A STUDY OF Ni-Cu WELD METALS FOR JOINING AUSTENITIC STAINLESS STEELS

A Thesis
Presented in Partial Fulfillment of
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By
Gustavo M. Guaytima, B.S

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The Ohio State University
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Master's Thesis Committee
Dr. John C. Lippold, Adviser
Dr. G. S. Frankel

Approved by

Adviser
Graduate Program in Welding Engineering
Abstract

Welding of austenitic stainless steels with matching filler metals results in the generation of hexavalent chromium (Cr\(^{6+}\)) in the welding fume, which is a known carcinogen. Permissible Exposure Limits (PELs) for this harmful ion are being severely reduced. Monel 60 filler metal (ERNiCu-7) was selected as a potential replacement filler metal for use with Type 304L base metal. This study evaluated the weldability issues associated with Monel 60/Type 304L dissimilar combinations. These included: compatibility, weld cracking susceptibility, microstructure evaluation, mechanical properties, and fume generation. A companion study evaluated the corrosion behavior of this dissimilar combination. Weld cracking was related to dilution of the Monel 60 filler metal by Type 304L base metal. When dilution was maintained below 30% cracking was avoided. The weld microstructure at all dilution levels was fully austenitic with segregation of Cu at the solidification grain boundaries and solidification subgrain boundaries. The mechanical properties of GTAW welds yielded compatible properties to welds made with matching filler metal (ER 308L). The ultimate tensile strength was 80 Ksi, yield strength was about 44 Ksi, while elongation was 44 %. The amount of Cr in the welding fumes during SMAW was reduced by a factor of 20 when comparing Monel 60 to E308-16.
Dedicated to Laura and my family
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VITA

March 30, 1976 ....................... Born in Comodoro Rivadavia, Argentina

2002 .................................. B.S Material Science Eng. Institute of
Technology of Argentina

2002-2003 ............................. Researcher,
   Welding and Joining Metallurgy Group
   The Ohio State University

2003-preset ........................... Graduate Researcher Associate
   Welding and Joining Metallurgy Group
   The Ohio State University

Publications

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FIELD OF STUDY

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CHAPTER 1

INTRODUCTION

The welding of stainless steel usually requires using a matching filler metal, which produces fumes containing Chromium (Cr). This element is considered very harmful for welder’s health. In particular, hexavalent Chromium (Cr$^{6+}$) may cause serious illness such as skin and lung cancer, as well as other respiratory problems [Ref. 1, 2, 3, 4, 5].

This concern resulted in a lot a work dedicated to find a solution to this problem. All the proposed solutions have focused on minimizing the total amount of fume by introducing changes in the welding process, ventilation of the welding environment, or using personal respiratory protection (e.g. filter masks) [Ref. 1, 6, 7]. Special emphasis has been focus on the development of different welding fluxes containing certain oxide that reduce the amount of fumes [Ref. 8, 9, 10]. However, these welding procedures still use matching filler metal, which is the main source of hazardous Cr$^{6+}$ found in the welding fumes. In this sense, a low (or free) chromium filler metal may reduce the amount of Cr generated from welding. Nevertheless, the implementation of low chromium filler metals must
maintain the corrosion resistance and the mechanical properties of the weldment relative to those properties with matching filler metals. Another aspect which must be considered with the new filler metal is galvanic corrosion. In general in a dissimilar weld the chemical composition of the filler is very different from that of the base metal, and this produces a galvanic couple [Ref. 11]. Thus, the galvanic potential of base metal and filler must be taken in account during the selection of the new filler metal. From the galvanic corrosion stand point, Ni-Cu alloys are compatible with Type 304L. This can be seen in the galvanic potential series for different alloys, which shows that Ni-Cu alloys in sea water have a slightly more cathodic behavior respect to Type 304 [Ref. 12] (see Appendix).

The most suitable Cu-Ni alloy is Monel 60 filler metal (ERNiCu-7). Therefore, this work was focused on Monel 60/Type 304L dissimilar welding. Referring to this particular dissimilar combination, hot cracking has been related to the dilution of Monel 60 by Type 304L base metal; however, the cracking phenomenon is avoided if dilution is kept below a certain threshold value [Ref. 13, 14, 15, 16, 17]. Other welding issues such as porosity and lack of the fusion have been associated with this dissimilar combination [Ref. 16, 18].

