Development of a High Chromium Ni-Base Filler Metal Resistant to Ductility Dip

Cracking and Solidification Cracking

DISSERTATION

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Abstract

Many nuclear reactor components previously constructed with Ni-based alloys containing 20 wt% Cr have been found to be susceptible to stress corrosion cracking. The nuclear power industry now uses high chromium (~30wt%) Ni-based filler metals to mitigate stress corrosion cracking. Current alloys are plagued with weldability issues, either solidification cracking or ductility dip cracking (DDC). Solidification cracking is related to solidification temperature range and the DDC is related to the fraction eutectic present in the microstructure. It was determined that an optimal alloy should have a solidification temperature range less than 150°C and at least 2% volume fraction eutectic. Due to the nature of the Nb rich eutectic that forms, it is difficult to avoid both cracking types simultaneously. Through computational modeling, alternative eutectic forming elements, Hf and Ta, have been identified as replacements for Nb in such alloys.

Compositions have been optimized through a combination of computational and experimental techniques combined with a design of experiment methodology. Small buttons were melted using commercially pure materials in a copper hearth to obtain the desired compositions. These buttons were then subjected to a gas tungsten arc spot weld. A type C thermocouple was used to acquire the cooling history during the solidification process. The cooling curves were processed using Single Sensor Differential Thermal Analysis to determine the solidification temperature range, and indicator of solidification cracking susceptibility. Metallography was performed to determine the fraction eutectic
present, an indicator of DDC resistance. The optimal level of Hf to resist cracking was found to be 0.25 wt%. The optimal level of Ta was found to be 4 wt%.

\(\gamma/\text{MC}\) type eutectics were found to form first in all Nb, Ta, and Hf-bearing compositions. Depending on Fe and Cr content, \(\gamma/\text{Laves}\) eutectic was sometimes found in Nb and Ta-bearing compositions, while Hf-bearing compositions had \(\gamma/\text{Ni}_7\text{Hf}_2\) as the final eutectic to solidify. This study found that the extra Cr in the current generation alloys promotes the \(\gamma/\text{Laves}\) phase eutectic, which expands the solidification temperature range and promotes solidification cracking. Both Ta-bearing and Hf-bearing eutectics were found to solidify at higher temperatures than Nb-bearing eutectics, leading to narrower solidification temperature ranges.

Weldability testing on the optimized Ta-bearing compositions revealed good resistance to both DDC and solidification cracking. Unexpectedly, the optimized Hf-bearing compositions were quite susceptible to solidification cracking. This led to an investigation on the possible wetting effect of eutectics on solidification cracking susceptibility, and a theory on how wetting affects the solidification crack susceptibility and the volume fraction of eutectic needed for crack healing has been proposed. Alloys with eutectics that easily wet the grain boundaries have increased solidification crack susceptibility at low volume fraction eutectics, but as the fraction eutectic is increased, experience crack healing at relatively lower fraction eutectics than alloys with eutectics that don’t wet as easily. Hf rich eutectics were found to wet grain boundaries significantly more than Nb rich eutectics. Additions of Mo were also found to increase the wetting of eutectics in Nb-bearing alloys.
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CHAPTER 1
INTRODUCTION

Solid solution strengthened Ni-based filler metals are commonly used for cladding, overlaying, and joining dissimilar materials. Depending on composition, these filler metals can exhibit excellent corrosion resistance with moderate strength. The nuclear power industry uses nickel based filler metals with high Cr (20-30 wt%) to join dissimilar metals. Alloys with approximately 20 wt% Cr, such as FM82, have been found to be susceptible to primary water stress corrosion cracking. Because of this, alloys such as FM52 and 52M (ERNiCrFe-7/7A), with approximately 30 wt% Cr, are currently used for repair welding of safe ends to the nuclear pressure vessel in Pressurized Water Reactors (PWRs), and are proposed for use in new construction [1-5].

Shortly after its introduction, FM52 was found to be susceptible to a phenomenon known as ductility dip cracking (DDC) [6]. This phenomenon is associated with solidification grain boundaries that migrate immediately following solidification to become very straight. These straight crystallographic boundaries then slide due to residual stresses and cracks can form at elevated temperatures either on cooling, or by reheating from subsequent passes. By adding elements that form eutectic at the end of solidification, such as Nb, these grain boundaries can be pinned and stay tortuous at elevated temperatures. As a result of this grain boundary pinning effect, alloys with a few wt% Nb, such as FM52i and FM52MSS, have increased resistance to DDC.
Increasing the Nb content of high Cr Ni-based filler metals causes increased susceptibility to solidification cracking [7, 8]. This was found to be related to low melting eutectics and liquid films present at grain boundaries at the end of solidification. There is a positive correlation between solidification temperature range (STR) and solidification cracking susceptibility. Alloys with lower Nb, such as FM52M, have greater resistance to solidification cracking due to a narrower STR.

Due to the contrasting effects of Nb in high-Cr Ni-based alloys, there is a fine balance needed in composition to avoid both forms of cracking. This work will investigate replacing Nb with another element that will promote the formation of eutectic phases at the end of solidification, but with a higher terminal eutectic temperature than that of current alloys. This will allow eutectic constituents to be generated for DDC resistance while keeping the solidification temperature range narrow for solidification cracking resistance.

Elements used for Nb replacement in this study are Ta and Hf. A combination of thermodynamic modeling and experimental validation were used to determine the nature of the eutectic constituents that may form when these elements are present. Based on that, a design of experiment (DOE) was used to determine a set of experimental compositions. The actual solidification temperature range and fraction eutectic present were determined for each composition. Regression analysis was then used to identify optimized compositions. These optimized compositions were verified using button melting and microstructure characterization. Finally, actual filler metal heats were cast and drawn into wire for actual welding trials and extensive weldability testing.
Based on some early unexpected results, a corollary study was initiated to evaluate the wetting characteristics of eutectic liquid films at grain boundaries. A novel modified sessile drop test was employed to study the contact angle of liquid eutectic compositions on a Ni-base substrate. These results provided insight into how wetting, along with solidification temperature range, play a role in solidification crack susceptibility. This was verified theoretically against some well-known aluminum alloy solidification cracking data.

The work presented here demonstrates how a combination of computational and experimental techniques can be used to facilitate filler metal development. The use of Thermo-Calc® and other thermodynamic-based computational programs can quickly evaluate the effect of different alloying additions on important weldability metrics such as solidification temperature range and fraction eutectic. When these computational programs are coupled with simple laboratory techniques such as button melting, Single Sensor Differential Thermal Analysis (SS DTA®), optical microscopy, and scanning electron microscopy, it is possible to identify candidate compositions without the use of “trial-and-error” approaches that are still widely used for alloy development.
CHAPTER 2
STRESS CORROSION CRACKING IN NICKEL BASED ALLOYS

Stress corrosion cracking is somewhat difficult to define due to its nature. Jones and Ricker define it as "simultaneous environmental exposure and application of stress" that causes "time-dependent subcritical crack propagation". [9] Subcritical crack propagation is important here because while the corrosion may generate some flaws that cause the stress intensity factor to increase, it does not ever reach the materials $K_{\text{crit}}$. But the crack is propagating, and as such, one can define a stress intensity factor $K_{\text{SCC}}$ to define the critical size of cracks that will propagate under stress and a corrosive environment.

With this in mind, one can begin to look at the various mechanisms that cause SCC. While the exact mechanism is a complex interaction of processes, Jones and Ricker have proposed a way of determining the propagation rate by determining the rate limiting step [9]. Figure 1 shows a schematic of a crack tip and possible steps required for crack propagation. Any one of these steps could be the rate limiting step depending on the conditions. In such a case, the effects of the other steps will be negligible, unless however, one of those steps becomes rate limiting.
Figure 1 - Schematic showing possible rate-limiting steps in the SCC process [9].

Once possible rate limiting steps are defined, variables that affect these steps can be brought into consideration. Changing these variables will in effect change the rate of SCC. Jones and Ricker detailed a non-comprehensive list consisting of:

- Temperature
- Pressure
- Solute species
- Solute activity
- pH
- Electrochemical potential
- Solution viscosity
- Solution flow
- Stress level
- Stress state (plane stress or plane strain)
- Loading mode
- Alloy composition
- Microstructure state (precipitates, grain size, etc.)
- Crack geometry

For SCC in primary water environments within nuclear reactors, some of these factors become more important than others. Temperature, pressure (which dictates stress), composition of the primary water, composition of the metal, and microstructure variations (from welding or heat treatments), will all be of great concern in this case.

2.1 Initiation of Stress Corrosion Cracks

Since SCC is essentially corrosion assisted crack growth, then the process must start with crack initiation. There are multiple ways cracks could initiate, given a plethora of initial conditions. Jones and Ricker describe three main methods [9]. The first is initiation due to surface discontinuities. These areas could provide sites for crevice corrosion to take place, which would be the beginnings of a crack. Another method described involves pitting corrosion. Deep and narrow pits could essentially be considered as a crack, and generally are when the depth to width ratio is over 10. The third mechanism detailed is initiation due to intergranular corrosion. Alloys with chemical compositions at grain boundaries that are more susceptible to corrosion than the matrix could experience intergranular corrosion; these can be crack initiation sites. This is the most likely method of initiation in FM82 welds. The chromium can segregate during solidification, becoming depleted at the boundaries. Additionally, due to the relatively high carbon of FM82, chromium rich M$_{23}$C$_6$ carbides can form during post weld heat treatment, further reducing matrix chromium levels at the grain boundary.
2.2 Growth of Stress Corrosion Cracks

After initiation, the conditions change. There is now a situation more like the one detailed in Figure 2. From this point, we can look thermodynamically at either an anodic dissolution process or a cathodic hydrogen evolution process. If conditions are right for anodic dissolution, they must be such that there is more dissolution at the crack tip than the crack walls, shown in Figure 2 [9]. If not, then the crack will self-blunt. Reasons for higher dissolution could be related to stagnation, mass transport issues, ohmic potential drops, or loss of protective oxide. The strain at the crack tip could also increase the activity on the surface. If the material is susceptible to hydrogen embrittlement, then a cathodic condition at the crack tip could cause hydrogen to evolve and diffuse into the tip. Since there is increased strain at the crack tip, cracks could propagate in this manner.

![Figure 2 - Schematic showing transport of anions (A) and metal cations (M) to and from the crack wall and crack tip [9].](image-url)
These two cases, anodic and cathodic, give rise to multiple explanations for how the cracks actually propagate. Jones and Ricker detail various models that have been proposed in the literature, the two main ones will be discussed here, the film rupture model, and the hydrogen embrittlement model [9].

The film rupture model says that the stress acts to crack the protective film, and then corrosion happens at the surface of the exposed metal. The crack will grow by dissolution and could possibly repassivate, at which point the film will crack again, and the process repeats itself. This generally happens in anodic regions, where passivation is possible, but not entirely stable. Of course, conditions are difficult to measure right at the crack tip due to transport and stagnation issues. Polarization curves shown in Figure 3 have been correlated with SCC in stainless steels and show regions where SCC is possible [10]. If the passive layer is not stable at all, then the sidewalls of the crack will corrode, effectively reducing the sharpness of the crack.
Figure 3 - General polarization curve showing regions of passive film breakdown, where SCC is most likely [10].

If conditions cause a more cathodic situation, or cathodic protection is applied to the material, then the film rupture model doesn't apply due to lack of anodic dissolution. However, cracking can still occur. Since atomic hydrogen is evolved at the surface in a cathodic reaction, it has the potential to diffuse into the material, especially at grain boundaries where the diffusion coefficient is higher [9]. It could also surface diffuse and combine with another hydrogen atom to form molecular hydrogen gas. Impurities, usually segregated at grain boundaries, can also increase the uptake of hydrogen. Figure 4 shows this mechanism schematically.
Figure 4 - Schematic showing hydrogen entry at grain boundaries in cathodic situations. Hydrogen entry can also cause cracking [9].

### 2.3 Methods for Evaluating Susceptibility to Stress Corrosion Cracking

There are many methods of testing to determine susceptibility to stress corrosion cracking. Jones and Ricker divide them into three groups [9].

- Tests on statically loaded smooth samples
- Tests on statically loaded pre-cracked samples
- Tests using slowly straining samples

Statically loaded smooth samples are tested at constant load, and in the environment of interest. These tests are repeated for several stress levels, and the time to cracking and time to failure recorded. The result is a graph like the one in Figure 5. This can give an
indication of the stress level for which cracking will not occur. Some of these tests are covered under ASTM standards G49 and G129.

![Typical results from statically loaded smooth samples](image)

**Figure 5 - Typical results from statically loaded smooth samples [9].**

Statically loaded pre-cracked samples are tested at a constant load in the environment of interest. They also have a crack of specific geometry introduced into the sample before testing. This allows for more careful study on how the stress intensity factor affects the growth rate of the crack, as the stress intensity factor can be tested by changing the crack geometry. Variants of this test can have the stress intensity factor increase as the crack grows. These test give results similar to the one shown in Figure 6 [9]. There are three different regions that appear in the results. In the first region, just above the threshold stress intensity for crack growth, the growth rate increases dramatically with increasing K. In region 2, the crack growth rate does not vary much with K. This is due to rate
limiting factors such as mass transport to the crack tip. The third region, the crack growth rate increases dramatically again as $K$ is approaching the material's inherent critical stress intensity factor.

![Graph showing the crack growth rate](image)

Figure 6 - Typical results from statically loaded pre-cracked samples [9].

Slow strain rate testing is similar to a tensile test, with a slower pulling speed and the sample encased in the environment of interest. Usually, the sample is tested with and without the environment of interest, and the ductility is plotted vs. the strain rate. Figure 7 shows an example of this. [9] These types of tests are relatively quick compared to the other tests previously detailed. This allows for variables such as microstructure to be altered, say from welding or heat treatments. When this is done, the variable of interest
can be plotted on the x axis, for a constant strain rate. Since most structures have variations in microstructure for numerous reasons, this test is quite useful.

![Graph](image)

Figure 7 - Typical results from slow strain rate tests [9].

### 2.4 Stress Corrosion Cracking of Ni-base Alloys in Primary Water

Since there are a variety of mechanisms to describe and predict crack growth rates during SCC, it would be useful to know the specific mechanism responsible for Ni-base alloys in primary water environments. Since most proposed mechanisms offer some way of predicting the crack growth rate, Rebak and Szklarska-Smialowska tried to fit these mechanisms to some crack growth data in the literature [11]. None of the mechanisms could fully predict the crack growth rate as a function of $K$, but some offered more insight than others. Specifically, they found that the film rupture model can fit the data quite well. Other methods such as the coupled environment fracture model, which involves a charge neutrality equation, didn't fit so well. They also investigated possible
mechanisms to describe the crack induction time. In service, cracks were not detected on the primary side for about 15 years. The authors propose that this suggests a diffusion process. They used an equation for void size in diffusional creep to describe the incubation time. The void size \( \delta \), is given by Equation 1.

\[
\delta \leq 1.8 \times \varepsilon \times d
\]

\( \varepsilon \) is the creep rate and \( d \) is the grain size. The authors found that voids could form that reach the surface that were between 1.5 to 120 \( \mu \)m in size within 15 years. These voids could crack the oxide and cause accumulation of impurities such that corrosion could begin to happen at the crack tip, shown schematically in Figure 8.
Figure 8 - Schematic of proposed mechanism for crack induction time [11].

The authors concluded that there isn't one primary mechanism for crack growth; rather it is probably a combination of methods. They were, however, able to correlate crack incubation times observed in the field with a simple diffusional creep model as the mechanism for crack initiation. This is important as there could be implications with crack incubation times as new generations of power plants strive to operate at higher, more efficient temperatures.

2.5 Welding Effects on Stress Corrosion Cracking

Welding is a highly non-linear process with a multitude of variables. Any of these could have an effect on stress corrosion cracking in these environments. A few variables that are known to be of importance are choice of weld metal, process used, joint geometry,
and cooling rate. These variables will affect local chromium levels, final microstructure, and residual stress, all of which will have an effect on the imitation and growth of SCC.

Recently, Alexandreanu et al. have done extensive studies on joint geometry and crack growth rates in weld metals [12]. They used a compact pre-cracked tensile specimen to determine crack growth rates for various conditions. They tested samples with two different weld geometries using the industry standard filler metal, Alloy 182. The two weld geometries, double-J and a deep-groove, are shown in Figure 9. The pre-cracked tensile specimens were oriented as shown in Figure 10.

![Figure 9 - Weld geometries used for SCC testing, (a) Double J, and (b) Deep-Groove](image-url)

Figure 9 - Weld geometries used for SCC testing, (a) Double J, and (b) Deep-Groove [12].
Figure 10 - Schematic of how compact tensile specimens were taken from weld geometries, showing location of crack notch [12].

The results, shown in Figure 11, clearly showed an increase in crack growth rate over base metal Alloy 600, as much as an order of magnitude [13]. This can be attributed to a multitude of factors, such as residual stresses, compositional gradients, and carbide precipitation. Compositional gradients arise from the solidification process. As the material solidifies, some elements segregate to the liquid. Chromium is known to segregate to the solid, such that the solidification grain boundaries are slightly depleted in Cr. Subsequent weld passes can cause material below to heat up into the carbide precipitation range. At certain temperatures, Cr-rich \((\text{Cr}_2\text{C}_6)\) carbides form along grain boundaries and locally deplete the surrounding matrix of Cr. These mechanisms are consistent with the crack paths seen in the weld metal. Cracks were observed to follow solidification grain boundaries in most cases. The authors also showed a slight difference in crack growth rates depending on weld geometry. The deep-groove weld performed slightly better than the double-J. No explanation for this difference was offered, though
one could speculate it may be related time spent in the carbide precipitation range, or
differences in residual stresses due to geometry.

Figure 11 - Crack growth rate data for the different weld geometries, along with median
Alloy 600 curve for comparison [12].

Ni-base filler metals containing 30 wt% Cr, such as FM52 and FM52M, have been used
to replace 20 wt% Cr alloys, like FM82, in nuclear power applications which require
resistance to primary water stress corrosion cracking (PWSCC) [14]. Compositions of
these alloys and other relevant alloys are shown in Table 1. These alloys were chosen to
withstand the primary water environment, which generally consists of deaerated pure
water near 325 °C, with 3000 ppb H₂, 1200 ppm B, and 2 ppm Li [15]. There have been
cases where cracks were found ultrasonically in FM82 welds [16]. These cracks were
determined to be stress corrosion cracks. The mechanism, while complex, seems to be related to the Ni/NiO stability along with hydrogen embrittlement at the crack tip [15].

Table 1 - Relevant alloy compositions in weight percent (wt%) with balance nickel of alloys used in primary water environments. Alloy 600 and 690 are base materials, all others are filler metals.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr</th>
<th>Fe</th>
<th>Nb</th>
<th>Mo</th>
<th>Ti</th>
<th>C</th>
<th>Si</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 600</td>
<td>14.0-17.0</td>
<td>6.0 max</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.15 max</td>
<td>0.5 max</td>
<td>0.015 max</td>
<td>-</td>
</tr>
<tr>
<td>FM 82</td>
<td>18.0-22.0</td>
<td>3.0 max</td>
<td>2.0-3.0</td>
<td>-</td>
<td>0.75 max</td>
<td>0.1 max</td>
<td>0.5 max</td>
<td>0.015 max</td>
<td>0.030 max</td>
</tr>
<tr>
<td>Alloy 690</td>
<td>27.0-31.0</td>
<td>7.0-11.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.05 max</td>
<td>0.5 max</td>
<td>0.015 max</td>
<td>-</td>
</tr>
<tr>
<td>FM 52</td>
<td>28.0-31.5</td>
<td>7.0-11.0</td>
<td>0.1 max</td>
<td>0.5 max</td>
<td>1.0 max</td>
<td>0.04 max</td>
<td>0.5 max</td>
<td>0.015 max</td>
<td>0.020 max</td>
</tr>
<tr>
<td>FM 52M</td>
<td>28.0-31.5</td>
<td>7.0-11.0</td>
<td>0.5-1.0</td>
<td>0.5 max</td>
<td>1.0 max</td>
<td>0.04 max</td>
<td>0.5 max</td>
<td>0.015 max</td>
<td>0.020 max</td>
</tr>
<tr>
<td>FM 52Mn</td>
<td>26.0-28.0</td>
<td>2.0-3.0</td>
<td>2.0-2.8</td>
<td>0.01 max</td>
<td>0.4 max</td>
<td>0.055 max</td>
<td>0.5 max</td>
<td>0.015 max</td>
<td>0.020 max</td>
</tr>
<tr>
<td>FM 52MSS</td>
<td>28.0-31.5</td>
<td>7.0-11.0</td>
<td>1.5-3.5</td>
<td>3.0-5.0</td>
<td>0.5 max</td>
<td>0.03 max</td>
<td>0.5 max</td>
<td>0.015 max</td>
<td>0.020 max</td>
</tr>
</tbody>
</table>

Studies were performed by Akashi showed that increasing Cr content greatly improves resistance to stress corrosion cracking [17]. The author proposed the Stress Corrosion Resistance Index (SCRI) as a measure of susceptibility to SCC, shown in Equation 2. SCRI values below 30 indicate significant susceptibility. Carbon is deleterious because it can form Cr-rich carbides along grain boundaries. This is reflected in its large negative coefficient in the equation. These Cr-rich carbides deplete the surrounding area of Cr, causing increased SCC susceptibility at the grain boundaries. Carbide formers such as Nb and Ta have a beneficial effect by tying up the carbon before Cr-rich carbides form.

Equation 2 - Stress Corrosion Resistance Index equation showing compositional effects on stress corrosion cracking resistance. Values below 30 indicate significant susceptibility [17].

\[
SCRI = Cr + 5 \times (Nb + Ta) + 10 \times Ti - 116.5 \times C
\]
In light of this relationship, FM52, FM52M, and FM52MSS are good candidates for resistance to PWSCC, having around 30 wt% Cr and SCRI values over 30, compared with FM82 which has 20 wt% Cr and an SCRI of around 25. Direct comparisons between FM52M and FM82 have been made with regard to SCC. Jacko et al. devised an accelerated SCC test using a doped (Cl, F, and SO$_4^{2-}$) water chemistry at 400 °C [4]. Samples were strained using a 4 point bending fixture. They found a 5 fold increase in crack initiation times in FM52M compared to FM82.
CHAPTER 3
WELDING METALLURGY OF NICKEL BASED ALLOYS

Filler metals for use in repair and construction of nuclear power plant components have been identified by the industry [1-5]. These alloys contain around 30 wt% Cr to resist PWSCC as discussed previously. Some of these alloys and their variants have been used successfully in overlays for repair, however, many times cracking is discovered during mock-ups, or found during ultrasonic inspection. This can cause delays during repair as welds have to be ground down and re-welded, costing money as the plant has to extend its shutdown time. As a result of this, extensive research has been done to determine the nature of the cracks and why they form during welding [7, 18-26].

The main types of cracking that occur in these alloy systems are either ductility dip cracking or solidification cracking. There are many factors that control the formation of these cracks, dealing with either the nature of liquid films for solidification cracking, or the nature of migrated grain boundaries for ductility dip cracking. Before discussing these cracking phenomena, it is necessary to have a background on welding metallurgy, solidification, and the types of weld metal boundaries that these cracks form on.

3.1 Regions of a Weld

Regions of a fusion weld have been defined by Savage et al. [27]. One region is the fusion zone, which consists of two sub regions, the composite region and the unmixed
zone. Other regions defined by Savage et al. are the partially melted zone, and the true heat affected zone. The fusion zone defines the region of the weld where metal has been completely melted and re-solidified. The composite region is where there has been a complete mixing of base metal and filler metal, whereas the unmixed zone consists of melted and solidified base metal that was not mixed with the filler metal. There can be a small transition region between the composite zone and the unmixed zone, where a composition gradient exists. These distinctions are particularly important for dissimilar metal welds, where the filler metal composition is drastically different from the base metal. The partially melted zone is the region next to the fusion boundary where base metal was heated between the liquidus and solidus. The true heat affected zone encompasses base metal that has undergone metallurgical reactions in the solid state.

