. The Scheil equation describes solute redistribution during case-two solidification; therefore it best describes microsegregation at the interdendritic level. The Scheil equation is provided in Equation 2.1; where $C_s$ is the composition of the solid, $k$ is the partitioning coefficient, $C_0$ is the nominal composition of the alloy, and $f_s$ is the fraction solid.

$$C_s = k \cdot C_0 (1 - f_s)^{k-1}$$

Equation 2.1: The Scheil equation [52]
2.5.2. Weld-Metal Boundaries

In general, three types of weld-metal boundaries are discussed within this investigation; these boundaries are illustrated in Figure 2.10. The first type of boundary is a solidification grain-boundary (SGB). These boundaries form when two adjacent solidifying grains impinge upon each other during the competitive growth of the solidification process. These boundaries initially have a high level of crystallographic misorientation between each other. Solidification cracking occurs primarily along this type of boundary.

The second type of boundary is the solidification subgrain-boundary (SSGB). This type of boundary is formed between adjacent dendrites during solidification. These boundaries have a low level of crystallographic misorientation, and are therefore referred to as low-angle boundaries. Although solidification cracking may occur along these boundaries if sufficient restraint is present, both solidification cracking and ductility-dip cracking are generally not associated with subgrain boundaries.

The third type of boundary is a migrated grain-boundary (MGB). This type of boundary occurs when the crystallographic portion of a solidification grain-boundary ‘migrates’ away from it’s original location. The driving force for boundary migration is a minimization of the Gibbs free energy associated with the surface area of the boundary; therefore, migrated grain-boundaries are often very straight as compared to solidification grain-boundaries. This long, straight boundary morphology makes migrated boundaries particularly susceptible to ductility-dip cracking.
2.5.3. Recrystallization

The final metallurgical concept to be discussed is the concept of recrystallization. However, recrystallization may not be discussed without discussing two other strongly related phenomena: recovery and grain-growth. Figure 2.11 illustrates the processes of recovery, recrystallization, and grain growth. When a metal is heavily cold worked, the dislocation density of the metal is greatly increased; these dislocations are organized somewhat randomly within the polycrystalline material. When such a metal is heated such that the dislocations become sufficiently mobile, the processes of recovery, recrystallization and grain-growth begin to occur.

In the low-temperature recovery process, the dislocations arrange themselves into a polygonized subgrain structure. During this process, the dislocation density remains unchanged and the mechanical properties of the metal are relatively unaffected. When
the metal is heated further, above the recrystallization temperature, recovery occurs rapidly and new grains form along the polygonized subgrain structure. During this process the dislocation density of the metal is greatly reduced, giving the recrystallized metal a lower strength and higher ductility. If the metal is heated still further, both recovery and recrystallization occur rapidly and grain-growth occurs as smaller grains are consumed by larger favored grains.

Figure 2.11: Schematic illustration of the processes of recovery, recrystallization, and grain-growth. (A) cold-worked metal (B) recovery of the cold-worked metal, (C) recrystallization of the recovered metal, and (D) grain-growth within the recrystallized metal [70]

If the deformation illustrated in Figure 2.11A occurs at a high enough temperature, recovery and recrystallization may occur ‘dynamically’ during the deformation process. Dynamic recrystallization is pertinent to this investigation, as it may occur during the strain-to-fracture or hot-ductility tests at the upper end of the testing temperature range.
CHAPTER 3

OBJECTIVES

One of the important intended uses for Alloy C-22 is as a canister material in the Yucca Mountain Project. In such a critical application, fabrication related defects are simply unacceptable. As such, the weldability of Alloy C-22 is an important issue. Two of the most common forms of weld defects in Ni-base alloys are solidification cracking and ductility-dip cracking. The principal objectives of this investigation are:

1. To assess the solidification cracking susceptibility of Alloy C-22
2. To assess the ductility-dip cracking susceptibility of Alloy C-22
3. To assess the effect of compositional variation (namely Mo, W, and Fe) on the solidification cracking and ductility-dip cracking susceptibility of the alloy
CHAPTER 4

EXPERIMENTAL APPROACH

Testing methods have been selected such that a comprehensive understanding of the cracking behavior of Alloy C-22 was achieved. The testing methods selected were the Transvarestraint test for solidification cracking, and both the hot-ductility and strain-to fracture-tests for ductility-dip-cracking.

4.1. Solidification Cracking

The varestraint weldability test was developed by Savage and Lundin [9] in the mid-sixties. The Varestraint test is a relatively inexpensive test that produces repeatable results. The testing apparatus is simple in nature, and test samples require little preparation. The test uses augmented strain to simulate the shrinkage stresses experienced by highly restrained weldments. The use of augmented strain, as opposed to self-restraint, isolates the mechanical, metallurgical, and process related effects, allowing these effects to be evaluated individually.

The Varestraint test was designed to be a “universal test” for the evaluation of hot-cracking susceptibility; such as test has the following properties:

1. Correlation to service behavior
2. A high level of reproducibility
3. A high sensitivity to small changes in test variables
4. The ability to show the effects of welding parameters
5. The ability to be conducted economically
6. Applicability to all welding processes

The Varestraint test has proven capable of satisfying the above six criterion. An additional benefit of the Varestraint test is that it is possible to cause cracking in all materials. This is an advantage over other testing methods, namely self-restraint, which are unable to produce cracking in many resistant materials.

The Transvarestraint test is a variation of the Varestraint test. In the Transvarestraint test, the augmented strain is applied in a direction transverse to the welding direction. The main advantage of the Transvarestraint test is that it requires less material per sample as compared to the original Varestraint test, and is therefore more economical.

Although Varestraint tests are highly repeatable, poor correlation often exists between laboratories using the test to evaluate the same cracking phenomenon. The reason for this is the large number of welding parameters that must be selected to perform the test. As a result, Finton and Lippold [39] performed work on standardizing the Transvarestraint test. The following conclusions were developed from this work:

1. Arc lengths between 0.05 and 0.15 inches did not have a substantial effect on cracking response
   a. Voltage changes of ±1.5V did not affect cracking response
2. The minimum recommended sample size for a specimen, parallel to the direction of welding, for 0.25 in thick plate, is 3 inches
3. A current range of 160-190A produced the most consistent cracking response
4. Travel speeds between four and six inches per minute are recommended
5. A ram travel speed of six to ten inches per second produced the most consistent cracking response

4.2. Ductility-Dip Cracking

The most common test to evaluate elevated temperature ductility is the hot-ductility test. In the hot-ductility test a sample of known dimensions is pulled to failure at an
elevated temperature; reduction in area, or elongation, is used to evaluate the ductility of the sample at failure. If a sequence of these tests is conducted over an appropriate elevated temperature range, a ductility vs. temperature curve may be plotted. A material that experiences a loss of ductility at elevated temperatures will display a noticeable dip in ductility at temperatures below the solidus temperature of the alloy.

Although the hot-ductility test is simple and effective for revealing elevated temperature ductility loss, the information provided by this test relates to the failure condition of the material. As a result, an alternative test (the strain-to-fracture test) was developed by Nissley and Lippold [26]. The main advantage of the strain-to-fracture test over the hot-ductility test is that it provides information relating to the initiation of cracking at elevated temperatures, which is more pertinent with respect to ductility-dip in weldments.

The strain-to-fracture test is a Gleeble-based test that uses “dog-bone” samples with spot-welds on the opposing faces of the gauge section. Much greater detail on the intricacies of the strain-to-fracture test and sample preparation are provided within the experimental procedure section of this report. The spot welds on the gauge section of the sample produce a microstructure that is both susceptible to ductility-dip cracking, providing the test with a high level of sensitivity, and repeatable in nature. Additionally, the Gleeble thermal-mechanical system allows for close control of both temperature and strain. The precise control of microstructure, temperature, and strain associated with the strain-to-fracture test eliminates much of the variability that makes ductility-dip cracking difficult to understand in complicated, highly-restrained, multi-pass weldments.

4.3. Compositional Variation

The effects of compositional variation on the solidification cracking and ductility-dip cracking susceptibility of Alloy C-22 were examined using both thermodynamic simulations and button-melting experiments. Thermodynamic simulations are a fast and inexpensive way of investigating metallurgical phenomena that occur in complex multi-component alloys. The bulk of the thermodynamic simulations in this investigation were
performed on the JMatPro v4.1 software package, although ThermoTech Version-P was employed for certain tasks. The JMatPro v4.1 software was selected primarily for its ease of use, diversity of calculations, and post-processing options.

A button melter uses a GTAW torch as a heat source to melt and stir precise quantities of metal in a water cooled copper hearth. This technique can quickly and inexpensively produce small quantities of experimental alloys. This technique may be coupled with single-sensor differential thermal analysis to determine the transition temperatures of such experimental alloys. Single-sensor differential thermal analysis is a technique developed to measure transition temperatures *in-situ* during solidification or solid-state reactions. This technique uses a single thermocouple and mathematically generated reference curves, which mimic the reference curve of conventional differential thermal analysis techniques, to determine transition temperatures. Single-sensor differential thermal analysis has proven to be a simple and reliable method of measuring the transition temperatures of an alloy.
CHAPTER 5

EXPERIMENTAL PROCEDURE

The following sections outline the materials, equipment, and experimental procedures used within this investigation.

5.1. Materials

The following two sections provide information about the base-metal used within the initial testing of Alloy C-22, as well as the commercially pure lots of material used within the button melting experiments.

5.1.1. Base Metal

Materials for the initial testing phase were provided by Haynes International. Approximately fifteen square-feet of two separate commercial heats of quarter-inch thick Hastelloy C-22 plate were obtained from Haynes International. The compositions of these two heats are listed in Table 5.1. Note the similarity of the compositions of the two heats.
<table>
<thead>
<tr>
<th>Heat Number</th>
<th>Chemical Analysis (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>2277-3-3114</td>
<td>0.0039</td>
</tr>
<tr>
<td>2277-3-3119</td>
<td>0.0050</td>
</tr>
</tbody>
</table>

Table 5.1: Composition of the two heat of Haynes Hastelloy C-22 used for initial testing

Heats 2277-3-3114 and 2277-3-3119 had ASTM grain sizes of 3.5 and 3.0 respectively. Optical microscopy revealed the microstructures of the longitudinal and transverse directions to be equivalent. The grain structure of the base-metal consists of equiaxed grains, many of which are heavily twinned (see Figure 5.1A). Backscattered electron imaging revealed the microstructure of the base metal to be free of secondary phases and remarkably homogenous (see Figure 5.1B).

The following paragraphs describe the processing steps involved in the fabrication of Alloy C-22 plate [65]. Each heat is melted in a 15 ton electric arc furnace, where each charge consists of a mix of internal scrap and raw material. The chemistry is checked during melting and the composition adjusted to be with internal melt control limits, which are tighter than the external ASTM material specifications. After arc melting, the liquid metal is transferred by ladle to an Argon-Oxygen Decarburization (AOD) vessel for final metal refining and chemistry control. The molten metal is poured into rectangular cast iron molds; the resulting solidified ingots are stripped and sent for Electroslag Remelting (ESR). The result is a sound ingot, 30.5 cm (12 in) in thickness, weighing approximately 4,536 kg (10,000 lbs).

These ingots are heated to approximately 1204°C (2200°F) and hot rolled to an intermediate thickness of around 17.8 cm (7 in). The intermediate thickness slabs are air
cooled and subsequently surface conditioned. These slabs are reheated and rolled to thinner slabs, air cooled, and receive additional surface conditioning and inspection. Final plate product is then rolled from these thinner slabs. The final plates are annealed at 1121°C (2050°F), water quenched, and cleaned by molten salt de-scaling and acid pickling.

![Figure 5.1: (A) Orientation imaging of Alloy C-22 base-metal, and (B) backscattered electron imaging of Alloy C-22 base-metal revealing the absence of secondary phases and the homogeneity of the microstructure](image)

Table 5.2 lists the room temperature mechanical properties provided by the manufacturer. A number of other physical, mechanical, electrical, and thermal properties are provided in Appendix A.
<table>
<thead>
<tr>
<th>Heat</th>
<th>0.2% Yield Strength</th>
<th>UTS</th>
<th>Elongation</th>
<th>HRB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MPa</td>
<td>ksi</td>
<td>MPa</td>
<td>ksi</td>
</tr>
<tr>
<td>2277-3-3114</td>
<td>400</td>
<td>58</td>
<td>755</td>
<td>109.5</td>
</tr>
<tr>
<td>2277-3-3119</td>
<td>393</td>
<td>57</td>
<td>758</td>
<td>110.0</td>
</tr>
</tbody>
</table>

Table 5.2: Manufacturer provided Alloy C-22 mechanical properties

5.1.2. Commercially Pure Metals

Small quantities of commercially pure metals were obtained in order to conduct the button-melting experiments. These metals included batches of nickel, chromium, molybdenum, tungsten, iron, and cobalt; all having a minimum purity of 99.90%.

5.2. Equipment

The following sections outline the equipment used within the experimental and characterization phases of this project.

5.2.1. The Varestraint Machine

The varestraint machine was used to perform the tests that determined the susceptibility of Alloy C-22 to solidification cracking. This machine is located at the Edison Welding Institute (EWI), adjacent to the Welding Engineering Department at The Ohio State University. The machine consists of a GTAW torch, power-supply, and a hydraulic system, all of which are computer controlled. A schematic of the Varestraint machine is provided in Figure 5.2.
Computer control of the X, Y, and Z-axis of the GTAW torch allows the torch to travel along the surface of the test specimen at a specified arc gap, travel speed, and distance. The hydraulic system of the Varestraint machine is used to conform the test plate around a die block of known radius, which induces augmented strain. Computer control of the hydraulic system, in coordination with the GTAW torch, allows the hydraulic system to bend the test plate around the die block using a specified stroke and stroke rate, at a user specified time in the GTAW weld sequence.

5.2.2. The Gleeble Thermal-Mechanical Simulator

The Welding and Joining Metallurgy Group in The Ohio State University’s Welding Engineering Department operates a Gleeble® 3800 thermal-mechanical simulator. A picture of the Gleeble® 3800 system is shown in Figure 5.3. The following system
specifications have been taken from the manufacturers (Dynamic Systems Inc.) website [46].

The Gleeble® 3800 thermal system uses direct resistance heating to heat specimens at rates anywhere between steady-state temperature holds to a maximum of 10,000°C/sec (18,000°F/sec). Water cooled conductive grips normally control the maximum possible cooling rate of the sample; an optional quenching system allows for cooling rates in excess of 10,000°C/sec (18,000°F/sec) at the sample surface. Thermocouples or an infrared pyrometer are used to accurately control the thermal feedback loop. All

Figure 5.3: the Gleeble® 3800 thermal-mechanical simulator, located in the Welding Engineering Department at The Ohio State University [45]
specimens for this investigation used K-type thermocouples to monitor, control, and record specimen temperature.

The Gleeble® 3800 mechanical system is capable of applying up to 20 tons of static force in compression or 10 tons in tension. Displacement rates up to 2000 mm/sec (78.7 in/sec) can be achieved. Transducers and load cells provide the feedback used to accurately control the mechanical aspects of the test. The operator may program changes from one control mode to another during any given test, providing a versatility that allows simulation of most thermal-mechanical processes. Typical mechanical control modes include stroke displacement, force, and extensometer feedback.

A Series 3 Digital Control System allows the Gleeble® 3800 to be operated by computer, by manual control, or by a combination of computer and manual control.

5.2.3. The Button-Melter

The button-melter is a water cooled copper hearth that uses a GTAW torch as a heat source to melt and stir small charges of metal. A quartz cylinder and a brass lid, into which the GTAW torch enters, create an air-tight chamber through which argon flows to provide a protective atmosphere. A schematic of the button melting system is provided in Figure 5.4.
5.2.4. Metallographic Equipment

Various pieces of metallographic equipment were used to section, mount, polish, and etch the samples that were characterized within this investigation. Sectioning was primarily accomplished using a Leco CM-15 cut-off machine and a Mark V CS600-A saw, both of which used SiC abrasive cutting wheels.

Mounting was accomplished using either a 1-¼ in Leco PR-10 mounting press or a 1-½ in Leco PR-32 mounting press. Grinding of the samples was accomplished using three separate pieces of equipment; a Leco BG-30 abrasive belt grinder, a Leco DS-20 grinding strip assembly, and a Buehler Metaserv 2000 grinding wheel. Coarse polishing steps were conducted on a Leco Spectrum System 1000 polishing wheel, and final polishing was conducted on a Buehler Vibromet 2 vibratory polisher.
Samples to be examined using EBSD were electropolished using a Struers Lectropol-5 electropolisher. Electrolytic etching was accomplished using an Electro Industries Digi-35A power supply.

5.2.5. Optical Microscopy

Optical microscopy was accomplished using a Nikon Epiphot microscope and a PAXcam 2MP digital camera using PAX-it™ software. Image analysis, of both optical and electron micrographs, was accomplished using ImageJ v1.37 software. Low magnification images were captured using a Nikon SMZ1000 stereoscope and a Nikon DS-2Mv 2MP digital camera.