One of the goals of this investigation was to develop a low Cr fume emission welding process to weld austenitic stainless steels, trying to find
out how suitable Monel filler metal is to replace the extensively used matching filler metal 308L in welding type 304L austenitic stainless steel. Of course that this evaluation has to be made not only from the weldability and mechanical point of view, but also from the corrosion point of view. For that reason, this study was a multidisciplinary investigation between the Fontana Corrosion Center at OSU and the Welding and Joining Metallurgy Group at OSU. The present work only addresses the issues related to welding. From that perspective, solidification cracking and other welding issues will be discussed.
CHAPTER 2

MONEL/TYPE 304L DISSIMILAR WELD

2.1. Introduction

Dissimilar welding involves the joining of two or more different materials, and it is extensively applied to the joining of stainless steels with other materials. This takes special attention in components that need the combination of good mechanical properties and corrosion resistance. The high fabrication costs of those components entirely made of stainless steel can be reduced if the structure or components are constructed in the following way: only the parts that are exposed to the aggressive environment are made of stainless steel, while the rest of the structure is made of a cheaper structural material such as carbon steel. Then welding is used to join the stainless steel to the cheaper material, producing what it is called dissimilar welding. Type 304 is the most extensively used austenitic stainless steel in all applications that require a good combination between corrosion resistance and mechanical properties. Usually, it is welded with AISI 308 filler metal type, which basically is matching filler; that is, the filler metal and the base metal have similar chemical composition except that the filler has a
higher chromium content to enhance weldability and corrosion resistance of the weld (Table 1). Since in this work ER308L was switched for Monel Filler 60, then this produces a dissimilar weld.

Monel is a nickel-copper alloy with high strength (relative to stainless steels) and excellent corrosion resistance in a range of media including sea water, hydrofluoric acid, sulfuric acid, and alkalies. It is used for marine engineering, chemical and hydrocarbon processing equipment, valves, pumps, shafts, fittings, fasteners, and heat exchangers (Table 2)[Ref. 19].

<table>
<thead>
<tr>
<th>Element</th>
<th>AISI 304L [Ref. 20]</th>
<th>ER308L [Ref. 21]</th>
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<tr>
<td>Cr………..</td>
<td>18-20…………………</td>
<td>20.3</td>
</tr>
<tr>
<td>Ni……………</td>
<td>8-10…………………</td>
<td>10</td>
</tr>
<tr>
<td>Mn……………</td>
<td>2.0 max……………</td>
<td>1.8</td>
</tr>
<tr>
<td>C……………</td>
<td>0.08 max……………</td>
<td>0.03 max</td>
</tr>
<tr>
<td>S……………</td>
<td>0.03 max……………</td>
<td>-</td>
</tr>
<tr>
<td>P……………</td>
<td>0.045 max…………</td>
<td>-</td>
</tr>
<tr>
<td>Si……………</td>
<td>1.0 max……………</td>
<td>0.5 max</td>
</tr>
<tr>
<td>Fe……………</td>
<td>Balance……………</td>
<td>balance</td>
</tr>
</tbody>
</table>

Table 1: Typical chemical composition of AISI 304 and ER308L

| Ni+Co…………… | 62.0-69.0 | Cu………………… | Remainder |
| C……………… | 0.15 max | Al………………… | 1.25 max  |
| Mn…………… | 4.0 max  | Ti………………… | 1.5-3.0   |
| Fe…………… | 2.5 max  | P………………… | 0.020 max |
| S…………… | 0.015 max | Others…………… | 0.50 max  |
| Si…………… | 1.25 max |                   |           |

Table 2: Typical chemical composition for Monel 60 alloy [% wt] [Ref. 22]
2.1.1. Mechanical Properties

From the mechanical point of view, Monel/Type 304L dissimilar weld has very good tensile properties and toughness. Typically it’s ultimate strength is around 490 Mpa and impact toughness (Charpy-V) 150 Joule [Ref. 14], which are similar to those value for AISI 304 and Monel (Table 3) [Ref. 19].