3.2 Weld Solidification

The solidification of welds is a complex phenomenon that has many variables that influence the final microstructure and properties of the fusion zone. Virtually all weld metals are multi-component alloys, however many of the basic concepts can be described more simply using a binary eutectic system as a reference. One major factor in weld solidification is the partition coefficient, $k$. For a given composition $C_0$, $k$ is defined as the composition of solid divided by composition of the liquid. The value for $k$ can be determined at any point in the two phase region by using tie lines. This value is usually not constant, especially in multi-component systems as the solidus and liquidus lines are not straight. Each solute element will have its own value of $k$. When $k$ is less than 1, the solute will partition to the liquid, and the final liquid to solidify will be enriched in solute.
When \( k \) is greater than 1, solute will partition to the solid and the final liquid will be depleted in solute. This natural phenomenon will cause compositional gradients across various regions and boundaries in the weld that will be discussed in the next section.

Another important set of factors during weld solidification are the temperature gradient in the liquid (\( G_L \)) and the solidification growth rate (\( R \)). These factors control the solidification mode of the metal. There are 5 solidification modes, starting with plane front solidification. When the \( G_L \) is high and \( R \) is low, the solid liquid interface will be very smooth and will progress along as a plane front. Plane front solidification is not very typical in welding due to the relatively high solidification rates. This interface is unstable and usually breaks down into different morphologies, starting with cellular, progressively becoming more dendritic. Figure 12 shows this schematically. Additionally, increases of both \( G_L \) and \( R \) simultaneously will cause a similar solidification mode but a finer structure.

![Diagram](image.png)

Figure 12 - Effect of \( G_L \) and \( R \) on solidification mode [28].
In addition to $G_L$ and $R$, the composition of the alloy can play a role in the solidification mode, more specifically, when the planar growth interface becomes unstable. Chalmers has proposed the constitutional supercooling theory to describe this instability. Figure 13 shows this schematically. Due to most alloying elements having a $k$ value not equal to 1, the liquidus temperature varies with composition. Additionally, there is a solute gradient ahead of the interface, which will be described in more detail in the next section. This solute gradient sets up a gradient of liquidus temperatures ahead of the interface. If the actual temperature gradient crosses the tangent to this curve, solid is predicted to form ahead of this interface. The region where this occurs is the ‘region of constitutional supercooling’. When this happens the planar growth interface breaks down into cellular or dendritic.
3.3 Weld Metal Boundaries

There are 3 main types of boundaries in weld metals. Solidification sub grain boundaries (SSGB) exist between individual cells or dendrites that formed during solidification. As a packet of cells or dendrites grows along the <100> direction, segregation during solidification is happening on the microscopic scale. The region between these dendrites will be enriched or depleted in solute, depending on the k value for that solute. There will exist a compositional gradient across the cell or dendrite for each alloying element with k not equal to 1. This gradient can be described by the Scheil equation, see Equation 3.
Equation 3 - Scheil equation which describes the composition of the solid as a function of $k$, $C_0$, and the fraction solidified, $f_s$.

$$C_s = kC_0(1 - f_s)^{k-1}$$

If the composition goes above the solubility limit, secondary phases such as eutectics can solidify at the SSGB. It is worth noting that these SSGBs do not have a significant misorientation at the boundary, as the cells or dendrites are growing together along the $<100>$ direction.

Another boundary type is the solidification grain boundary (SGB). Grains start to solidify epitaxially from the base metal. Packets of cells or dendrites grow along the $<100>$ direction off of the existing grains. As solidification progresses, these packets will be cut off from one another as ones that are more favorably oriented to the solidification direction out compete others. Where these packets meet, grain boundaries form, with potentially significant grain misorientation. There is also macroscopic segregation that occurs at these boundaries. The composition at the boundary will be enriched or depleted of solute depending on $k$, similar to what happens at the SSGB. Eutectics may also solidify here if the composition is rich enough.

The final type of boundary is the migrated grain boundary (MGB). This type of boundary can be seen when the crystallographic part of the SGB migrates away from the compositional differences at the boundary. This typically happens on cooling or during reheating of weld metal, and is essentially a grain growth phenomenon. If some amount of eutectic forms at the end of solidification as described previously, the boundary can essentially be pinned, and prevented from migrating. Typically boundaries become quite
straight when they migrate as this lowers the free energy. This boundary straightness is important for ductility dip cracking, which will be discussed in the next section.

3.4 Solidification Cracking

Weld solidification cracking is a cracking phenomenon that occurs near the end of solidification. There are a few theories that seek to describe the phenomenon fundamentally, but not all are in agreement. It is generally accepted to be related to liquid films at solidification grain boundaries being pulled apart by stresses. These stresses can be a combination of material shrinkage due to solidification, as well as restraint due to fixturing or section thickness. The wetting angle of the final liquid to solidify also plays a role in crack susceptibility [30]. The theories proposed over the years include the Shrinkage-Brittleness Theory, the Strain Theory, the Technological Strength Theory, the Generalized Theory, and the Modified Generalized Theory. [30-34]

The Shrinkage-Brittleness Theory was proposed by Bochvar in 1947 [32]. This theory describes an effective interval of solidification below which a coherent network of solid exists in the liquid + solid region. In this region, strain can accumulate due to the bridging of the solid, and cracks can form. According to this theory, cracking can only occur in this region. It is important to note that this theory allows for crack healing if the composition forms enough eutectic, as there will be sufficient liquid present at the end of solidification before strain can accumulate.

The Strain Theory, proposed by Pellini in 1952, is similar to the Shrinkage-Brittleness Theory, as it divides solidification into two stages, except it considers a mushy stage and a film stage during solidification [31]. In this theory, cracking occurs in
the film stage, where liquid is only present at grain boundaries due to segregation of solute. This is likely closer to what happens during actual cracking, as the fracture surfaces seen in real solidification cracks do not show evidence of solid-solid bridging, but rather smooth or dendritic surfaces. However, this theory has no way to account for crack healing, which is seen in some weld metals.

The Technological Strength Theory proposed by Prokhorov takes a mechanical approach to describe cracking [34]. It defines a brittle temperature range (BTR) over which the ductility of the material is reduced due to presence of some liquid. This theory simply describes cracking as the point where the buildup of strain exceeds the ductility of the material.

The Generalized Theory proposed by Borland also uses a coherency temperature, much like the Shrinkage Brittleness theory [30]. However, more stages are considered. Stage 1 is the mushy stage, just after solidification starts. No cracking can occur in this stage. Stage 2 is the coherency range, where solid-solid bridging starts but cracks can be healed by excess liquid. Stage 3 is the critical temperature, where cracks can only be healed if the strain is low. Stage 4 is where solidification is complete and no cracks can form.

The Modified Generalized Theory proposed by Matsuda is an extension and unification of the previous theories [33]. The researchers used an in-situ high-speed camera to observe actual solidification cracks forming in a weld. Based on these observations, Stage 3 of the Generalized Theory was able to be divided into two stages, 3H (liquid film stage), and 3L (droplet stage). During Stage 3H, liquid films are present
on grain boundaries and cracks may nucleate and propagate. During Stage 3L, liquid is present in discrete droplets along the grain boundaries and cracks may only propagate. These stages are shown schematically on Figure 14.

![Schematic phase diagram showing location of stages of solidification cracking in the Modified Generalized Theory proposed by Matsuda [33].](image)

**Figure 14** - Schematic phase diagram showing location of stages of solidification cracking in the Modified Generalized Theory proposed by Matsuda [33].

### 3.5 Ductility Dip Cracking

Many face centered-cubic (FCC) materials such as nickel based alloys experience a drop in ductility at 50-70 % of their melting temperature [35]. Depending on the severity of the drop in ductility, and the severity of strains induced from welding or other thermomechanical processing, so called ductility dip cracks (DDC) may form [36]. Much like solidification cracking, there is no fundamental theory that describes the cracking
mechanism, however, much work has been done to try and improve resistance to DDC, and a handful of theories have arisen from these works.

One of the first theories to describe DDC was proposed by Rhines and Wray in 1961 [35]. They experienced cracks during hot forming of various metals, and speculated that a grain boundary shearing phenomena similar to creep rupture was at play. They found that above the recrystallization temperature, formation of new grains makes crack formation difficult.

Young et al. have proposed a precipitation induced cracking mechanism to explain DDC [26]. They have correlated the DDC temperature range to the M_{23}C_{6} precipitation range, as well as observed such carbides on fracture surfaces. They propose that the large misfit between the matrix and the carbides causes large tensile stresses to aggregate at grain boundaries. While this mechanism may aggregate DDC, this theory cannot explain DDC in highly pure materials such as Ni-200, which do not precipitate such carbides.

Some researchers have explained the cracking as a segregation and embrittlement effect. Yamaguchi et al., Matsuda, and Nishimoto, have all found that increased sulfur content aggravates DDC cracking, and related the mechanism to sulfur segregating to grain boundaries at intermediate temperatures [37-39]. However, recent work by Ramirez and Lippold showed that materials with extremely low impurity content were still susceptible to DDC, and proposed a different mechanism.

The mechanism proposed by Ramirez, Collins, and Lippold, and further corroborated by Noecker and DuPont, is related to grain boundary sliding [6, 23, 40-42].
They found that by altering the character of the grain boundaries to be more tortuous, the cracking susceptibility could be decreased. Alloys which had no second phase had extremely straight boundaries and were highly susceptible to DDC. The authors showed that by forming a eutectic at the end of solidification, boundaries can be pinned and will have a more tortuous character. However, certain eutectics can widen the solidification temperature range and cause a potential solidification cracking problem, so care needs to be taken on type and amount of eutectic forming elements.
CHAPTER 4
EUTECTICS IN HIGH CHROMIUM NICKEL BASED ALLOYS

4.1 Current Alloys and the Role of Eutectics in Crack Resistance

As previously mentioned, alloys such as FM52 and FM52M have been identified as candidates for construction and repair in certain nuclear power applications, due to their high Cr content (~30 wt%). For existing structures an overlay technique has been developed to mitigate further crack growth [2, 3]. These overlays have been evaluated for their effectiveness and are currently being used. The studies show that overlaying causes a compressive stress to develop on the existing crack tip, slowing the growth rate. They also show that if the crack does grow to the overlay weld, use of 30 wt% Cr alloys will prevent further crack growth. Since the overlay is also structural, it can bear the normal load on its own if a crack did grow all the way through the existing weld. A schematic of such an overlay is shown in Figure 15.
While FM52 eliminated PWSCC issues, it was found to be susceptible to ductility dip cracking [6]. Nissley and Lippold developed the Strain to Fracture (STF) test using the Gleeble thermo-mechanical simulator to assess DDC susceptibility [43]. This test allows precise control of strain and temperature. The test involves making a spot weld on a dog-bone shaped sample and straining at temperature in the Gleeble. The spot weld creates a weld metal microstructure with grain boundaries oriented at various angles to the direction of strain. The sample is then checked for cracks under a binocular microscope. In this way, a threshold strain for cracking can be determined and plotted versus temperature. Nissley and Lippold further propose comparing alloys at 950 °C, the temperature where most alloys have their ductility minimum. Some alloys of interest are plotted in Figure 16. The numbers on the figure are the number of cracks found at the applied strain. The horizontal lines represent the threshold strain to fracture.
It can be seen that FM52 is quite susceptible to DDC due to its low threshold strain for cracking. Conversely, alloy FM52MSS has good resistance to DDC, its threshold strain is 10 %. Nissley and Lippold propose that the extra Nb in this alloy, which forms a eutectic at the end of solidification, ties up the grain boundaries so that they are tortuous and cannot migrate at intermediate temperatures. Without sufficient eutectic phase present at the grain boundaries, grain boundaries become very straight and can easily slide relative to each other. Figure 17 shows how grain boundary precipitates and tortuosity affects DDC resistance.
While increases in Nb help with DDC resistance, they can be detrimental to solidification cracking resistance [7]. As previously discussed, a generally accepted theory of solidification cracking involves the presence of both residual stress and liquid films at the end of solidification [30, 33]. When residual stresses, which build up from thermal shrinkage, overcome the strength of liquid films, cracks will form. There are many metallurgical factors that influence crack susceptibility. Solidification temperature range (STR) is important, because it is related to the width of the mushy zone, which is the region where solidification cracks will form in a weld. The morphology of the liquid present at the end of solidification is also important [44]. Nakata and Matsuda investigated the effect of wetting angle of the final liquid to solidify on cracking resistance. They found that when liquid wets out along grain boundaries, cracking was
more severe, as shown in Figure 18. Metallurgical factors such as impurity concentration or eutectic formation are important, as they can affect both the STR and the wetting characteristics of the final liquid to solidify.

![Figure 18 - Left, effect of grain boundary liquid wetting on solidification crack susceptibility [44]. Right, schematic showing the mechanism [45].](image)

Specifically for Ni-base alloys, there are a few key factors in determining solidification crack susceptibility. DuPont et al. have correlated the solidification temperature range (STR) to crack susceptibility using the Transvarestraint test [46]. They found alloys with a higher STR had higher crack susceptibility, as shown in Figure 19. DuPont has also investigated metallurgical factors that influenced the solidification microstructure in Nb-bearing Ni-base superalloys [47, 48]. Increasing Nb content caused more eutectic constituent to form. This eutectic can either be $\gamma$/NbC or $\gamma$/Laves, which starts to form around 1350°C, and 1250°C, respectively. Increasing C caused the eutectic to be mostly $\gamma$/NbC. Increasing Fe and Si promoted formation of $\gamma$/Laves at the expense of $\gamma$/NbC. This difference in eutectic formation can also be seen in Figure 19, where two distinct
groups of alloys can be observed. The alloys with a STR around 75°C only formed γ/NbC eutectic, whereas the alloys with a STR around 175°C formed some combination of both eutectics. Thus, it can be concluded that the formation of γ/Laves eutectic is detrimental to solidification cracking susceptibility because it increases the STR by about 100°C when it forms.

![Graph showing relationship between STR and maximum crack length](image)

Figure 19 - Relationship between STR determined by DTA and Maximum Crack Length (MCL) in the Transvarestraint test [46].

Since γ/Laves eutectic needs to be avoided, it is useful to know what alloying elements play a role in promoting its formation. As mentioned previously, DuPont established that Fe and Si promote the formation of Laves phase [48]. Work done by Chang found that similar to Fe, Cr promotes Laves phase on solidification [49]. These factors may explain the relatively good weldability of FM82 vs. FM52MSS. Both of these alloys have around 2.5 wt% Nb. FM82 is fairly resistant to DDC most likely due to the formation of a fair amount of γ/NbC eutectic [43]. FM52MSS is very resistant to DDC because of formation
of large amounts of γ/NbC and γ/Laves, but is quite susceptible to solidification cracking [7]. The extra (30 wt% versus 20 wt%) Cr in FM52MSS promotes γ/Laves, which expands the STR and increases the cracking susceptibility.

Since increases in Fe content will promote γ/Laves, this can also present a problem with dilution. DuPont also found Fe decreased the partition coefficient, k, of Nb, a measure of the segregation that happens during solidification [47]. This decrease causes Nb to segregate more strongly to the solidification grain boundaries, increasing the amount of eutectic constituent that forms. Studies have been performed by Hope et al. that directly measured the crack susceptibility as a function of dilution [50]. A direct positive correlation between dilution and cracking susceptibility was observed.

4.2 Alternatives to Niobium

It is evident that no matter what the level of Nb in high-Cr nickel based alloys, such alloys can be susceptible to either solidification cracking or ductility dip cracking. These alloys need a eutectic to form to prevent DDC, and a narrow STR to prevent solidification cracking. Based on the previous research, this is just not possible with Nb, due to the low melting Laves eutectic that forms. As such, alternative eutectic forming elements need to be investigated.

4.2.1 Tantalum Rich Eutectics

Baeslack et al. investigated substituting Ta for Nb in Inconel 718 weld metal [51]. They performed Spot-Varestraint and Mini-Varestraint tests on heats of modified and unmodified 718. Gleeble heat affected zone (HAZ) tests were also performed to
determine the liquation temperature. The authors found improvement in liquation and solidification cracking for the alloys with Ta instead of Nb, shown in Figure 20. They attributed this to the higher liquation temperature of the Ta-rich γ/Laves eutectic relative to the Nb-rich γ/Laves eutectic. The liquation temperatures of the Laves phases were 1225°C and 1175°C, respectively.

![Figure 20](image)

Figure 20 - Total crack length versus augmented strain in the Mini-Varestraint test for standard 718 and Ta-modified 718 alloys [51].

### 4.2.2 Hafnium Rich Eutectics

Hafnium is another potential replacement for Nb in these high Cr nickel base alloys. Historically, Hf has been added to cast superalloys to modify the grain boundary carbide morphology [52]. MC carbides form upon solidification and are generally Hf-rich [53]. A study by Dmitrieva et al. found the γ/HfC eutectic to solidify at 1330°C [54]. Furthermore, a study by Nash and West found no evidence of Laves phase in a ternary Ni-Cr-Hf system [55]. Nash and West melted samples of varying composition and
determined the solidus temperature, as well as phases present by XRD. They found two eutectic phases that could solidify, shown in Figure 21. The first was the binary Ni-Hf eutectic, Ni$_5$Hf, which solidified at 1227°C. The second, Ni$_7$Hf$_2$, formed when 30 at% Cr was present, and also formed at a higher temperature of 1288°C. This is promising because when carbon is exhausted on solidification, other eutectic phases may form, such as Laves in systems containing Nb or Ta. The Ni$_7$Hf$_2$ phase, which could form when Hf is present and C has been exhausted, has a much higher eutectic temperature than both the Nb or Ta-rich Laves eutectics. This is expected to improve solidification cracking resistance over Nb or Ta eutectics by narrowing the solidification temperature range.

![Figure 21 - Schematic representation of primary solidification regions in Ni-rich portion of Ni-Cr-Hf ternary system [55].](image)

**4.2.3 Effect of Hf on DDC Resistance**

Some previous work has been done by Unfried and Ramirez on the influence of Hf and Mo additions to high Cr Ni-based alloys to determine their effect on DDC resistance [56-
The authors found that both Mo and Hf increased the resistance to DDC in these alloys. They added 0.36 wt% Hf and found that numerous HfC particles formed at the end of solidification that contributed to grain boundary tortuosity. The effect of Mo was attributed to the increase in stacking fault energy of the matrix at high temperatures, affecting dislocation mobility. However, the authors studied Hf additions in an alloy that also had around 2.5 wt% Nb, and they also observed Nb rich Laves phase in interdendritic regions which may poorly affect solidification cracking resistance.

4.2.4 Effect of Molybdenum

A number of researchers have found a beneficial effect of around 4 wt% Mo on DDC resistance [6, 59, 60]. The exact reason for this is not quite clear, but recent published work by Afonso theorizes that the strain hardening effect of the segregated Mo at the grain boundaries might play a role. It is also important to note that Afonso also found that while Mo segregated to grain boundaries during solidification, it was rejected by the eutectic carbides that form, and was present only in the matrix. This has implications for the wetting experiments performed in this study, and will be discussed later.

Additionally, recent work at OSU by Wheeling has shown that Mo may have a beneficial effect on solidification cracking resistance [61, 62]. The beneficial effect however, was only realized in alloys containing 6 wt% Nb, and not 4 wt% Nb. This can be seen in Figure 22, which shows the cracking response as determined by the Cast Pin Tear Test (CPTT) for different Nb and Mo levels. Upon investigation of the pins with 6 wt% Nb and 4 wt% Mo, extensive crack healing was found, as shown in Figure 23. This was
hypothesized to be related to a wetting effect, which is investigated and discussed later in this work.

Figure 22 - Cracking data from the CPTT showing the healing effect of Mo at higher levels of Nb [61].
Figure 23 - SEM micrograph of a 6Nb-4Mo sample showing extensive crack healing [62].
CHAPTER 5

OBJECTIVES

The need for the nuclear industry to use Ni-based alloys containing 30 wt% Cr to mitigate primary water stress corrosion cracking in repair of existing power plants, and construction of new ones, has led to the development of many alloys with varying Nb contents that are either susceptible to ductility dip cracking (low Nb) or solidification cracking (high Nb). The nature of the eutectic reaction in these Nb-bearing high Cr alloys makes it difficult to eliminate one cracking type without exacerbating the other. As such the main goal of this work was to identify alternative eutectic forming elements to Nb, and optimize a composition that could be used to mitigate both forms of cracking. The initial boundary conditions were to maintain the solidification temperature range below 150°C while assuring that a minimum of 2 vol% eutectic is present to control solidification cracking and ductility dip cracking, respectively. Based on some of the results of this work, an additional task was added to better understand how wetting of eutectic liquids at the end of solidification might play a role in solidification cracking. Specifically, the objectives of this work are as follows:

1. Through a thorough literature review and computational thermodynamic simulations, identify potential eutectic forming elements that can be used as a replacement for Nb in 30 wt% Cr Ni-based alloys.
2. Using a combination of computational and experimental techniques, along with design of experiment methodology, determine elemental effects of eutectic forming elements along with C, Fe, and Mo on the solidification behavior.

3. Based on the results from the design of experiment methodology, optimize compositions that should be resistant to solidification cracking and ductility dip cracking, that can be recommended for commercial wire production, and later further full-scale weldability testing.

4. Quantify the wetting behavior of relevant eutectics to determine how liquid wetting on the grain boundary influences solidification cracking resistance.

5. Propose a theory on how wetting behavior of eutectics plays a role in solidification cracking and crack healing phenomena.
6.1 Development of Optimized Filler Metal Composition

The first part of the work performed attempted to identify compositions that use alternative eutectic forming elements to Nb. Based on the review of the literature, Ta and Hf, and Mo were selected as potential candidates. Varying amounts of these elements were added to a base composition of Ni-30Cr (wt%). The Fe content was also varied slightly to determine how dilution with steels might play a role on eutectic formation. A set of compositions containing Nb was also tested as a baseline.

A design of experiment methodology (DOE) was used to generate a set of compositions to test that would be able to determine the elemental effects on solidification temperature range (STR) and the fraction eutectic measured. These responses were selected to represent cracking susceptibility: STR has been shown to be a predictor of solidification cracking susceptibility, and a sufficient level of eutectic can prevent ductility dip cracking.

Initially, a range of compositions was chosen and simulated using the Scheil module within Thermo-Calc®, and entered into the DOE model. Based on these results, compositions were selected for experimental testing also using the DOE. Finally, an optimized composition was generated using the data. This work on optimization of a
filler metal composition was performed in conjunction with Eric Fusner, a Master’s student at The Ohio State University. The author and Fusner have published a paper with much more detail on this procedure which is attached in Appendix 1 [19]. Additionally, the Master’s thesis of Fusner has more detail on the statistical parts of this work [63]. As such, this technique will be covered briefly in the following sections.

6.1.1 Design of Experiment Methodology

Throughout testing, many different DOE software packages were used to generate datasets and analyze results; however Design Expert® was used in the final analysis due to its robust graphical capabilities and ease of use [64]. Most DOE software packages utilize similar statistical formulas and routines so similar results can be obtained regardless of the software used.

Since Ta and Hf were identified as potential elements to replace Nb, three ‘groups’ of alloys were tested separately, each containing either Ta, Hf, or Nb. A group containing Nb was added to be used as a baseline, since there is already considerable research done on Nb-bearing high Cr Ni-based alloys. Each group contained Ni, Cr, Fe, C, Mo, and X, where X was either Ta, Hf, or Nb. Cr was held at 30 wt%, while the other elements were varied. Table 2 shows the amount the elements were varied within each group. These ranges were input into the DOE software, and a response surface model was chosen. This type of model allows for some curvature in the responses as a function of composition, while keeping the number of experimental runs lower than a full factorial design. After experiments are run, the results, or responses, are put back into the software for analysis. The software can then determine which factors are significant, and what
effect they have on the responses. An equation that predicts the response as a function of composition can then be generated.