5.2.6. Electron Microscopy

Electron microscopy was conducted at the Campus Electron Optics Facility within the Material Science and Engineering Department at The Ohio State University. All electron microscopy was accomplished using a Quanta scanning electron microscope (SEM). The Quanta is a heated tungsten filament SEM equipped with a range of detectors including a secondary electron detector, a backscattered electron detector, and an internal CCD camera.

The Quanta is also equipped with an Energy Dispersive Spectrometer (EDS) for chemical analysis using x-rays, and an Electron Backscattered Pattern (EBSP) detector for mapping and phase analysis. EDS was accomplished using an EDAX Genesis Spectrum software collection and analysis software. Likewise, EBSD was accomplished using EDAX TSL OIM™ collection and analysis software.

5.3. The Transvarestraint Test

The Transvarestraint (TV) test was used to quantify the solidification cracking susceptibility of Alloy C-22. Six TV samples were cut from both heats of quarter-inch thick plate. The samples were three by eight inch rectangular pieces, with each of these samples able to accommodate three TV bends.
Prior to testing, the surfaces of the samples were prepared by grinding, and cleaning with acetone. The parameters for TV testing were selected from the recommendations of Finton and Lippold [39]; these parameters are listed in Table 5.3. A combination of current and travel speed was selected such that a weld bead with a width of approximately 1-cm (0.4-in) was produced. This weld bead width is standard for the Transvarestraint test, and permits comparison with other tested alloys.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>180 amps</td>
</tr>
<tr>
<td>Voltage</td>
<td>10 volts</td>
</tr>
<tr>
<td>Arc-Gap</td>
<td>0.08 inches</td>
</tr>
<tr>
<td>Travel Speed</td>
<td>5 inches per minute</td>
</tr>
<tr>
<td>Pre-Bend Weld Length</td>
<td>1.5 inches</td>
</tr>
<tr>
<td>Total Weld Length</td>
<td>2.0 inches</td>
</tr>
</tbody>
</table>

Table 5.3: Transvarestraint test parameters

After testing, cracking of the sample surfaces was evaluated using a low magnification stereomicroscope. The measurement of particular interest in assessing cracking susceptibility was the Maximum Cracking Distance (MCD). The MCD, or the longest crack in a direction perpendicular to the local solidification front at the instant of strain application, was measured using a filar scale within the ocular of the stereomicroscope.

5.4. The Strain-to-Fracture Test

The STF test was used to evaluate the DDC susceptibility of Alloy C-22. Twenty Gleeble ‘dog-bone’ samples were sectioned from heat 2277-3-3114 using standard machining techniques. The nominal dimensions of an STF sample are presented in Figure 5.5.
A spot weld, approximately 1-cm (0.4-in) in diameter, was made on each side of the reduced section of the STF samples. The spot welds were autogenous GTAW welds made using the parameters listed in Table 5.4.
Copper chill blocks were used to fixture the samples during spot welding (Figure 5.6). These blocks ensured that the spot welds would not grow larger than the width of the reduced section in diameter. The spot weld is made on the samples as to create a reproducible microstructure that is susceptible to DDC. The slow radial solidification of the weld pool produces large columnar grains that are oriented at all angles to the axis of tensile strain experienced by the samples during the STF test.

Figure 5.6: STF sample fixture using a copper chill-block
Gauge marks, located 4 mm (0.16 in) apart, are stamped on the top and bottom of the reduced section of the samples using diamond shape indenter and a special location tool. These gauge marks serve two purposes: (1) they are measured before and after testing to determine the actual amount of plastic strain induced in the sample during testing, and (2) they serve as anchor points for the ceramic prongs of the longitudinal extensometer used in the Gleeble STF program. The distance between the gauge marks is measured before and after testing on the micrometer controlled stage of a Leco M-400-H1 microhardness testing machine, which has a resolution of 0.001 mm (0.00004 in).

Making a spot-weld on the faces of the reduced sections creates an uneven surface due to weld cratering; this surface is unfavorable for post-testing optical examinations. As a result, these faces are ground flat prior to testing. Grinding of the reduced section was accomplished using a 17.8 cm (7 in) diameter by 19 mm (0.75 in) wide aluminum oxide grinding wheel.

Samples ready for Gleeble testing have K-type thermocouples percussion welded to the center of the reduced gauge section. The samples are then loaded into the Gleeble chamber with a free span of 50.8 mm (2 in). The Gleeble jaws used for the STF test are stainless steel ‘hot jaws’ with hardened steel serrated inserts, used to grip the sample during tests involving tensile forces. These jaws are termed ‘hot jaws’ because stainless steel is considerably less conductive than the standard copper jaws. Limiting the conductivity of the jaws allows for a flatter temperature profile across the free-span of the sample, which is beneficial in many types of testing. The samples are pre-loaded at room temperature to allow the serrated inserts of the hot-jaws to ‘bite’ into and grip the sample, preventing slippage during testing.

Once the sample has been successfully loaded, the sample chamber closed, evacuated to 2.0x10^{-1} torr, and backfilled with argon gas. This procedure is repeated twice to decrease the amount of sample oxidation during testing. Initially the Gleeble heats the sample at 100°C/sec (180°F/sec) to the desired testing temperature; the temperature of the sample is then kept constant for 10 seconds as the gauge section is allowed to come to
an equilibrium temperature profile. During these initial steps, the mechanical system is under force control, and the sample experiences 0 kg (0 lbs) force.

The mechanical system is next switched to stroke control mode in order to strain the sample. A control loop strains the sample at a constant stroke rate of 0.06 cm/sec (0.024 in/sec) until a specified extension of the gauge length, as measured by a longitudinal extensometer, is reached. This specified extension is determined prior to testing, based upon the desired level of strain, using Equation 5.1. This equation was developed empirically from previous testing of similar solid-solution nickel based alloys [45].

\[
HZT = \frac{(S - 0.3573)}{84.363} \cdot L_0
\]

Equation 5.1: Formula used to estimate the required gauge extension during the STF test. HZT = extensometer elongation (mm), S = strain (%), and L₀ = initial gauge length (mm)

After the desired gauge length extension is reached, the thermal and mechanical systems are turned off, and the sample is allowed to free cool under negligible tensile force. The sample gauge marks are re-measured following strain-to-fracture testing. The difference between the initial and final gauge lengths is noted, and the strain of the gauge section is calculated and recorded.

Samples are next sectioned to separate the gauge section from the shoulders of the specimens. The gauge sections are mounted in bakelite, ground flat, and polished to a 1μm finish. This mirror surface is next examined under a stereomicroscope equipped with a fluorescent ring-light for illumination. All cracks on the sample surface are counted and recorded. The samples are next broken out of the bakelite mold, the opposite sample face is mounted, ground, and polished to count and record the number of cracks. The number of cracks reported per sample is the average of the number of cracks on the two faces.
After a sufficient number of samples have been tested, the cracking data is plotted on a strain-vs-temperature graph. Based on the data, a line is drawn on the graph that represents the threshold strain, below which cracking will not occur. This threshold strain line creates the cracking susceptibility envelope for the particular alloy.

5.5. The Hot Ductility Test

Hot ductility testing was performed on Alloy C-22 base-metal and weld-metal. All samples were machined from heat 2277-3-3114 of Haynes Hastelloy C-22. Base-metal samples were created by sectioning 100 mm x 6.4 mm x 6.4 mm (4 in x 0.25 in x 0.25 in) samples from 6.4 mm (0.25 in) thick Alloy C-22 plate. Weld metal samples were created in a similar fashion from plate with the center section consisting entirely of autogenous weld metal. The center sections of all samples were subsequently ground on all four faces to produce a 19 mm (0.75 in) gauge section that allowed for heat and strain concentration during Gleeble testing. Grinding was accomplished using a 17.8 cm (7 in) diameter by 19 mm (0.75 in) wide aluminum oxide grinding wheel. The nominal dimensions of the hot-ductility samples are displayed in Figure 5.7.

![Figure 5.7: Hot-ductility sample schematic](image)

The autogenous weld-metal center sections of the weld-metal samples were created by first running a deep penetrating GTAW weld on the face of the Alloy C-22 plate; the weld parameters of which are listed in Table 5.5. The plate was then flipped over, and an
identical weld was made on the opposing face of the plate such that the second weld penetrated into the weld metal of the first pass, creating a center section of through-thickness weld-metal.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc Current</td>
<td>250 A</td>
</tr>
<tr>
<td>Arc Voltage</td>
<td>9.0 V</td>
</tr>
<tr>
<td>Travel Speed</td>
<td>3 ipm</td>
</tr>
<tr>
<td>Shielding</td>
<td>Argon</td>
</tr>
<tr>
<td></td>
<td>20 cfh</td>
</tr>
</tbody>
</table>

Table 5.5: GTAW parameters for hot-ductility sample production

The Gleeble testing parameters for the hot-ductility test are listed in Table 5.6. The Nil-Strength-Temperature (NST) of the metal is determined by putting the sample under a minute load (approximately 20kg) and heating at a rate of 111°C/sec (200°F/sec) until sample breakage. The point where the recorded temperature begins to deviate from the programmed temperature is determined to be the NST.

On-heating samples are heated at a rate of 111°C/sec (200°F/sec) to the testing temperature and immediately pulled to failure. On-cooling samples are heated at a rate of 111°C/sec (200°F/sec) to a temperature just below the NST. The samples are then free cooled, through conduction with the Gleeble jaws, down to the desired testing temperature, where they are immediately pulled to failure.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>On-Heating</th>
<th>On-Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>Argon</td>
<td></td>
</tr>
<tr>
<td>Jaws</td>
<td>Stainless steel (with serrated grip inserts)</td>
<td></td>
</tr>
<tr>
<td>Sample free-span</td>
<td>25.4-mm (1-in)</td>
<td></td>
</tr>
<tr>
<td>Heating Rate</td>
<td>111°C/sec (200°F/sec)</td>
<td></td>
</tr>
<tr>
<td>Peak Temperature</td>
<td>$T_{\text{test}}$</td>
<td>$\text{NDT} &lt; T_{\text{test}} &lt; \text{NST}$</td>
</tr>
<tr>
<td>Cooling Rate</td>
<td>N/A</td>
<td>Free-cool</td>
</tr>
<tr>
<td>Hold Time</td>
<td>0 sec</td>
<td></td>
</tr>
<tr>
<td>Stroke Rate</td>
<td>50.8 mm/sec (2 in/sec)</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.6: Hot-ductility Gleeble testing parameters

After testing, the dimensions of the fracture surface were measured with a Mitutoyo Absolute Digimatic micrometer, having a resolution of 0.01 mm (0.0004 in), and the area of the fracture surface is calculated. This area is compared to the area of the gauge prior to testing, and the percent reduction in area is calculated. Plotting the reduction in area versus testing temperature allows for the creation of a ductility ‘signature’.

5.6. Thermodynamic Simulations

The thermodynamic simulations were conducted using both the JMatPro v4.1 and Thermo-Calc Version-P thermodynamic simulation programs; both programs utilized the ThermoTech Ni-DATA V.7 thermodynamic database. These programs were used to create a number of diagrams that helped in understanding the welding metallurgy and phase transformation sequence of Alloy C-22, including pseudo-binary phase diagrams, CCT diagrams, TTT diagrams, and stacking-fault energy analysis.

However, the module that was most frequently used to understand the behavior of Alloy C-22 weld-metal was the Scheil-Gulliver non-equilibrium solidification module. Two quantities derived from the Scheil-Gulliver simulations were of particular importance: (1) the solidification temperature range, and (2) the volume fraction of
secondary phases present at the end of solidification. The solidification temperature range is thought to be related to the susceptibility of the alloy to solidification cracking, and the volume fraction of secondary phases is thought to be proportional to the ability of the alloy to resist ductility-dip cracking.

A response surface method (RSM) experimental approach was used to conduct the Alloy C-22 Scheil-Gulliver simulations in this investigation. The elements that are significantly enriched or depleted during solidification of Alloy C-22 were chosen as the factors to be varied. According to Cieslak et al. [17] the elements that are enriched or depleted in the terminal solidification constituents of Alloy C-22 are Mo, W, and Fe (see Table 5.7).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Mo</th>
<th>W</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>μ</td>
<td>38.7</td>
<td>6.3</td>
<td>2.1</td>
</tr>
<tr>
<td>P</td>
<td>37.4</td>
<td>5.3</td>
<td>2.2</td>
</tr>
<tr>
<td>σ</td>
<td>34.9</td>
<td>4.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Alloy C-22</td>
<td>13.4</td>
<td>3.3</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Table 5.7: Composition of terminal solidification constituents in Alloy C-22 [17]

The nominal composition of Alloy C-22 used within these simulations was determined as the average composition of the elements from the two heats of Haynes Hastelloy C-22 used within this study (heats 2277-3-3114 and 2277-3-3119); these compositions are provided in Table 5.8. The compositional limits that define an alloy as “C-22” are provided in Table 5.9.
Table 5.8: Nominal composition of Alloy C-22 elements in wt%

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Fe</th>
<th>Co</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>V</th>
<th>O*</th>
<th>N*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bal.</td>
<td>21.36</td>
<td>13.46</td>
<td>2.99</td>
<td>3.67</td>
<td>1.36</td>
<td>0.0045</td>
<td>0.24</td>
<td>0.0265</td>
<td>0.13</td>
<td>0.005</td>
<td>0.0025</td>
<td></td>
</tr>
</tbody>
</table>

*Assumed levels of O and N during GTAW as specified by Eagar [50]

The low (-1), intermediate (0), and high (+1) values for the RSM matrix were selected based upon the compositional limits of Alloy C-22; these values are provided in Table 5.10. Accordingly, the full RSM matrix for the variation of Mo, W, and Fe is provided in Table 5.11; this RSM design is a three-factor EIMSE-Optimal RSM design [51].

Table 5.9: Compositional Limits of Alloy C-22 in wt%

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
<th>W</th>
<th>Co</th>
<th>Mn</th>
<th>V</th>
<th>Si</th>
<th>C</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min</td>
<td>bal.</td>
<td>20</td>
<td>12.5</td>
<td>2.0</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Max</td>
<td>bal.</td>
<td>22.5</td>
<td>14.5</td>
<td>6.0</td>
<td>3.5</td>
<td>2.5</td>
<td>0.5</td>
<td>0.35</td>
<td>0.08</td>
<td>0.015</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 5.10: RSM matrix -1, 0, +1 values

<table>
<thead>
<tr>
<th></th>
<th>Mo</th>
<th>W</th>
<th>Fe</th>
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<tbody>
<tr>
<td>-1</td>
<td>12.5</td>
<td>2.5</td>
<td>2.0</td>
</tr>
<tr>
<td>0</td>
<td>13.5</td>
<td>3.0</td>
<td>4.0</td>
</tr>
<tr>
<td>+1</td>
<td>14.5</td>
<td>3.5</td>
<td>6.0</td>
</tr>
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</table>
Table 5.11: RSM matrix for compositional variation

<table>
<thead>
<tr>
<th>Run</th>
<th>Mo</th>
<th>W</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.5</td>
<td>2.5</td>
<td>6.0</td>
</tr>
<tr>
<td>2</td>
<td>13.5</td>
<td>3.0</td>
<td>4.0</td>
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<tr>
<td>3</td>
<td>14.5</td>
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<td>2.0</td>
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<tr>
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</tr>
<tr>
<td>7</td>
<td>14.5</td>
<td>3.5</td>
<td>6.0</td>
</tr>
<tr>
<td>8</td>
<td>13.5</td>
<td>2.5</td>
<td>6.0</td>
</tr>
<tr>
<td>9</td>
<td>12.5</td>
<td>3.0</td>
<td>6.0</td>
</tr>
<tr>
<td>10</td>
<td>14.5</td>
<td>3.5</td>
<td>2.0</td>
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<td>12.5</td>
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<td>6.0</td>
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<tr>
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<td>14.5</td>
<td>3.0</td>
<td>2.0</td>
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<tr>
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<td>12.5</td>
<td>2.5</td>
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<tr>
<td>14</td>
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<td>4.0</td>
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<td>16</td>
<td>12.5</td>
<td>3.5</td>
<td>6.0</td>
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</tbody>
</table>

Sulfur and phosphorus are known to promote the formation of continuous liquid films along grain boundaries at the end of solidification; as a result, these two elements strongly encourage solidification cracking. Unfortunately, sulfur and phosphorus do not exist in the ThermoTech Ni-DATA V.7 thermodynamic database; as such, they have not been included in these simulations. It is however noted that the sulfur and phosphorus levels of the base-metal used in this investigation (see Table 5.1), and the pure metals used for the button-melting experiments are all very low in these two elements. The parameters used to conduct the Scheil-Gulliver simulations are listed in Table 5.12.
Solidification cut-off | Fraction liquid = 0.02%
---|---
Start Temperature | 1450°C
Temperature Step | 1°C

*Take all solid phases into account*

Table 5.12: JMatPro Scheil simulation parameters

5.7. Button-Melting Experiments

Button melting experiments were performed to physically replicate the Scheil simulations performed in the thermodynamic simulation phase of the project. The first step in this process was the creation of Ni-Xx binary alloys; the compositions of these alloys are listed in Table 5.13.