<table>
<thead>
<tr>
<th>Property</th>
<th>Monel [Ref. 22]</th>
<th>AISI 304L [Ref. 20]</th>
<th>ER308L [Ref. 21]</th>
</tr>
</thead>
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<tr>
<td>Ultimate Tensile Strength Mpa, (Ksi)</td>
<td>483 (70)</td>
<td>505 (73)</td>
<td>645 (93)</td>
</tr>
<tr>
<td>Yield Strength Mpa (Ksi)</td>
<td>240 (34)</td>
<td>215 (31)</td>
<td>450 (65)</td>
</tr>
<tr>
<td>Elongation at break [%]</td>
<td>48</td>
<td>70</td>
<td>36</td>
</tr>
<tr>
<td>Charpy impact Energy [Joule]</td>
<td>191</td>
<td>325</td>
<td>170</td>
</tr>
</tbody>
</table>

Table 3: Typical mechanical properties of Monel 400 alloy, AISI 304, and ER308L.
2.1.2. Corrosion Behavior of Monel ® 400.

Monel ® alloy 400 exhibits resistance to corrosion by many reducing media [Ref. 19, 23]. It is also generally more resistant to attack by oxidizing media than higher copper alloys. This versatility makes alloy 400 suitable for service in a variety of environments. Monel ® Alloy 400 is widely used in marine applications. Despite its very low corrosion rate in flowing seawater, stagnant conditions have been shown to induce crevice and pitting corrosion. Alloy 400 is also resistant to stress corrosion cracking and pitting in most fresh and industrial waters. It offers exceptional resistance to hydrofluoric acid in all concentrations up to the boiling point. Finally, Monel is also resistant to many forms of sulfuric and hydrochloric acids under reducing conditions [Ref. 19].

2.1.3. Welding issues:

From the welding point of view, the main problem with Monel-AISI 304L dissimilar welding is hot cracking [Ref. 13, 14, 15, 16, 17]. The dilution of Fe and Cr, which come from the base metal, has a harmful effect on hot cracking susceptibility. Consequently, dilution is the main variable to control.
The key to achieve this goal is to try to keep dilution level below a certain threshold value in order to avoid hot cracking (see section 2.5).


In general, the molten metal of nickel base alloys has two distinctive characteristics: low viscosity, and poor wetting [Ref. 13, 18]. These characteristics cause some problems, which may be related with penetration. For example, partial filling may occur in cases which the metal has to flow in a close section such as the tip of a V-groove on plate. That also may produce other welding defects such as lack of fusion.

The fluid characteristics of the molten metal in welding may be sensitive changed by slight changes in the chemical composition [Ref. 24]. For example, very small changes in the S content in the weld pool can change the fluid motion mode completely, producing a large change in the penetration (Marangoni Effect). The presence of important amount of slag islands on the surface of the weld pool may change also the motion mode of the molten metal, and consequently, it may affect weld penetration.

In the case of Monel-304 dissimilar welding, the presence of titanium can affect the performance of the weld. Ti is added to tie up N and O in
the weld metal [Ref. 25], but has a secondary effect related with weld protection and penetration. This detrimental effect is due to the ability of Ti to react with oxygen.
2.2. General Mechanism of Hot Cracking:

Since one of the main issues related with this dissimilar welding is hot cracking, a brief introduction to this phenomenon is presented.

2.2.1. Introduction

The term hot cracks refers to those welding defects which are associated with the presence of liquid in the system and are localized in either the fusion zone (Weld Metal) or in the zones adjacent to the weld (heat affected zone) [Ref. 24].

This phenomenon results from a local depression of the solidification temperature in the grain boundaries, causing that some liquid film remains there while the rest of the material is in the solid state [Ref. 24]. Those zones containing liquid films are mechanically very weak, thus cracks can be form under the application of tensile stress. The stress is always present during welding, resulting from the following factors: shrinkage during solidification of the weld, the thermal contraction, and some external imposed forces such as fixture or clamping forces. In general, all these forces are referred to restraint.
The hot cracking phenomenon is divided into three subcategories [Ref. 24]:

**Weld Solidification Cracking** (WSC), which occurs at the end of the solidification in the weld fusion zone.

**Heat Affected Zones (HAZ) liqation cracking**, which occurs on cooling in the region closest to the fusion boundary* (Partially Melted Zone).

**Weld metal liqation cracking**, which takes places in multipass welding when a previous pass is reheated by the new weld taking place in the joint.