Table 2 - Nominal levels of elements varied in the DOE.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Nb, Hf, or Ta</th>
<th>C</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level (wt%)</td>
<td>Bal.</td>
<td>30</td>
<td>8-18</td>
<td>0.5-2</td>
<td>0.04-0.08</td>
<td>0-4</td>
</tr>
</tbody>
</table>

This technique was first carried out using computational thermodynamic modeling as the ‘experiment’. Since this saves time and material, many experiments can be run and a general idea of elemental effects on STR and fraction eutectic can be determined. These results were used to verify that the composition ranges were reasonable before proceeding with experimental validation by button melting.

6.1.2 Computational Modeling

The Scheil solidification module within Thermo-Calc® was used to calculate STR and the fraction eutectic for various alloy compositions as defined by the DOE software. After some preliminary tests, the TCNi5 Database was chosen to be used for all calculations as it contained phases predicted to form in the Ni-Cr-Hf system that don’t form in the Ni-Cr-Ta or Ni-Cr-Nb system. The Scheil equation predicts the solute redistribution during solidification. It has been shown to accurately model solidification across dendrites [65, 66].

When combined with a thermodynamic software package such as Thermo-Calc®, the solidification temperature range as well as the fraction eutectic can be determined for
multi-component systems. The results from the computational part of the DOE are then used to create a narrower set of compositions to test experimentally.

Thermo-Calc® was also used to generate pseudo-binary phase diagrams of Ni-30Cr-8Fe alloys with either Hf, Ta, or Nb. Fe was fixed at 8 wt%, as is the nominal level in commercial alloys of the same type. Two phase diagrams were calculated for each eutectic former. All of the eutectic forming elements will first form an MC (M = Hf, Ta, or Nb) carbide eutectic until carbon is exhausted. One such MC carbide eutectic diagram was calculated for each carbide forming element. Nb and Ta are known to form a Laves phase (M₂(Ni,Cr,Fe)) eutectic when carbon has been exhausted and there is sufficient Nb or Ta in the liquid at the end of solidification. Hf will form Hf₇Ni₂ under similar conditions. Separate pseudo-binary diagrams were developed for these eutectics as well.

6.1.3 Experimental Validation

Based on the elemental effects determined by the computational DOE, a narrower set of compositions is chosen for experimental testing. This consists of casting a small (~20 g) button of material at the desired composition. A novel thermocouple plunging technique is performed to determine the actual solidification temperature range. The resulting microstructure is then observed optically to determine the phase fraction of eutectic constituent present.

6.1.3.1 Button Melting

To create alloys used in the study, a button melting technique was used. Figure 24 shows the button melting device, which consists of a tungsten arc torch over a water cooled
copper hearth. The glass chamber is purged with argon five times before use. Material to be melted is placed on the hearth and melted with a $\frac{1}{4}$” arc length and 200 A of current. If multiple components are being melted together, or alloys are being mixed, the sample is flipped over post solidification and re-melted several times to ensure homogeneity. When creating alloys used in the study, high purity (> 99.9 %) pure metals were weighed out on a high precision balance. Masses were controlled to within 1 % of the target mass. The target mass was typically 20 g, unless buttons were to be used for Cast Pin Tear Testing, in which case masses ranged from 10-16 g. Raw materials were ultrasonically cleaned in alcohol then dried prior to melting. This technique produces a cast microstructure with dendrite arm spacing of 30-50 microns, depending on button mass. In some cases with the Hf-bearing alloys, considerable oxidation was seen on the surfaces of the buttons. Luskin has measured the oxygen level in the button melting chamber and found to be only 12ppm after purging five times [67]. This is quite low; however Hf is known to have a very high affinity for oxygen. Since the oxides float to the surface during button melting and cast pin tear testing, it was a minor issue in this investigation; however it could be a more serious issue during actual welding.
6.1.3.2 Phase Transformation Analysis

To determine the actual solidification temperature range of created compositions, a novel thermocouple plunging technique was used in combination with a thermal analysis technique. A schematic of the thermocouple plunging technique is shown in Figure 25. A 20 g button of desired composition is subjected to a tungsten arc for 4 seconds at 250 A. The arc length is 2 mm, and argon shielding is used. Immediately upon extinction of the arc, a type C thermocouple is plunged into the center of the resulting spot weld pool. The thermal history is acquired at 1 kHz from this point down to room temperature. The data is then analyzed by a novel thermal analysis technique.
The thermal analysis technique, Single Sensor Differential Thermal Analysis (SS-DTA®), was developed at The Ohio State University by Alexandrov and Lippold [68, 69]. This technique is similar to a conventional DTA technique, except that a reference sample is not used. A special software algorithm uses the Rosenthal equation along with the acquired thermal cycle to generate a reference curve. In this way, in situ determinations of phase transformations can be made during welding cycles or heat treatments, with cooling rates much faster than what can be achieved during normal DTA. Figure 26 shows a representation of a cooling curve acquired during the plunging technique described in Figure 25, with the reference curves plotted on the same graph. The software then generates a separate plot of the differences between the two curves, so that the relevant transformation temperatures can be determined accurately. This
technique has been used previously to determine the STR of high Cr nickel based alloys by Alexandrov et al., and results correlated well with industry cracking data [7].

![Thermal History](image)

Figure 26 - Representation of acquired cooling curve and reference curves generated by SS-DTA\textsuperscript{®} that assist in determining transformation temperatures.

6.1.3.3 Metallographic Image Analysis

All samples that were subjected to the thermocouple plunging technique previously described were sectioned, mounted, and polished through 0.05 µm colloidal silica. They were then electrolytically etched with a 10 % chromic acid solution at 5 V for 5-15 seconds. Figure 27 shows a macrograph of a typical button sample that has undergone the thermocouple plunging experiment. Optical micrographs were taken in random locations in the spot weld at 500x. These images were converted to binary and black pixels were counted using the analysis software, ImageJ\textsuperscript{®} [70]. This allows for an
area fraction of eutectic constituent to be determined for each sample. Area fractions were assumed to approximate to volume fraction.

Figure 27 - Macrograph of a typical button sample with spot weld from thermocouple plunging technique clearly visible.

The samples containing Hf were not readily etched by the chromic acid or other conventional means, which made eutectic analysis difficult optically. Therefore, samples were analyzed in the un-etched condition using the backscatter mode of the SEM. The high Hf content of the eutectics allowed for good Z-contrast. Images were taken randomly from the spot weld at 1000x, and analyzed using ImageJ®. Figure 28 shows an example of the binary conversion used by ImageJ®, in this case on an SEM image. Values were averaged and the resulting eutectic fractions were used in DOE analysis.
6.1.4 Optimization of Composition via Genetic Algorithm

To determine an optimized composition based on the results obtained from thermo-couple plunging and image analysis, a genetic algorithm was employed. This software was custom written at The Ohio State University by Professor Ted Allen and Sayak Roychowdhury, a graduate student at the time. The software allows for multiple objectives to be optimized simultaneously, based experimental results from the DOE. A genetic algorithm takes an evolutionary approach to optimization. It starts with a random population of input variables which, in this case, are different chemical compositions. The response variables are then computed using the data and regression equations determined from the DOE; these are STR and fraction eutectic for this work. Input variables that yield responses close to the desired values are then used to ‘breed’ a new generation of input variables. Some ‘mutation’ or randomness is added with each generation. The number of generations can be selected by the user, and the end result is one or more optimum inputs which give the desired response. Genetic algorithms are widely used in statistics and optimization, and the reader is referred to read a widely referenced book by Goldberg for more information on their inner workings [71].
6.2 Weldability Testing

To evaluate the weldability of select compositions of material, weldability tests that can accommodate limited quantities of material were chosen. To evaluate solidification crack susceptibility, the Cast Pin Tear Test (CPTT) was used. To evaluate ductility dip cracking susceptibility, a slightly modified Strain to Fracture test was used. It would have been desirable to also perform the Transvarestraint test, or an unmodified Strain to Fracture test, however these tests require a significant amount of filler wire to create V-groove welds that are used for sample coupons.

6.2.1 Cast Pin Tear Testing

After select compositions containing either Hf, Ta, or Nb were identified, further weldability testing was performed using the Cast Pin Tear Test (CPTT). This solidification cracking susceptibility test was originally developed by Hull in the late 1950s [72]. The basic premise involves casting a charge of molten material into a pin shaped copper mold. This mold is shaped such that internal stresses can build up in the material during solidification and cooling. The lengths of the molds can be varied, which varies the level of stress that builds up. Materials that are susceptible to solidification cracking will crack at shorter mold lengths than more resistant alloys. In this way solidification cracking susceptibility of different alloys can be compared. It has since been modified by Luskin and Alexandrov at The Ohio State University [12, 67]. The new design incorporates an induction levitation coil to heat and melt charges of material. Figure 29 shows a schematic of the test setup. The design differs from Hull’s design in several ways. An optical pyrometer has been incorporated that can precisely control the
casting temperature, this allows for consistent levels of superheat above the liquidus temperature. The mold material has also been changed to a UNS C63000 alloy, which causes the cooling rate to be slower and closer to rates experienced during welding. The mass of the samples varies from 10-16 g, depending on mold length. More detail on specific parameters used can be found in [67].

![Figure 29 - Schematic of the updated Cast Pin Tear Testing Device developed at OSU [67].](image)

A collection of data from the CPTT is shown in Figure 30. The X-axis shows the various mold lengths, with increasing mold length causing more strain on solidification. The Y-axis shows the maximum cracking response, as a percentage of the circumference. Three or more pins are cast at each length and the pin with the most cracking is recorded.
Reporting of maximum cracking instead of average cracking has been shown to correlate better with industry experience of crack susceptibility by Przybylowicz [73]. Alloys which lie more to the left are more susceptible to cracking, while alloys more towards the right are more resistant. Particularly, the threshold for cracking, defined as the longest pin length where no cracking is observed, is used for comparing alloy susceptibility.

![Diagram showing cracking susceptibility](image)

Figure 30 - CPTT data from some commercially available alloys to demonstrate how crack data is interpreted. Adapted from Przybylowicz [73].

**6.2.2 Strain-to-Fracture Test**

The Strain-to-Fracture (STF) test was developed by Nissley and Lippold to simulate and rank DDC susceptibility in alloys [43]. The test uses a dogbone sample that is either machined out of an all weld metal coupon, or is machined from a V-groove coupon such that the reduced gauge section is comprised entirely of weld metal. A spot weld is made on the gauge section with carefully controlled parameters specified by Nissley. The
purpose of this spot weld is to develop a uniform microstructure in the sample (eliminating local variations that may occur in multipass welds), as well as create grain boundaries that are oriented at all angles with respect to the loading direction. The sample is then placed in the Gleeble, where it is heated to 950°C, held for 10 s, and pulled to a pre-determined strain level at a stroke rate of 0.06 cm/s. The sample is then allowed to free cool, and is inspected for DDC cracks. The spot welding and Gleeble test parameters have recently been investigated for robustness by Kreuter [74]. Kreuter used a DOE matrix of parameters and found that the parameters put forth by Nissley produced clear differences in alloy susceptibility, and were tolerant to slight variations.

Due to limitations on material, dogbone samples could not be machined from full size weld coupons. To overcome this limitation, a novel sample design was used, which has been previously demonstrated to be effective by Sowards [75]. Samples of Alloy 690 were machined to the standard STF dogbone geometry. A conical hole was drilled into the face of the gauge section, where small buttons of desired composition were placed. This was then manually melted using a GTAW torch. The surface was ground flat, and the standard STF spot weld procedure was then carried out. Dilution was calculated to be less than 20 % by examining weld cross sections of pre-ground samples. Figure 31 shows a typical STF sample and the steps used to create it.
6.3 Phase Extraction Technique

To determine the eutectic phases present in the alloy systems under study, a phase extraction technique was performed. The ASTM standard E963-95, which describes electrolytic extraction of secondary phases in Ni and Ni-Fe superalloys, was followed [76]. Samples were made using the button melting technique previously described. During the technique, the matrix of the sample is dissolved and the secondary phases remain as solids in the solution. The resulting solution is then filtered and analyzed using X-ray diffraction. Buttons and the filter are weighed before and after the experiment so that a mass phase fraction can be calculated. The electrolytic cell set-up is shown in Figure 32. The ASTM procedure was followed closely; the only modification was the use of a vacuum filtering system and a 0.2 µm PTFE filter.
6.4 Eutectic Wetting Angle Tests

During weldability testing of optimized compositions, large differences were found in cracking susceptibility of some alloys that did not correlate with differences in solidification range. This was speculated to be related to differences in wetting angles of the eutectics liquids. More on this theory will be discussed in the results section. To evaluate differences in wetting of eutectic liquids, a wetting angle experiment that is similar to a standard sessile drop test was developed and performed using eutectic compositions relevant to this study.

Using the pseudo-binary diagrams calculated in Thermo-Calc®, the compositions of the lowest temperature, or last to solidify, eutectic liquids were determined. These compositions are shown in Table 3. Mo was also added to one composition as previous research has shown beneficial effects of Mo, it was not known if this could possibly be related to weldability [6, 59, 60]. Since the wetting of the eutectic is taking place on a
grain boundary, an Alloy 600 substrate was used, since it is close to the alloy matrix composition. While Mo segregates during solidification to the dendrite boundaries, it is not clear whether Mo ends up as part of the eutectic, or stays in the matrix. As such, another substrate, Alloy C22 was chosen as it has a similar composition to Alloy 600, and contains 13 % Mo. Compositions of the substrates are listed in Table 4.

Table 3 - Compositions of eutectic constituents as determined by Thermo-Calc® simulations for use in button wetting experiments.

<table>
<thead>
<tr>
<th>Eutectic</th>
<th>Ni</th>
<th>Cr</th>
<th>Nb, Hf, or Ta</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb-Laves</td>
<td>53</td>
<td>24.5</td>
<td>22.5</td>
<td>0</td>
</tr>
<tr>
<td>Nb+Mo-Laves</td>
<td>48</td>
<td>22</td>
<td>22</td>
<td>8</td>
</tr>
<tr>
<td>Ta-Laves</td>
<td>45</td>
<td>24</td>
<td>31</td>
<td>0</td>
</tr>
<tr>
<td>Ni$_2$Hf$_2$</td>
<td>58</td>
<td>15</td>
<td>27</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4 - Nominal compositions (in wt%) of substrates used in button wetting experiments.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>C</th>
<th>Mo</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 600</td>
<td>Bal.</td>
<td>17</td>
<td>8</td>
<td>&lt;0.15</td>
<td>0</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Alloy C22</td>
<td>Bal.</td>
<td>22</td>
<td>3</td>
<td>&lt;0.01</td>
<td>13</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>

Several techniques were tried when attempting to melt the eutectic on to the substrate. Furnace and vacuum furnace techniques were attempted, but oxidation proved to be too much of a problem, even when forming gasses were used. It was also difficult to know when the sample melted. Heating well above the liquidus temperature of the eutectic was undesirable, as wetting angle is a strong function of temperature above the melting point, and the eutectics all had different melting temperatures. An arc melting technique was finally settled on. Small 1 g buttons were created according to compositions in Table 3.
They were placed on top of a 1 x 1 x ¼” substrate, which had been ground to 600 grit finish and cleaned with ethanol. The 1 g button was placed on the substrate as shown in Figure 33. This was placed in the button melter, which was purged with argon. A 100 A arc was struck over the button, with an arc length of 2 mm. The arc was extinguished manually as soon as the 1 g button was melted and wet onto the substrate.

![Figure 33 - Schematic of button wetting experiment.](image)

The sample was then observed with a KEYANCE 3-D optical microscope at 100x. This microscope generates a 3-D image by focusing through the Z direction in 5 µm increments, stitching together the areas that are in focus. The contact angles can then be measured accurately in the resulting 3-D micrograph. Each sample was repeated three times, and measured in 3 random locations around the circumference of the button. An example of the 3-D image results is shown in Figure 34. While this technique does not simulate the presence of two solid interfaces at the grain boundary, it produces clear differences in wetting angles, which can be used to compare the wettability of different
eutectics on different substrates. More on the wetting angle and how it relates to surface tension, and potentially crack susceptibility will be discussed in Chapter 10.

Figure 34 - KEYANCE Microscope setup and resultant 3-D image of wetting angle.

6.5 Characterization Techniques

Throughout this study, a number of characterization techniques were used to evaluate microstructural features and determine the type and distribution of eutectic phases present. This section will briefly discuss the equipment and methodology used throughout.

6.5.1 Metallography

To prepare samples for optical and scanning election microscopy, buttons, or other welded samples were cross sectioned and mounted in conductive Bakelite. Samples were ground with SiC papers from 240-800 grit, and then polished with diamond compound from 9 \( \mu \text{m} \) to 1 \( \mu \text{m} \). A final vibratory polish was performed using 0.05 \( \mu \text{m} \) colloidal silica.
on a Buhler Vibromet. Samples were inspected in both the etched and unetched condition. Etching was performed electrolytically, at 5 V with a 10 % chromic acid solution for 2-10 seconds. The sample was the cathode and a stainless steel foil was used as the anode.

6.5.2 Optical Microscopy

Optical micrographs were taken with an Olympus GX-71 microscope. Magnifications from 12.5x to 1000x were used. In some cases, a differential interference contrast (DIC) filter was used. This provides extra contrast in the form of color differences based on topographical differences in the sample. This technique combined with etching sometimes provided greater detail in micrographs.

6.5.3 Scanning Electron Microscopy

Scanning electron micrographs were taken using a Philips XL-30 ESEM. Excitation voltages ranged from 10-20 keV. In some cases, energy dispersive spectroscopy (EDS) was performed to obtain compositional information. X-Rays were collected with an EDAX brand silicon drift detector.

6.5.4 Transmission Electron Microscopy

Transmission electron microscopy (TEM) was used to assist in identifying phases in the Hf-bearing alloys. TEM samples were prepared from the spot weld regions of buttons using a Helios 600 dual beam FIB/SEM system. The TEM samples were then analyzed on a Philips CM-200 microscope operating at 200 kV. Selected area diffraction patterns were then taken from the eutectic regions.
6.5.5 X-Ray Diffraction

X-Ray diffraction was also used to assist in determining eutectic phases present in alloys.

Filters from the phase extraction technique outlined previously were placed in a Rigaku Smart Lab XRD. The X-ray source voltage was 30kV, with a current of 20mA.

Continuous 2θ scans were made from 20-80° over a 20 minute scan time.
CHAPTER 7

OPTIMIZATION OF FILLER METAL COMPOSITIONS VIA
COMPUTATIONAL AND EXPERIMENTAL TECHNIQUES

7.1 Introduction

The first step of the project was to identify the elemental effects of various elements on solidification behavior. Before deciding to investigate Hf and Ta as alternatives to Nb, pseudo-binary phase diagrams were constructed with Thermo-Calc®. This allowed the determination of terminal eutectic temperatures, which gives an estimate of the solidification temperature range.

The DOE software generated a set of compositions based on desired ranges defined previously in Table 2. The compositions generated for testing by the software are shown in Table 5. These compositions were then simulated with the Thermo-Calc® Scheil module, to obtain fraction eutectic and solidification temperature range values. Buttons of these compositions were created using the button melter. More detail on the results is outlined in Appendix A. Major results will be discussed in the following sections, which consist of regression equations that can be used in optimization, as well as graphs that help visualize compositional influences. It is important to note that throughout this chapter, the target volume fraction eutectic for an ideal alloy was chosen to be 2 vol%. This was chosen based on image analysis of a precursor alloy to FM52MSS.
heats tested by Lippold and Nissley [6]. They showed that this alloy has good resistance to DDC, due to the eutectic that forms at the end of solidification causing tortuous migrated grain boundaries as a result of additions of Nb and Mo. For solidification cracking, past data of Transvarestraint and Cast Pin Tear Test data were analyzed [7, 47, 48, 77]. Alloys which were quite resistant to solidification cracking had solidification temperature ranges less than 150°C.

Table 5 - Compositions (wt%) generated by DOE software for elemental effects study.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>C</th>
<th>X*</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-1,2</td>
<td>Bal.</td>
<td>30</td>
<td>8</td>
<td>0</td>
<td>0.02</td>
<td>2.0</td>
</tr>
<tr>
<td>X-3,4</td>
<td>Bal.</td>
<td>30</td>
<td>8</td>
<td>0</td>
<td>0.06</td>
<td>0.5</td>
</tr>
<tr>
<td>X-5,6</td>
<td>Bal.</td>
<td>30</td>
<td>8</td>
<td>4</td>
<td>0.02</td>
<td>1.25</td>
</tr>
<tr>
<td>X-7,8</td>
<td>Bal.</td>
<td>30</td>
<td>8</td>
<td>4</td>
<td>0.04</td>
<td>0.5</td>
</tr>
<tr>
<td>X-9,10</td>
<td>Bal.</td>
<td>30</td>
<td>8</td>
<td>4</td>
<td>0.06</td>
<td>2.0</td>
</tr>
<tr>
<td>X-11,12</td>
<td>Bal.</td>
<td>30</td>
<td>13</td>
<td>0</td>
<td>0.02</td>
<td>0.5</td>
</tr>
<tr>
<td>X-13,14</td>
<td>Bal.</td>
<td>30</td>
<td>13</td>
<td>0</td>
<td>0.06</td>
<td>2.0</td>
</tr>
<tr>
<td>X-15,16</td>
<td>Bal.</td>
<td>30</td>
<td>13</td>
<td>2</td>
<td>0.04</td>
<td>1.25</td>
</tr>
<tr>
<td>X-17,18</td>
<td>Bal.</td>
<td>30</td>
<td>13</td>
<td>4</td>
<td>0.02</td>
<td>2.0</td>
</tr>
<tr>
<td>X-19,20</td>
<td>Bal.</td>
<td>30</td>
<td>13</td>
<td>4</td>
<td>0.06</td>
<td>0.5</td>
</tr>
<tr>
<td>X-21,22</td>
<td>Bal.</td>
<td>30</td>
<td>18</td>
<td>0</td>
<td>0.02</td>
<td>2.0</td>
</tr>
<tr>
<td>X-23,24</td>
<td>Bal.</td>
<td>30</td>
<td>18</td>
<td>0</td>
<td>0.06</td>
<td>0.5</td>
</tr>
<tr>
<td>X-25,26</td>
<td>Bal.</td>
<td>30</td>
<td>18</td>
<td>2</td>
<td>0.06</td>
<td>2.0</td>
</tr>
<tr>
<td>X-27,28</td>
<td>Bal.</td>
<td>30</td>
<td>18</td>
<td>4</td>
<td>0.02</td>
<td>0.5</td>
</tr>
<tr>
<td>X-29,30</td>
<td>Bal.</td>
<td>30</td>
<td>18</td>
<td>4</td>
<td>0.04</td>
<td>2.0</td>
</tr>
<tr>
<td>X-31,32</td>
<td>Bal.</td>
<td>30</td>
<td>18</td>
<td>4</td>
<td>0.06</td>
<td>1.25</td>
</tr>
</tbody>
</table>

* X = Hf, Ta, or Nb-bearing samples, respectively.

7.2 Pseudo-Binary Phase Diagrams

To assess the feasibility of Hf and Ta eutectic forming elements relative to Nb in high Cr nickel base alloys, Thermo-Calc® was used to create pseudo-binary phase diagrams. These diagrams can give an idea of the terminal eutectic temperatures for each eutectic
possible in the system. Depending on the eutectic, the simulation conditions were slightly different. All simulations used a Ni-30Cr-8Fe fixed composition. Nb, Ta, and Hf all form MC carbides as a eutectic, so for these diagrams M and C were varied in a 1:1 atomic ratio along the X axis. For Nb and Ta, it is known that a Laves ((Ni,Cr)₂M) type eutectic forms, so the X axis is just Nb or Ta in these cases. For Hf, Nash and West found that for a Ni-30 at% Cr system, a Ni₁Hf₂ eutectic formed. In this case Hf is increased along the X axis. Figure 35 shows the results for Nb-bearing Ni-30Cr-8Fe alloys. These values are in good agreement with data from DuPont that shows STR for alloys that form either NbC or Laves as their terminal eutectics [47, 48]. It also shows how much the solidification temperature range is expanded when carbon is exhausted, and Laves becomes the terminal eutectic, as the terminal eutectic temperature drops from ~1275°C to ~1175°C. It is important to note that the eutectic does not necessarily solidify at a single temperature since these are not binary systems. Some eutectics can solidify over a range of temperatures, such as the γ+NbC in this case.
The Ta-bearing diagrams calculated for Ni-30Cr-8Fe are shown in Figure 36. These diagrams are very similar to the Nb-bearing system, with the exception of different eutectic temperatures. Ta behaves very similarly to Nb in these alloy systems. The eutectic temperatures are slightly higher in both cases.
Figure 36 - Left: Pseudo-binary diagram for Ni-30Cr-8Fe & TaC. Right: Similar diagram showing Ta-rich Laves eutectic.