The binary alloys were created by melting together specific quantities of pure nickel and pure solutes in the button-melting apparatus displayed in Figure 5.4. Accurate weight measurements of nickel and solute additions were performed on a Mettler P163 scale, having a resolution of ±0.01 g (±0.0004 oz). The reasons for initially creating these binary alloys were two-fold: (1) the binary alloys allowed for more precise addition of small quantities of alloying additions, such as cobalt, and (2) the binary alloys allowed for easier addition of high melting point elements such as molybdenum, utilizing the Ni-Mo eutectic composition. An intermediate compositional check, using Energy Dispersive Spectrometry (EDS), was conducted on the binary alloys before they were subsequently sectioned for use in the creation of the final button compositions.
Table 5.13: Ni-Xx binary alloy compositions

Once the compositions of the binary alloys were verified, precise quantities of the binaries were sectioned along with precise quantities of commercially pure nickel and chromium. These charges were melted together in the button-melter to form the desired compositions of the final buttons of the RSM matrix. Energy dispersive spectrometry, utilizing pure metal standards, was used to verify the final composition of the sixteen RSM buttons. Good correlation between the desired (Table 5.11) and measured compositions (Table 5.14) is noted.
Table 5.14: RSM final button compositions as measured by EDS with pure element standards

<table>
<thead>
<tr>
<th>Mo</th>
<th>W</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.7</td>
<td>29</td>
<td>6.3</td>
</tr>
<tr>
<td>14.2</td>
<td>31</td>
<td>4.4</td>
</tr>
<tr>
<td>15.6</td>
<td>31</td>
<td>2.1</td>
</tr>
<tr>
<td>13.9</td>
<td>40</td>
<td>2.4</td>
</tr>
<tr>
<td>14.5</td>
<td>32</td>
<td>4.3</td>
</tr>
<tr>
<td>12.6</td>
<td>36</td>
<td>2.4</td>
</tr>
<tr>
<td>13.6</td>
<td>37</td>
<td>6.4</td>
</tr>
<tr>
<td>14.4</td>
<td>28</td>
<td>6.2</td>
</tr>
<tr>
<td>12.8</td>
<td>38</td>
<td>6.0</td>
</tr>
<tr>
<td>14.9</td>
<td>41</td>
<td>2.3</td>
</tr>
<tr>
<td>12.6</td>
<td>31</td>
<td>6.2</td>
</tr>
<tr>
<td>15.1</td>
<td>33</td>
<td>2.2</td>
</tr>
<tr>
<td>12.9</td>
<td>30</td>
<td>4.3</td>
</tr>
<tr>
<td>13.9</td>
<td>32</td>
<td>4.3</td>
</tr>
<tr>
<td>13.0</td>
<td>30</td>
<td>2.1</td>
</tr>
<tr>
<td>12.6</td>
<td>38</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Three 0.8 g (0.028 oz) samples were sectioned from each of the sixteen RSM compositions, along with three 0.8 g (0.028 oz) samples from heat 2277-2-3114 of Haynes Hastelloy C-22. These samples were subsequently melted in the button-melter to produce spherical shaped samples appropriate for the next phase of testing. These spherical samples were placed on top of a special copper mold designed for use in capturing the thermal history of solidifying samples. The body of this copper mold, schematically diagramed in Figure 5.8, has two channels running through it; one channel is for the thermocouple and the other is an argon backfilling line. A short pulse from a GTAW torch (115A for 1 sec) is used to melt the sample; the sample conforms to the copper mold and contacts the thermocouple.

The thermal histories of the samples were digitally recorded at 1000Hz using an Instrunet Model 100 digital input/output system coupled with iNet32.dII v2.0.4.0 software. The thermocouples used in the button-melting experiments were C-type
thermocouples (W-5%Re/W-26%Re), selected primarily for their high useable temperature range and sensitivity.

Figure 5.8: an illustration of the set-up used to acquire the thermal histories of the Ni-Cr-Mo alloys during solidification. (A) the sample is melted by an arc from a GTAW torch, (B) the molten sample conforms to the mold, making contact with the thermocouple, and (C) the thermal history of the sample is digitally recorded during the solidification event.

The thermal histories of each sample were analyzed after collection. The transition temperatures during solidification, being the liquidus and solidus temperatures, were determined using a technique known as single-sensor differential thermal analysis (SS-DTA). This technique uses a mathematically generated reference curve, which simulates a sample that does not undergo a phase change, to compare against the actual cooling curve of the experimental sample. The point at which the actual cooling curve begins to deviate from the reference curve is determined to be the transition temperature. To determine the liquidus temperature of the alloy, the reference curve is fit to the experimental cooling curve just above the liquidus temperature. Likewise, to determine
the solidus temperature, the reference curve is fit to the experimental cooling curve just below the solidus temperature. This process is illustrated in Figure 5.9.

![Figure 5.9: (A) The experimental (blue) cooling curve and mathematically generated reference curve (red) used to determine the liquidus temperature of an alloy, and (B) similar determination of the solidus temperature of an alloy](image)

The volume factions of secondary phases of the various alloys were determined through metallographic techniques. The samples were metallographically prepared to a finish of 0.05 μm, and examined in the Quanta SEM in the unetched condition. As a result of the high molybdenum and tungsten content of the secondary phases, these phases were clearly visible in the backscattered electron imaging mode. Using image analysis software, thirty electron micrographs (taken at 2000X) of each composition were analyzed to determine the volume fraction of secondary phases.

It is noted that this technique reveals only the total volume fraction of secondary phases; it does not provide a distinction between these phases. This investigation did not attempt to identify, or determine the relative volume fractions of secondary phases within the alloys; previous research has been conducted to resolve these issues [17]. Table 5.7 illustrates the closeness in composition of the secondary phases; standard chemical
analysis (*i.e.* EDS) is incapable of accurately distinguishing between \( \mu \), \( \sigma \), and P phase in the metal. Diffractive techniques are necessary to positively identify these secondary phases.

5.8. Metallographic Preparation

Samples to be examined using Light-Optical Microscopy (LOM), and samples that were to be electropolished were mounted in Buehler Epomet molding compound. Samples that were to be examined using SEM were mounted in Buehler Probemet conductive molding compound. Buehler recommended temperatures, pressures, and times were used to mount all specimens.

All metallographic samples were ground from 180-grit to 800-grit using progressively finer grits of SiC paper; intermediate grinding steps included 240, 320, 400, 600, and 800C grits. Samples were next vibratory polished in a neutralized Buehler Mastermet® 2 colloidal silica polishing suspension for approximately three hours. Care was taken such that samples to be etched were not dried and exposed to air after the final polish, as recommended by the manufacturer [48].

Two etching methods were used to reveal the structure of the metal. A light etching of the structure was accomplished using a ten-percent chromic acid solution at an applied voltage of 2.5V for approximately thirty seconds. This light etch proved excellent in delineating the secondary phases from the matrix during SEM observation, as well as preferentially staining intradendritic regions, which was useful in both LOM and SEM examinations.

A heavier etch was accomplished using a 95 mL HCl + 5 g oxalic-acid solution at an applied voltage 6V for two to five seconds. This heavier etch proved excellent in causing relief of interdendritic regions, revealing the general structure of weld-metal samples. Additionally, this heavy etch appeared to lightly reveal high-angle boundaries when examining at high magnifications.

Samples that were to be electropolished required an additional step before mounting. A thermocouple wire was percussion welded to the face of the sample opposite the
desired face of examination. This wire provided a conductive path, through the non-conductive bakelite, for the negative electrode of the electropolishing procedure. After mounting, the back side of the mount was ground on 180-grit SiC paper until the thermocouple wire was exposed.

<table>
<thead>
<tr>
<th>90 mL Distilled Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>730 mL Ethanol (Ethyl Alcohol)</td>
</tr>
<tr>
<td>100 mL Ethylene Glycol Monobutyl Ether</td>
</tr>
<tr>
<td>78 mL Perchloric Acid</td>
</tr>
</tbody>
</table>

Table 5.15: Struers A2 electropolishing solution recipe

Table 5.15 contains the recipe for the electrolyte used in the electropolishing procedure; Struers A2 solution. The A2 solution contains perchloric acid and therefore requires perchloric acid handling procedures during both mixing and use; explosions and adverse reactions are hazards when using this highly oxidizing acid. The parameters used in the electropolishing procedure are listed in Table 5.16.

<table>
<thead>
<tr>
<th>Time</th>
<th>10 sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>20°C (70°F)</td>
</tr>
<tr>
<td>Voltage</td>
<td>22V</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>10</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>Struers A2 Solution</td>
</tr>
</tbody>
</table>

Table 5.16: Electropolishing parameters
CHAPTER 6

RESULTS AND DISCUSSION

The following sections present the results and discussion from the initial testing and compositional variation phases of this investigation.

6.1. Initial Testing

The following sections present the results and discussion from the initial testing phase of this investigation. This phase includes the assessment of solidification cracking susceptibility of Alloy C-22 using the Transvarestraint test, as well as the assessment of the ductility-dip cracking susceptibility of the alloy using both the strain-to-fracture test and the hot-ductility test.

6.1.1. Solidification Cracking

Figure 6.1 displays the results from the Transvarestraint testing of Alloy C-22. The blue line represents heat 2277-3-3114 and the red line represents heat 2277-3-3119. One can see that strain saturates at approximately two-percent augmented strain; that is, further increases in augmented strain does not lead to an increased cracking response.
Figure 6.1: Alloy C-22 Transvarestraint testing results

As mentioned previously, MCD is of particular interest because it is proportional to the temperature range over which solidification cracking occurs. The relationship between MCD and the solidification cracking temperature range (SCTR) is given in Equation 6.1; maximum cracking distance past the point of saturated strain is multiplied by the cooling rate of the weld (as measured through thermocouple plunges), all divided by the travel speed of the GTAW torch during the Transvarestraint test.
The calculated solidification cracking temperature ranges of the two heats of Alloy C-22 are presented in Table 6.1. An SCTR of approximately 50°C (90°F) demonstrates excellent resistance to solidification cracking; this SCTR ranks Alloy C-22 only slightly behind highly crack resistant alloys duplex SS 2205, austenitic SS 304 (FN6), and duplex SS 2507 in cracking susceptibility [52].

Examine Figure 6.1, it is interesting to note that heat 2277-3-3119 has a higher cracking response than heat 2277-3-3114 throughout the entire range of augmented strain. However, the error bars in Figure 6.1 and the standard deviations listed in Table 6.1 indicate that this effect lies on what might be considered the border of statistical significance. That is, the standard deviation of one series often extends to the median of the other series, but rarely extends past the median. This is especially true when considering only the lower levels of augmented strain (below five-percent), which are more representative of real weldments.

<table>
<thead>
<tr>
<th>Heat Number</th>
<th>SCTR (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2277-3-3114</td>
<td>45.8 (±6.2)</td>
</tr>
<tr>
<td>2277-3-3119</td>
<td>55.6 (±9.9)</td>
</tr>
</tbody>
</table>

Table 6.1: Calculated SCTR of the two commercial heats of Alloy C-22
Examining Table 5.1, one detects both heats to be extremely close in composition. Accordingly, Scheil simulations predict both heats to have virtually identical solidification temperature ranges. It is however noted that the Scheil simulations do not account for sulfur or phosphorus, and heat 2277-3-3119 has approximately nine-percent more (S + P) than heat 2277-3-3114. Perhaps this minor compositional difference, albeit between elements that are well known to aggravate hot cracking, explains the difference in the cracking response of the two heats. Lastly, the reader is cautioned that this discussion point is not intended to suggest that heat 2277-3-3119 is high in sulfur and phosphorus; both heats have extremely low levels of these two impurity elements.

Standard metallographic techniques found cracking to occur primarily along solidification grain boundaries (SGB), and to a lesser extent along solidification sub-grain boundaries (SSGB). Visual examples of cracking occurring along a SGB and a SSGB are displayed in Figure 6.2. It is noted that these solidification grain boundaries and solidification sub-grain boundaries were identified using only the misorientation of the dendritic structure; orientation imaging was not employed for this purpose.

![Figure 6.2](image_url)

Figure 6.2: (A) solidification cracking along a SGB, and (B) solidification cracking occurring along a SSGB
During the characterization phase, three distinct regions were noted within the fracture surfaces of the Transvarestraint solidification cracks; these regions are indicated in Figure 6.3. The following sections utilize fractography, compositional analysis, and standard metallographic preparations to develop a deeper understanding of the behavior of Alloy C-22 during the Transvarestraint test.

Figure 6.3: Plan view of a solidification crack in a Transvarestraint sample from heat 2277-3-3114 (five-percent augmented strain). Three distinct regions were noted within the solidification cracks of the Transvarestraint samples. Region-A: Typical/bulk cracking morphology; Region-B: Backfilled face; and Region-C: Backfilled region, through which a crack has propagated.
Figure 6.4 is used to illustrate the difference between Region-A and Region-B of the fracture surface of Alloy C-22 solidification cracks from the Transvarestraint test. Figure 6.4A shows a lower magnification electron-micrograph of an area of the fracture surface transitioning from the typical Region-A morphology to the Region-B morphology of the backfilled face. The columnar dendritic structure along which cracking occurs is easily observed within this electron-micrograph. In Figure 6.4B a closer view of the Region-B fracture surface is displayed. As compared to Region-A (Figure 6.4C), it is evident that more liquid is present in this area as solidification occurs.

Figure 6.4C displays the typical or bulk fracture surface observed within all solidification cracks; this morphology covers approximately three-quarters of the fracture surface. It is somewhat surprising how sharp the features of the fracture surface are for a solidification crack; this indicates that very little liquid is present on the boundaries along which cracking occurs. This observation is in agreement with the excellent cracking resistance of the alloy, as noted by the experimentally determined SCTR values (Table 6.1).
Figure 6.4: (A) Fractograph showing a portion of the solidification crack transitioning from Region-A to Region-B, (B) a closer view of Region-B, and (C) a closer view of Region-A
Figure 6.5 displays the Region-C fracture surface morphology observed in solidification cracks that have cracks propagating through an area that has backfilled. This fracture surface has the classic ‘egg-crate’ appearance that is most often associated with solidification cracking. The reason that cracks are seen to propagate through areas that are backfilled is that straining does not occur instantaneously during varestraint testing, but rather over a finite period of time. Accordingly, higher levels of augmented strain require longer stroke distances and longer stroking times. Robino et al. [53] used high-speed cinematography to demonstrate that cracking has a ‘dynamic’ component; that is, a certain portion of the total crack length is opened as the stroke is being applied.

It appears that during the transvarestraint test, specifically at higher levels of augmented strain, capillary action draws molten metal backwards into the leading (hot) edge of opening cracks. This molten metal begins to solidify as the torch moves further away from the backfilled region. If the partially molten metal in the backfilled region is within the correct temperature/coherency range as the stroke is still being applied, then cracking will occur in the backfilled region. This phenomenon explains a subtle trend observed in Figure 6.1, which shows a gentle increase in MCD (especially for heat 2277-3-3119) past the point of saturated strain. Understanding that cracking in the backfilled region was included in the MCD measurements explains this trend.
Energy dispersive spectrometry of the fracture faces revealed Regions B and C to be significantly enriched in molybdenum, whereas Region-A had virtually the same composition as the base-metal. Additionally, secondary and backscattered electron imaging of lightly etched plan-views of the cracks revealed the backfilled regions to be significantly enriched in secondary phases as compared to the matrix (see Figure 6.6). Chemical analysis and standard metallographic techniques demonstrate that the liquid that is drawn backwards into these cracks is enriched in solute.
Figure 6.6: Secondary and backscattered electron imaging of a backfilled region displaying an obvious increase in the amount secondary phases as compared to that of the matrix.

The reader is cautioned that the preceding characterization of ‘backfilled’ regions is not intended to suggest that backfilling, or eutectic healing, plays a role in the excellent resistance of Alloy C-22 to solidification cracking. This characterization is merely an account of experimental observations. Additionally, it is unlikely that a real weldment will ever experience the high levels of augmented strain (five- to seven-percent) experienced by the samples that typically displayed cracks propagating through backfilled regions. Therefore, it is debatable how representative this phenomenon is with regards to practical applications.

Summary:

1. Strain saturation (that is, the level past which further increases in augmented strain did not cause further increases in maximum crack distance) occurred at two-percent augmented strain.

2. Alloy C-22 was found to have a solidification cracking temperature range of approximately 50°C (90°F); this indicates that the alloy is resistant to
solidification cracking. The susceptibility of Alloy C-22 to solidification cracking is only slightly higher than very crack resistant alloys such as DSS2205, SS304(FN6), and DSS2507.

3. Heat 2277-3-3119 was observed to have a higher cracking response than heat 2277-3-3114 throughout the entire range of augmented strain. This difference in cracking response is believed to in part be due to the difference in the (S + P) levels of the two heats. However, the statistical significance of this conclusion is debatable.

4. Cracking occurred primarily along solidification grain boundaries, although cracking was sometimes observed to have occurred along solidification subgrain boundaries.

6.1.2. Ductility-Dip Cracking

The following sections present the results and discussion regarding the elevated temperature ductility of the Alloy C-22 weld-metal. The alloy was assessed using two separate testing methods: (1) the strain-to-fracture test, and (2) the hot-ductility test.