Pseudo-binary diagrams for Hf are slightly different than those for Nb or Ta, as can be seen in Figure 37. A Laves type phase does not form in this system, as investigated previously by Nash and West [55]. The Thermo-Calc® simulations also predict the Ni$_7$Hf$_2$ phase. At extremely high levels of Hf, a Hf-rich $\alpha$ phase is predicted to form, but this was not seen in alloys in this study as well as in alloys in the study by Nash and West [55]. A MC carbide is predicted to form, much like the MC carbide that forms in Nb and Ta-bearing alloys. The terminal eutectic temperatures are much higher than those seen in Nb-bearing alloys. The HfC carbide eutectic forms at a slightly lower temperature than the TaC eutectic, but the Ni$_7$Hf$_2$ forms at a higher temperature than the Ta-rich Laves eutectic.
The results of the calculated pseudo binary diagrams are summarized in Table 6. A marked improvement in potential terminal eutectic temperature can be had by switching to Hf or Ta. This will lead to a narrower STR, and potentially better solidification cracking resistance. These calculations were the basis for moving forward with investigation of Ta and Hf as alternatives to Nb in high Cr Ni-base alloys.

Table 6 - Summary of terminal eutectic temperatures as determined by calculated pseudo-binary phase diagrams.

<table>
<thead>
<tr>
<th></th>
<th>γ-MC Eutectic</th>
<th>γ-Laves Eutectic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>1280°C</td>
<td>1160°C</td>
</tr>
<tr>
<td>Ta</td>
<td>1330°C</td>
<td>1190°C</td>
</tr>
<tr>
<td>Hf γ-MC Eutectic</td>
<td>1310°C</td>
<td>γ-Ni₇Hf₂ Eutectic 1250°C</td>
</tr>
</tbody>
</table>

Figure 37 - Left: Pseudo-binary diagram for Ni-30Cr-8Fe & HfC. Right: Similar diagram showing Hf-rich Ni₇Hf₂ eutectic.
7.3 Analysis of Elemental Effects on Nb-Bearing Alloys

A study of the elemental effects on Nb-bearing alloys was conducted to use as a comparison with experimental Ta, and Hf-bearing alloys. Very good correlation between the computational STR and experimentally determined STR was found. The trends for fraction eutectic were also comparable between computational and experimental, however it is important to note that the fraction eutectic from the Thermo-Calc® Scheil module is a mole fraction and not a volume fraction, so the values cannot be directly compared without converting the mole fraction into volume fraction. This requires density information on the crystal structures, which is not available in the Themro-Calc® databases.

The experimental results affirmed what is currently known about Nb-bearing Ni-30Cr alloys. Much of the current research shows that these Nb-bearing alloys have either a solidification cracking or ductility dip cracking problem [5, 7, 78]. Solving the DDC problem by adding Nb expands the solidification temperature range and creates a solidification cracking problem. Figure 38, which shows results from the experimental DOE, demonstrates this very well. There is no region on the graph which has both >2% eutectic and <150°C STR, the criteria established in this work for resistance to both forms of cracking.
7.4 Analysis of Elemental Effects on Hf-Bearing Alloys

The DOE analysis on experimental results from Hf-bearing alloys from Table 5 is shown in Figure 39. These results are very promising as there is clearly an area of the diagram where greater than 2 vol% eutectic and <150°C STR co-exist. This is represented by the shaded area. The primary explanation for this has to do with the nature of the final eutectic to form in this alloy. For Nb-bearing alloys, when carbon is exhausted, Laves phase will form, with a terminal eutectic temperature of around 1150°C. In Hf-bearing alloys, when carbon is exhausted, a Ni$_7$Hf$_2$ eutectic phase forms, but at around 1250°C. This allows significant eutectic to be generated while keeping the STR relatively narrow. More discussion on eutectic phase formation will be provided in the following chapter.
7.5 Analysis of Elemental Effects on Ta-Bearing Alloys

The published paper in Appendix 1 did not include results from Ta-bearing alloys, as they were not available at that time. Unfortunately, none of the Ta-bearing alloys created from Table 5 contained anywhere near the target 2 vol% eutectic which was the target to resist DDC. Since Thermo-Calc® Scheil only outputs mole fraction, this was not caught until actual samples were examined metallographically. However, since Ta is known to behave very similarly to Nb during solidification, with the exception of a higher terminal Laves eutectic temperature [51], a simple solution to choose a composition was devised.

It is known that Alloys such as FM52MSS, with 2.5 wt% Nb and 4 wt% Mo are highly resistant to DDC, while being quite susceptible to solidification cracking due to the formation of Laves eutectic at low temperatures [7]. Simply switching to 2.5 wt% Ta
would not generate the same amount of eutectic, due to the large difference in atomic weight between Ta and Nb. By converting 2.5 wt% Nb to atomic fraction for these alloys, then using this amount for Ta, 4 wt% Ta becomes the value to achieve the same atomic fraction Ta as Nb. Therefore, this value was chosen, and buttons of Ni-30Cr-8Fe-4Ta (wt%), with and without 4 wt% Mo were created in the lab. Microstructurally, as seen in Figure 40, the microstructure is quite comparable to FM52MSS, with evenly distributed eutectic throughout the interdentritic regions. Experimentally, the STR was also found to be 134°C, which is much lower than that of FM52MSS, which was found to be 192°C by Alexandrov et al. [7].

![Figure 40 - Comparison of microstructures from CPTT tests of FM52MSS and a similar 4 wt% Ta-bearing alloy.](image)

**7.6 Optimized Compositions from Genetic Algorithm**

The genetic algorithm, developed by Ted Allen and Sayak Roychowdhury and described previously in 6.1.1 was used on the raw data for the Hf-bearing alloys to develop an optimized composition for further testing. Because of curvature in the responses with
respect to alloying additions, there may be multiple solutions for optimization. To detect this, the software should be run multiple times to find them, as the randomness in evolution may take a different path each time. Ultimately, the software will settle on the most optimal compositions. As shown in Table 7, three such compositions were found. The desirability value is a number assigned to each composition during evolution to determine which compositions survive to the next generation. Desirability values closest to one are more optimal. It is interesting to note that the level of Hf was essentially the same between all compositions; this is due to the 2 vol% eutectic requirement and the fact that Hf was the most potent factor in determining fraction eutectic. Additionally, Mo could either be 0 or 4 wt%, without changing the STR significantly. Moving forward, alloys were created with and without 4 wt% Mo since the data here was inconclusive about the effect of Mo on fraction eutectic and STR.

Table 7 - Three optimized Hf-bearing compositions that were identified using the genetic algorithm.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Mo</th>
<th>C</th>
<th>Hf</th>
<th>Response Values</th>
<th>Desirability</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.8</td>
<td>0.06</td>
<td>0.03</td>
<td>0.73</td>
<td>155.2</td>
<td>2.00</td>
</tr>
<tr>
<td>2</td>
<td>14.3</td>
<td>3.9</td>
<td>0.04</td>
<td>0.74</td>
<td>155.1</td>
<td>1.97</td>
</tr>
<tr>
<td>3</td>
<td>13.3</td>
<td>0.25</td>
<td>0.03</td>
<td>0.77</td>
<td>159.6</td>
<td>1.99</td>
</tr>
</tbody>
</table>

7.7 Conclusions

Overall, the combined computational and experimental technique proved to be very useful in not only determining an optimized composition for further testing, but allowed for some insight into how different elements affected the solidification behavior. Using
Thermo-Calc® to investigate potential eutectic formers and their terminal temperatures provided a basis on which to select potential elemental candidates. The use of Scheil simulations along with a DOE also provided useful trends that could be used to narrow down a composition space for experimental testing. Unfortunately, with the experimental Nb-bearing data, the effects of some elements, such as Fe and Mo, ended up being statistically insignificant (p > 0.05). This could have been for a number of reasons, such as the varied range of the element being too small, too much scatter in the data, or because some elements had a much stronger effect and obscured the effect of others. It is also interesting to note that Mo had no statistically significant effect on STR or fraction eutectic in either the Nb or Hf-bearing DOE groups. This is interesting because previous researchers have shown an effect of Mo on solidification cracking resistance [61]. This further suggests that the effect of Mo may be related to wetting, and would not show up in the STR data. However, the good thing about using a DOE to investigate such effects is that some software packages can provide recommendations about where in the design space one should perform additional experiments. Due to time constraints, and the fact that Nb-bearing alloys are already well understood, this was not carried out.
CHAPTER 8
EFFECT OF CHROMIUM AND IRON ON EUTECTIC PHASE FORMATION

8.1 Introduction

It should be noted that the Ni-base filler metal used previously in nuclear power plant construction, FM82, had few reported weldability issues. As shown in Table 1, FM82 has about 2.5 wt% Nb, and 20 wt% Cr. This is enough Nb to resist DDC by eutectic formation, as shown by Collins et al. [18, 40]. Alloys such as FM52MSS have a similar level of Nb, while having 30 wt% Cr, to resist PWSCC as discussed previously. Although FM52MSS is quite resistant to DDC, it is fairly susceptible to solidification cracking.

FM82 is quite resistant to both forms of cracking under moderate restraint conditions, and the only major difference in composition is the Fe and Cr content.

DuPont et al. have shown that the level of Fe in Nb-bearing superalloys has an effect on the partitioning coefficient of Nb, and promotes the formation of a Laves eutectic at the end of solidification. They have also shown that this increases the STR and solidification cracking susceptibility. While the level of Fe is higher in FM52MSS compared to FM82, it cannot explain the large difference in cracking susceptibility as shown by Przybylowicz and Alexandrov [7, 73].

There has not been much research on the effect of Cr on eutectic formation in Nb-bearing Ni-base alloys. Research by Chang et al. showed that in cast superalloys with
varied Fe, Cr, and Co levels, Fe and Cr promoted a Nb-rich Laves eutectic over the binary Ni-Nb eutectic [49]. Therefore, it is possible that the increased Cr levels in the new generation of alloys aggravate the solidification cracking problem.

Laves phase forms after carbon is consumed by formation of MC eutectic [79]. This solidification path, \( L \rightarrow L + \gamma \rightarrow L + \gamma + MC \rightarrow L + \gamma + MC + Laves \), is expected for Nb and Ta-bearing alloys. Based on the work of Nash and West, for a Hf-bearing alloy, the solidification path is expected to be \( L \rightarrow L + \gamma \rightarrow L + \gamma + MC \rightarrow L + \gamma + MC + Ni_7Hf_2 \) [55]. These are shown in Figure 41, which is a schematic liquidus projection for these alloy systems. The different lines show different solidification paths for alloys with high and low values of C and the carbide forming element (Nb, Ta, or Hf).

In Chapter 9, Ta and Nb-bearing alloys will be discussed together, since they form very similar phases. For these systems, results from Thermo-Calc® simulations are compared with experimental buttons. Experimentally, thermocouple plunges were performed to determine solidification temperatures, while XRD was used to determine the phases present. Hf-bearing alloys will be discussed separately as they do not form a Laves phase and a very different trend was found with respect to Cr content and STR. Thermodynamic data for Hf-bearing alloys was not as robust as the data for Nb and Ta-bearing alloys, and because of this the results from Thermo-Calc® simulations will not be discussed here. XRD was unsuccessful in identifying phases in the Hf-bearing weld metals, so the TEM was eventually used.
8.2 Effect of Chromium and Iron on Laves Phase Formation in Nb and Ta-Bearing Alloys

To study the effect of Cr and Fe on solidification of high-Cr Ni-base alloy, a matrix of Scheil simulations was designed according to Table 8. Fe was varied from 3-13 wt% as this range covers Fe contents seen in commercial alloys. Carbon was tested at two levels, 0.04 and 0.1 wt% as these are the max levels in commercial FM52 and FM82 alloys, respectively. To verify some of the Scheil simulations, buttons were tested according to the plunging procedure detailed in the experimental section. Buttons were made with varied Cr and C as described in Table 8, but with Fe held constant at 8 wt%.

Figure 41 - Schematic pseudo-ternary liquidus projection for eutectic formation in Ni-base alloys containing Nb, Ta, or Hf. Adapted from DuPont et al. [48].
Table 8 - Elemental levels used to perform Scheil simulations to determine solidification data. For experimental validation, the same levels were used except Fe was held at 8 wt%.

<table>
<thead>
<tr>
<th>Element</th>
<th>Levels (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0, 20, 30</td>
</tr>
<tr>
<td>Fe</td>
<td>3, 8, 13</td>
</tr>
<tr>
<td>C</td>
<td>0.04, 0.1</td>
</tr>
<tr>
<td>Nb or Ta</td>
<td>2.4 or 4</td>
</tr>
</tbody>
</table>

The calculated STR as a function of Fe content from the Scheil simulations is shown in Figure 42. The red lines are for 30 wt% Cr, while the blue lines are for 20 wt% Cr. Dashed lines are the low carbon level and the solid lines are the higher carbon level. For Nb-bearing alloys, Fe tends to increase the STR, except at the 30 wt% Cr level. This implies that the Laves eutectic, which expands the STR, is already forming at 30 wt% Cr levels, and the STR cannot be increased much further. The Ta-bearing alloys seem to be more resistant to Laves phase formation. However, a similar situation arises at the 30 wt% Cr and low carbon level, where Fe does not increase the STR significantly because Laves eutectic is already forming. Overall the maximum STR in the Ta-bearing systems is lower; this is because the Laves eutectic forms at a higher temperature in this system.
Figure 42 - Calculated effect of Fe and C on STR of Nb and Ta-bearing alloys for 20 wt% and 30 wt% Cr levels.

Figure 43 shows the STR from both the plunges and the Scheil simulations as a function of Cr and C content, for both Nb-bearing and Ta-bearing systems. The dashed lines are simulated results, and the different colors represent different C levels. In general, the Scheil simulations always over predict the STR, except for the 0 wt% Cr condition. This is not surprising as the Scheil simulation predicts the most extreme segregation possible during solidification, which may not be the case during actual solidification. However, the Scheil prediction is reasonably accurate at the 0 wt% Cr level, likely because the alloy system is simpler. Another major result is that Cr has a strong effect on increasing the STR, for both Nb and Ta-bearing systems, especially for the low carbon case. This strongly supports the hypothesis that Cr also promotes Laves phase, in the same way DuPont showed Fe promotes Laves phase [47]. However, the Cr effect on STR is not as strong when carbon is at 0.1 wt%. This can be easily explained by Figure 41, which is adapted from DuPont’s work. The higher carbon composition is represented by the green line, and the lower carbon by the red line on Figure 41. The higher carbon keeps the solidification path from reaching the point where Laves phase forms, as more of the Nb
or Ta is consumed by formation of MC eutectic during eutectic solidification. This keeps the STR relatively narrow. One interesting finding in this study is that the STR of the Ta-bearing alloys was only considerably narrower for compositions with less than 30 wt% Cr. This suggests that Laves phase could be detrimental to solidification cracking resistance in Ta-bearing alloys, just as it is in Nb-bearing alloys.

![Figure 43 - Elemental effects of Cr and C on STR of Nb and Ta-bearing alloys. Dashed lines represent Scheil results while solid lines are experimental data.](image)

While the STR gives insight into what eutectic forms, it still does not confirm the presence of any particular phase. For this reason, the phase extraction technique, described in section 6.3, was carried out on a matrix of buttons with varying Fe, Cr, C, and Ta or Nb. An example of the results for one XRD scan is shown in Figure 44. While primary $\gamma$ and MC carbides were found in all samples, Laves phase was not detected in any sample. Primary $\gamma$ should have been dissolved electrolytically, however it is possible that some grains were etched out and fell into the solution, where they were no longer part of the circuit. They would have then been picked up on the filter during filtration.
However, the Scheil simulations did predict some compositions to form Laves phase, and the experimental STR results also suggest Laves phase formation. This lack of detection by XRD could be due to the relatively small amounts of Laves phase that formed, or the possibility of the Laves phase being dissolved during the phase extraction technique. Therefore, the phases determined by Thermo-Calc® Scheil simulations are shown below in Table 9. It can be seen that both Fe and Cr promote Laves phase, while increases in carbon content help to mitigate Laves phase formation. This table is insightful as it helps explain why 20 wt% Cr variants such as FM82 have good resistance to cracking, since they do not form Laves eutectics unless the C is low and the Fe is high. Additionally, this
The table shows that Laves eutectic is present in 30 wt% Cr variants such as FM52MSS no matter the C or Fe content, explaining its high susceptibility to solidification cracking. The 4 wt% Ta-bearing system shows promise since at the 30 wt% Cr level, there are a few combinations of Fe and C that prevent Laves eutectic from forming.

Table 9 - Depiction of eutectic phases that form during solidification as a function of Cr, Fe, and C contents for systems containing 2.5 wt% Nb (left) and 4 wt% Ta (right), as determined by Scheil simulations.

<table>
<thead>
<tr>
<th>Fe</th>
<th>2.5 Nb</th>
<th>20 Cr Carbon</th>
<th>30 Cr Carbon</th>
<th>4 Ta</th>
<th>20 Cr Carbon</th>
<th>30 Cr Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>NbC</td>
<td>NbC</td>
<td>NbC</td>
<td>3</td>
<td>TaC</td>
<td>TaC</td>
</tr>
<tr>
<td>8</td>
<td>NbC</td>
<td>NbC</td>
<td>NbC</td>
<td>8</td>
<td>TaC</td>
<td>TaC</td>
</tr>
<tr>
<td>13</td>
<td>NbC</td>
<td>NbC</td>
<td>NbC</td>
<td>13</td>
<td>TaC</td>
<td>TaC</td>
</tr>
</tbody>
</table>

A more fundamental way to explain the increase in STR and eutectic phase formation as a function of composition is with the k values. The k values describe how much an element will segregate during solidification. This affects the final liquid to solidify, which ends up forming a eutectic. Figure 45 shows the k values as a function of composition, as determined by the Scheil simulations. It can be seen that the C content has no effect on k values. And much like the research published by DuPont et al., Fe has the effect of lowering the k value for Nb, as well as Ta [47]. Interestingly, Cr has a similar effect of lowering the k value for Nb or Ta. By lowering the k value for Nb or Ta, there will be a higher concentration of these elements at the dendrite and solidification grain boundaries, which will not only cause more eutectic to form, but can promote Laves phase since C.
will be exhausted and an appreciable level of Nb or Ta will remain before solidification is complete. This leads to a widening of the STR, and an increase in solidification cracking susceptibility. When directly comparing Nb and Ta, overall Ta has a higher k value, leading to less segregation during solidification. However at the high Fe levels, the k value for Ta is just as low as for Nb. This suggests possible problems with dilution of steel and stainless steel base metals, just as current Nb-bearing 30 wt% Cr alloys have solidification cracking issues with dilution.

![Figure 45 - Elemental effects of Fe, Cr, and C on k values in Nb and Ta-bearing alloys.](image)

**8.3 Effect of Chromium and Iron on Hafnium Eutectics**

As discussed previously, work by Nash and West showed that the Ni-Cr-Hf system does not form a Laves eutectic. Rather, a Ni₅Hf or Ni₇Hf₂ eutectic is possible, depending on the Cr content. They found that the Ni₅Hf eutectic formed at a much lower temperature than the Ni₇Hf₂ eutectic. This shows potential promise for a Hf-bearing alloy as the potential STR when the system terminates on a Ni₇Hf₂ eutectic is quite narrow. The Ni₅Hf and Ni₇Hf₂ phases could not be detected by XRD for any of the compositions
tested. These phases may have dissolved in the electrolyte used for the phase extraction technique, or they could have been present in amounts below the limit of detection.

Figure 46 shows the results of one scan on a Hf-bearing sample. HfC and HfO$_2$ were detected. Peaks from HfO$_2$ were not expected, however, Hf is very readily oxidized, and these may be surface oxides that did not dissolve in the electrolyte.

To determine the phases, a focused ion beam (FIB) was used to machine out TEM samples for selected area diffraction. However, at the optimized composition levels determined in the previous chapter, not enough eutectic was present to reliably FIB samples for analysis. Therefore for the purposes of phase identification, the level of Hf was increased to 5 wt%. This has the added benefit of increasing the size of the thermal effect of the eutectic on solidification, which makes the SS-DTA® analysis extremely
simple. Figure 47 shows the data from two thermocouple plunges, one at 0 wt% Cr and one at 30 wt% Cr. The liquidus, eutectic start, and solidus temperatures determined by the SS-DTA® software are labeled on the cooling curve. The thermal effects from the eutectic are clearly visible. A large difference in overall STR and eutectic start temperatures can be seen between the two alloys, which will be discussed in the next paragraph.

Figure 47 - Cooling curves for two alloys that were subjected to the thermocouple plunging technique. Solidification temperatures as determined by SS-DTA® are labeled on the curves.

Figure 48 shows the solidification temperatures as a function of Cr content for a Ni-5Hf system. A very similar result to that of Nash and West was found, where around 20 wt% Cr, the terminal eutectic switches from a low temperature to a higher temperature one. Additionally, at 20 wt% Cr, two individual thermal effects were seen in the cooling curve, around 1225°C and 1150°C. This further enforces that there are two different
eutectics that can form in these systems. It is important to note here that for Hf-bearing Ni-Cr alloys, the overall STR goes down as a function of Cr content. In Ta and Nb-bearing Ni-Cr alloys, the opposite is true.

![5Hf Solidification Temperatures](image)

Figure 48 - Solidification temperatures as a function of Cr content for a Ni-5Hf system.

Selected area diffraction patterns of the samples confirmed the phases present. These patterns for two selected samples are shown in Figure 49. Ni₅Hf has a cubic structure with a lattice parameter of 0.668 nm. Ni₇Hf₂ has a monoclinic structure, and has a cell of 1.21 x 0.82 x 0.46 nm³ < 90 x 95.5 x 90 >. Due to difficulties in finding zone axes of the eutectic phases, not enough measurement were taken to determine if there were any orientation relationships between the γ and the eutectic phases.
Figure 49 - Selected area diffraction patterns confirming presence of Ni$_5$Hf in: 0 wt% Cr sample (a), 5 wt% Cr sample (b). Ni$_7$Hf$_2$ found in: 20 wt% Cr sample (c), 30 wt% Cr sample (d).

To assist in indexing of patterns, especially Ni$_7$Hf$_2$, due to its low symmetry, the software SingleCrystal® was used to generate patterns at various zone axes to find a match. This also helped confirm the zone axis of complicated patterns and deconvolute selected areas that contained both γ and a eutectic phase, such as in (d) of Figure 49. Figure 50 shows one such generated pattern along the selected area diffraction pattern from the 20 wt% Cr sample.
Figure 50 - Left: Selected area diffraction pattern of Ni\(_7\)Hf\(_2\) phase found in 20 wt% Cr sample. Right: Generated diffraction pattern for Ni\(_7\)Hf\(_2\) phase along the [\(\overline{3}10\)] zone axis.

To further confirm the nature of phases, TEM EDS was performed on the eutectics to determine their atomic composition ratios, and compare that to the expected composition of the phases. As can be seen from Table 10, the composition ratios are quite close to the phases determined by the diffraction patterns. Some discrepancies may be attributed to the high energy X-rays emitted from Hf exciting nearby material and distorting the results.

Table 10 - TEM EDS results showing atomic ratios of Ni/Hf within secondary phases, confirming presence of either Ni\(_5\)Hf or Ni\(_7\)Hf\(_2\).