6.1.2.1. Strain-to-Fracture Test

Figure 6.7 displays the results of the strain-to-fracture test for Alloy C-22. Each circle represents an individual STF sample; the adjacent bracketed numbers are the number of cracks experienced by the corresponding sample. The dotted line represents the threshold level of strain to cause cracking. It is observed that Alloy C-22 has both a low cracking threshold, a wide temperature range over which cracking occurs, and no recovery of cracking resistance at the upper end of this susceptible temperature range.
Figure 6.7: Alloy C-22 strain-to-fracture test results; red dotted line represents the cracking threshold.

In Figure 6.8, the susceptibility of Alloy C-22 to ductility-dip cracking is compared to two other ductility-dip susceptible alloys that have been previously tested in the strain-to-fracture test: Filler-Metal 52 and Filler-Metal 82. The susceptibility of these three alloys is compared at 950°C (1742°F). This temperature is used for baseline comparisons as it often corresponds to the minimum of the ductility trough for susceptible alloys. In the strain-to-fracture test, Alloy C-22 is observed to have a ductility-dip cracking susceptibility on the same order as that of FM-52.
Figure 6.8: Baseline comparison between the ductility-dip cracking susceptibility of Alloy C-22, FM52, and FM82. Data provided courtesy of N.E. Nissley [45]

Normally, alloys that are susceptible to ductility-dip cracking have three distinct regions on the strain-versus-temperature plot: (1) a low temperature region associated with good resistance to cracking, (2) an intermediate temperature range susceptible to ductility-dip cracking, and (3) a high temperature range where the resistance to cracking is restored due to the onset of recrystallization.

However, Alloy C-22 does not recover its cracking resistance at the upper end of the cracking susceptible temperature range; instead, the intermediate ductility-dip temperature range of Alloy C-22 extends completely to the solidus temperature in the strain-to-fracture test. As a result, the characterization of the Alloy C-22 strain-to-fracture samples was subdivided into only two temperature regimes: (1) low temperature, high cracking resistance, and (2) high temperature, low cracking resistance.
It is noted that only one heat of Alloy C-22 (heat 2277-3-3114) was used within this investigation. Earlier unpublished research demonstrated that the minor compositional differences between heats 2277-3-3114 and 2277-3-3119 were insufficient to cause observable differences in cracking response during the strain-to-fracture test.

Optical, electron, and orientation imaging of ductility-dip cracks all found cracking to occur along high angle boundaries. Figure 6.9 displays two orientation images of ductility-dip cracks occurring along high-angle boundaries in strain-to-fracture specimens; Figure 6.9A is from a sample subjected to 17-percent strain at 800°C (1472°F) and Figure 6.9B is from a sample subjected to 3.6-percent strain at 1200°C (2192°F). Metallographic examinations also determined that cracking was not associated with secondary phases, i.e. secondary phases did not initiate cracking.

Figure 6.9: Orientation imaging of strain-to-fracture samples; cracking is observed to occur along high-angle boundaries in both images. (A) STF sample subjected to 17-percent strain at 800°C (1472°F), and (B) STF sample subjected to 3.6-percent strain at 1200°C (2192°F)
Closer examination of Figure 6.9B reveals an important piece of information about the behavior of Alloy C-22 during the strain-to-fracture test. The boundaries along which cracking has occurred are free of recrystallization; in fact, all boundaries are free of recrystallization. As mentioned previously, most alloys in the strain-to-fracture test have a recovery of the cracking resistance at the high end of the testing temperature range due to the onset of recrystallization. In these alloys, the weld-metal boundaries are covered in small recrystallized grains; this is not the case with Alloy C-22. This is in large part responsible for the fact that Alloy C-22 does not see a recovery of cracking resistance at the high end of the testing temperature range. This phenomenon will be discussed in much greater detail in subsequent sections that compare the results of the strain-to-fracture test to those of the hot-ductility test.

This absence of the recovery of cracking resistance also helps to explain another experimental observation. At high levels of augmented strain in the transvarestraint test, very narrow, long, and straight cracks were often observed to propagate from the trailing edge of solidification cracks. Fractography revealed these cracks to be solid-state cracks; that is, they are ductility-dip cracks.

The absence of the recovery of cracking resistance at high temperatures led to the propagation of ductility-dip cracks from solidification cracks in the transvarestraint test. As discussed previously, the higher levels of augmented strain in the transvarestraint test are likely not representative of actual weldments. Therefore, it is not suggested that ductility-dip cracks will propagate from solidification cracks in real weldments; rather, this finding is offered as an explanation to experimental observations, and conversely, in support of the strain-to-fracture test findings.

Aside from the absence of a recovery of cracking resistance in Alloy C-22, the most striking feature of Figure 6.7 is the extremely low cracking threshold. This finding is surprising based on the fact that Alloy C-22 is considered to be a very weldable alloy. Additionally, although Alloy C-22 (a fully austenitic alloy with very little secondary phases) would seem to be an excellent candidate for ductility-dip cracking, no instances of ductility-dip cracking were found within the literature search.
The reconciliation between the experimental and industrial findings (or lack thereof) involves two factors. The first part of the explanation involves the behavior of the alloy during the thermal cycle of the strain-to-fracture test; the second part of the explanation involves the method of crack counting employed within this investigation.

Re-examining Figure 6.9A and Figure 6.9B, attention is directed towards the grain-boundary morphology of the two specimens. The specimen that was tested at 800°C (1472°F) has a much more tortuous grain-boundary morphology than the specimen tested at 1200°C (2192°F). What is proposed is a migration of the grain boundaries during the thermal portion of the strain-to-fracture test. This grain boundary migration reduces the tortuosity of the boundaries and creates a microstructure that is more susceptible to ductility-dip cracking.

Each strain-to-fracture sample experiences a complex thermal cycle, which is illustrated in Figure 6.10. During the production of the spot weld, the copper fixture rapidly cools the sample after solidification. In this portion of the thermal cycle, the weld-metal spends very little time in the temperature regime where grain boundary migration would be expected; the result is a tortuous grain boundary morphology. It appears as if the secondary phases that form during solidification are effective in pinning the grain boundaries during this portion of the total thermal cycle.
Figure 6.10: Schematic of the total thermal history of a strain-to-fracture sample

During the strain-to-fracture test the sample spends a ten-second period in a thermal hold in order to allow the gauge section of the sample to come to a thermal equilibrium. It appears as if the secondary phases in Alloy C-22 weld metal are ineffective at pinning the grain boundaries during this time period, and boundary migration occurs; this phenomenon is illustrated in Figure 6.11. The secondary phases are not dissolved during this period; rather, whatever mechanism(s) allowed the secondary phases to pin the boundaries during spot-weld production are defeated during the thermal hold. Additionally, it is well known that boundary mobility obeys an Arrhenius relationship. Therefore, setting aside the recrystallization behavior of the alloy, it is not surprising to see the problem of cracking resistance exasperated in an exponential fashion with increasing temperature.
This postulate is also supported by fractography conducted on strain-to-fracture specimens. In a two-dimensional plane, boundary migration appears to be a straightening of the boundaries. However, in three-dimensions, boundary migration would appear in the form of a flattening of the surface. Figure 6.12 displays the fracture surfaces of one strain-to-fracture sample tested at 800°C (1472°F) and one tested at 1200°C (2192°F). Both images clearly show the dendritic structure of the fracture surface; however, the 1200°C (2192°F) sample is clearly much flatter in profile than the 800°C (1472°F) sample.
FIGURE 6.12: (A) The fracture surface of a strain-to-fracture sample tested at 800°C (1472°F), and (B) the fracture surface of a strain-to-fracture sample tested at 1200°C (2192°F)

This boundary migration phenomenon in the strain-to-fracture test could explain the discrepancy between the cracking susceptibility of Alloy C-22 observed in this laboratory test and the fact that ductility-dip cracking is not a reported problem with the alloy in industry. The manufacturer of Alloy C-22 recommends three processes for welding the alloy: GTAW, GMAW, and SMAW [54]. It is unlikely when using these processes that the weld-metal HAZ of a weldment would spend enough time in the temperature regime where boundary migration occurs such that the grain boundary morphology would lose its tortuosity.

A simple example is presented to illustrate this point. Haynes International provides recommended welding parameters for Alloy C-22 with the SMAW, GTAW, and GMAW processes [4]. Table 6.2 lists two sets of welding parameters for SMAW; the first set of parameters corresponds to the highest recommended heat-input, and the second set of parameters corresponds to a nominal heat-input. These parameters were used along with Rosenthal’s thick plate solution in order to calculate the amount of time necessary to cool
from the solidus temperature of the alloy, 1250°C (2282°F), completely through the ductility-dip temperature range, to 800°C (1472°F).

For the parameters corresponding to the highest recommended heat-input, the Rosenthal equation predicts that it would take 5.8-seconds to cool through the entire ductility-dip temperature range; for the parameters corresponding to the nominal heat-input, it would only take 2.5-seconds. In both of these cases, the weld-metal heat-affected-zones would spend significantly less time in the temperature range where boundary migration occurs than the gauge of a strain-to-fracture sample tested in the upper end of the testing temperature range.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Heat Input</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Highest Recommended</td>
</tr>
<tr>
<td>Current</td>
<td>180 A</td>
</tr>
<tr>
<td>Voltage</td>
<td>26 V</td>
</tr>
<tr>
<td>Travel Speed</td>
<td>4.23 mm/s (10 ipm)</td>
</tr>
<tr>
<td>Arc Efficiency</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 6.2: Manufacturer recommended SMAW parameters for Alloy C-22 corresponding to high heat-input and nominal heat-input situations

In fact, the manufacturer discourages the use of high heat-input processes such as SAW to weld the alloy [54]. The use of high heat-input processes is discouraged based on corrosion considerations; higher heat input allow the heat-affected-zone to spend more time at elevated temperatures, increasing the likelihood of secondary phase formation. But the fact that these processes are discouraged from use by the manufacturer may in part explain why ductility-dip cracking has not been seen in industrial applications.

Classically, when discussing boundary tortuosity with respect to ductility-dip cracking resistance, one assumes a level of tortuosity for a given composition. For
example, the compositional differences between FM-82 and FM-52 lead to FM-82 having a higher level of boundary tortuosity than FM-52. Furthermore, these levels of tortuosity (initially created during the solidification process) are assumed to remain constant during strain-to-fracture testing, and lead to the explained differences in the cracking response of the two alloys. The ‘meta-tortuosity’ experienced by Alloy C-22, where a portion of the boundary tortuosity is lost during the thermal portion of the strain-to-fracture test, appears to be either unique to this alloy or unreported in other alloys to date.

Unfortunately, this boundary migration versus heat input argument does not completely explain the low cracking threshold of the alloy. Alloy C-22 has a relatively low cracking threshold at 950°C (1742°F), a temperature where the ten-second holding period is likely insufficient to cause significant boundary migration.

Another possible reason for the poor reported cracking threshold values is the manner in which cracks were counted. This investigation is the first time that samples were ground flat and polished in order to assess cracking. It has always been understood that crack counting is a subjective process. During the course of this investigation it was noted that two investigators examining the same sample could report significantly different cracking numbers. Grinding samples flat and polishing them prior to crack counting eliminates much of this variability. However, cracks that may have previously gone unnoticed, cracks that may have previously been categorized as ‘grain boundary sliding’, or cracks that exist at some depth into the sample, are now included in the crack count. This could in part lead to a lower reported cracking threshold. On the other hand, it must also be mentioned that shallow surface cracks may be ground away during the process and therefore not included in the final count.

Additionally, all cracking on the sample surface was counted. Previous researchers have neglected cracks at the center of the sample, unsure of whether or not they were crater cracks that had opened during testing, as opposed to actual ductility-dip cracks. Unfortunately, with the samples in this investigation cracking was often found to initiate in the center of the sample and spread outwards with increasing levels of strain.
If center cracks are not to be counted, how far from the center must a crack be in order for it to be counted? Additionally, how is this distance kept constant from sample to sample? To eliminate this variability, the decision was made to count all cracks on the sample surface. The series of samples tested at 800°C (1472°F), displayed in Figure 6.7, provides confidence in this crack counting method. If center cracks really were crater cracks that had opened during testing, then the three samples below the cracking threshold would have had center cracks. This is not the case, and the center cracks at the higher levels of strain at 800°C (1472°F) are determined to be true ductility-dip cracks.

A brief discussion will now be presented on the adverse effects of ductility-dip cracks in weldments. Ductility-dip cracks are detrimental for two reasons: (1) structural integrity considerations, and (2) corrosion considerations, where cracks may become sites of localized corrosion. Suppose that a welding process with a sufficient level of restraint to cause ductility-dip cracking is used, and ductility-dip cracks are noted within the microstructure. How detrimental would such a situation be?

Consider an application such as the Yucca Mountain Project, where the alloy is selected based almost entirely upon corrosion considerations, and where structurally the alloy is not subjected to intense or cyclical loads. In this case, ductility-dip cracking may not be considered a critical discontinuity during the fabrication process. Ductility-dip cracking is a re-heat cracking phenomenon; that is, it occurs in the weld-metal heat-affected-zone of multipass weldments. This is illustrated in Figure 6.13, where one observes that ductility-dip cracking is a subsurface cracking phenomenon; i.e. the outer surfaces of the root and cap passes do not have exposed ductility-dip cracks. Therefore, even though cracking has occurred, the corrosion properties of the alloy remain strong.
Summary:

1. The threshold strain to cause ductility-dip cracking in the strain-to-fracture test for Alloy C-22 is very low. The threshold strain for cracking at 950°C (1742°F) was roughly two-percent; this is approximately the same threshold strain for cracking demonstrated by Filler-Metal 52, which is known to be susceptible to ductility-dip cracking.

2. Alloy C-22 has a wide temperature range over which ductility-dip cracking occurs in the strain-to-fracture test. Additionally, Alloy C-22 displays no recovery of cracking-resistance at the upper end of the testing temperature range.

3. All cracking was observed to have occurred along high-angle weld metal boundaries

4. Cracking was not associated with the presence of secondary phases, *i.e.* cracking did not initiate or terminate at secondary phases

5. Recrystallization was not noted along boundaries of samples tested in the upper end of the testing temperature range. This absence of recrystallization is in large
part responsible for the lack of recovery of cracking-resistance in this temperature range.

6. Metallurgical evidence suggests that grain boundary migration occurs during the thermal hold portion of the strain-to-fracture test. This phenomenon, which appears to be unique to Alloy C-22 as compared to previously tested alloys, creates less tortuous boundaries, a more susceptible microstructure, and a higher cracking response during testing. Actual Alloy C-22 welds may not experience such a prolonged duration in the temperature range where boundary migration occurs; as a result, the boundaries within actual weldments may remain tortuous and resistant to ductility-dip cracking.

7. A new crack counting method was used within this investigation in order to eliminate much of the subjectivity of the crack counting process. All samples were sectioned and polished to a finish of 1μm before examination. Cracks that may previously have gone unnoticed or misdiagnosed as ‘grain boundary sliding’ were now counted. Additionally, cracks within the center of the sample (traditionally uncounted) were included in the crack counting totals. These new crack counting methods likely contributed in part to the low cracking threshold of the alloy.

6.1.2.2. Hot-Ductility Test

Figure 6.14 displays the results from the hot-ductility testing of Alloy C-22 base-metal. Both the on-heating and on-cooling curves display excellent elevated temperature ductility, with no ductility-dip. The alloy is observed to have a narrow liquation cracking temperature range (LCTR), which indicates a low susceptibility towards HAZ liquation cracking. The LCTR is given by the difference between the nil-strength-temperature (NST) and the ductility-recovery-temperature (DRT), and represents the maximum temperature range over which liquid films will be present in the HAZ.
Figure 6.14: Hot-ductility results for Alloy C-22 base metal

Figure 6.15 displays the results of the weld-metal hot ductility testing. The nil-strength-temperature, nil-ductility-temperature (NDT), and ductility-recovery-temperature are similar to those of the base-metal samples. However, a pronounced difference in the ductility signature of the weld-metal is seen as compared to the base-metal. The ductility of the weld-metal is lower than that of the base-metal throughout the entire range of test temperatures. More importantly, there are obvious ductility-dips in both the on-heating and on-cooling ductility curves.
A comparison between Figure 6.14 and Figure 6.15 provides an excellent example of how welding processes are able to greatly affect the mechanical properties of an alloy. Significant differences in the microstructures of the base-metal and weld-metal hot-ductility samples likely account for the differences in elevated temperature ductility. The weld-metal samples have large columnar grains that have resulted from epitaxial nucleation and competitive growth during solidification. The base-metal samples have small equiaxed grains resulting from the thermal-mechanical processing steps involved in the production of Alloy C-22 plate. The smaller equiaxed grains of the base-metal have a correspondingly higher total grain boundary area; as a result, each individual grain boundary must accommodate less strain during the hot-ductility test as compared to the boundaries of the weld-metal samples. This is the proposed reason that the base-metal
samples outperform the weld-metal samples in the hot-ductility test. Table 6.3 summarizes the findings from the hot-ductility tests.