<table>
<thead>
<tr>
<th>Alloy (wt%)</th>
<th>Element (at%)</th>
<th>Ni/Hf Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni(K)</td>
<td>Hf(L)</td>
</tr>
<tr>
<td>Ni-0Cr-5Hf</td>
<td>84.2</td>
<td>15.8</td>
</tr>
<tr>
<td>Ni-5Cr-5Hf</td>
<td>84.1</td>
<td>15.9</td>
</tr>
<tr>
<td>Ni-20Cr-5Hf</td>
<td>77.7</td>
<td>20.7</td>
</tr>
<tr>
<td>Ni-30Cr-5Hf</td>
<td>78.9</td>
<td>19.1</td>
</tr>
</tbody>
</table>

Note: All errors were less than 1 at%.
The results from the TEM analysis are summarized in Table 11. Ni$_5$Hf was found in the 0 wt% Cr and 5 wt% Cr samples, while Ni$_7$Hf$_2$ was found in the 20 wt% Cr and 30 wt% Cr samples. No Ni$_5$Hf was found in the 20 wt% Cr sample; this could be related to the extremely limited area of extracted FIB samples. A distinct thermal effect was seen in all of the thermocouple plunging experiments at the 20 wt% Cr level; therefore it is presumed to exist to some extent at this composition.

Table 11 - Summary of phases detected via TEM analysis in Ni-5Hf samples with varied Cr content. Alloying in wt%.

<table>
<thead>
<tr>
<th>Alloy (wt%)</th>
<th>Ni$_5$Hf ?</th>
<th>Ni$_7$Hf$_2$ ?</th>
<th>STR (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-0Cr-5Hf</td>
<td>Yes</td>
<td>No</td>
<td>260</td>
</tr>
<tr>
<td>Ni-5Cr-5Hf</td>
<td>Yes</td>
<td>No</td>
<td>235</td>
</tr>
<tr>
<td>Ni-20Cr-5Hf</td>
<td>Presumed</td>
<td>Yes</td>
<td>215</td>
</tr>
<tr>
<td>Ni-30Cr-5Hf</td>
<td>No</td>
<td>Yes</td>
<td>170</td>
</tr>
</tbody>
</table>

A similar study was performed with varying Fe content instead of Cr content. However, a thermal effect was only seen around 1150°C for Fe contents up to 20 wt%. Therefore it is assumed that only the Ni$_5$Hf eutectic forms and varying Fe content does not influence the formation of another eutectic. This is important because in Nb and Ta-bearing systems, Fe, which can come from dilution of steel base metals, promotes the formation of Laves eutectics which expand the solidification temperature range. No significant change in STR was seen as a function of Fe content up to 20 wt% for a Ni-5Hf system.

8.4 Avoiding Low Temperature Eutectic Phases

Based on many studies of Nb-bearing Ni-base alloys, avoiding a large STR is a key to avoiding solidification cracking [7, 46]. It is also clear that a widening of the STR comes
about due to the formation of low temperature eutectics, such as Laves phase. DuPont has previously discussed how Fe can promote Laves phase, and his liquidus projection schematic, in Figure 41, shows that initial Nb and C levels can also play a role in avoiding Laves phase. It is clear from the work in this section that many of the problems with current generation 30 wt% Cr alloys stem from the increased Cr relative to previous alloys (such as FM82) by promoting Laves phase formation. This makes formation of a Laves eutectic unavoidable if Nb is at a sufficient level to resist DDC. This is also the case with Ta-bearing Ni-base alloys, although the terminal eutectic temperature for Ta-rich Laves is slightly higher than for Nb, providing some advantage by switching to Ta.

For Hf-bearing alloys, the situation is much different. A low melting temperature Laves phase is not favored to form, instead at 20 and 30 wt% Cr levels, a Ni$_7$Hf$_2$ eutectic forms. This eutectic has a much higher terminal temperature than the Laves eutectic in both Nb and Ta-bearing alloys, so its formation is not as problematic. Additionally, during metallographic analysis of Hf-bearing alloys from the DOE (Chapter 7, Table 5), there were 3 out of 16 compositions that only had a single eutectic morphology, whereas the rest has a dual morphology. Figure 51 shows this quite well. These compositions, regardless of Mo and Fe content, all had two things in common: Low Hf (0.5 wt%), and high C (0.06 wt%). These starting conditions can also be represented by the red and green lines that are drawn schematically on Figure 41, where the green line represents the low Hf and high C composition, and the red line represents compositions with more Hf and/or less C. The colors around the micrographs in Figure 51 are also meant to correspond with these lines. This means for a Hf-bearing Ni-base alloy, it is possible to only form HfC
eutectic, and prevent the lower temperature eutectic Ni$_7$Hf$_2$, at least in this composition space.

Figure 51 - SEM micrographs of eutectic morphologies in Hf-bearing DOE samples. Green box: the skeletal/blocky HfC carbide eutectic morphology found in all compositions with low Hf and high C. Red box: Dual eutectic morphology showing script Ni$_7$Hf$_2$ eutectic surrounding a blocky HfC eutectic found in all other samples.

8.5 Conclusions

The results from this section have revealed the reasons for solidification cracking problems in current 30 wt% Cr Nb-bearing alloys. Cr was found to act much like Fe to promote low temperature Laves eutectic at the end of solidification. Additionally, Ta-bearing alloys were found to behave similarly to Nb-bearing alloys, however they benefit from a higher Laves eutectic temperature, which narrows the STR and could reduce solidification cracking susceptibility. The eutectics in these Hf-bearing Ni-base alloys have been identified, and alloys with high Cr benefit from the relatively high Ni$_7$Hf$_2$ terminal eutectic temperature.
CHAPTER 9
WELDABILITY TESTING OF OPTIMIZED COMPOSITIONS

9.1 Introduction
The optimized Hf-bearing composition described in Chapter 7 was subjected to the Cast Pin Tear Test (CPTT) to validate its solidification cracking resistance prior to specifying the composition to a commercial facility for wire production. The results were suboptimal; therefore slight modifications were made to the composition before a composition was specified for a limited production of welding wire. The Ta-bearing composition was also recommended for production. Upon receipt of the production wires, the compositions were again tested using the CPTT, since some trace elements were present in the commercially-processed material that were not present in lab heats. Additionally, before limited heats of wire were drawn commercially, the DDC resistance was verified using the novel STF test procedure described in Section 6.2.2. This section will cover these results and discuss their impact.

9.2 Cast Pin Tear Testing of Previously Optimized Compositions
Cast Pin Tear Testing was performed on one of the optimized Hf-bearing composition (Alloy 1 from Table 7), as well as the selected 4 wt% Ta-bearing alloy. As Fe was shown to have little to no effect on STR or fraction eutectic by the models, 8 wt% Fe was used instead of 12.8 wt% as predicted by the genetic algorithm, and 8 wt% is the amount used
in commercial Ni-30Cr alloys. Table 12 shows the compositions used for these CPTT tests, along with a heat of FM82 used for comparison purposes since it is known to be resistant to solidification cracking. The CPTT results are compiled in Figure 52. Since Mo was optimized by the algorithm to be at 0 or 4 wt%, compositions for this round of testing were set at 0 wt%, with the intention of having two heats of wire made Mo-free and with 4 wt% Mo at the next step.

The data from Figure 52 was unexpected based on the predicted STR for the optimized Hf-bearing composition. The optimized composition, with 0.75 wt% Hf, was found to have extremely high cracking susceptibility. This led to a reduction in the amount of Hf to 0.5 wt%, in an attempt to improve the cracking resistance at the expense of some volume fraction eutectic. Results from the 0.5 wt% Hf composition were the same as the 0.75 wt% Hf alloy, so the composition was further reduced to 0.25 wt% Hf. At this Hf level, the threshold for cracking was slightly higher than that of FM82. This composition was then selected to be commercially cast and drawn for further analysis. The 4 wt% Ta alloy exhibited a threshold for cracking that was the same as FM82, so this composition was also selected to be commercially cast and drawn.

It is important to note here that during this stage of testing, the 3rd Generation Cast Pin Tear Test was being developed by Luskin at The Ohio State University. By the time the commercially drawn wire arrived, some parameters of the test were changed and optimized. Luskin found that the chamber pressure and the mold material had a large impact on cracking response, and changed these parameters to yield a microstructure more representative of a typical gas tungsten arc weld. More information can be found in
his Master’s thesis [12]. In light of this, these results should not be compared to other cast pin data presented later in this chapter.

Table 12 - Compositions of alloys tested via CPTT to evaluate solidification crack susceptibility prior to having heats of wire commercially cast and drawn. Values in wt%.

<table>
<thead>
<tr>
<th>Alloy (wt%)</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>C</th>
<th>Hf, Ta, or Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Opt-Hf(0.75Hf)</td>
<td>Bal.</td>
<td>30</td>
<td>8</td>
<td>0</td>
<td>0.04</td>
<td>0.75</td>
</tr>
<tr>
<td>Opt-Hf(0.5Hf)</td>
<td>Bal.</td>
<td>30</td>
<td>8</td>
<td>0</td>
<td>0.04</td>
<td>0.5</td>
</tr>
<tr>
<td>Opt-Hf(0.25Hf)</td>
<td>Bal.</td>
<td>30</td>
<td>8</td>
<td>0</td>
<td>0.04</td>
<td>0.25</td>
</tr>
<tr>
<td>Opt-Ta(4Ta)</td>
<td>Bal.</td>
<td>30</td>
<td>8</td>
<td>0</td>
<td>0.04</td>
<td>4</td>
</tr>
<tr>
<td>FM82 (Nb-bearing)</td>
<td>Bal.</td>
<td>19.4</td>
<td>1.1</td>
<td>0</td>
<td>0.06</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Figure 52 - CPTT cracking data of optimized Hf and Ta compositions, along with modified versions with less Hf. Data from a select heat of FM82 that is known to be resistant to solidification cracking is shown for comparison. Note: Tested prior to CPTT parameter optimization.
9.3 Commercially Drawn Filler Metal

Table 13 shows the compositions of the filler metals that were commercially cast and drawn. Variant #1 and #2 are the Hf-bearing heats, with and without 4 wt% Mo. Variant #5 and #6 are the Ta-bearing heats, with and without 4 wt% Mo. Variants #3 and #4 were produced without a eutectic forming element. These heats were created to allow modification of the Hf- and Ta-bearing heats, whereby these heats can be used to dilute the concentration of Hf or Ta down to a level that would produce better solidification cracking results. Such an approach may decrease the DDC resistance, but this was considered less of a concern than solidification cracking. At the time of publication, these two eutectic-free variants have not been used for this purpose, and are not discussed or characterized in this work.

Table 13 - Compositions of different variants of FM52, based on optimization work in this study that were commercially cast and drawn for weldability testing. Values in wt%.

<table>
<thead>
<tr>
<th>Variant</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>Hf</th>
<th>Ta</th>
<th>C</th>
<th>Al</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1-Hf</td>
<td>Bal.</td>
<td>29.04</td>
<td>8.04</td>
<td>&lt;0.005</td>
<td>0.27</td>
<td>&lt;0.005</td>
<td>0.004</td>
<td>0.033</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>#2-Hf-Mo</td>
<td>Bal.</td>
<td>29.67</td>
<td>8.41</td>
<td>3.87</td>
<td>0.25</td>
<td>&lt;0.002</td>
<td>0.036</td>
<td>0.025</td>
<td>0.002</td>
</tr>
<tr>
<td>#3</td>
<td>Bal.</td>
<td>29.93</td>
<td>7.78</td>
<td>&lt;0.005</td>
<td>&lt;0.01</td>
<td>&lt;0.005</td>
<td>0.003</td>
<td>0.018</td>
<td>0.011</td>
</tr>
<tr>
<td>#4-Mo</td>
<td>Bal.</td>
<td>29.65</td>
<td>8.21</td>
<td>3.83</td>
<td>&lt;0.01</td>
<td>&lt;0.002</td>
<td>0.037</td>
<td>0.014</td>
<td>0.002</td>
</tr>
<tr>
<td>#5-Ta</td>
<td>Bal.</td>
<td>29.83</td>
<td>7.99</td>
<td>&lt;0.005</td>
<td>&lt;0.01</td>
<td>3.88</td>
<td>0.035</td>
<td>0.007</td>
<td>0.004</td>
</tr>
<tr>
<td>#6-Ta-Mo</td>
<td>Bal.</td>
<td>29.76</td>
<td>8.05</td>
<td>3.86</td>
<td>&lt;0.01</td>
<td>3.82</td>
<td>0.033</td>
<td>0.010</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Unfortunately, Variant #1 and #3, which were cast as a split heat, were produced with the incorrect amount of carbon. The carbon level was an order of magnitude lower than the desired amount. It could not be re-cast in a timely manner as work already started on the next heats. This heat could not be tested in this condition as γ/HfC eutectic would not
form in appreciable amounts; $\gamma$/Ni$_7$Hf$_2$ would form instead widening the STR. To remedy this so that the alloy could be evaluated in the CPTT, 5% by weight 1080 steel wire was mixed with Variant #1 in the button melter. Via a dilution calculation, shown in Table 14, this addition would bring the carbon level to about 0.04 wt%, the desired amount. While this will add about 4 wt% Fe, the solidification behavior of the Hf-bearing system is not expected to change significantly based on the previous discussion. It also adds other trace elements such as Si, Mn, S, and P, but in amounts that also are not expected to have a large effect on solidification behavior.

Table 14 - Composition of 1080 steel wire used to add carbon to Variant #1-Hf, and how the resultant composition after mixing.

<table>
<thead>
<tr>
<th>Element</th>
<th>Variant #1</th>
<th>1080 wire</th>
<th>Variant #1 + 5% 1080</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>61.64</td>
<td>0</td>
<td>58.561</td>
</tr>
<tr>
<td>Fe</td>
<td>7.78</td>
<td>98.392</td>
<td>12.311</td>
</tr>
<tr>
<td>C</td>
<td>0.003</td>
<td>0.81</td>
<td>0.043</td>
</tr>
<tr>
<td>Mn</td>
<td>0.005</td>
<td>0.55</td>
<td>0.032</td>
</tr>
<tr>
<td>S</td>
<td>0.0005</td>
<td>0.007</td>
<td>0.0008</td>
</tr>
<tr>
<td>P</td>
<td>0.002</td>
<td>0.011</td>
<td>0.0025</td>
</tr>
<tr>
<td>Mo</td>
<td>0.005</td>
<td>-</td>
<td>0.005</td>
</tr>
<tr>
<td>Hf</td>
<td>0.25</td>
<td>-</td>
<td>0.238</td>
</tr>
<tr>
<td>Al</td>
<td>0.018</td>
<td>-</td>
<td>0.017</td>
</tr>
<tr>
<td>Co</td>
<td>0.01</td>
<td>-</td>
<td>0.010</td>
</tr>
<tr>
<td>Cr</td>
<td>29.93</td>
<td>-</td>
<td>28.434</td>
</tr>
<tr>
<td>Si</td>
<td>0.01</td>
<td>0.23</td>
<td>0.021</td>
</tr>
<tr>
<td>Ti</td>
<td>0.011</td>
<td>-</td>
<td>0.010</td>
</tr>
<tr>
<td>N</td>
<td>0.0061</td>
<td>-</td>
<td>0.006</td>
</tr>
<tr>
<td>W</td>
<td>0.01</td>
<td>-</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Note: All values are in wt%.

Since the CPTT test can only rank alloy susceptibility to solidification cracking, a baseline for susceptible and resistant alloys was needed. Przybylowicz used the 3rd
Generation CPTT with the optimized parameters that Luskin developed to test a wide range of alloys and compare them with industry experience [12, 73]. 52MSS-C, a current generation high-Cr alloy with 3.5 wt% Mo and 2.5 wt% Nb, is known to be moderately susceptible to solidification cracking. FM82, with 0 wt% Mo, and 2.4 wt% Nb, is quite resistant to solidification cracking based on industry experience. Both of these alloys are also quite resistant to ductility dip cracking because of the amount of eutectic they form based on their similar Nb contents. Also, the resistance of FM82 to solidification cracking is associated with its lower Cr and Fe content. The additional Cr and Fe, as discussed previously, promotes formation of $\gamma$/Laves eutectic, which widens the STR.

Table 15 - Commercial alloys that are known to be susceptible (52MSS-C) and resistant (FM82) to solidification cracking that were used as baselines for comparison in the CPTT.

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>Nb</th>
<th>C</th>
<th>Al</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>52MSS-C</td>
<td>Bal.</td>
<td>29.24</td>
<td>8.79</td>
<td><strong>3.51</strong></td>
<td><strong>2.51</strong></td>
<td>0.02</td>
<td>0.13</td>
<td>0.18</td>
</tr>
<tr>
<td>FM82 (YB8908)</td>
<td>Bal.</td>
<td>19.15</td>
<td>0.98</td>
<td>-</td>
<td><strong>2.38</strong></td>
<td>0.044</td>
<td>0.021</td>
<td>0.37</td>
</tr>
</tbody>
</table>

The alloys from Table 13, and Variant #1 + 5% 1080 wire from Table 14, were tested using the 3rd generation CPTT with the parameters optimized by Luskin, to be comparable to the data from Przybylowicz [12, 73]. Due to limitations in the amount of material, not all lengths could be tested, so most material was used to determine the threshold for cracking instead of testing the full range of pin lengths. The results from the tests are shown in Figure 53. The Ta-bearing Variants #5 and #6, performed as expected, with cracking resistance better than 52MSS-C and slightly worse than FM82. There
appears to be no significant effect of Mo on the cracking resistance in the Ta-bearing variants.

The results for the Hf-bearing Variant #1 and #3 were again unexpected. There was no discernible effect of Mo on the cracking resistance in these alloys. Additionally, the threshold for cracking was at the shortest pin length possible to cast, showing solidification cracking resistance worse than 52MSS-C. These results were highly unexpected, as the STR for Variant #1 + 5% 1080 wire was experimentally determined to be 115°C. This contradicts the widely held belief that STR correlates with solidification crack susceptibility. This was later theorized to be related to a wetting effect of the eutectics, and is discussed further in Chapter 10.

![Figure 53 - CPTT results from optimized variants from Table 13. 52MSS-C and FM82 data are from Przybylowicz [73].](image-url)
9.4 Strain to Fracture Testing

The Strain to Fracture (STF) test normally requires dogbone samples to be machined from either all weld metal overlays, or a V-groove filled in with the material of interest. Due to delays with the production of weld wire, small buttons were made with the nominal optimized compositions without Mo. For the Hf-bearing composition, this was Ni-30Cr-8Fe-0.25Hf-0.04C (in wt%). For the Ta-bearing, this was Ni-30Cr-8Fe-4Ta-0.04C (in wt%). These buttons were then used in the modified STF sample preparation described in the experimental procedures. Because of material limitations, only a few tests could be run for each composition.

The results from the tests are shown in Figure 54. Data from two other alloys, tested previously by Nissley, FM52M and FM52MSS are plotted for reference. These are examples of how susceptible (FM52M) and resistant (FM52MSS) alloys perform in this test. The most important metric for ranking alloys is the threshold strain to fracture at 950°C. This is defined as the highest strain that can be applied without cracking. The optimized compositions performed as expected. The Ta-bearing composition, which has the same at% of Ta as the at% of Nb in FM52MSS, has a very similar response to FM52MSS. The Hf-bearing composition, which had been reduced from 0.75 wt% Hf to 0.25 wt% Hf because of solidification cracking concerns, has a slightly lower susceptibility. The 0.75 wt% Hf composition was optimized to produce 2 vol% fraction eutectic, which was roughly equivalent to the eutectic fraction of FM52MSS. Since it had to be lowered to address solidification cracking concerns, it is not surprising that its DDC
resistance is slightly lower. However, it still has a threshold significantly higher than that of FM52M, and would likely be more resistant than FM52M in real world applications.

Figure 54 - Strain to fracture results of optimized Hf and Ta-bearing compositions, without Mo. Data from Nissley of FM52M, which is known to be susceptible to DDC, and FM52MSS, which is resistant, are shown for comparison [6].

Grain boundaries from untested spot welds of the STF samples were characterized by optical microscopy. Throughout the spot weld, relatively tortuous migrated grain boundaries could be found. Examples of such boundaries for the Hf-bearing (A) and Ta-bearing (B) compositions are shown in Figure 55. These tortuous boundaries are a result of the eutectic in each sample pinning the boundaries as they migrate. The eutectic in each sample is evenly distributed. Analysis of eutectic by averaging three random binary images from each sample with ImageJ® determined that the Hf-bearing sample had 1.2 +/- 0.12 area% eutectic, while the Ta-bearing sample had 1.8 +/- 0.15 area% eutectic.
The Hf-bearing sample’s eutectic fraction is much lower than the desired 2% as the level of Hf was reduced from 0.75 to 0.25 wt% to combat solidification cracking issues, as discussed previously. However, the nature of the grain boundaries is still fairly tortuous and as discussed, the DDC resistance lies somewhere between that of FM52M and FM52MSS.

Figure 55 - Micrographs of untested STF samples of Ni-30Cr-8Fe-0.25Hf-0.04C (A) and Ni-30Cr-8Fe-4Ta-0.04C (B), showing tortuous migrated grain boundaries.

9.5 Characterization of Optimized Compositions

Cross sections of select cast pins were made to assess the nature of the eutectic that forms in the different variants. Figure 56 shows SEM micrographs of the Ta-bearing Variants #5 and #6. The general nature and distribution of the eutectic is very similar with and without 4 wt% Mo additions. The eutectic is evenly distributed along subgrain boundaries and exists as discreet, separate particles. There were no places where it appeared that the eutectic had ‘spread out’ along a subgrain boundary. The main difference is the solidification mode, with Variant #6 exhibiting a cellular dendritic mode.
and Variant #5 exhibiting a cellular mode. This is not attributed to the Mo additions, as different pins were observed to have different solidification modes depending on where the section was taken. Additionally, qualitative EDS showed enrichment of Ta and C in the eutectic particles when compared to the matrix. There was also an enrichment of Mo in the interdendritic regions in Variant #6. The eutectic constituents were too small to determine whether Mo was present within the eutectic or just enriched in the area around the eutectic. It was not feasible to assess migrated grain boundary character in the cast pin samples, as the cooling rate is quite fast post solidification, and there isn’t much time for grain boundary migration.

![Figure 56 - SEM cross sections of Ta-bearing cast pins. (A) Variant #6, with Mo, and (B) Variant #5, without Mo.](image)

To compare the eutectic morphologies of Hf-bearing and Ta-bearing alloys, Ta-Mo-bearing and Hf-Mo-bearing cast pins were sectioned and observed in the SEM
(Variants #6 and #2). As Variant #1 was made with the incorrect carbon content, it was not used for comparison with Variant #5. Figure 57 shows the same Ta-Mo-bearing Variant #6 micrograph from Figure 56, along with a cross section of a Hf-Mo-bearing pin, Variant #2. There is slightly less eutectic in Variant #2, but this is expected since the Hf content was lowered below the optimized value as discussed earlier. The nature of the eutectics is also different. There were some small discrete eutectics in the interdendritic regions, but occasionally long spread out eutectics could be found along sub grain boundaries. It is not clear if this is related to a wetting effect.

Figure 57 - SEM cross sections of a Ta-bearing cast pin, (A) Variant #6, with Mo, and a Hf-bearing cast pin, (B) Variant #2, with Mo.

Fracture surfaces of the Variant #2 Hf-Mo pins were investigated due to the extremely poor resistance to solidification cracking. While the cross sections show mostly discrete eutectic with a relatively low volume fraction, the fracture surface is much different. A
secondary electron image of the fracture, Figure 58 A, exhibits the characteristic egg-crate morphology indicative of solidification cracking. The backscattered image, Figure 58 B, shows a large fraction of the surface with higher Z contrast, indicating presence of heavier elements. Qualitative EDS analysis showed these regions to be largely enriched in Hf. The area fraction of eutectic on this surface is much greater than that of the cross section, indicating that a significant amount of eutectic liquid was present at the time of fracture.

Figure 58 - Secondary electron image (A), and backscatter electron image (B) of a cracked Hf-Mo Variant #2 pin.