<table>
<thead>
<tr>
<th></th>
<th>Base-Metal</th>
<th>Weld-Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDT</td>
<td>1250°C (2282°F)</td>
<td>1240°C (2264°F)</td>
</tr>
<tr>
<td>NST</td>
<td>1298°C (2368°F)</td>
<td>1289°C (2352°F)</td>
</tr>
<tr>
<td>DRT</td>
<td>1250°C (2282°F)</td>
<td>1240°C (2264°F)</td>
</tr>
<tr>
<td>LCTR</td>
<td>48°C (86°F)</td>
<td>49°C (88°F)</td>
</tr>
</tbody>
</table>

Table 6.3: Hot-ductility testing results

It is unclear why the base-metal does not experience a ductility-dip. However, an attempt was not made to resolve this discrepancy; rather, focus was placed on explaining the differences between the weld-metal in the hot-ductility and strain-to-fracture tests. Accordingly, only the weld-metal hot-ductility samples were characterized in this investigation.

Because of the difficulties associated with etching Alloy C-22 (namely, etching of high-angle boundaries), it is difficult to tell how cracks have propagated along the failure surface of the broken samples. However, all samples characterized had internal cracks. All internal cracks were noted to have occurred along high-angle boundaries. Figure 6.16 displays a micrograph of a crack propagating along a high-angle boundary in a weld-metal sample. As with the strain-to-fracture test, cracking did not appear to be associated with secondary phases; i.e. cracks did not initiate at secondary phases.
Summary:

1. In both the on-heating and on-cooling conditions, the base-metal samples demonstrated excellent ductility without intermediate temperature ductility-dips.

2. In both the on-heating and on-cooling conditions, the weld-metal samples demonstrated lower ductility through the entire testing temperature range as compared to the base-metal samples. The weld-metal on-heating and on-cooling ductility signatures had pronounced intermediate temperature ductility-dips. The ductility minimum of the on-heating signature occurred at 900°C (1652°F), while
the ductility minimum of the on-cooling signature occurred at 1000°C (1832°F). Recovery of ductility occurred at the upper end of the testing temperature range in both the on-heating and on-cooling conditions.

3. The base-metal and weld-metal samples had liquation cracking temperature ranges (NST – DRT) of approximately 50°C (90°F). This is a narrow value that indicates that the alloy is not susceptible to heat-affected-zone liquation cracking.

4. Differences in the microstructures of the base-metal and weld-metal samples account for the respective differences of the ductility signatures. The small equiaxed grains of the base-metal are better able to distribute and accommodate the strain as compared to the elongated columnar grains of the weld-metal samples; as a result, the base-metal demonstrates markedly better performance in the hot-ductility test.

5. All internal cracks, at some distance from the fracture face, in the weld-metal samples were found to have occurred along high-angle boundaries.

6. Cracking was not associated with the presence of secondary phases, *i.e.* cracking did not initiate or terminate at secondary phases.

6.1.2.3. Strain-to-Fracture vs. Weld-Metal Hot-Ductility Comparison

In comparing the results from the strain-to-fracture and weld-metal hot-ductility tests, it is necessary to make distinction between the phenomena of cracking resistance and ductility. It is noted that care has been taken within this investigation to use the terminology ‘cracking resistance’ when referring to the results from the strain-to-fracture test, as opposed to ductility. Although these two quantities are certainly linked, where alloys resisting the initiation of cracks are often very ductile, they are in fact separate phenomena.

This is especially evident in the results of the strain-to-fracture test and weld-metal hot-ductility test at the higher end of the testing temperature range. At 1200°C (2192°F)
the alloy is very poor at resisting the initiation of cracks (strain-to-fracture test), yet relatively ductile having transitioned out of the intermediate temperatureductility-dip temperature range (hot-ductility test). It is proposed that the weakest links of the microstructure (long, straight migrated-grain-boundaries oriented favorably to the tensile axis) easily separate to form cracks. However, the bulk of the microstructure remains ductile and resistant to the propagation of cracks, resulting in a good overall ductility at high levels of strain.

This discrepancy in the testing of Alloy C-22 is an excellent example of how the hot-ductility test is inadequate at explaining the ductility-dip behavior of an alloy in real welding situations. The hot-ductility test provides information on the failure condition of the metal, and is likely more appropriate to describe certain hot working processes. The strain-to-fracture test provides information on the initiation of cracks in a material. This is more appropriate for welding, where the initiation of cracks is important from structural integrity and/or corrosion perspectives.

The most striking difference between the results from the strain-to-fracture test (Figure 6.7) and the hot-ductility test (Figure 6.15) is the high temperature behavior of the alloy. In the hot-ductility test there is a recovery of ductility at the upper end of the testing temperature range; whereas, there is no recovery of cracking resistance in this temperature range in the strain-to-fracture test. This phenomenon is in large part explained by the recrystallization behavior of the alloy.

Figure 6.17 displays orientation images of an internal crack from a weld-metal hot-ductility specimen tested at 1100°C (2012 °F) in the on-heating condition. The boundaries of this sample are decorated with a vigorous amount of recrystallization. The recrystallized grains are heavily twinned equiaxed grains with an average diameter of approximately 5-μm (Figure 6.17B).
Figure 6.17: (A) Orientation imaging of an internal crack in a weld-metal hot-ductility specimen tested at 1100°C (2012°F) in the on-heating condition, and (B) a zoomed in view of the region within the white-box in ‘A’. Noted is the vigorous recrystallization along the boundaries.

This microstructure is compared to that of the 1200°C (2192°F) strain-to-fracture sample (Figure 6.9B), where the boundaries are completely absent of recrystallization. In the hot-ductility test, recrystallization has worked to dynamically annihilate internal strain, allowing for higher levels of deformation before the eventual failure. This condition produces the recovery of ductility at the high end of the testing temperature range.

This is not the case during the strain-to-fracture test. As a result, one of three possibilities explains this behavior of Alloy C-22 in the strain-to-fracture test:

1. Cracking occurs easily at the high end of the testing temperature range because the alloy is sluggish to recrystallize
2. The alloy does not recrystallize because the boundaries are so weak that cracking occurs before enough strain accumulates in the microstructure to cause recrystallization
3. A combination of both of these factors

It is difficult to quantify the boundary cohesiveness of one metal versus another. However, an examination of the recrystallization behavior of Alloy C-22 is possible. Reed-Hill [55] states that “Dynamic recovery occurs most strongly in metals of high stacking-fault energies and is not readily observed in metals of very low stacking-fault energies”, and that “Alloying normally reduces the stacking-fault energy of a metal.”

A stacking fault can be considered an extended dislocation, see Figure 6.18. The length of the stacking fault is a balance between the energy associated with the surface area of the fault and the repulsion of partial dislocations that bind the fault on each end. Metals with low stacking fault energies have physically wider stacking faults; the wider the stacking fault, the larger the impediment to the mobility of dislocations through the matrix. Because recovery and recrystallization are associated with dislocation movement, it is easy to see how a material with low stacking fault energy will have retarded recrystallization as compared to a material with high stacking fault energy.

Figure 6.18: Stacking fault schematic; the dotted box represents the surface energy associated with the stacking fault, and the arrows represent the repulsive forces between the partial dislocations that bind the fault on each end
Both stacking-fault-energy and alloying content, are examined for Alloy C-22 and compared to other materials previously tested in the strain-to-fracture test [56]. Table 6.4 displays the compositions of the alloys used in this comparison.

<table>
<thead>
<tr>
<th></th>
<th>Austenitic Stainless Steels</th>
<th>Nickel-Base Alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>304SS</td>
<td>310SS</td>
</tr>
<tr>
<td>C</td>
<td>0.062</td>
<td>0.083</td>
</tr>
<tr>
<td>Fe</td>
<td>70.69</td>
<td>53.82</td>
</tr>
<tr>
<td>Cr</td>
<td>18.5</td>
<td>24.75</td>
</tr>
<tr>
<td>Ni</td>
<td>8.6</td>
<td>18.72</td>
</tr>
<tr>
<td>Mn</td>
<td>1.53</td>
<td>1.42</td>
</tr>
<tr>
<td>Cu</td>
<td>0.32</td>
<td>0.23</td>
</tr>
<tr>
<td>Si</td>
<td>0.42</td>
<td>0.46</td>
</tr>
<tr>
<td>Al</td>
<td>0.062</td>
<td>0.29</td>
</tr>
<tr>
<td>V</td>
<td>0.014</td>
<td>0.054</td>
</tr>
<tr>
<td>Mg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td></td>
<td>0.17</td>
</tr>
<tr>
<td>Mo</td>
<td>0.12</td>
<td>0.27</td>
</tr>
<tr>
<td>Nb</td>
<td>0.041</td>
<td>0.23</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0.041</td>
<td>0.23</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>0.034</td>
<td>0.024</td>
</tr>
<tr>
<td>S</td>
<td>0.008</td>
<td>0.004</td>
</tr>
<tr>
<td>W</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.4: Compositions of the austenitic stainless steels and nickel-base alloys used in the stacking-fault-energy comparison [56]

The stacking-fault-energies of the alloys in Table 6.4 were calculated in JMatPro v4.1. The software calculates the stacking-fault-energy by determining the difference between the Gibbs free energy of the FCC and HCP crystal structures of the alloy. Aside from viewing a stacking-fault as an extended dislocation, a stacking-fault may be visualized as, or understood to be, a thin layer of HCP within the FCC matrix; this is demonstrated in Figure 6.19.
Figure 6.19: (A) FCC stacking sequence, (B) FCC stacking sequence with a stacking-fault, and (C) HCP stacking sequence; note the similarity between the stacking-fault region in ‘B’ and the HCP stacking sequence [66]

Table 6.5 displays the stacking-fault-energies of the materials in Table 6.4, at 1200°C (2192°F). It is noted that Alloy C-22 has the lowest predicted stacking-fault-energy of all these materials. This indicates that Alloy C-22 is the most resistant to recrystallization; i.e. Alloy C-22 will require the highest level of strain before recrystallization begins. Accordingly, as indicated in the shaded cells of Table 6.4, Alloy C-22 is the most highly alloyed of the nickel-base alloys cited in this comparison.
### Table 6.5: Stacking-fault-energy comparison, as calculated by JMatPro v4.1

<table>
<thead>
<tr>
<th>Material</th>
<th>Stacking Fault Energy at 1200°C (2192°F) mJ/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>304</td>
<td>268.5</td>
</tr>
<tr>
<td>310</td>
<td>243.9</td>
</tr>
<tr>
<td>AL-6XN</td>
<td>209.7</td>
</tr>
<tr>
<td>Alloy 690</td>
<td>212.6</td>
</tr>
<tr>
<td><strong>Alloy C-22</strong></td>
<td><strong>174.3</strong></td>
</tr>
<tr>
<td>FM52</td>
<td>192.7</td>
</tr>
<tr>
<td>FM82</td>
<td>329.1</td>
</tr>
</tbody>
</table>

**Summary:**

1. Alloy C-22 behaves very differently in the hot-ductility and strain-to-fracture tests. This difference in behavior provides an excellent example why the strain-to-fracture test, which provides information specifically on crack initiation, is more applicable to cracking in real weldments than the simpler hot-ductility test.

2. A recovery of ductility is noted in the hot-ductility test, whereas no recovery of cracking resistance was noted within the strain-to-fracture test. The recrystallization behavior of the alloy explains this discrepancy. Orientation imaging revealed considerable recrystallization along boundaries in hot-ductility specimens tested at the upper end of the testing temperature range; these samples were subjected to greater than forty-percent strain. Recrystallization was completely absent from the strain-to-fracture samples tested within this temperature range; these samples were subjected to less than ten-percent strain.

3. The ‘sluggishness’ of the recrystallization of Alloy C-22 was quantified through stacking-fault-energy analysis of a total of seven Ni-base alloys previously
examined in the strain-to-fracture test. Alloy C-22 was found to have the lowest stacking-fault-energy, and therefore the highest resistance to recrystallization, of the alloys analyzed.

6.2. Compositional Variation

The following sections present the results from the compositional variation phase of this investigation. This phase had two stages: thermodynamic simulations and button-melting experiments.

6.2.1. Thermodynamic Simulations

The following sections present the results of the thermodynamic simulations conducted in this investigation. These sections include simulations performed on the nominal Alloy C-22 composition, simulations performed on alloys of varied compositions within the Alloy C-22 compositional range, and experimental finding that support the methodology of compositional variation.

6.2.1.1. Nominal Alloy C-22

Figure 6.20 displays the results of the Scheil simulation for a C-22 alloy of nominal composition. Table 6.6 displays the start temperatures and volume fraction of phases present at the end of solidification. It is noted that although P-Phase does not form in the composition used for this simulation, it does form as a solidification constituent in other compositions within the Alloy C-22 range.
Figure 6.20: Scheil simulation for an alloy of nominal Alloy C-22 composition

It is noted that this simulation, which used the Scheil model, predicts a slightly different solidification sequence than the Mehrabian-Flemings model used by Perricone et al. [18] to describe the solidification of Hastelloy alloys. This is not surprising considering that the Scheil model describes microsegregation, whereas the Mehrabian-Flemings model describes macrosegregation. It is however noted that both models, utilizing thermodynamic algorithms to examine complex multi-component systems, predict P-Phase as a solidification constituent in certain compositions of Alloy C-22. This differs from Cieslak et al. [17], who originally proposed that P-Phase in Alloy C-22 weld metal resulted from a solid-state transformation.
Table 6.6: Tabulated results from the Scheil simulation of a C-22 alloy of nominal composition

<table>
<thead>
<tr>
<th></th>
<th>Start Temperature</th>
<th>Fraction Present at T_s</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_L$</td>
<td>1374°C (2505°F)</td>
<td>N/A</td>
</tr>
<tr>
<td>$M_2O_3$</td>
<td>&gt;1450°C (&gt;2642°F)</td>
<td>0.02%</td>
</tr>
<tr>
<td>Sigma</td>
<td>1304°C (2379°F)</td>
<td>2.16%</td>
</tr>
<tr>
<td>P-Phase</td>
<td>N/A</td>
<td>0.00%</td>
</tr>
<tr>
<td>$M_6C$</td>
<td>1282°C (2340°F)</td>
<td>0.01%</td>
</tr>
<tr>
<td>$T_s$</td>
<td>1281°C (2338°F)</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Also examined were the segregation trends of the major elements in an alloy of nominal Alloy C-22 composition, see Figure 6.21. It is observed that the predicted segregation trends match very well with the experimentally determined segregation profiles of an Alloy C-22 weldment. The only element whose predicted trend did not match the experimental trend was tungsten. However, in Figure 6.21B one observes that the microprobe data for tungsten contains a lot of data scatter, and the trend-line drawn for the segregation of tungsten may not be wholly representative of the actual trend.
Figure 6.21: (A) Predicted (Scheil simulations), and (B) experimentally determined (microprobe analysis [17]) elemental partitioning of Alloy C-22 weld-metal. The dendrite core and interdendritic regions are represented via decreasing temperatures in the Scheil simulations, and labeled DC and ID respectively in the microprobe analysis.

Figure 6.22 is an equilibrium fraction-phase vs. temperature diagram for a C-22 alloy of nominal composition. Table 6.7 displays the start and finishing temperatures of the equilibrium phases present in Figure 6.22.
Figure 6.22: Fraction-phase vs. temperature plot for a C-22 alloy of nominal composition

By examining and comparing the results from the Scheil simulations (non-equilibrium) and the fraction-phase vs. temperature (equilibrium) plot, the metastable solidification constituents can be determined. The equilibrium plot (Figure 6.22) indicates that Alloy C-22 is single phase until 1072°C (1962°C), below which temperature P-Phase begins to form. Therefore, sigma-phase and M₆C-carbides are metastable solidification constituents in Alloy C-22; this is also true of P-Phase in compositions of Alloy C-22 that form this phase during solidification.
Table 6.7: Tabulated results for a fraction-phase vs. temperature plot of a C-22 alloy of nominal composition

<table>
<thead>
<tr>
<th>Phase</th>
<th>Start Temperature $^{\circ}C$</th>
<th>End Temperature $^{\circ}C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>$T_L = 1373.94$</td>
<td>$T_S = 1343.43$</td>
</tr>
<tr>
<td>P-Phase</td>
<td>1072.33</td>
<td>N/A</td>
</tr>
<tr>
<td>$M_6C$</td>
<td>1045.57</td>
<td>701.28</td>
</tr>
<tr>
<td>MN</td>
<td>750.65</td>
<td>N/A</td>
</tr>
<tr>
<td>$M_{23}C_6$</td>
<td>703.55</td>
<td>N/A</td>
</tr>
<tr>
<td>MU (ThermoCalc)</td>
<td>682</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Figure 6.23 displays the continuous cooling transformation (CCT) diagram created for an alloy of nominal C-22 composition, using the JMatPro v4.1 software. Cooling from the all gamma phase region at 1250°C, the most rapidly forming phase is the P-phase. The nose of the curve for P-phase coincides with a time of greater than seven hours. This indicates that phases that do not form as a result of partitioning during solidification will certainly not form in the solid-state during the cooling of a weld cycle, nor should they form in the solid-state during subsequent reheating from overlying passes.
Figure 6.23: CCT diagram for a C-22 alloy of nominal composition

The predicted CCT curve in Figure 6.23 correlates well with unpublished experimental observations by the author [58], who found that significant precipitation of secondary phases occurs somewhere between 1hr and 5hrs of aging at 800°C (1472°F), as displayed in Figure 6.24. However, it is noted that Rebak et al. [59] have reported partial grain-boundary precipitation of secondary phases in Alloy C-22 after as little as 1hr at 800°C (1472°F).
Pseudo-binary phase diagrams were created in ThermoCalc using the `define-diagram` function in the Poly (version 3.32) module. These diagrams vary the composition of a single alloying element versus nickel, while holding the rest of the alloying elements at the nominal levels of Alloy C-22. It is noted that oxygen and nitrogen were not included in these calculations because the processing time for the simulations with these two elements included was prohibitive.

The Ni-Mo, Ni-Fe, and Ni-W pseudo-binary phase diagrams are presented in Figure 6.25 through Figure 6.27; other Ni-Xx pseudo-binary phase diagrams (including those for Cr, Co, C, Mn, Si, and V) are located in Appendix B. The thin red vertical line on these diagrams indicates the nominal Alloy C-22 composition. One can see the correspondence between the path traveled along the line of nominal composition, and the fraction-phase vs. temperature plot for the nominal Alloy C-22 composition (Figure 6.22). Traveling downward in temperature from 1400°C to 600°C along these lines, each pseudo-binary phase diagram follows the same path:
L \rightarrow L + \gamma \rightarrow \gamma \rightarrow \gamma + P \rightarrow \gamma + P + M_6C \rightarrow \gamma + P + M_{23}C_6 \rightarrow \gamma + P + M_{23}C_6 + MU

It is also noted that the temperatures at the intersections of the nominal composition lines and the lines separating the phase regions corresponds to the start and finish temperatures of the fraction-phase vs. temperature plot (Figure 6.22). Overall, the pseudo-binary phase diagrams show that varying the composition of Alloy C-22, within the limits that define the alloy as C-22, has little effect on the start temperatures of the equilibrium phases, and zero effect on which phases form.

Figure 6.25: Ni-Mo pseudo-binary phase diagram
Figure 6.26: Ni-Fe pseudo-binary phase diagram
Another interesting set of diagrams that have been created to explain the welding metallurgy of Alloy C-22 are termed “non-equilibrium pseudo-binary solidification diagrams”. To create these diagrams, a number of multi-component Scheil simulations were run at varied levels of Mo, Fe, and W. For instance, five Scheil simulations were run with the nominal Alloy C-22 composition and 11.5, 12.5, 13.5, 14.5, and 15.5 wt% Mo respectively. The results from these simulations were subsequently pieced together to reveal the phase fields of the non-equilibrium solidification range over this range of molybdenum.

This type of diagram is much better at revealing the expected microstructure of weld-metal than a conventional equilibrium pseudo-binary phase diagram. The results of the non-equilibrium pseudo-binary phase diagrams are presented in Figure 6.28 to Figure
6.30. The most interesting information that is derived from these diagrams is the composition ranges over which P-phase forms. In each diagram, P-phase is observed to begin forming during solidification at compositions slightly richer in Mo, Fe, and W than the nominal compositions of the alloy. If P-phase were found to be particularly detrimental to the mechanical or corrosion properties of the alloy, an engineer may specify ordering heats of material which are leaner in Mo, Fe, and W than these ‘critical’ compositions.

Figure 6.28: Ni-Mo non-equilibrium, pseudo-binary, solidification diagram
Figure 6.29: Ni-Fe non-equilibrium, pseudo-binary, solidification diagram
Figure 6.30: Ni-W non-equilibrium, pseudo-binary, solidification diagram

**Summary:**

1. Scheil simulations using the nominal composition of Alloy C-22 predict a solidification temperature range of 93°C (167°F), with slightly more than two volume-percent of secondary phases.

2. The equilibrium phase-fraction vs. temperature plot for the nominal composition of Alloy C-22 reveals $\sigma$-phase and $M_6C$ carbides to be metastable solidification products.

3. The nose of the most rapidly forming secondary phase (P-phase) on the continuous-cooling transformation diagram for the nominal composition of Alloy C-22 occurs at a time of greater than seven hours. This indicates that secondary
phases will not form on-cooling from a weld cycle, or in subsequent reheating from adjacent or overlying weld passes.

4. Non-equilibrium pseudo-binary solidification diagrams indicate that P-phase begins to form as a solidification constituent at levels of molybdenum, tungsten, and iron slightly richer than the nominal Alloy C-22 compositions.

6.2.1.2. Alloy C-22 Variants

The following sections examine the individual effects of Mo, W, and Fe on the non-equilibrium solidification temperature range \((T_L-T_S)\) and the volume fraction of secondary phases at the end of solidification in Alloy C-22. These effects have been determined using a response-surface-methods experimental design approach, as outlined in the procedure section.

Regression analysis of the factors and responses from the experimental design matrix was performed using the software package Minitab-14. All results are presented in the form of main effects plots; these plots use the mean value of all but one factor to show the individual effect of the remaining factor on the response.

The non-equilibrium solidification temperature range has been selected for examination because it is proportional to the solidification cracking temperature range (SCTR). Therefore, it is an indicator of the susceptibility of the alloy to solidification cracking. The predicted relationship between the weight-percent of Mo, W, and Fe in the alloy and the non-equilibrium solidification temperature range is provided by Equation 6.2.

\[
T_L - T_S = 92.8940 + 5.1409 \cdot \text{Mo} - 5.2684 \cdot \text{W} + 0.4363 \cdot \text{Fe} \\
- 0.3396 \cdot \text{Mo}^2 + 0.1115 \cdot \text{W}^2 - 0.0105 \cdot \text{Fe}^2 \\
+ 0.2626 \cdot \text{Mo} \cdot \text{W} - 0.0957 \cdot \text{Mo} \cdot \text{Fe} + 0.0212 \cdot \text{W} \cdot \text{Fe}
\]

Equation 6.2: The effects of Mo, W, and Fe on the non-equilibrium solidification temperature range
The main effects plots showing the individual effects of Mo, W, and Fe on the non-equilibrium solidification temperature ranges are displayed in Figure 6.31. Unexpectedly, it is found that the predicted solidification temperature ranges are decreased as the alloy becomes richer in Mo, W, and Fe; with Mo having the most pronounced effect. However, examining the scale of the Y-axis in Figure 6.31, it is observed that over the Mo, W, and Fe composition ranges that define Alloy C-22, the solidification temperature range is only affected by a few degrees Celsius. This level of response to the compositional variation of Alloy C-22 would not be expected to significantly effect the solidification cracking susceptibility of the alloy.

The volume fraction of the secondary-phases that form during solidification are examined because they are believed to be proportional to the resistance of the alloy to ductility-dip cracking. Provided that these phases are effective at pinning migrating grain boundaries, a higher volume fraction of secondary-phases will result in a more tortuous grain boundary morphology. Tortuous grain-boundary morphologies create a mechanical locking effect, which improve the resistance of the alloy to ductility-dip cracking.

Equation 6.3 provides the predicted relationship between the weight-percent Mo, W, and Fe and the volume-percent of secondary phases in Alloy C-22 weld-metal. The main effects plots derived from this equation are presented in Figure 6.32. As one might expect, the volume fraction of secondary phases increases with increasing concentrations of Mo, W, and Fe. These three elements are predicted to have approximately the same potency in increasing the amount of secondary phases in the weld-metal.

\[
\text{vol}^\%_{\text{2nd phases}} = 15.7785 - 2.7209 \cdot \text{Mo} + 0.5194 \cdot \text{W} - 0.5672 \cdot \text{Fe} \\
+ 0.1172 \cdot \text{Mo}^2 + 0.0061 \cdot \text{W}^2 + 0.0023 \cdot \text{Fe}^2 \\
- 0.0081 \cdot \text{Mo} \cdot \text{W} + 0.0548 \cdot \text{Mo} \cdot \text{Fe} - 0.0113 \cdot \text{W} \cdot \text{Fe}
\]

Equation 6.3: the predicted relationship between the volume fraction of secondary phases and weight-percent Mo, W, and Fe in Alloy C-22
Summary:

1. Scheil simulations revealed that increasing the amount of molybdenum, tungsten, and iron (within the compositional limits of Alloy C-22) decreased the solidification temperature range, thereby decreasing the susceptibility to solidification cracking. However, this decrease was less than ten degrees Celsius, and therefore would not significantly affect the cracking susceptibility of the alloy.

2. Scheil simulations revealed that increasing the amount of molybdenum, tungsten, and iron (within the compositional limits of Alloy C-22) increased the volume fraction of secondary phases that formed during solidification, and would presumably decrease the susceptibility to ductility-dip cracking. Each element demonstrated roughly the same potency in promoting the formation of secondary phases.
Figure 6.31: The predicted effect of Mo, W, and Fe on the non-equilibrium solidification temperature range of Alloy C-22, as derived from the response surface methods Scheil simulations.
Figure 6.32: The predicted effect of Mo, W, and Fe on the volume fraction of secondary phases in Alloy C-22 weld-metal, as derived from the response surface method Scheil simulations
6.2.1.2.1. Secondary Phases and Elevated Temperature Ductility

The assumption that an increase in the non-equilibrium solidification temperature range indicates an increase in the susceptibility of an alloy to solidification cracking is easily accepted. Additionally, previous research [24] has demonstrated the maximum crack length (which is very similar to maximum cracking distance and therefore proportional to the solidification cracking temperature range) of a number of nickel base alloys to be linearly related to the solidification temperature range of the alloy (see Figure 6.33).

![Figure 6.33: Relationship between maximum crack length (MCL) and solidification temperature range for a number of nickel base alloys [24]](image)

However, the assumption that an increase in the volume fraction of secondary phases will decrease the susceptibility of the alloy to ductility-dip cracking is significantly more tenuous considering the complex nature of this cracking mechanism. As a result, a small set of experiments were undertaken in order to verify this assumption. Several weld-metal hot-ductility and strain-to-fracture samples were heat treated to purposefully form
secondary phases. These samples were heat treated, under an argon atmosphere, for twelve-hours at 990°C (1814°F); this time and temperature corresponded to the nose of the time-temperature-transformation diagram for Alloy C-22, as predicted by JMatPro v4.1. The fraction-phase vs. temperature plot (see Figure 6.22), also created using JMatPro v4.1, reveals that the secondary phases formed during this heat treatment are a mixture of predominately P-phase with a very small amount of M₆C.

Figure 6.34 demonstrates the quantity and morphology of the secondary phases in the weld-metal before and after this heat treatment. The respective volume fractions of secondary phases in the two microstructures was measured to be 0.19-percent and 2.19-percent for the as-welded and heat-treated microstructures respectively, a tenfold increase. Figure 6.34B demonstrates that the formation of secondary phases first occurred along boundaries within in the weld-metal.

Figure 6.34: (A) Backscattered electron imaging of Alloy C-22 weld-metal in the unetched condition, and (B) Backscattered electron imaging of Alloy C-22 weld-metal that has been heat-treated at 990°C (1814°F) for twelve hours, in the etched condition.

Figure 6.35 displays the results of the hot-ductility testing of the heat-treated weld-metal samples versus those of the as-welded samples, both in the on-heating condition. It
is observed that the samples with the higher volume fraction of secondary phases are significantly more ductile over the testing temperature range. Reduction in area data is not plotted for the 800°C (1472°F) and 900°C (1652°F) heat-treated weld-metal samples because necking and failure occurred in the base-metal of these samples. The heat-treatment had actually strengthened the weld-metal beyond that of the (cooler) surrounding base-metal during the Gleeble hot-ductility test.

![Graph: The Effect of Secondary Phases on the Hot-Ductility of Alloy C-22 Weld-Metal](image)

Figure 6.35: A comparison between the elevated temperature ductility of as-welded Alloy C-22 weld-metal and Alloy C-22 weld-metal subjected to a heat-treatment of 990°C (1814°F) for twelve hours.

Figure 6.36 displays an orientation image of one of the heat-treated weld-metal samples, which was tested at 1100°C (2012°F) in the on-heating condition. The secondary phases (black globules) are observed to exist along boundaries that have been
aligned in the direction of tensile strain. The boundaries of this metal have been so strengthened by the presence of secondary phases that before failure sufficient strain accumulates to cause a complete recrystallization of the microstructure.

Figure 6.36: Orientation image of a heat-treated weld-metal hot-ductility sample that has been tested at 1100°C (2012°F) in the on-heating condition. The vertical colonies of black-globules in the microstructure are secondary phases along boundaries which have been aligned in the direction of tensile strain.

The formation of secondary phases also improved the performance of the alloy in the strain-to-fracture test. Figure 6.37 displays the results from the strain-to-fracture testing of as-welded and heat-treated Alloy C-22 samples, at a testing temperature of 1200°C (2192°F). A significant improvement in the cracking resistance of the heat-treated samples is noted; the cracking threshold has climbed from below two-percent to above four-percent strain. Additionally, the rise in the rate of crack initiation appears to be lower with increasing levels of applied strain.
The Effect of Volume Fraction of Secondary Phases on DDC in Alloy C-22

Figure 6.37: Comparison of the behavior of as-welded and heat-treated Alloy C-22 weld-metal in the strain-to-fracture test at a testing temperature of 1200°C (2192°F)

Figure 6.38 displays the microstructure of a heat-treated strain-to-fracture sample, which was tested at 1200°C (2192°F) and 10.6-percent strain. Secondary phases are present on the boundary along which cracking has occurred. Additionally, recrystallization is now observed in the microstructure; recrystallization is not observed in the as-welded strain-to-fracture samples. Similar to the hot-ductility tests of heat-treated weld-metal, the secondary phases that have formed as a result of heat-treatment have significantly strengthened the boundaries of the metal. This allows for enough strain to accumulate before cracking such that recrystallization may occur at this elevated temperature.
A brief discussion will now be presented on the mechanism by which secondary phase formation has increased the elevated temperature ductility and cracking resistance of the Alloy C-22 weld-metal. In resisting crack initiation, the boundaries of a weld-metal can be strengthened four ways:

1. Increasing the grain-to-grain cohesiveness of the boundary itself
2. Increasing the tortuosity of the boundary, thereby providing a mechanical ‘locking’ effect
3. Formation of secondary phases along the boundaries, creating a mechanical ‘knitting’ of adjacent grains
4. Any combination of the above three mechanisms
Aside from the elimination of harmful trace impurities, little can be done to increase the grain-to-grain cohesiveness of the boundary itself. The tortuosity of the boundary is a remnant of the solidification process; secondary phases which form at the end of solidification act to pin grain boundaries during elevated temperature boundary migration, creating a tortuous morphology.

The difference in the behavior of the as-welded and heat-treated weld-metals in the hot-ductility and strain-to-fracture tests cannot be explained by these first two mechanisms of boundary strengthening. Therefore, it is deduced that the secondary phases that formed during the heat-treatment act to strengthen the boundaries primarily through some type of mechanical ‘knitting’ of adjacent grains.

With this conclusion in mind, the reader should understand that a one-to-one relationship (with regards to elevated temperature ductility) will not exist between these heat-treated weld-metal samples and a hypothetical Ni-Cr-Mo-Fe-W weld-metal with an equivalent amount of secondary phases. Such a hypothetical weld-metal would likely have some combination of mechanical locking from grain-boundary tortuousity and mechanical knitting from the secondary phases. How this combination of mechanical locking and knitting would compare to the knitting effect of the heat-treated samples is impossible to say without experimental trials.

Aside from boundary strengthening, a more subtle mechanism may have played a role in the increased ductility and cracking-resistance of the heat-treated Alloy C-22 samples with the higher volume-fraction of secondary phases. This mechanism is known as Particle Stimulated Nucleation (PSN), and has been widely studied in aluminum alloys [67]. This phenomenon occurs in alloys that contain coarse non-deformable particles; when such alloys are subjected to strain, from cold- or hot-working, a highly deformed region forms around these particles. In subsequent annealing, recrystallization occurs preferentially in the highly strained immediate vicinity of these particles; this phenomenon can presumably be extended to participate in dynamic recrystallization. Additionally, aside from producing recrystallization in situations where it may not be
expected, particle-stimulated-nucleation also increases the kinetics of the recrystallization process.

If the P-phase of the heat-treated Alloy C-22 samples is in fact non-deformable, this mechanism may have occurred during the hot-ductility and strain-to-fracture tests. This mechanism would act to annihilate the internal strains within the material during the test (through dynamic recrystallization) and allow for higher strain levels to be achieved before the initiation of cracking in the strain-to-fracture test, or before failure in the hot-ductility test. This mechanism would of course be more active in the upper region of the testing temperature range, where dynamic recrystallization becomes possible.

It is noted that other researchers have found the opposite trend, with regards to secondary phases versus elevated temperature ductility, to be true in similar alloys. Kim et al. [42] hot-ductility tested as-cast and solutionized Alloy C-276 samples. It was found that reducing the amount of secondary phases, specifically P-phase, improved the hot ductility of these specimens. Within the present investigation, solutionizing of Alloy C-22 hot-ductility samples prior to testing resulted in approximately the same ductility as samples tested in the as-welded condition.