9.6 Conclusions

The further weldability testing revealed that the optimized Hf-bearing compositions had poor solidification crack resistance, which was unexpected based on the STR. However, it should be noted that CPTT and the modified STF test used to evaluate weldability in
this chapter are good tests for screening limited sets of compositions without making actual welds, which requires filler wire and can be costly. The optimized Ta and Hf-bearing compositions had a evenly distributed eutectic morphology that contributed to their relatively good DDC resistance. The optimized Ta-bearing composition also had good solidification crack resistance, which has lead to this composition being the primary candidate for the nuclear power industry moving forward. Since the optimized Hf-bearing composition had unexpectedly poor solidification crack resistance, even though the STR was narrow, a study on the possible influence of eutectic wetting on crack susceptibility has been performed.
CHAPTER 10
ROLE OF WETTING ON SOLIDIFICATION CRACK SUSCEPTIBILITY

10.1 Introduction

To address differences in expected solidification cracking resistance, a novel theory involving differences in eutectic wetting was proposed. It was expected that the Hf-bearing alloys, which had narrow STRs, and should have been resistant to solidification cracking. The hypothesis is that these alloys were susceptible because the Hf-rich eutectics wet the grain boundaries and caused the final liquid to solidify to be present as a film instead of discrete droplets. It turns out that elements such as Hf and Zr are intentionally added to brazing alloys to improve wettability, and this fact was what sparked this investigation.

Another facet to this theory involves the amount of eutectic to promote crack healing. It is generally regarded that weld metals can be resistant to solidification cracking by having enough eutectic to promote extensive crack healing, as shown in Figure 59 [28]. In region 1 on the figure, alloys are not susceptible because they do not have enough eutectic to form continuous liquid films. In region 2, there is enough eutectic to form continuous liquid films that can be pulled apart due to internally or externally applied strains. This is supported by the observation of “clean” dendritic fracture surfaces that are characteristic of solidification cracking. In region 3, there is
enough eutectic to backfill cracks if and when they form. This is actually taken advantage of in the 4000 series (Al-Si) of aluminum alloys. These alloys are known to be very weldable due to eutectic backfilling [28, 80]. What is not known is the level of eutectic that is needed to promote healing, and if this amount is consistent across alloy systems. More on how this applies to the theory proposed will be discussed in Section 10.4.

![Figure 59 - Schematic of cracking susceptibility and fraction eutectic as a function of composition, showing the healing effect that occurs at high levels of fraction eutectic [28].](image)

**10.2 Challenges with Wetting Experiments**

Before settling on the arc melting sessile drop test a more traditional sessile drop method was attempted, involving a vacuum furnace. Even with a rough vacuum, and later the use of a forming gas (Ar-5%H₂), there were many problems with oxidation, likely due to the long times held at high temperatures as a result of the relatively slow heating and cooling rates. Oxides are known to adversely affect wettability, and as such, reliable results could
not be obtained. Additionally, there was no way to monitor the temperature of the samples accurately. The sample was as close to the furnace control thermocouple as possible, but wetting could not be achieved without going at least 100°C above the calculated eutectic temperatures. This is problematic because wetting of liquid metals is known to increase strongly as a function of temperature above the melting temperature [81]. For some eutectics, adding 100°C to the eutectic temperature could put the furnace temperature close to, or over, the melting temperature of the substrate used. Also, the slow heating and cooling rates could give ample time for diffusion to occur at the interface, which is likely not experienced during actual welding. These issues combined with the oxidation issues were the basis for a new, modified sessile drop test, which used an electric arc to quickly melt the button onto the substrate. This technique has been outlined in section 6.4.

10.3 Results of Modified Sessile Drop Test

The compositions of the final liquids to solidify were determined by performing Scheil simulations in Thermo-Calc® as described in the experimental procedures. The compositions used are listed in Table 3. All eutectics tested are the lowest temperature eutectic possible in the system as it was too difficult to add carbon in high enough levels via button melting to simulate a pure γ/MC eutectic. However, the lowest temperature eutectics, in this case γ/Laves or γ/Ni₇Hf₂, likely better represent the composition of the final liquid to solidify.

Before discussing the results, a small background on contact angles will be presented. The Young equation describes the relationship between the contact angle and
the interfacial energies of the solid, liquid, and gas with respect to each other [82]. The equation is shown below as Equation 4.

Equation 4 - Young equation describing relationship between interfacial energies and the contact angle [82].

\[
\cos(\theta) = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}
\]

In Equation 4, \( \theta \) is the internal contact angle as shown in Figure 60, \( \gamma_{SG} \) is the solid-gas interfacial energy, \( \gamma_{SL} \) is the solid-liquid interfacial energy, and \( \gamma_{LG} \) is the liquid-gas interfacial energy. Smaller values of \( \theta \) indicate increased wetting angles measured on the 3D images from the Keyence microscope are the outside angle, so the contact angle is 180 minus the measured angle.

![Figure 60 - Schematic showing the internal angle \( \theta \) for a droplet on a surface. Smaller \( \theta \) is a result of increased wetting.](image)

The arc melting sessile drop technique was performed as detailed in the experimental section on combinations of the alloys and substrates listed in Table 3 and Table 4. The results of the wetting angles are shown in Figure 61. It can be seen that Nb and Ta \( \gamma \)/Laves eutectics have similar contact angles, even if Mo is added to the eutectic.
However when Alloy C22 is used as the substrate, the contact angle decreases substantially. In this case the Mo is present in the substrate and not in the eutectic itself. Work done by Afonso et al. has shown that when Mo is added to Nb-bearing Ni-base weld metals, the Mo segregates during solidification, but does not end up in the eutectic phase, and is present in higher concentrations just next to the eutectics [18]. Using Alloy C22 as a substrate was an attempt to simulate this. This shows that adding Mo to such weld metals has a significant effect on the wetting of the final eutectic to solidify.

The $\gamma$/$\text{Ni}_7\text{Hf}_2$ eutectic also had a much lower contact angle, and thus increased wetting compared to the Nb and Ta $\gamma$/Laves eutectics. This is consistent with the hypothesis that Hf was causing an increase in the wetting of the final liquid to solidify. This helps explain the discrepancy between the narrow STR of the optimized Hf-bearing
composition, and the poor solidification cracking resistance observed in the CPTT. For a small amount of eutectic liquid, increased wetting will promote spreading of that liquid along grain boundaries, which leads to the presence of continuous liquid films at the end of solidification. These films are then easily pulled apart by shrinkage and/or external stresses.

However, a different explanation is needed to explain how Mo, which has now been shown to also increase wetting of eutectics by its enrichment of the area around the eutectics, can improve solidification cracking resistance as shown by Wheeling in Figure 22 [61]. In short, this increased wetting caused the Hf-bearing alloys to be more susceptible to cracking, and caused alloys with relatively high levels of Nb tested by Wheeling to be more resistant. A hypothesis to explain this deals with the amount of eutectic formed. It is speculated that at low fraction eutectics, increased wetting causes liquid films to spread along grain boundaries, increasing susceptibility to cracking. At higher fraction eutectics, this increased wetting promotes capillary flow which helps to heal cracks that form. There may even be a viscosity component to this theory, but this has not been explored in this work.

10.4 Fraction Eutectic and Crack Healing in Aluminum Alloys

The theory described in the previous section gives rise to the question of how much eutectic liquid is needed to promote crack healing. In aluminum alloy systems, solidification cracking during welding is a major issue, due to the large STR and high thermal contraction during solidification. This creates a significant amount of stress as the material solidifies. The crack healing phenomena is taken advantage of in some weld
metals such as the 4000 (Al-Si) series. These alloys generate a significant amount of eutectic that backfills cracks that form during solidification. One classic diagram that demonstrates this phenomenon, developed by Dudas and Collins, compiles historical data of crack susceptibility for various binary aluminum alloy systems [80]. Similarly to Figure 59, this diagram shows how cracking susceptibility increases, then decreases, as the composition is enriched with solute. Dudas and Collins did not quantify the amount of eutectic for these alloys, and only discussed how backfilling occurred when ‘enough’ eutectic was present. This diagram has been modified here to show the volume fraction eutectic at the point where the crack susceptibility curves begin to level off due to backfilling, indicated by the red line in Figure 62. To determine the volume fraction eutectic, JMatPro® (Al-Alloy Database) was used to perform a Scheil simulation for the compositions at the red lines. JMatPro® was used over Thermo-Calc® as its databases include density information and as such it can calculate a volume fraction from the mole fraction results.

From Figure 62 without the volume fraction eutectic information, it can be seen that the shapes of the curves are very different among alloy systems. Additionally, the concentrations of solute where crack healing begins to take effect are also different. This could initially be assumed to be because these systems have different solid solubility for these elements, and therefore the fraction eutectic values might all be similar at these points. However, the JMatPro® calculations clearly show this is not the case.
Figure 62 - Relative solidification crack susceptibility curves for various Al-alloys. Fraction eutectic was calculated by JMatPro® for compositions shown by red lines, which is where the crack susceptibility drops down due to healing effects. Diagram adapted from Dudas and Collins [80].

The Al-Si and Al-Cu systems both have low susceptibility due to healing at around 11-12 vol%, while in Al-Mg and Al-Mg₂Si systems this occurs around 4 vol%. To better visualize these differences, the data in Figure 62 were re-plotted against calculated fraction eutectic, instead of wt% alloying element. Figure 63 shows the data this way, and gives a much clearer picture of the amount of eutectic needed for healing. Al-Si and Al-Cu systems behave similarly in cracking response vs. fraction eutectic. Al-Mg and Al-Mg₂Si also have a similar response that is much different from Al-Si and Al-Cu. These differences could be due to differences in wetting characteristics and possibly even viscosity. To assess this, JMatPro® was used to calculate the surface tensions of the final
liquids to solidify, at their eutectic temperatures. The compositions of the final liquid to solidify for each system were determined from the previously calculated Scheil simulations. The surface tension essentially represents the $\gamma_{LG}$ term in Equation 4, in vacuum, which is a good approximation for an internal crack or a grain boundary.

JMatPro® was also used to calculate the surface tension of the solid aluminum, also in vacuum, close to the melting temperature, which was 1020 mN/m. This would represent $\gamma_{SG}$ in Equation 4. Unfortunately, $\gamma_{SL}$ is difficult to calculate, it is typically determined after contact angle measurements have been made. However, things can be simplified somewhat since Equation 4 deals with the cosine of the angle. For contact angles less than 90°, a smaller value for $\gamma_{LG}$ will lead to a larger value for $\cos(\theta)$. This leads to a smaller contact angle as $\gamma_{LG}$ decreases. Therefore, a final liquid to solidify with lower surface tension more easily wets a grain boundary.
Figure 63 - The same curves from Figure 62, with the data re-plotted to match the calculated volume fraction eutectic instead of the wt% alloying element. The JMatPro® calculated surface tensions for the final liquid to solidify for each system are also displayed.

The shapes of these curves give some insight on how wetting effects solidification cracking susceptibility in multiple ways. Eutectic liquids that have higher surface tension, such as those from the Al-Si and Al-Cu system, and do not wet boundaries as easily, have moderate resistance to solidification cracking at low volume fraction eutectic amounts. Their susceptibility is not at a maximum until around 5-6 vol% eutectic. However, they do not experience significant crack healing until well over 10 vol% eutectic. Conversely, eutectic liquids with lower surface tension, such as those in the Al-Mg and Al-Mg₂Si systems, experience their maximum susceptibility around 1-2 vol% eutectic. For these
systems, the increased wetting of the final liquid to solidify likely causes this liquid to spread out along boundaries, causing them to be continuous along the boundary and susceptible to rupture under stress. However, these two alloys experience crack healing with as little as 5-6 vol% eutectic. In this case, the increased wetting is likely promoting backfilling by capillary action immediately after cracks form.

10.5 Effect of Eutectic Wetting on Solidification Crack Susceptibility

The effect of surface tension on wetting and how that relates to solidification cracking for aluminum alloys can also be applied to the alloys tested in this study. The optimized Hf-bearing alloy, with around 1-2 vol% eutectic, had extremely poor solidification cracking resistance as shown in Figure 53. The Ni₂Hf₂ eutectic was also shown to have increased wetting over other eutectics. The small amount of eutectic present likely spread along grain boundaries at the end of solidification and caused poor solidification cracking resistance. Wheeling showed that Ni-30Cr-6Nb alloys with and without Mo additions had similar fraction eutectics, in this case around 7 vol% [61]. However, the alloy without Mo was extremely susceptible to solidification cracking while additions of Mo caused extensive healing and good resistance to cracking. In this work, the additions of Mo to the substrate caused an increase in wetting of Nb Laves eutectics. This is an example of where the increased wetting promoted more crack healing for a similar fraction eutectic.

After analyzing all of the data from the aluminum alloys, alloys from Wheeling’s research, and alloys in the authors work, a generalized theory on how wetting and fraction eutectic affect solidification cracking is proposed. This theory is summarized in Figure 64 and Figure 65. For alloys with low fraction eutectic, if the final liquid to
solidify has a low $\theta$ (more wetting), it will be more susceptible to solidification cracking than an alloy with the same fraction eutectic and liquid with a high $\theta$ (less wetting). The converse is true for a slightly higher fraction eutectic. If the final liquid to solidify has a low $\theta$, it can be quite resistant due to increased backfilling. For the same eutectic fraction, liquids with high $\theta$ will be more susceptible to cracking, as there is not enough liquid to promote backfilling and the poor wettability does not assist in feeding liquid into cracks that have formed.

Figure 64 - Generalized theory on how alloys have different solidification crack susceptibility as a function of fraction eutectic, when the eutectics have either low $\theta$ (more wetting) or high $\theta$ (less wetting).
**10.6 Conclusions**

It is proposed that solidification temperature range can still be a good metric for predicting solidification cracking behavior, provided that the wetting characteristics of the eutectic liquids are comparable within a given composition range, and the composition is not rich enough to get over the peak on the susceptibility curve in Figure 64. For alloys with eutectics that have high $\theta$ (less wetting), such as Nb and Ta-bearing alloys, increasing the Nb or Ta will increase the fraction eutectic, STR, and crack susceptibility simultaneously over a wide range of compositions, before crack healing.
will take over. This was clearly seen when comparing Nb and Ta-bearing alloys, as the eutectics that form in these systems are not only similar (γ/MC and γ/Laves), but the wetting characteristics of each were nearly equivalent as well. Since they had similar eutectic wetting characteristics, reducing the STR of the Ta-bearing alloy relative to a Nb-bearing alloy also reduced the susceptibility.

For alloys with eutectics that have low θ (more wetting), even if the STR is low, even a relatively low fraction eutectic can cause susceptibility to be quite high. STR can likely still predict cracking susceptibility up until the peak on Figure 64, but the range of fraction eutectics where this is possible could be very narrow. Additionally, the STR values should not be used to compare solidification cracking susceptibility to other alloys that may have different eutectic wetting behavior. Avoiding solidification cracking in an alloy with low θ is likely best done by getting over this peak, as crack healing will become more prevalent at lower fraction eutectics than an alloy with a higher θ.
CHAPTER 11

CONCLUSIONS

The main goal of this work was to improve the weldability of Ni-30Cr filler metals by identifying alternative eutectic forming elements to Nb, and then optimize compositions that could be resistant to both solidification cracking and ductility dip cracking. Along the way, many other useful observations were made, with regards to elemental effects on solidification behavior, and how wetting can affect the solidification cracking response with respect to fraction eutectic. The main conclusions are as follows:

1. Through computational modeling and literature review, Ta and Hf were identified as potential alternatives to Nb in high Cr Ni-based alloys, due to their higher terminal eutectic temperatures, which allow them to form sufficient eutectic for DDC resistance, while keeping the STR below 150°C, preventing solidification cracking.

2. Through the use of computational and experimental techniques combined with a design of experiment methodology, elemental effects on solidification behavior were determined for Nb, Ta, and Hf-bearing systems, and compositions were then optimized using a genetic algorithm that should be resistant to both DDC and solidification cracking.
3. The eutectics that form in Ta and Hf-bearing high Cr Ni-based alloys were identified to be $\gamma$/Laves and $\gamma$/Ni$_7$Hf$_2$, respectively. $\gamma$/MC eutectics form in both systems.

4. It was also found that similar to Fe additions, additional Cr also promotes the formation of $\gamma$/Laves eutectic in Nb and Ta-bearing Ni-base alloys. This helps explain the poor resistance to solidification cracking of 30 wt% Cr alloys such as FM52MSS as compared to 20 wt% Cr alloys such as FM82, even though they both have around 2.5 wt% Nb.

5. Additions of Cr do not promote a $\gamma$/Laves phase in Hf-bearing Ni-based alloys, but instead promote the $\gamma$/Ni$_7$Hf$_2$ eutectic, which has a terminal eutectic temperature of around 1250°C, which leads to a much narrower STR compared to Nb and Ta-bearing alloys.

6. The optimized Ta-bearing composition, Ni-30Cr-8-Fe-4Ta-0.04C, was found to have DDC resistance comparable with that of alloy FM52MSS, and solidification cracking resistance comparable to that of FM82.

7. The optimized Hf-bearing composition, Ni-30Cr-8Fe-0.25Hf-0.04C, was found to have DDC resistance in between alloy FM52M and FM52MSS, and solidification cracking resistance that was very poor, even though the STR was much narrower than susceptible alloys.
8. A wettability study was devised as a result, and found that the $\gamma$/Ni$_7$Hf$_2$ eutectic wets out much more on an Alloy 600 substrate than Nb and Ta rich $\gamma$/Laves eutectics. It was also found that Mo, when present in the substrate, caused an increase in wetting of Nb rich $\gamma$/Laves eutectic.

These results, along with a cursory study of some historical solidification crack susceptibility data in Al-alloy systems, led to the development of a theory on how wetting affects solidification cracking and crack healing as a function of fraction eutectic. Eutectics that wet more have their crack susceptibility vs. fraction eutectic peak shifted more to the left, while eutectics that wet less have their peaks shifted more to the right. This development will be very important for future researchers when designing new alloys with weldability in mind.
CHAPTER 12
FUTURE WORK

Since the wetting characteristics of the Hf-bearing alloys caused the solidification crack susceptibility to be very poor at the target fraction eutectic, the optimized Ta-bearing composition looks the most promising moving forward. At the time of publication, the commercial wire has not been drawn down to a size acceptable for GTA welding. As such, making actual welds for qualification is a main task in the near future. These welds will need to be inspected for cracks, as well as tested to meet all AWS code requirements. Penetration and general welding characteristics might also be different, and optimal welding parameters for applications such as cladding or joining will need to be determined. Although not predicted to be an issue, corrosion testing of such welds will need to be carried out, to ensure good PWSCC resistance.

The wetting study performed in this work has brought to light a previously unexplored facet with respect to the mechanism of solidification cracking. The previous method of using STR to predict susceptibility only holds when comparing alloys with similar eutectic wetting behavior, and within a limited composition space. This study only looked at the influence of surface tension of the final liquid to solidify on crack susceptibility, but it is possible that viscosity may also play a role. More viscous liquids might have trouble flowing into cracks to heal them. Additionally, this study only investigated a few eutectic compositions and substrate combinations to determine their
wetting characteristics. A study that combines this wetting data with actual crack susceptibility data from a test such as the CPTT, over a range of fraction eutectics, could help make the schematic shown in Figure 64 much more accurate.

There might be a way to quantify the eutectic wetting by looking at the morphology at the grain boundaries, i.e. how spread out it is, for a given volume fraction eutectics. This would eliminate the complications and difficulties in performing a sessile drop test on liquid metals with relatively high melting temperatures.
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APPENDIX A: DEVELOPMENT OF HIGH-CR, NI-BASED FILLER METALS USING COMBINED COMPUTATIONAL & EXPERIMENTAL TECHNIQUES

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Development of High-Cr, Ni-Based Filler Metals Using Combined Computational and Experimental Techniques

Filler metals with optimized solidification behavior are designed to reduce susceptibility to solidification and ductility-dip cracking

BY E. W. FUSNER, A. T. HOPE, AND J. C. LIPPOLD

ABSTRACT

Nickel-based filler metals containing 30 wt-% chromium are required in the nuclear power industry in order to provide resistance to primary water stress corrosion cracking. Existing filler metals have exhibited susceptibility to solidification and ductility-dip cracking, thus the motivation for this study was to develop filler metals resistant to both these cracking phenomena. A design of experiment methodology used in conjunction with computational and experimental techniques was employed to statistically determine the effects of Fe, Mo, C, Hf, and Nb on the solidification behavior of a Ni-30Cr base composition. Target solidification behavior included a solidification temperature range of 125°C and a fraction eutectic constituent of 2 vol-% to mitigate solidification and ductility-dip cracking, respectively. Regression analysis of data gathered from solidification experiments and volume fraction eutectic measurements were used to develop response surfaces relative to compositional factors included in the investigation. Statistical optimization based on solidification temperature range contour plots overlaid with volume-fraction eutectic revealed that an optimum fraction eutectic was achievable with Hf-bearing filler metals relative to those containing Nb, while maintaining a narrower solidification temperature range. Statistical optimization of experimental solidification temperature range and fraction eutectic data based on desirable solidification criteria using genetic algorithm-based design software have identified several compositions for further microstructural characterization and weldability testing. This paper demonstrates how a combination of computational and experimental techniques provides an efficient methodology for filler metal development.

Introduction

Welding electrode Inconel®82 (IN82) and filler metal Inconel®82 (IN82) were used extensively in pressurized water reactor (PWR) and boiling water reactor (BWR) steam generators (SGs) as matching consumables for Inconel®600 (IN600) after intergranular stress corrosion cracking (IGSsC) failures of sensitized Type 304 stainless steels in the 1960s brought about the need for base materials and consumables more suited to these environments (Ref. 1). These two alloys also served as the filler metals of choice for dissimilar metal welds (DMWs) made between low-alloy pressure vessel steel and 300-series austenitic stainless steel because of a coefficient of thermal expansion intermediate of the steels. IN82 and IN82 contained Nb (1–3 wt-%), an alloying addition known to form niobium carbide (NbC) via a eutectic reaction at the end of solidification. Initially, Nb was intentionally added to tie up excess free carbon during similar and DMWs on base materials with relatively high carbon contents. Eventually, Nb was removed from solid solution strengthened, Ni-based filler metals (such as IN52) until serious problems with ductility dip cracking (DDC) resulted in the reintroduction of Nb in high-Cr filler metals such as 52M, 52MSS, and 52I (Refs. 2, 3).

In 1974, failure analysis of an IN600 safe-end forging from the recirculation inlet nozzle of a BWR at the Duane Arnold Nuclear Power Plant determined the root cause as IGSsC. The failure initiated in the heat-affected zone (HAZ) of an IN600/IN82 weldment and propagated through the weld metal, raising questions regarding the IGSsC susceptibility of both materials (Ref. 4). Soon after, Inconel®820 (IN600) was proposed as a replacement for IN600 in both BWR and PWR SGs. With nominally 30 wt-% Cr, IN600 demonstrated superior corrosion performance in primary water, high-temperature caustic, acid sulfate, and oxygenated chloride environments relative to IN600, and was eventually designated as the replacement alloy for primary water applications (Ref. 5). IN182 and IN82 continued to serve as leading consumables for IN690 when repair welding SGs, as well as for safe end DMWs between pressure vessel steels and austenitic stainless steels.

In 1988, nondestructive testing of PWR safe-end joints indicated primary water stress corrosion cracking (PWSSCC) degradation in DMWs between IN182/IN82 and austenitic stainless steel, driving the need for 30 wt-% Cr, Ni-based filler metals that would match the intergranular corrosion resistance of IN690 (Refs. 6–8). As a result, both welding electrodes Inconel®152 (IN152) and filler metal IN52 with nominally 30 wt-% Cr were introduced.

These new filler metals exhibited excellent resistance to IGSC and surface corrosion (Ref. 9), but IN52 was found to be susceptible to DDC. The cracking was observed along straight, migrated grain

KEYWORDS

Ni-Based Filler Metals
Solidification
Cracking
Ductility-Dip Cracking
Filler Metal Development
Computational Techniques
WELDING RESEARCH

Fig. 1 — Flow chart of the steps taken in this study.