Finally, it must be mentioned that these experiments involving the formation of secondary phases in the weld-metal have been conducted merely for demonstrative purposes. Secondary phase formation in Alloy C-22 weld-metal is known to be detrimental to corrosion resistance, and therefore discouraged.

**Summary:**

1. Heat-treating to purposely increase the volume fraction of secondary phases demonstrated that an increase in the volume fraction of secondary phases increases both the elevated temperature ductility and DDC cracking resistance of the alloy

2. Aside from a strengthening of the weld-metal boundaries by the secondary phases, particle-stimulated-nucleation (PSN) may be partially responsible for the
increased elevated temperature ductility and cracking-resistance of the heat-
treated alloy with a higher volume fraction of secondary phases

6.2.2. Button-Melting Experiments

The following sections present and discuss the results of the button-melting
experiments and compare these results to those of the thermodynamic simulations.

6.2.2.1. Response Surface Method

The following sections present and discuss the results of the response-surface-method
button melting experiments and compare these results to those predicted by the JMatPro
Scheil simulations. The experimental and predicted results are displayed in Table 6.8.

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Table 6.8: Results from the (Scheil) simulated and experimental response-surface-method
button melting experiments

Figure 6.41 provides a comparison between the predicted and experimentally
determined non-equilibrium solidification temperature ranges. Unfortunately, a poor
correlation exists between these two sets of results. The predicted solidification
temperature ranges are wider than the experimental ranges and show linear trends, with
the experimental findings showing parabolic trends.

However, a closer examination of the results reveals further information. Figure 6.42
shows the effect of tungsten on the liquidus temperature, solidus temperature, and
solidification temperature range of the Alloy C-22 variants from the response-surface-
method trials. The predicted trends are plotted as the black lines, and the ranges of the
experimental trends are bracketed by the dotted red lines.

Examining the relationship between the predicted liquidus temperature and the range
of the experimentally determined trend, it is observed that the predicted liquidus
temperature falls completely within the experimental range. The predicted solidus
temperature is approximately ten-degrees Celsius below the experimental solidus
temperature range, and accordingly the predicted solidification temperature range is
approximately ten-degrees Celsius wider than the range of the experimentally determined
temperature range. These trends are repeated in the effects of both molybdenum and iron
on the liquidus temperatures, solidus temperatures, and solidification temperature ranges
of the alloy.

The reader is now asked to consider the fact that the ranges of the experimentally
determined liquidus temperatures directly overlap the predicted trends. This indicates
that the experimental method for determining the liquidus temperatures, solidus
temperatures, and solidification temperature ranges is accurate, but not precise enough to
resolve the fine trends that are predicted by the thermodynamic simulations. Figure 6.39
illustrates the difference between accuracy and precision.

Therefore, the ranges of the experimentally determined trends are correct, but the
trends observed within these ranges are erroneous. Re-examining the parabolic trends of
the experimentally determined solidification temperature ranges of Figure 6.41, and
understanding that the regression analysis of a response-surface-method model fits the
data to a quadratic equation, it can be easily understood how the range of the predicted
values can be correct, yet the parabolic trend within this range be incorrect.
A brief discussion will now be presented on the differences noted between the predicted (Scheil simulations) and experimentally measured solidification temperature ranges. A possible reason for this difference involves the rate of solidification that the experimental buttons experience during solidification. At very low solidification rates (approaching equilibrium), the solidification front is planar and the liquidus and solidus temperatures are equal. As solidification rate increases, perturbations are formed as the planar front becomes unstable; the liquidus temperature (perturbation tip) and solidus temperature (perturbation trough) begin to diverge. With further increases in solidification rate, these perturbations grow into elongated dendrites and a wider difference is noted between the liquidus and solidus temperature of the solidifying alloy.

However, as solidification rate continues to increase, there is a point past which the dendrite tips become unstable. Past this point, increasingly planar solidification fronts are favored, and the liquidus and solidus temperatures once again begin to converge. This phenomenon has been experimentally demonstrated in Fe-C-Al-Mn steels by Babu et al. [68]. A schematic of the phenomenon is provided in Figure 6.40. In the button melting experiments, a very small amount of molten metal (0.8g) is quickly solidified through conduction with a copper mold of significant mass. If the buttons are solidifying
at a rate past the point were the liquidus and solidus temperatures begin to converge, and the Scheil simulations correspond to a slower solidification rate, then this phenomenon will explain why the experimentally measured solidification temperature ranges were approximately ten degrees Celsius narrower than the solidification temperature ranges of the Scheil simulations.

Figure 6.40: Schematic explaining the effect of solidification rate on the liquidus and solidus temperatures of an alloy.

Summary:

1. The solidification temperature ranges predicted by the Scheil simulations were approximately 10°C (18°F) wider than the experimentally measured solidification temperature ranges. This may be due to the rapid solidification rates experienced by the experimental buttons. At very high solidification rates dendrite tips become unstable, the liquidus and solidus temperatures begin to converge, and the solidification temperature range is narrowed.

2. The experimental method used to determine the solidification temperature ranges of the Alloy C-22 variants proved to be accurate, yet not precise enough to resolve the fine trends predicted by the Scheil simulations. As a result, a smaller set of experiments with an expanded compositional range was conducted.
Figure 6.41: Comparison of the predicted (Scheil simulations) and experimentally measured non-equilibrium solidification temperature ranges of the Alloy C-22 variants tested in the response-surface-methods trials.
Figure 6.42: The effect of tungsten on the liquidus temperature, solidus temperature, and non-equilibrium solidification temperature range of the Alloy C-22 variants of the response-surface-method trails. The predicted trends (Scheil simulations) are represented by the black lines, and the ranges of the experimental trends are bracketed by the dotted red lines.
6.2.2.2. Fractional Factorial

Because the technique used to determine the liquidus and solidus temperatures of the alloys during solidification was not precise enough to resolve the fine trends predicted by the thermodynamic simulations, a smaller set of experiments with a wider compositional range was performed. A wider compositional range creates larger differences in the transition temperatures, which are more easily resolved.

This set of experiments used a fractional factorial experimental design. The alloys of this phase of the investigation were created and tested using the same button-melting techniques that were used for the compositions of the response-surface-method trials. Table 6.9 displays the desired and experimental compositions of the alloys (as measured by EDS using pure metal standards) within this phase of the investigation.

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Table 6.9: Desired and actual compositions of the fractional factorial button compositions

In this section, the results and discussion for the simulations and the button-melting experiments will be presented simultaneously. Table 6.10 provides the simulated and experimentally determined liquidus temperatures, solidus temperatures, and solidification temperature ranges for the fractional factorial trials. It is observed that the liquidus temperatures from the button-melting experiments are very close to those from the simulations. However, the same cannot be said of the experimental and predicted solidus temperatures and the corresponding solidification temperature ranges.
Regression analysis of the data in Table 6.10 was performed using Minitab-14 software. It is noted that the predicted (Scheil simulations) trends for the liquidus temperature, solidus temperature, and solidification temperature range are virtually identical when comparing the fractional factorial trials to the more rigorous response-surface-method trials. For example, in the response-surface-method simulations, the liquidus temperature is decreased by the addition of both molybdenum and tungsten (with molybdenum having a more pronounced effect), while iron slightly increases the liquidus temperature. These exact same trends are observed with the fractional factorial simulations, although the magnitudes of the trends are different as a result of the differences in the composition ranges.
Figure 6.43: a comparison of the predicted (Scheil simulations) and experimental non-equilibrium solidification temperature ranges of the fractional factorial composition range.
Figure 6.43 displays the main effects plots for the predicted and experimentally determined relationships between composition and the solidification temperature range of the alloy. Molybdenum, tungsten, and iron are all predicted to narrow the solidification temperature range of the alloy. However, the experimentally determined trends indicate that additions of molybdenum and tungsten have little effect on the solidification temperature range, and iron is observed to slightly widen the temperature range.

This discrepancy between the predicted and experimentally determined solidification temperature ranges suggests the following. The predicted trend, especially visible in the molybdenum main effects plot, suggests a eutectic system past the point of maximum solid solubility, where increases in composition narrow the solidification temperature range. On the other hand, the experimentally determined trends suggest a eutectic system below the point of maximum solid solubility, where increases in composition do not lead to significant changes in the solidification temperature range of the alloy. This situation is illustrated in Figure 6.44.
The discussion of this observation will now focus on the effect of molybdenum on the solidification temperature range, as molybdenum provides the most demonstrative example. Figure 6.45 displays the Ni-Mo binary phase-diagram and Figure 6.46 displays the Ni-Mo pseudo-binary phase-diagram for Alloy C-22. Comparing these two diagrams, it is observed that the addition of solute to the Ni-Mo system results in a predicted shift of the eutectic composition of the system from roughly forty-five weight-percent to below twenty-five weight-percent molybdenum. Table 6.11 provides data on the segregation behavior of molybdenum during the solidification simulations of the fractional factorial compositions of Table 6.10.
Table 6.11: Segregation of molybdenum during the solidification simulations of the fractional factorial compositions. Bold numbers denote the leanest dendrite core and richest interdendritic region compositions.

The encircled region in Figure 6.46 indicates the range of possible segregation during the solidification of the fractional-factorial alloys. That is, the lower bound of the encircled region (10.5 weight-percent) represents the leanest dendrite core composition of these trials, as predicted by JMatPro v4.1, and the upper bound (26 weight-percent) corresponds to the richest interdendritic region.

Figure 6.45: Ni-Mo binary phase-diagram [62]
This segregation data overlaid onto the Ni-Mo pseudo-binary phase-diagram indicates that segregation during solidification is predicted to push the compositions of the terminal liquid into a range corresponding to the Ni-Mo eutectic. Therefore, the pseudo-binary phase diagram also predicts the fractional factorial alloys to behave like a eutectic system past the point of maximum solid solubility during solidification. However, the experimental determination of the solidification temperature ranges disagrees with these predictions. Therefore, the thermal histories of the fractional factorial buttons suggest that the thermodynamic software has over estimated the shift of the Ni-Mo eutectic with the addition of solute to the system.

Figure 6.46: Ni-Mo pseudo-binary phase diagram; encircled is the composition range of interest
The metallographic evidence in some ways supports and some ways contradicts the findings of the single-sensor differential thermal analysis. Figure 6.47 displays backscattered electron images of the fractional factorial alloys; secondary phases appear bright-white due to compositional contrast. Factorial runs one, two, and four do not appear to have formed eutectics; run-two contains no secondary phases whatsoever, and runs one and four contain globular secondary phases within enriched interdendritic regions.

However, the most solute rich run of the fractional factorial experiments (run-three) displays a lamellar morphology of secondary phases, which is clearly a eutectic that has formed in interdendritic regions at the end of solidification. Run-three contains 12.7 volume-percent eutectic, as quantified through image analysis. In plain terms, run-three (which is significantly richer in Mo, W, and Fe than the upper compositional limits of Alloy C-22) is only slightly above the point of maximum solid solubility for this multi-component eutectic system. This finding is schematically illustrated in Figure 6.48. Overall the metallographic evidence supports the postulate that the thermodynamic software has over estimated the shift of the eutectic point resulting from additions of solute.
Figure 6.47: Backscattered electron imaging of the fractional factorial alloys. (A) Run-1, (B) Run-2, (C) Run-3, and (D) Run-4. Inset in ‘C’ is a higher magnification of a colony of secondary phases displaying the lamellar arrangement of a eutectic.
Table 6.12 displays the predicted and experimentally determined volume fractions of secondary phases in the fractional factorial alloy compositions. Ranking the runs from least to most volume fraction of secondary phases (two→four→one→three), the predicted and experimental results show an excellent correlation. However, the magnitude of the volume fraction of secondary phases formed does not share such a good correlation.
Table 6.12: Predicted and experimentally determined volume fraction of secondary phases in the fractional factorial alloys

<table>
<thead>
<tr>
<th>Run</th>
<th>Mo</th>
<th>W</th>
<th>Fe</th>
<th>Volume Fraction Secondary Phases</th>
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<tr>
<td></td>
<td>Mo</td>
<td></td>
<td></td>
<td>JMatPro</td>
</tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>6.0</td>
<td>7.0</td>
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</tr>
<tr>
<td>4</td>
<td>10.5</td>
<td>6.0</td>
<td>1.0</td>
<td>1.11%</td>
</tr>
</tbody>
</table>

Figure 6.50 displays the main effects plots for the volume fraction of secondary phases from the simulations and button-melting experiments. Again it is noted that the predicted trends observed in the fractional-factorial simulations are virtually identical to the predicted trends of the response-surface-method simulations. In both the fractional-factorial and response-surface-methods simulations, the volume fraction of secondary phases is predicted to increase with increasing levels of molybdenum, iron, and tungsten; each element having relatively the same potency.

From Figure 6.50, it would appear as if there is excellent correlation between the predicted and experimental findings. However, a closer examination of the raw data (Table 6.12) indicates that this is not true. In fractional-factorial experimental designs, the regression analysis produces a linear equation. The trend produced by the data within Table 6.12 is likely not linear; compositions one, two, and four produce very little secondary phases, yet run three produces copious amounts of secondary phases. This is especially noticeable in the experimental results.

From this data, it appears as if the formation of secondary phases during solidification is dependant more upon the total amount of solute than the individual contributions of molybdenum, tungsten, or iron. An attempt was made to develop further understanding of this phenomenon; over fifty Scheil simulations were conducted using the nominal compositions of Alloy C-22 (Table 5.8), plus randomized levels of molybdenum, tungsten and iron. Molybdenum was varied from 10.5 to 18 weight-percent, tungsten varied from 0 to 7.5 weight-percent, and iron varied from 1 to 8.5 weight-percent.
Figure 6.49 displays the results from these Scheil simulations. It appears as if the formation of secondary phases over this composition range is strongly dependant upon the combined level of molybdenum and tungsten. In fact, the volume-percent of secondary phases increases exponentially with an increase in \((\text{Mo} + \text{W})\). Iron, by comparison, was found to have a much less pronounced effect on the secondary phase formation.

![Graph showing the relationship between Mo + W and Secondary Phases (%)](image)

\[ R^2 = 0.8969 \]

Figure 6.49: The predicted effect (Scheil simulations) of molybdenum, tungsten, and iron on the volume fraction of secondary phases in the expanded fractional-factorial composition range

**Summary:**

1. Scheil simulations predict the solidification temperature range of the fractional factorial alloys to decrease with increasing levels of molybdenum, tungsten, and
iron. This appears to predict a eutectic system past the point of maximum solid solubility, where an increase in composition produces a narrower solidification temperature range.

2. Single-sensor differential thermal analysis found the solidification temperature range of the alloys to be insensitive to molybdenum, tungsten, and iron additions. This finding suggests a eutectic system below the point of maximum solid solubility.

3. Metallographic evidence revealed the richest composition of the fractional factorial runs to produce 12.7 volume-percent eutectic products. Eutectic products were not observed in the fractional factorial runs with leaner compositions.

4. The single-sensor differential thermal analysis and the metallographic results suggest that the thermodynamic software overestimates the shifting of the eutectic composition of the multi-component system with solute additions.

5. Both metallography and extensive Scheil simulations suggest that the volume fraction of secondary phases increases exponentially with an increase in the combined level of molybdenum and tungsten (i.e. Mo + W)
Figure 6.50: A comparison of the predicted (Scheil simulations) and experimental volume fraction of secondary phases in the fractional factorial composition range.
CHAPTER 7

CONCLUSIONS

1. Solidification Cracking (*Transvarestraint Test*)
   
   a. Strain saturation (that is, the level past which further increases in augmented strain did not cause further increases in maximum crack distance) occurred at two-percent augmented strain.
   
   b. Alloy C-22 was found to have a solidification cracking temperature range of approximately 50°C (90°F); this indicates that the alloy is resistant to solidification cracking. The susceptibility of Alloy C-22 to solidification cracking is only slightly higher than very crack resistant alloys such as DSS2205, SS304(FN6), and DSS2507.
   
   c. Heat 2277-3-3119 was observed to have a higher cracking response than heat 2277-3-3114 throughout the entire range of augmented strain. This difference in cracking response is believed to in part be due to the difference in the (S + P) levels of the two heats. However, the statistical significance of this conclusion is debatable.

   d. Cracking occurred primarily along solidification grain boundaries, although cracking was sometimes observed to have occurred along solidification subgrain boundaries

2. Ductility-Dip Cracking
a. Strain-to-fracture test

i. The threshold strain to cause ductility-dip cracking in the strain-to-fracture test for Alloy C-22 is very low. The threshold strain for cracking at 950°C (1742°F) was roughly two-percent; this is approximately the same threshold strain for cracking demonstrated by Filler-Metal 52, which is known to be susceptible to ductility-dip cracking.

ii. Alloy C-22 has a wide temperature range over which ductility-dip cracking occurs in the strain-to-fracture test. Additionally, Alloy C-22 displays no recovery of cracking-resistance at the upper end of the testing temperature range.

iii. All cracking was observed to have occurred along high-angle weld metal boundaries

iv. Cracking was not associated with the presence of secondary phases, i.e. cracking did not initiate or terminate at secondary phases

v. Recrystallization was not noted along boundaries of samples tested in the upper end of the testing temperature range. This absence of recrystallization is in large part responsible for the lack of recovery of cracking-resistance in this temperature range.

vi. Metallurgical evidence suggests that grain boundary migration occurs during the thermal hold portion of the strain-to-fracture test. This phenomenon, which appears to be unique to Alloy C-22 as compared to previously tested alloys, creates less tortuous boundaries, a more susceptible microstructure, and a higher cracking response during testing. Actual Alloy C-22 welds may
not experience such a prolonged duration in the temperature range where boundary migration occurs; as a result, the boundaries within actual weldments may remain tortuous and resistant to ductility-dip cracking.

vii. A new crack counting method was used within this investigation in order to eliminate much of the subjectivity of the crack counting process. All samples were sectioned and polished to a finish of 1μm before examination. Cracks that may previously have gone unnoticed or misdiagnosed as ‘grain boundary sliding’ were now counted. Additionally, cracks within the center of the sample (traditionally uncounted) were included in the crack counting totals. These new crack counting methods likely contributed in part to the low cracking threshold of the alloy.

b. Hot-ductility test

i. In both the on-heating and on-cooling conditions, the base-metal samples demonstrated excellent ductility without intermediate temperature ductility-dips

ii. In both the on-heating and on-cooling conditions, the weld-metal samples demonstrated lower ductility through the entire testing temperature range as compared to the base-metal samples. The weld-metal on-heating and on-cooling ductility signatures had pronounced intermediate temperature ductility-dips. The ductility minimum of the on-heating signature occurred at 900°C (1652°F), while the ductility minimum of the on-cooling signature occurred at 1000°C (1832°F). Recovery of ductility occurred at the upper end of the testing temperature range in both the on-heating and on-cooling conditions.
iii. The base-metal and weld-metal samples had liquation cracking temperature ranges (NST – DRT) of approximately 50°C (90°F). This is a narrow value that indicates that the alloy is not susceptible to heat-affected-zone liquation cracking.

iv. Differences in the microstructures of the base-metal and weld-metal samples account for the respective differences of the ductility signatures. The small equiaxed grains of the base-metal are better able to distribute and accommodate the strain as compared to the elongated columnar grains of the weld-metal samples; as a result, the base-metal demonstrates markedly better performance in the hot-ductility test.

v. All internal cracks, at some distance from the fracture face, in the weld-metal samples were found to have occurred along high-angle boundaries.

vi. Cracking was not associated with the presence of secondary phases, *i.e.* cracking did not initiate or terminate at secondary phases.

c. Hot-Ductility versus Strain-to-Fracture

i. Alloy C-22 behaves very differently in the hot-ductility and strain-to-fracture tests. This difference in behavior provides an excellent example why the strain-to-fracture test, which provides information specifically on crack initiation, is more applicable to cracking in real weldments than the simpler hot-ductility test.

ii. A recovery of ductility is noted in the hot-ductility test, whereas no recovery of cracking resistance was noted within the strain-to-fracture test. The recrystallization behavior of the alloy explains
this discrepancy. Orientation imaging revealed considerable recrystallization along boundaries in hot-ductility specimens tested at the upper end of the testing temperature range; these samples were subjected to greater than forty-percent strain. Recrystallization was completely absent from the strain-to-fracture samples tested within this temperature range; these samples were subjected to less than ten-percent strain.

iii. The ‘sluggishness’ of the recrystallization of Alloy C-22 was quantified through stacking-fault-energy analysis of a total of seven Ni-base alloys previously examined in the strain-to-fracture test. Alloy C-22 was found to have the lowest stacking-fault-energy, and therefore the highest resistance to recrystallization, of the alloys analyzed.

3. Compositional Variation

   a. Thermodynamic Simulations

   i. Nominal Alloy C-22 Composition

      1. Scheil simulations using the nominal composition of Alloy C-22 predict a solidification temperature range of 93°C (167°F), with slightly more than two volume-percent of secondary phases

      2. The equilibrium phase-fraction vs. temperature plot for the nominal composition of Alloy C-22 reveals σ-phase and M₆C carbides to be metastable solidification products.

      3. The nose of the most rapidly forming secondary phase (P-phase) on the continuous-cooling transformation diagram
for the nominal composition of Alloy C-22 occurs at a time of greater than seven hours. This indicates that secondary phases will not form on-cooling from a weld cycle, or in subsequent reheating from adjacent or overlying weld passes.

4. Non-equilibrium pseudo-binary solidification diagrams indicate that P-phase begins to form as a solidification constituent at levels of molybdenum, tungsten, and iron slightly richer than the nominal Alloy C-22 compositions

ii. Alloy C-22 Variants

1. Scheil simulations revealed that increasing the amount of molybdenum, tungsten, and iron (within the compositional limits of Alloy C-22) decreased the solidification temperature range, thereby decreasing the susceptibility to solidification cracking. However, this decrease was less than ten degrees Celsius, and therefore would not significantly affect the cracking susceptibility of the alloy.

2. Scheil simulations revealed that increasing the amount of molybdenum, tungsten, and iron (within the compositional limits of Alloy C-22) increased the volume fraction of secondary phases that formed during solidification, and would presumably decrease the susceptibility to ductility-dip cracking. Each element demonstrated roughly the same potency in promoting the formation of secondary phases.

b. Button-melting

i. Response Surface Methods Experiments
Compositional variation within the limits of Alloy C-22

1. The solidification temperature ranges predicted by the Scheil simulations were approximately 10°C (18°F) wider than the experimentally measured solidification temperature ranges. This may be due to the rapid solidification rates experienced by the experimental buttons. At very high solidification rates dendrite tips become unstable, the liquidus and solidus temperatures begin to converge, and the solidification temperature range is narrowed.

2. The experimental method used to determine the solidification temperature ranges of the Alloy C-22 variants proved to be accurate, yet not precise enough to resolve the fine trends predicted by the Scheil simulations. As a result, a smaller set of experiments with an expanded compositional range was conducted.

ii. Fractional Factorial Experiments

Compositional variation expanded beyond the limits of Alloy C-22

1. Scheil simulations predict the solidification temperature range of the fractional factorial alloys to decrease with increasing levels of molybdenum, tungsten, and iron. This appears to predict a eutectic system past the point of maximum solid solubility, where an increase in composition produces a narrower solidification temperature range.

2. Single-sensor differential thermal analysis found the solidification temperature range of the alloys to be
insensitive to molybdenum, tungsten, and iron additions. This finding suggests a eutectic system below the point of maximum solid solubility.

3. Metallographic evidence revealed the richest composition of the fractional factorial runs to produce 12.7 volume-percent eutectic products. Eutectic products were not observed in the fractional factorial runs with leaner compositions.

4. The single-sensor differential thermal analysis and the metallographic results suggest that the thermodynamic software overestimates the shifting of the eutectic composition of the multi-component system with solute additions.

5. Both metallography and extensive Scheil simulations suggest that the volume fraction of secondary phases increases exponentially with an increase in the combined level of molybdenum and tungsten (i.e. Mo + W)

4. Heat Treatment, Secondary Phases, and Elevated Temperature Ductility

a. Heat-treating to purposely increase the volume fraction of secondary phases demonstrated that an increase in the volume fraction of secondary phases increases both the elevated temperature ductility and DDC cracking resistance of the alloy.

b. Aside from a strengthening of the weld-metal boundaries by the secondary phases, particle-stimulated-nucleation (PSN) may be partially responsible for the increased elevated temperature ductility and cracking-resistance of the heat-treated alloy with a higher volume fraction of secondary phases.
CHAPTER 8

FUTURE WORK

Solidification Cracking

1. Investigation of the effect of travel speed on the distribution of macrosegregation in the solidified weld-metal
   
   a. It is hypothesized that a teardrop shaped weld-pool would create a continuous string of macrosegregation along the weld centerline. Using a combination of travel speed and current to create a teardrop shaped weld-pool, plus subsequent characterization of the weldment, it will be possible to either verify or negate this hypothesis.

Ductility-Dip Cracking

1. Simple experiments have demonstrated that secondary phases within the Alloy C-22 microstructure are effective at improving the elevated temperature ductility and cracking resistance of the alloy. However, formation of these phases is known to be detrimental to the corrosion resistance of the alloy. It is therefore of interest to know the relationship between the volume fraction of secondary phases and elevated temperature ductility and cracking resistance. This can be accomplished one of two ways:
a. Strain-to-fracture testing of a series of Alloy C-22 variants with progressively increasing volume fractions of secondary phases (preferred), or

b. Strain-to-fracture testing of a series of Alloy C-22 sample that have been heat-treated at a designated temperature, for times that correspond to the formation of progressively increasing volume fractions of secondary phases

Coupling this data with data from corrosion testing of these hypothetical microstructures, it may be possible to determine a ‘sweet-spot’ where the elevated temperature ductility and cracking resistance of the alloy is significantly improved, yet the corrosion properties of the weld-metal do not markedly suffer.

2. In this investigation, the total volume fraction of secondary phases was demonstrated to significantly improve the elevated temperature cracking-resistance of the alloy. It is of interest to know the relative potency of the secondary phases that form during solidification (σ, P, and M₆C), with regards to grain boundary pinning, tortuosity, and the subsequent effect on elevated temperature cracking resistance. This would require a somewhat intensive study with the following four steps:

a. Thermodynamic simulations to understand the compositional variations necessary to create study-alloys (Alloy C-22 variants) with maximized and/or minimized volume fractions of particular secondary phases

b. Selection and casting of a small number of these study alloys

c. Strain-to-fracture testing of the selected study-alloys, and
d. TEM work to confirm the presence of the expected secondary phases

3. Characterization has demonstrated that grain-boundary migration occurs during the thermal cycle of the strain-to-fracture test. This is believed to be in part responsible for the discrepancy between the poor performance of Alloy C-22 during the strain-to-fracture test, as compared to the weldability of the alloy within industry. If boundary migration during the test is indeed a contributing factor to the reported cracking susceptibility, then lessening the effect of the thermal cycle during the test should prove to increase the resistance of the alloy to cracking. This may be demonstrated with a small set of experiments:

a. Strain-to-fracture testing of approximately five samples at 1200°C (2192°F) using an accelerated temperature upslope and no thermal hold period. It should be kept in mind that such a thermal cycle will not allow the gauge section of the sample to come to a thermal equilibrium. As such, the sample will have a higher thermal gradient, and the results may not be as representative of the reported testing temperature as compared those from the regular thermal cycle. For instance, the majority of cracking observed on the sample surface in this situation may occur at locations corresponding to temperatures significantly above or below the reported testing temperature.

b. Conversely, the effect of boundary migration in Alloy C-22 could be demonstrated by purposefully attempting to cause ductility-dip cracking in a real weldment. Multi-pass welding of a thick-section, highly-restrained Alloy C-22 joint using a high heat-input process such as SAW would force the weld-metal and HAZ to spend more time in the temperature regime where boundary migration occurs. Cracking occurring in such a weldment would further evidence the effect of boundary migration on the cracking-resistance of the alloy, and further
explain the discrepancy between the performance of Alloy C-22 in the strain-to-fracture test and the reported cracking-resistance of the alloy within industry.

4. Although the strain-to-fracture test offers significant advantages over the hot-ductility test, refinement of this test is still necessary at this point. Among the chief concerns are the repeatability of the crack counting method and the intensive sample preparation and testing procedures.

a. Efforts have been made in this investigation to reduce or eliminate the subjectivity of crack counting by assessing the samples in the polished condition. Although this procedure clearly identifies cracking on the sample surface, several questions remain. Should two cracks that clearly occur along the same boundary be counted together or separately? Should the number of cracks be the only criterion for evaluating the severity of cracking? For instance, is cracking more severe in a sample with many small cracks or a sample with a few large cracks? Recently, Sowards [63] has proposed a method in which total crack area, normalized by spot area, is plotted versus testing temperature; initial results have been promising.

b. One of the main barriers to the wide-spread use of the strain-to-fracture test is the intensity of sample preparation and testing procedure, as compared to that of the hot-ductility test. Anything that may be done to lessen the number of samples necessary for testing will make the strain-to-fracture test more ‘competitive’ with the hot-ductility test. Wider spread use of the strain-to-fracture test, will further accelerate the refinement of the test and provide the academic community and industry with valuable information on ductility-dip cracking in weldments.
Compositional Variation

1. Solidification Cracking
   
   a. Although the assumption that an increase in the solidification temperature range of an alloy will also increase the SCTR of the alloy is sound, direct testing is required to verify this assumption. Casting of a lean and a rich composition from the fractional factorial trials, and subsequent transvarestraint testing of these compositions would further validate the findings of the button-melting experiments.

2. Ductility-Dip Cracking
   
   a. Although it has been experimentally demonstrated that increasing the volume fraction of secondary phases in Alloy C-22 weld-metal will improve the elevated temperature ductility and cracking resistance of the alloy, no direct testing of the button-melting compositions was conducted. Casting of an Alloy C-22 variant with a moderate increase in the volume fraction of secondary phases, and subsequent strain-to-fracture testing of this composition, would further validate the findings of the button-melting experiments.
REFERENCES


52. Lippold, J.C.; WE715 Class Notes, The Ohio State University, Summer Quarter 2005.


58. M.L. Gallagher, Unpublished Research, 2004, The Ohio State University, Columbus, OH.


64. Finton, T.; 2003; “Standardization of the Transvarestraint Test”; M.S. Thesis; Ohio State University; Columbus, OH.


APPENDIX A

SELECT PROPERTIES OF ALLOY C-22

The following tables display selected physical, mechanical, electrical, and thermal properties of Alloy C-22; some properties as functions of temperature. This data is provided by the manufacturer, Haynes International, Inc., for 6.4-19.1 mm (0.25-0.75 in) plate that has been solution heat treated at 1121°C (2050°F) to dissolve all secondary phases, and rapidly quenched to room temperature.

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<th>Value</th>
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<td>Melting Temperature Range</td>
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Table A.1: Select physical properties of Alloy C-22 as provided by Haynes International, Inc. [2]
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Table A.2: Select mechanical properties of Alloy C-22 as functions of temperature, as provided by Haynes International, Inc. [2]
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Table A.3: Impact properties of Alloy C-22 as provided by Haynes International, Inc. [2]

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</tbody>
</table>

Table A.4: Electrical resistivity of Alloy C-22 as a function of temperature, as provided by Haynes International, Inc. [2]
<table>
<thead>
<tr>
<th>Temperature</th>
<th>Coefficient of Thermal Expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>°F</td>
</tr>
<tr>
<td>24-93</td>
<td>75-200</td>
</tr>
<tr>
<td>24-204</td>
<td>75-400</td>
</tr>
<tr>
<td>24-316</td>
<td>75-600</td>
</tr>
<tr>
<td>24-427</td>
<td>75-600</td>
</tr>
<tr>
<td>24-538</td>
<td>75-1000</td>
</tr>
<tr>
<td>24-649</td>
<td>75-1200</td>
</tr>
<tr>
<td>24-760</td>
<td>75-1400</td>
</tr>
<tr>
<td>24-871</td>
<td>75-1600</td>
</tr>
<tr>
<td>24-982</td>
<td>75-1800</td>
</tr>
</tbody>
</table>

Table A.5: Coefficient of linear expansion of Alloy C-22 as a function of temperature, as provided by Haynes International, Inc. [2]

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Specific Heat</th>
<th>Thermal Conductivity</th>
<th>Thermal Diffusivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>°F</td>
<td>J/g-°C</td>
<td>BTU/lb-°F</td>
</tr>
<tr>
<td>21</td>
<td>70</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>48</td>
<td>118</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>52</td>
<td>126</td>
<td>0.414</td>
<td>0.099</td>
</tr>
<tr>
<td>100</td>
<td>212</td>
<td>0.423</td>
<td>0.101</td>
</tr>
<tr>
<td>200</td>
<td>390</td>
<td>0.444</td>
<td>0.106</td>
</tr>
<tr>
<td>300</td>
<td>570</td>
<td>0.460</td>
<td>0.110</td>
</tr>
<tr>
<td>400</td>
<td>750</td>
<td>0.476</td>
<td>0.114</td>
</tr>
<tr>
<td>500</td>
<td>930</td>
<td>0.489</td>
<td>0.117</td>
</tr>
<tr>
<td>600</td>
<td>1100</td>
<td>0.514</td>
<td>0.123</td>
</tr>
</tbody>
</table>

Table A.6: Selected thermal properties of Alloy C-22 as functions of temperature, as provided by Haynes International, Inc. [2]

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APPENDIX B

PSEUDO-BINARY PHASE-DIAGRAMS

Figure B.1: Ni-Cr pseudo-binary phase diagram
Figure B.2: Ni-Co pseudo-binary phase diagram
Figure B.3: Ni-C pseudo-binary phase diagram
Figure B.4: Ni-Mn pseudo-binary phase diagram
Figure B.5: Ni-Si pseudo-binary phase diagram
Figure B.6: Ni-V pseudo-binary phase diagram