Fig. 2 — Button melting device for casting small experimental heats of material.

Fig. 3 — Plunger device schematic for acquiring weld solidification thermal histories.

| Table 1 — Solidification Temperature Range (STR) Data for Commercially Available High-Cr Ni-Based Filler Metals Filter Metals (from Alexandrow et al., Ref. 2) |
|---|---|---|---|
| Source | 52M | 52MSS | 52I |
| STR (°C) | 144 | 192 | 232 |

of DDC and the intergranular precipitation of M23C6 carbides may play a role in exacerbating cracking (Ref. 13). Recent testing at The Ohio State University (OSU) has also shown that extremely low levels of S and P caused an increase in DDC. Noecker and DuPont also found that when coarse intergranular eutectics such as NMC formed, DDC resistance was high.

It was well known that Nb formed an MC carbide via a eutectic reaction with austenite in the final stages of solidification, so a new 30 wt-% Cr filler metal, IN52M, reintroduced Nb (≈1 wt-%) to solid solution strengthened Ni-based consumables. Subsequent testing and microstructural examination at OSU concluded that IN52M was also susceptible to DDC due to insufficient second-phase formation to create tortuous MGBs. Using the strain-to-fracture test, the threshold strain to induce cracking in IN52/52M2 filler materials was found to be on the order of ~2% at 950°C (Ref. 14). The susceptibility to DDC of these filler metals has also been experienced in practice.

Considerable research has led to the development of DDC-resistant filler metals such as 52MSS with 2.5 wt-% Nb and 4 wt-% Mo, and 52I with 2.5 wt-% Nb and 3 wt-% Mn (Refs. 15–17). Single-sensor differential thermal analysis (SS-DTA™) (Refs. 18–21),transverse, and cast pin tear testing demonstrated that 52MSS and 52I have increased susceptibility to solidification cracking relative to 52M and 52 due to an expansion of the STR related to the addition of Nb (Refs. 2, 3, 21). Table 1 shows their STRs as determined by Alexandrow et al (Ref. 2).

IN52M was found to be susceptible to solidification cracking after liquid penetrant testing of structural weld overlays performed on PWR safe-end joints indicated cracks at the DMW interface between the IN52M filler metal and Type 308 stainless steel substrate (Ref. 8). The IN52M overlay technique was a repair methodology adopted by the Electric Power Research Institute (EPRI) to form a new, PWSCC-resistant pressure boundary for the safe-end joint due to through-thickness PWSCC degradation of the existing IN182/IN52 weld metal. These overlays, commonly known as structural weld overlays, also produced compressive stresses at the root pass of the DMW to mitigate future PWSCC initiation and propagation (Refs. 6, 7).

The solidification cracking of IN52M was attributed to unexpectedly high dilution by the austenitic stainless steel substrate, leading to increased Fe content in the weld metal and the formation of low-melting eutectic constituents, particularly Laves phase (Ref. 6).

The major material factors that contribute to the solidification cracking susceptibility of high-Cr, Ni-based alloys are solidification temperature range (STR), fraction euteutic (fₑ), and the nature of the last-to-solidify interfacial liquid (i.e., the wetting characteristics and morphology) (Ref. 23).
By definition, STR is the temperature range from $T_{\text{Liq}}$ to $T_{\text{fus}}$. Assuming these temperatures can be either predicted or measured, the STR can be determined and correlated with the solidification cracking susceptibility of an alloy. The magnitude of the STR is influenced by composition and the occurrence of eutectic reactions that promote low-melting constituents, such as a Laves phase. A larger STR equates to a wider mushy zone incapable of accommodating the restraint that develops during weld solidification and concentrates along continuous liquid films at the solidification grain boundaries during the final stages of solidification.

Of the two remaining material factors important to solidification cracking, $T_{\text{fus}}$ is important to this preliminary investigation because the amount of liquid present during the terminal stages of solidification controls the distribution of the liquid (Ref. 23). Cynx and Kueh showed that 1–10 vol-% terminal liquid coupled with low solid/liquid surface tension created continuous liquid films along GBS that resulted in solidification cracking of continuously cast austenitic stainless steels (Ref. 24). Conversely, terminal liquid < 1 vol-% formed isolated liquid globules that increased the hot cracking resistance of the steels (Ref. 24). When the liquid fraction is greater than 10 vol-%, healing of solidification cracks by liquid backfilling is possible (Refs. 24, 25), but it is unclear if higher levels of eutectic constituents are deleterious to the properties of solid-solution strengthened high-Cr, Ni-based alloys investigated in this study.

Fraction eutectic is also important to DDC cracking susceptibility. Higher amounts of eutectic will contribute strongly to grain boundary tortuosity, which can control DDC susceptibility. Images analyzed from research done by Collins, Nisley, and Lippold show that resistant alloys have on the order of 2 vol-% eutectics (Refs. 10, 14). Therefore, 2 vol-% eutectic was chosen as the target value for this work.

This paper describes an approach for the development of a Ni-30Cr filler metal that is resistant to both solidification and ductility-dip cracking. The goal was to identify alternative carbide-forming elements that would maintain the tortuous MGBs to mitigate DDC while reducing the STR relative to Nb-containing filler metals. The filler metal development process utilized in this investigation involved a DOE methodology used in conjunction with rigorous computational modeling to develop clear relationships between independent compositional factors and dependent solidification responses.

The steps taken are outlined in Fig. 1 as a flow chart. Initially, suitable ranges for $H$ and concentration were identified based on work by Unfried et al. (Refs. 26–28). A DOE methodology was then employed to create compositions for experimental study. Subsequent statistical analysis of responses for optimization of compositional factors were based on specific solidification criteria. Experimental work involved direct measurement of solidification behavior through thermocouple plunging experiments and quantitative microstructural examination. When applicable, experimental results are compared with results from the computational analysis. Computational and experimental DOE groups with Nb as the carbide former were also investigated and compared to the Nb-bearing groups. Finally, an optimized composition is determined, and can be tested further.

**Experimental Procedures**

**Design of Experiment and Statistical Analysis: Computational Experiments**

An initial investigation was conducted to statistically determine the relative elemental effects of Fe, Mo, C, and Hf (or Nb) on the solidification behavior of Ni-based filler metals containing 30 wt-% Cr. Values for the ranges of Mo, C, and Nb in the computational Nb DOE group were chosen to represent those in current commercially available Nb-bearing filler metals including 52M, 52SS, and 52L. The values for Mo and C were chosen to be the same for the computational Hf DOE group due to a lack of published data, and to facilitate comparison of the two systems. The Fe was varied to determine if there was any effect on segregation of other alloying elements, similar to work done by Dupont (Ref. 29). Such Fe ranges also give some insight into the effect of dilution by pressure vessel steels. Values for the range of Hf were chosen based on those studied in the limited amount of literature available pertaining to the use of Hf in Ni-based alloys (Refs. 26–28, 30–35).
Two groups of 30 wt.% Cr, Ni-based alloys were generated for computational study via DOE using MINTAB®. The composition ranges and constants used to generate the DOE are shown in Table 2. A four-factor, response surface method DOE was chosen to explore the relationship between composition and output data from the Scheil Module within Thermo-Calc®. The response surface methodology is beneficial because it is capable of determining if any curvature exists in the response plot, while reducing the number of compositions required for testing. The solidification response variables of interest included the liquidus and solidus temperatures \( T_{lq} \) and \( T_{sq} \), STR, eutectic start temperature \( T_{es} \), and fraction eutectic \( f_{es} \). Since Thermo-Calc® cannot provide reliable mass fraction values, the molar fractions were used. While not ideal, it still gives an idea of relative amounts of eutectic. A Scheil simulation for each of 30 compositions generated by the DOE was conducted. The values for the responses were extracted from Thermo-Calc®, input back into MINTAB®, and then analyzed. Main effects plots were created to determine the change in response produced at each of five levels of the factors tested. Regression analyses were conducted to develop quantitative equations that describe the response surfaces in terms of Fe, Mo, C, and Hf (or Nb) on a weight-percentage basis.

Two Thermo-Calc® databases, TCNi5 and TTNi7, were evaluated in this investigation. The TCNi5 database was chosen because it contained thermodynamic data for Ni3Hf2, which was identified to exist in the experimental Hf DOE group via transmission electron microscopy (TEM) and selected area diffraction (Ref. 36).

When performing Scheil calculations, the user must have some knowledge of the potential phases that form on solidification of a particular alloy system in order to get the best information possible from the simulation. Based on this, the TTNi7 database was deemed to be nonoptimum since it did not include at least one compound that had been identified experimentally. Also, the TTNi7 database was not able to handle compositions with Hf values >1 wt.%, resulting in errors and unreliable data when trying to perform the simulation.

**Design of Experiment and Statistical Analysis: Experimental Alloys**

Based on results from the computational work, a separate DOE methodology was utilized to study similar effects on experimental alloys. The experimental technique is detailed in the next section. Optimized compositions based on minimizing the STR for solidification cracking resistance, while ensuring sufficient \( f_{es} \) for DDC resistance, were also developed as an objective of this work. The statistical software package JMP®9 was used to create a “custom” four-factor, three-level DOE resulting in two sets (experimental Nb and Hf DOE groups) of 16 alloys for study via thermocouple plunging experiments and quantitative \( f_{es} \) analysis.

Although the chosen DOE was not a response surface method, which would have resulted in five levels of each factor requiring testing of 30 alloys for each group, the “custom” DOE was designed such that interaction and squared terms would be identified by the regression analysis. The nominal alloy compositions are summarized in Table 3. A duplicate sample of each composition was made, totaling 32 samples per group, and 64 total solidification experiments.

The limits for Mo represented the high and low values that are seen in current commercially available Nb-bearing high-Cr, Ni-based filler metals (52M and 52MS). The range for Hf was chosen based on results of Scheil simulations and previous research.
(Refs. 26–28, 30–35), while the Nb alloys were given the same value as Hf for the purpose of direct comparison. Carbon levels (0.02–0.06 wt-%) represent the range that can be expected in these filler metals. Alloys were prepared and tested to determine \( T_{\text{eq}} \), \( \text{STR} \), and \( T_{\text{eq}} \).

**Alloy Preparation**

Twenty-gram “buttons” of the nominal compositions listed in Table 3 were made from high-purity materials weighed on a Mettler-Toledo AB15-S balance with masses of individual components controlled to ±0.005 g. Carbon was introduced to the alloys via plain carbon 1080 steel wire. Raw materials were ultrasonically cleaned in ethyl alcohol prior to casting on a copper hearth, resulting in so-called “buttons” because of their shape. The casting was done with a gas tungsten arc (GTA) torch under argon shielding at 200 A and \( 15/2 \) in. arc gap in the button melting device shown in Fig. 2. The buttons were flipped and remelted several times to ensure complete homogenization. A cast, cellular dendritic microstructure was produced with an observed primary dendrite arm spacing in the range of 30–50 \( \mu \)m.

The compositions of the experimental Nb DOE group alloys were analyzed using an Ametek® manufactured SPECTROMAX™ machine via optical emission spectroscopy, which has the ability to measure carbon. The measured compositions were used to refine statistical models once experimentally determined response variables were input back into MINITAB®*, Design Expert®*, and a statistical optimization program developed at OSU (Ref. 37). Results of the chemical analyses are reported in Table 4.

Comparing the nominal values of the experimental Nb DOE group buttons (Table 3) to the measured values (Table 4), it can be seen that the techniques used to control composition were fairly accurate.

The Hf DOE group alloys could not be analyzed on the same machine due to a lack of standards. To verify that the compositions were controlled with similar accuracy to the Nb group, four samples were chosen to be sent out for composition analysis by an independent lab. Inductively coupled plasma mass spectroscopy was used. The results of the chemical analysis are shown in Table 5. The values are in close agreement with the nominal values. Since all the samples could not be analyzed, the nominal values were used for further optimization.

**Solidification Experiments: Solidus Temperature Determination**

The solidus temperatures of the alloys listed in Table 3 were measured using thermocouple plunge experiments in conjunction with the SS-DTA™ technique (Refs. 18–21). After casting, a GTA spot weld was made on each button with a fixed GTA torch. The parameters for this spot weld were as follows: current 250 A, arc length 0.08 in., voltage 12 V, and weld time 4 s. At the moment the arc extinguished, a Type C thermocouple was plunged directly into the center of the molten spot according to the schematic shown in Fig. 3. The on-cooling thermal history was acquired from the liquid state down to room temperature. The thermal histories were processed with SS-DTA™ and \( T_{\text{eq}} \) was determined as determined by Thermo-Calc™ to determine the STR. Due to issues with the timing of the thermocouple plunge, \( T_{\text{eq}} \) cannot be acquired every time. In instances where it was, the computationally determined \( T_{\text{eq}} \) was found to be in good agreement with the measured \( T_{\text{eq}} \), and as such was used in determining STR. The values were input into MINITAB®, Design Expert®, and the optimization software for subsequent statistical analysis and development. Tables 4 and 6 present the raw experimental data that resulted from the solidification experiments.

**Volume Fraction Eutectic Analysis**

Light optical microscopy (LOM) was conducted on the experimental Nb DOE groups.
group buttons after the solidification experiments were performed in order to determine the solidification front. All measurements were made in the remelted region on the top of the button. A cross section was metallographically prepared for each composition, an example of which can be seen in Fig. 5. The samples were mounted, ground, vibratory polished through 0.05 μm with colloidal silica, and electrolytically etched with a 10% vol chromic acid aqueous solution at 5 V for 10-15 s. Quantitative image analysis (QIA) was conducted on three separate light optical micrographs 500x magnification of the air-solidified SS-DTA samples. ImageJ software was used for binary conversion of the images, and to determine area fractions of total eutectic constituents. No attempt was made to determine relative amounts of individual eutectic constituents, namely, γNbC and γN-Hf2. Area fractions were assumed to be equivalent to volume fractions.

Figure 6 shows an example LOM image, along with the converted binary image created by ImageJ. It can be seen that the conversion process adequately described the total eutectic constituent for quantification. The average of three f\text{tot} values for each composition was input into Minitab®, Design Expert®, and the optimization software for subsequent statistical analysis. Tables 4 and 6 also present the raw experimental data that resulted from the volume fraction eutectic analyses.

For the Hf-bearing alloys, a chromic acid etch was unsuitable. Therefore, volume fraction eutectic analysis was conducted on samples in the unetched condition using a scanning electron microscopy (SEM). An XL30 FESEM was used in backscattered electron (BSE) imaging mode with 20-kV accelerating voltage and a spot size of 5. Images were taken at 1000x magnification. Figure 7 shows an example SEM image and its binary conversion.

### Results and Discussion

#### Computational Determination of Elemental Effects on Solidification Behavior

Thermo-Calc® (TNCI5 database) was used to conduct Schell simulations on two groups of high-Cr, Ni-based filler metal compositions generated by Minitab® via a four-factor, response surface method.
DOE. All simulations were run with carbon included as a fast diffusing species. The phases retained in the system when conducting Scheil simulations for the Hf DOE group alloys were liquid, FCC, HCC, Laves, and Ni3Hf2. Dissolution experiments in conjunction with X-ray diffraction were used to show the existence of HfC in the experimental Hf DOE group alloys, as discussed later (Ref. 26). Ni3Hf2 has been observed experimentally in similar Ni-alloy compositions containing Cr and Hf via selected area diffraction in TEM (Ref. 36). The phases retained for simulations of the Nb DOE group alloys were liquid, FCC, NBC, and Laves, which have been shown to form on solidification of Nb-bearing, Ni-based filler metals (Ref. 23, 38–42).

The values for $T_{\text{sol}}$, $T_{\text{Liq}}$, $T_{\text{STC}}$, and $c_{\text{ext}}$ were determined for each composition, extracted from Thermo-Calc™, and input into MINITAB™ for further analysis. Table 7 shows the average and standard deviation for each response calculated over the entire range of compositions for each of the two alloy groups. Comparing row 3 of Table 7, it can be seen that the Hf DOE group alloys presented a narrower STR (on average) relative to the Nb DOE group. These computational data suggest that the Hf DOE group alloys should demonstrate slightly improved solidification cracking resistance (based on the STR value) in the composition space defined by the DOE.

Comparing the standard deviation for $T_{\text{ext}}$ of both groups (Table 7, row 2), it can be seen that the value for the Nb DOE group is considerably larger than that of the Hf DOE group. This demonstrates the disparity between possible terminal eutectic reaction temperatures that could occur in each system. Cieslak et al. used differential thermal analysis (DTA) to show that the disparity between the terminal γ/NbC and γ/Laves eutectic reaction temperatures was as large as 98°C for Alloy 625 (Ref. 40) and as large as 131°C in Alloy 625 plus (Ref. 39).

The standard deviation for $T_{\text{ext}}$ of the Hf DOE group is smaller, which indicates that the disparity between the terminal γ/HfC and γ/Ni3Hf2 eutectic reaction temperatures is also smaller. Hope et al. showed that this disparity was as small as 65°C based on computational pseudo-binary diagrams created by Thermo-Calc™ using the TCNi5 database (Ref. 38).

Nash and West reported the equilibrium solidus temperature of a Ni-30Cr-7Hf alloy containing the γ/Ni3Hf2 eutectic phase to be 1280 ± 12°C (Ref. 43). Frey and Holleck determined the eutectic melting point of HfC in pure Ni to be 1320 ± 20°C via DTA (Ref. 44). Although the

### Table 5 — Chemical Analysis Results of Select Experimental Hf DOE Group Buttons

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>C</th>
<th>Hf</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF-1</td>
<td>30.15</td>
<td>8.08</td>
<td>0.001</td>
<td>0.024</td>
<td>2.13</td>
</tr>
<tr>
<td>HF-10</td>
<td>30.37</td>
<td>8.03</td>
<td>3.97</td>
<td>0.009</td>
<td>2.68</td>
</tr>
<tr>
<td>HF-20</td>
<td>29.95</td>
<td>13.30</td>
<td>4.99</td>
<td>0.008</td>
<td>0.40</td>
</tr>
<tr>
<td>HF-27</td>
<td>30.07</td>
<td>18.29</td>
<td>3.82</td>
<td>0.020</td>
<td>0.40</td>
</tr>
</tbody>
</table>

All values in wt-%. (Ref. 28).

### Table 6 — Nominal Alloy Compositions and Responses for the Experimental Hf DOE Group

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>C</th>
<th>Hf</th>
<th>$T_{\text{Liq}}$</th>
<th>$T_{\text{sol}}$</th>
<th>STR</th>
<th>$c_{\text{ext}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF-1</td>
<td>Bal.</td>
<td>30*</td>
<td>8</td>
<td>0</td>
<td>0.02</td>
<td>2</td>
<td>1343**</td>
<td>1187</td>
<td>156</td>
<td>0.036</td>
</tr>
<tr>
<td>HF-2</td>
<td>Bal.</td>
<td>30</td>
<td>8</td>
<td>0</td>
<td>0.02</td>
<td>2</td>
<td>1336</td>
<td>1161</td>
<td>175</td>
<td>–</td>
</tr>
<tr>
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<td>Bal.</td>
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<td>8</td>
<td>0</td>
<td>0.06</td>
<td>0.5</td>
<td>1346</td>
<td>1143</td>
<td>203</td>
<td>0.009</td>
</tr>
<tr>
<td>HF-4</td>
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<td>30</td>
<td>8</td>
<td>0</td>
<td>0.06</td>
<td>0.5</td>
<td>1351</td>
<td>1147</td>
<td>204</td>
<td>–</td>
</tr>
<tr>
<td>HF-5</td>
<td>Bal.</td>
<td>30</td>
<td>8</td>
<td>4</td>
<td>0.02</td>
<td>1.25</td>
<td>1341</td>
<td>1136</td>
<td>205</td>
<td>0.023</td>
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<td>4</td>
<td>0.02</td>
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<td>201</td>
<td>–</td>
</tr>
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<td>4</td>
<td>0.04</td>
<td>0.5</td>
<td>1335</td>
<td>1199</td>
<td>136</td>
<td>0.009</td>
</tr>
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<td>8</td>
<td>4</td>
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<td>0.5</td>
<td>1334</td>
<td>1192</td>
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<td>–</td>
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<td>8</td>
<td>4</td>
<td>0.06</td>
<td>2</td>
<td>1320</td>
<td>1138</td>
<td>182</td>
<td>0.05</td>
</tr>
<tr>
<td>HF-10</td>
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<td>30</td>
<td>8</td>
<td>4</td>
<td>0.06</td>
<td>2</td>
<td>1323</td>
<td>1144</td>
<td>179</td>
<td>–</td>
</tr>
<tr>
<td>HF-11</td>
<td>Bal.</td>
<td>30</td>
<td>13</td>
<td>0</td>
<td>0.02</td>
<td>0.5</td>
<td>1342</td>
<td>1269</td>
<td>73</td>
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</tr>
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<td>HF-12</td>
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<td>13</td>
<td>0</td>
<td>0.02</td>
<td>0.5</td>
<td>1353</td>
<td>1287</td>
<td>66</td>
<td>–</td>
</tr>
<tr>
<td>HF-13</td>
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<td>13</td>
<td>0</td>
<td>0.06</td>
<td>2</td>
<td>1335</td>
<td>1164</td>
<td>171</td>
<td>0.045</td>
</tr>
<tr>
<td>HF-14</td>
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<td>13</td>
<td>0</td>
<td>0.06</td>
<td>2</td>
<td>1342</td>
<td>1161</td>
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<td>–</td>
</tr>
<tr>
<td>HF-15</td>
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<td>13</td>
<td>2</td>
<td>0.04</td>
<td>1.25</td>
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</tr>
<tr>
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<td>2</td>
<td>0.04</td>
<td>1.25</td>
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<td>1120</td>
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<td>–</td>
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<tr>
<td>HF-17</td>
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<td>4</td>
<td>0.02</td>
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</tr>
<tr>
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<td>13</td>
<td>4</td>
<td>0.02</td>
<td>2</td>
<td>1340</td>
<td>1158</td>
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<td>–</td>
</tr>
<tr>
<td>HF-19</td>
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<td>30</td>
<td>13</td>
<td>4</td>
<td>0.06</td>
<td>0.5</td>
<td>1330</td>
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<tr>
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<td>13</td>
<td>4</td>
<td>0.06</td>
<td>0.5</td>
<td>1331</td>
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<td>0.02</td>
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<td>0</td>
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<td>2</td>
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<td>1130</td>
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</tr>
<tr>
<td>HF-23</td>
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<td>0.06</td>
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</tr>
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<td>4</td>
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<td>1.25</td>
<td>1308</td>
<td>1160</td>
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<td>–</td>
</tr>
</tbody>
</table>

All values in wt-%; all temperatures in °C.
permently values presented here represent equilibrium conditions and aren’t necessarily indicative of welding conditions, they suggest that the difference between these two terminal eutectic reactions is small, corroborating the computational findings presented here.

The disparity between terminal eutectic reaction temperatures is important to understand because the fusion zone zone position modification arising from DMW on pressure vessel or stainless steels can result in the formation of undesirable eutectics that expand the STR (Refs. 23, 38–42). The larger the difference between the possible eutectic reaction temperatures, the greater the risk of producing solidification cracks when the fusion zone composition enters a regime that promotes the lower melting eutectic phase.

Responses with large standard deviations were chosen for further analysis to determine the change in response produced at each level of the factor, i.e., the main effects of each factor on a particular response. These responses included T$_{e}$, T$_{s}$, STR, and T$_{f}$. The chosen response surface method DOE was a full, central composite design resulting in five levels of each factor tested. The central composite design was chosen because it allows for curvature in the response with less points than a full three-level factorial. These data are presented graphically via main effect plots in Figs. 8 and 9. The overall mean value of the responses is indicated on the plots with a solid horizontal line. Main effects plots are useful when trying to determine which factors affect the response the most. Table 8 summarizes these effects with the indicated symbols used to signify the relative effect.

Rows 1 and 2 of Table 8, and the top-left plots in Figs. 8 and 9 show that Fe and Mo act individually to decrease T$_{e}$ slightly (–30° to 890°C) when increased from 0 to 20 wt% and 0 to 4 wt%, respectively, for both the computational HF and Nb DOE groups. HF and Nb both work to depress T$_{e}$ but do so to a much greater extent due to the fact that these elements are responsible for the previously mentioned eutectic reactions. It should be noted that Ni is more potent at reducing T$_{e}$ relative to HF across the ranges studied in this investigation. From the top-left plot in Figs. 8 and 9, it can be seen that Nb decreases T$_{e}$ by ~100°C when increased from 0 to 3 wt% as compared to HF, which only reduces T$_{e}$ by ~100°C when increased from 0 to 2 wt%. Since the liquidus temperatures showed only minor fluctuations in both systems (as evident by comparing standard deviations in Table 7, row 1), the main effect plots for the STR response are simply an inverse of the T$_{e}$ plots — Figs. 8 and 9, right plot.

The same discussion of the T$_{e}$ main effects applies for STR, but in an opposite sense, meaning that a decrease in T$_{e}$ corresponds to an increase in STR, with the exception of Mo in the HF DOE group whose effect on STR was essentially negligible.

Fe and Mo both acted to slightly increase T$_{s}$ in the HF DOE group (Fig. 8, lower left, Table 8, row 5) and the Nb DOE group (Fig. 8, lower left, Table 8, row 6) but the Mo contribution to T$_{s}$ was almost negligible in the Nb DOE group. HF and Nb were both strong contributors to T$_{s}$ as was C for both groups (Figs. 8 and 9 lower left, Table 8, rows 5 and 6). It can be seen that HF and Nb were stronger contributors relative to C, which would be expected because the Ni, HF, and Laves phases are essentially C-free, but contain HF and Nb, respectively.

The main effect plots for T$_{s}$ (Figs. 8 and 9, lower right) show that C acts to substantially increase T$_{s}$. Carbon has been experimentally shown to increase the start temperature of the γ-NiC eutectic reaction, which promoted significant improvements in solidification cracking resistance (Ref. 23). Results of Varestraint testing showed that experimental Ni-based superalloys containing >2 wt% Nb and C ≥ 0.052 wt% had maximum crack length ≤05 mm at ≥25% augmented strain, supporting this observation (Ref. 23). DuPont et al. related the increase in solidification resistance seen in Varestraint testing to the effect of C on the solidification path. By increasing T$_{s}$, the solidification path intersects the line of twofold saturation between NCB and γ at relatively high temperatures, which restricts the temperature range of the primary γ → solidification event, resulting in larger amounts of solid-solution γ networks earlier in the solidification process capable of sustaining weld shrinkage strain (Ref. 23).

The effect of Fe, Mo, C, and Hf (or Nb) on T$_{s}$, STR, and T$_{f}$ on a weight percentage basis was determined. Equations 1–8 present the empirical formulas that describe a particular response surface in terms of the significant contributors defined as those with p-value ≤ 0.05. The high correlation coefficients (R) indicate that the regression analysis of the response surface DOE describe the effects of Fe, Mo, C, and Hf (or Nb) on the solidification behavior of high-Cr, Ni-based filler metals with great accuracy. It should be pointed out, however, that these data are only computational and require experimental validation.

### Computational HF DOE Group Equations

T$_{e}$ (°C) = 1315 – 12.5Mo + 95.6Hf + 28000°C + 42.5 Hf + 1.8Fe + 95°C (R$^2$ = 95.3)  

(1)

T$_{s}$ (°C) = 87 + 89.7Hf + 2008°C + 42.3Fe + 1.7Fe + 85°C Hf (R$^2$ = 95.7)  

(2)

T$_{f}$ (°C) = 1200 + 1.8Fe + 3182°C – 3516°C (R$^2$ = 96.0)  

(3)
\[ \text{f}_{\text{crit}} (\%) = 2.26 \times \text{Hf} + 4.24 \times \text{Fe}\text{C} + 0.065 \times \text{Fe}\text{Hf} + 76 \times \text{Cr} \text{Hf} (R^2 = 98.9) \] (4)

Computational Nb DOE Group Equations

\[ T_{\text{rod}} (\text{C}) = 1367 - 5.34 \times \text{Fe} - 116 \times \text{Nb} + 17.63 \times \text{Nb}^2 + 1.5 \times \text{Fe}\text{Nb} (R^2 = 93.7) \] (5)

\[ \text{STR (C)} = 4.44 \times \text{Fe} + 109 \times \text{Nb} - 17.93 \times \text{Nb}^2 - 1.57 \times \text{Fe}\text{Nb} (R^2 = 91.3) \] (6)

\[ T_{\text{rod}} (\text{C}) = 1246 - 12 \times \text{Mo} + 4280 \times \text{C} - 78667 \times \text{C}^2 + 417 \times \text{C}^3\text{Nb} (R^2 = 96.8) \] (7)

\[ \text{f}_{\text{crit}} (\%) = 0.78 + 0.23 \times \text{Mo} + 62.9 \times \text{C} + 1.25 \times \text{Nb} - 1236 \times \text{C} - 0.14 \times \text{Nb}^2 + 2.71 \times \text{Fe}\text{C} + 0.07 \times \text{Fe}\text{Nb} + 8.1 \times \text{Fe}\text{C}\text{Nb} (R^2 = 99.9) \] (8)

Considering Equations 1 and 5, it can be seen that various elements act individually, as squared terms, or in tandem with other elements to reduce \( T_{\text{rod}} \) depending on the alloy system. In both systems, the carbide formers have the strongest effect of reducing \( T_{\text{rod}} \). This is to be expected because Hf and Nb in the Ni-based system are responsible for the eutectic reactions. Considering the regression coefficient for Fe in the Nb DOE group, it is obvious that Fe also has a strong effect at reducing \( T_{\text{rod}} \).

At the maximum value for Fe used in this analysis (20 wt-%), the empirical relationship suggests that \( T_{\text{rod}} \) of Nb-bearing alloy would decrease by 107°C. This indicates that increasing the Fe content changes the terminal solidification reaction from the \( \gamma\text{N} \)C eutectic to the \( \gamma\text{Laves} \) eutectic. Cieslak et al. experimentally showed that the as-cast Laves phase constituent had considerable solubility for Fe (25 wt-%) (Ref. 41). Since the liquids temperature is essentially constant in these alloys, the reduction in \( T_{\text{rod}} \) due to Fe and Hf/Nb additions results in an expansion of the STR (Equations 2, 6).

The regression equations for \( T_{\text{rod}} \) (Equations 3, 7) are affected most by increases in C that act to increase \( T_{\text{rod}} \). This result is expected, considering that C additions have been shown experimentally to stabilize the \( \gamma\text{N} \)C eutectic (Ref. 41) and that the \( \gamma\text{M} \)C eutectics have higher reaction temperatures (Refs. 23, 36, 38–42). DuPont et al. experimentally showed that C additions increased the start temperature of the \( \gamma\text{N} \)C eutectic reaction, which induced a constant increment of the temperature interval over which the primary \( L \rightarrow \gamma \) reaction occurred, stating that this promoted a significant improvement in solidification cracking resistance of 20 wt-% Cr, Ni-based superalloys (Ref. 23).

### Experimental Determination of Elemental Effects on Solidification Behavior

One goal of this investigation was to experimentally determine the elemental effects of Fe, Mo, C, and Hf (or Nb) on solidification behavior of high-Cr, Ni-based weld metals as a means of comparing the hot cracking susceptibility of both alloy systems. Wherever applicable, experimental results are compared to the computational results presented earlier. Comments pertinent to the overall filler metal development project goals and combined resistance to solidification and ductility drop cracking are also made.

Thermocouple plunging experiments were used in conjunction with SS-DTA to determine the solidus temperatures of the experimental Hf and Nb DOE alloys whose nominal compositions are presented in Table 3. Actual compositions for the Nb DOE group alloys as determined by optical emission spectroscopy are listed in Table 4. STR was calculated by subtracting the experimental solidus temperatures from the computational liquidus temperatures computed by Thermocalc™. The QIA was performed on light optical and scanning electron micrographs of the odd-numbered alloys to determine \( f_{\text{crit}} \) after thermocouple plunging experiments were completed. Table 9 shows the average and standard deviation of each response calculated over the whole range of compositions encompassed by the DOE. From rows 3 of Table 9, it can be seen that the computationally determined \( T_{\text{rod}} \) for both groups were essentially identical and did not fluctuate significantly as evidenced by small standard deviation. Based on this, \( T_{\text{rod}} \) did not warrant investigation and only \( T_{\text{rod}} \) was investigated to determine STR.

Contrary to the computational results presented in Table 7, as well as experimental results from the literature (Refs. 43, 44), \( T_{\text{rod}} \) for the experimental Hf DOE group alloys were determined to be much lower on average than that of the Nb DOE group alloys (Table 9, row 2). A lower \( T_{\text{rod}} \) means a wider STR (Table 9, row 3).

Since the goal is to balance solidification cracking susceptibility with DDC susceptibility, it is useful to compare the two eutectic formers by looking at the ratio of the STR to fraction eutectic. This can help compare the efficiency of a eutectic former to form eutectic without drastically increasing the STR. By dividing row 3 by row 4 in Table 9, the STR/\% ratio can be found. For Hf as the eutectic former, this is 77°C%. In other words, for every 1% eutectic formed, the STR will expand by 77°C. With Nb as the eutectic former, this ratio is 114°C%. This result helps make the case for using Hf over Nb in high-Cr Ni-based alloy systems.

A regression analysis performed with MINITAB determined the effect of Fe, Mo, C, and Hf (or Nb) on the experimental responses \( T_{\text{rod}} \), STR, and \( f_{\text{crit}} \). Only terms with \( p \leq 0.05 \) were considered significant and were included in the models. The resulting models that describe the response surfaces are shown in Equations 9–14.

### Experimental Hf DOE Equations (Hf-# Alloys)

\[ T_{\text{rod}} (\text{C}) = -1.25 + 19 \times \text{Fe} - 239 \times \text{Hf} - 0.065 \times \text{Fe}\text{Hf} + 488 \times \text{Mo} + 580 \times \text{Hf} \text{C} \text{Hf} (R^2 = 89.7) \] (9)
STR (°C) = 232°F - 20°F + Fe²⁺ + Fe₃⁺ - 94.3°HF - Fe⁶+Mo - 223°F+C + 4°F+H⁻ - 483°Mo⁻C - 593°C⁴H (R² = 87.5)

\[ f_{out} (%) = 1.84\cdot 10^{-3} (R² = 97.4) \]

Experimental Nb DOE Equations (Nb-# Alloys)

\[ T_{out} (°C) = 1177 - 19.2\cdot Nb (R² = 31.9) \]

\[ STR (°C) = 198 + 17.2\cdot FeMo (R² = 35.0) \]

\[ f_{out} (%) = 0.87 + 1.4\cdot Nb + 0.72\cdot C\cdot Nb (R² = 99.6) \]

The high correlation coefficients (R² values) for the experimental HF DOE group responses indicate that the regression models describe the effects of Fe, Mo, C, and Nb on the STR and f_{out} of HF-bearing, high-Cr, Ni-based filler metals with great accuracy. The R² values for the experimental Nb DOE group STR regression equation were too low to be considered valid. The predictability of the f_{out} model for the Nb DOE group was considered valid based on the high correlation coefficient (R² = 99.6). The image analysis technique employed always gave consistent results, whereas the thermocouple plunging technique had much variability. This variability is what caused the R² values to be lower for the STR regression models.

Comparing Equations 1 and 9, it can be seen that the computational and experimental T_{out} surfaces have similar mean values (1325°C and 1315°C, respectively). Both models predict that Nb has the strongest effect at reducing T_{out}, which was shown to be much more pronounced of an effect experimentally. The experimental evidence suggests that Thermo-Calc™ is underestimating the disparity between the γ'HIC and γ'Ni₃H₅C eutectic reaction temperatures. Some other points of agreement between Equations 1 and 9 are the positive effect of the H⁺Fe interaction term. Once again, the effect of each was determined to be more pronounced experimentally. The reason for the positive H⁺Fe term can be explained by eutectic formation in this composition space. For low amounts of H⁺, the higher terminal temperature eutectic γ'HIC is the only eutectic to form. As the composition approaches higher amounts of H⁺, the solubility begins to level off as the terminal γ'Ni₃H₅C eutectic temperature is reached. From Equations 2 and 10, it can be seen that the agreement in significant terms between the experimental and computational STR models is the same as was discussed for T_{out}. Each effect was determined to be greater experimentally than was predicted by Thermo-Calc™. The regression models for the HF DOE group f_{out} response (Equations 4, 11) also agreed well in terms of the relative effect of H⁺ increasing f_{out}, but the regression model for the H⁺ computational DOE included some interaction terms that weren't determined to be significant experimentally. Based on Equation 11, it can be seen that H⁺ is the sole predictor of f_{out}.

Microstructural examination of the H⁺ DOE group alloys showed that the γ'Ni₃H₅C eutectic was the major constituent (as opposed to the γ'HIC eutectic). This was likely why C wasn't determined to be a significant factor for describing the f_{out} response. Based on the regression model for f_{out}, the ideal amount of H⁺ should be in the range of 0.7 to 1.2 wt-%. This would equate to 1.3-2.2 vol-% eutectic. This amount of eutectic should be sufficient to develop the tortuous GBs that are associated with good DDC resistance, but weldability testing will be required to verify this.

Comparing the f_{out} regression models for the Nb DOE groups (Equations 8, 14), it can be seen that the major source of agreement between the two models is the effect of Nb. The regression coefficient associated with the Nb term in both the computational and experimental models agreed in terms of magnitude (1.25 and 1.5, respectively). The additional squared and interaction terms in Equation 8 most likely resulted from the overestimation of f_{out} by Thermo-Calc™, as evident by looking at Table 7, row 5 and considering the microstructural examination of the experimental Nb DOE group alloys showed that the maximum f_{out} observed based on the composition space defined in Table 4 was 4.1 vol-%. The maximum f_{out} value observed experimentally was below the average value listed in Table 7, and well below the maximum (8.5 vol-%) predicted by Thermo-Calc™.

The software package Design Expert™ was used to analyze the experimental STR and f_{out} data for the HF and Nb DOE groups. An optimization procedure based on overlaying the f_{out} contour plot onto the STR contour plot was conducted to establish a composition space that meets specific solidification criteria that would be ideal for solidification cracking and DDC resistance. The overlaid contour plots for each experimental group can be seen in Figs. 10, 11. The plots were created by holding the Fe and Mo concentrations at their low values of 8 and 0 wt-%, respectively. These values are representative of commercially available Nb-bearing filler metals. The composition space defined by an STR between 125°C and 150°C, as well as a f_{out} = 2 vol-%, is significant on the HF STR contour plot by the purple region — Fig. 10. The value for STR was chosen to be at or below the STR of 52M from Table 1.

From Fig. 10, it can be seen that the optimized STR that accompanied 2 vol-% eutectic was ~110°C, which agreed with the rough calculation presented earlier. These data predict that an optimized HF-bearing, high-Cr, Ni-based filler metal composition containing ~0.8-1.1 wt-% H⁺ and 0.02-0.04 wt-% C would equate to an STR < 150°C and a f_{out} < 2 vol-%.

From Fig. 11, it can be determined that the composition space that meets the same criteria does not exist in the Nb-bearing system. It should be noted that the correlation coefficient for the Nb group STR regression model was quite low, so the STR values on the plot are most likely inaccurate. However, in order for an alloy in the Nb DOE group to meet the same solidification criteria previously described, the C would have to be increased well above 0.10 wt-%. This can be visualized by extrapolating the constant 155°C STR and 2.0 vol-% eutectic contour lines outside of the studied composition space where it appears that these lines would finally intersect. This assumes that the validity of these contours remain intact outside the composition space defined by the DOE.

Akashi et al. showed that increasing C increased the start temperature of the γ'NbC eutectic reaction when Nb was below ~2 wt-%. This would in turn increase the effective solidification temperature of the alloy and would subsequently reduce the STR, while increasing f_{out} (Ref. 26). The same behavior of C is observed here, but concerns of increasing the stress corrosion cracking (SCC) susceptibility of the alloy prevents extensive carbon additions.

Akashi developed a stress corrosion resistance index (SCRI) that quantifies the SCC resistance in terms of alloying additions such as Cr, Nb, Ta, Ti, and C while studying the effects of Cr and Nb on the SCC susceptibility of “Alloy 600-type” Ni-based alloys (Ref. 45). Equation 15 describes this relationship between C, Ni, Nb, Ta, and Ti to increase the SCRI, while C has a huge detrimental effect.

\[ SCRI = Cr + 5(Nb + Ta) + 10Ti - 116.5°C \]
development process for the intended service environment.

Figures 10 and 11 provided the first convincing experimental evidence that the STR, of Hf-bearing, high-Cr, Ni-based alloys could be minimized within the constraint of maximizing $f_{\text{Hf}}$.

### Optimized Compositions Based on Experimental HF DOE Group Responses

The experimental STR and $f_{\text{Hf}}$ data for the experimental HF DOE group alloys were input into a statistical optimization program recently developed at OSU (Ref. 37). The software differs from commercially available statistical programs such as MINITAB™, JMP®/SAS, and Design Expert™ in that it uses a genetic algorithm search heuristic to generate inputs and create solutions to the optimization routine. The software first performs a regression analysis based on the composition data and the recorded experimental values for the responses. Once the regression equations have been determined, the user inputs values for population size and number of generations and selects the optimization criteria based on minimizing, maximizing, or targeting a specific value for multiple responses, in this case STR and $f_{\text{Hf}}$. The population size dictates how many sets of randomly chosen values for the factors that the genetic algorithm chooses and inputs into the regression models. Once the set of response values is calculated from the randomly chosen inputs in the first generation, the genetic algorithm decides which inputs resulted in the best-fit for the optimization criteria selected by the user. The solutions that best match the optimization criteria in the first generation are used by the algorithm to decide the next population of inputs, but the algorithm is designed such that the new population is selected based on phenomena in natural evolution such as in-hertance, mutation, selection, and crossover. This process repeats itself as many times as determined by the number of generations selected. The software is capable of assigning a composite desirability value that indicates how well the solutions meet the optimization criteria and also outputs the value of the responses based on the optimized composition.

The compositions in Table 10 represent the solutions to an optimization routine in which an STR of 125°C and a $f_{\text{Hf}}$ of 2 vol.% were chosen as targeted response values in the HF group. A population size of 50 was chosen to undergo 50 generations, meaning that the software initially de-
cided 250 sets of randomly chosen inputs for the STR and $f_{\text{Hf}}$ regression models in the first generation. This process repeated 50 times, producing an optimized compo-
sition based on the criteria selected. Table 10 presents the three solutions to the optimization routine. The table also includes the composite desirability, as well as the response values.

From Table 10, it can be seen that an STR of 125°C could not be achieved based on the desired $f_{\text{Hf}}$ of 2 vol.%; however, a reasonable value of STR (155–160°C) is shown to accompany the desired $f_{\text{Hf}}$ of 2 vol.%. The desirability (0.84-0.87) indicates that the solutions to the optimization routine adequately met the optimization criteria even though the desired STR could not be attained based on the experimental data. There was considerable agreement amongst the three solutions to the optimization problem, namely the level of Fe, C, and Hf needed to obtain the desired $f_{\text{Hf}}$ and a minimum STR. Based on the values for Fe, it can be seen that all three solutions predicted the Fe to be between ~12–15 wt.%. Smith et al. stated that the nominal Fe concentration in IN690 (7–11 wt.%) was sufficient to mitigate the long-range ordering of Ni3Cr (Ref. 5). Based on this, the amount of Fe needed to achieve the desired $f_{\text{Hf}}$ and STR is greater than the amount necessary to ensure long-term structural stability of a Hf-bearing filler metal at typical service temperatures.

Ideally, the value of Fe could be reduced to ~8–10 wt.%, as is common with most commercially available, Nb-bearing filler metals such as 52Mo or 52MSS, without negatively impacting $f_{\text{Hf}}$ and STR. Had the optimized value of Fe been less than 10 wt.%, some concerns over the long-term structural stability of the resulting filler metal would have resulted in a need for more Fe, which would in turn equate to a larger STR and $f_{\text{Hf}}$. Since the optimized value of Fe was greater than that necessary to achieve a structurally stabi-
able alloy, decreasing this value to 9 wt.% would benefit the weldability of the re-
sulting alloy by decreasing the STR, without reducing $f_{\text{Hf}}$.

From column 4 in Table 10 it can be seen that the optimized level of Hf for all three solutions to the optimization problem were in excellent agreement. This is consistent with Equation 11, which indicates that $f_{\text{Hf}}$ is solely a function of Hf content. Based on this analysis, the nominal value for Hf in an experimental heat of material should be ~0.75 wt.%. The optimized values for C (0.03–0.04 wt.%) did vary somewhat but are in agreement with range for C in commercially available Nb-bearing filler metals. Previous DDC testing has shown that Mo reduces DDC suscepti-
bility at equivalent Nb contents in IN690-type alloys (Ref. 10). The result here shows that in a Hf-bearing alloy, Mo was not important in determining an optimi-
zed composition. This is seen in Table 10 as one result composition has 3.9 wt.% Mo, and the others have almost no Mo. However, EBSL analysis and weldability testing of 30 wt.% Cr, Hf-bearing, Ni-based alloys containing 0.75 wt.% Hf and 0–4 wt.% Mo is still needed to assess whether or not Mo is beneficial and/or needed in the (final filler metal). Based on this optimization, such a composite should have ST less than 175°C, and $f_{\text{Hf}} < 2$ vol.%. These values should provide good solidification cracking and ductility dip cracking resistance. Further weldabil-
ity testing will be conducted to verify this.

### Summary

- A DOE methodology was employed to computationally determine the elemental effects of Fe, Mo, C, and Hf (or Nb) on the solidification behavior of 30 wt.% Cr, Ni-based alloys using data extracted from Thermo-Calc™.
- Main effects plots created from solidi-
dication data described effects of individual factors on solidus temperature ($T_s$), solidification temperature range (ST), fraction eutectic ($f_{\text{Eut}}$), and eutectic tem-
perature ($T_{\text{Eut}}$) using analysis of variance calculations.
- Regression analyses of solidification data provided empirical relationships that described the response surfaces in terms of Fe, Mo, C, and Hf (or Nb) on a weight percentage basis.
- Thermodynamic plugging experiments and quantitative image analysis of LOM and SEM images, used in conjunction with a DOE methodology, allowed for the experimental determination of the elec-
tmental effects of Fe, Mo, C, and Hf (or Nb) on the STR and $f_{\text{Hf}}$ of 30 wt.%, Ni-based filler metals.
- Regression analyses of experimental solidification data provided empirical rela-
tionships that described the response surfaces in terms of Fe, Mo, C, and Hf (or Nb) on a weight percentage basis.
- Optimization of STR and $f_{\text{Hf}}$ data using constraint optimization resulted in Hf-bearing filler metal compositions for further weldability testing and microstructural characterization.

### Conclusions

- Nb was found to be the most potent factor for decreasing $T_s$ and increasing the STR, followed by Hf, Fe, and Mo, while C was found to increase $T_{\text{Eut}}$ therefore reducing the STR.
- Hf, Nb, and C contributed significantly to increases in $f_{\text{Eut}}$ compared to Fe and Mo, which only increased $f_{\text{Eut}}$ slightly.
- C significantly increased $T_{\text{Eut}}$ due to promotion of MC carbide eutectic in lieu of lower-temperature eutectic reactions.
- Recursive optimization of experimen-

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tal data using contour plots of the STR and $f_{Pe}$ response surfaces, as a function of the carbide former (Nb or Hf) and C, demonstrated that a larger $f_{Pe}$ was achievable with a smaller STR in the Nb-bearing alloys relative to the Nb-bearing alloys. The composition space defined by $f_{Pe}$ from 0.8 to 1.3 wt-% and C from 0.03 to 0.04 wt-% C ensured $f_{Pe}$>2 vol-% with an STR $<1.75^\circ C$.

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