### 2.2.2. Grain Boundaries in Welding

Three different types of grain boundaries can be typically distinguished in welding (Figure 1)[Ref. 26].

**Solidification Grain Boundary (SGB)**: generated during solidification when two or more dendrites meet producing a boundary with high segregation and high crystallographic misfit.

**Solidification Sub grain Boundary (SSGB)**: generated during solidification inside of the grain due to the rejection of solute and impurities.

* The fusion boundary is the limit between the metal melted during welding (weld metal) and the metal that was partially or not melted.
SSGB and SGB have similar characteristics, except that this boundary type has a very low crystallographic misfit angle.

**Migrated Grain Boundary (MGB):** formed right after solidification or when the temperature is high. As a general role, every grain boundary tends to move when the temperature is high enough (Minimization of free Energy). As mentioned before, SGB has basically two components: high segregation and crystallographic misfit. Since the segregated elements are usually heavy elements (e.g. Cr, Ni, Mo), then they are not able to move with the boundary. Thus just the crystallographic component of SGB can move, generating what is referred as Migration Grain boundary.
2.2.3. Formation of liquid films:

In all alloys, segregation occurs simply because there is always rejection (when the partition coefficient $k < 1$) or removal (for alloys with $k > 1$) of alloying and impurities from the surrounding liquid [Ref. 24]. This fact is due to the difference in solubility of those elements between the liquid and the solid state. Solidification starts in many points inside of the weld pool. During solidification of stainless steel and the rest of the alloys with $k < 1$, many dendrites with different orientation start to grow, which causes the rejection of solute and
impurities into the surrounding liquid. This liquid eventually will be enriched in solute and impurities. Thus, when two or more dendrites meet, the enrichment will be even higher. Consequently, if the system presents eutectic phases, eventually the eutectic composition may be reached (Figure 2). This narrow high segregated zones leads to the formation of eutectic liquid films.
Figure 2: Solute redistribution during weld solidification at a SGB for $k < 1$. The solute rejection enriches the liquid around, which eventually reach the eutectic composition ($C_e$) [Ref. 27].
2.2.4. Essential Factors for Weld Solidification Cracking

In the case of Monel-AISI304L dissimilar welding only Weld solidification Cracking (WSC) type is reported in the literature. Regarding to this type, there are two essential elements to cause cracking: 1) a susceptible microstructure, 2) restraint.

2.2.4.1. Susceptible microstructure:

The fact that one particular microstructure is susceptible or not to WSC depends on the composition of the alloy. In particular, it depends on the presence of certain impurities that can result in an increment of the cracking susceptibility. The elements considered as impurities depend on the alloy system. For example, in the case of steels the most common impurities are phosphorous (P), sulfur (S), and boron (B). Impurities are associated with a series of factors that have a strong influence on the cracking susceptibility, e.g., strong segregation in the grain boundaries, widening of solidification range, formation of eutectic phases, and sensitive drop in the local solidification temperature.

The composition of the alloy determines what kind of microstructure will be present during solidification. In the case of austenitic stainless steels such as AISI 304, the molten weld metal can solidify as ferrite, austenite, or a mixture of those phases. In any case, the type of phase present during solidification will be stipulated by: a) quantity of liquid at the grain
boundaries, and b) the wetting characteristics of the liquid. With regard to these
two factors, the presence of primary ferrite during solidification has strong
influence on the cracking susceptibility.

2.2.4.2. Restraint

Regarding to restraint, the weld geometry plays an important role
on reducing cracking susceptibility [Ref. 24]. To illustrate this fact, Figure 3
presents two opposite cases. On the left of the figure a weld with a concave shape
concentrates the restraint in the middle of the weld, where the metal always
solidifies last and liquid films may remain. Therefore, this is not a desirable
situation. In contrast, in the geometry on the right of the figure a convex weld
presents a concentration of restraint at the side of the weld rather than in the
middle. Thus, when the restraint builds up during solidification this zone has
already solidified, reducing the susceptibility.

In the particular case of dissimilar weld presenting hot cracking
like the case of Monel60/type 304, heat input is associated with restraint also. To
illustrate this, imagine a welding geometry like in Figure 3 that has to be
completed. If single pass welding is compared with multipass welding, then single
pass welding will always use more energy than multipass welding. The reasons
are obvious: in the first case the entire cross section has to be filled in just one
step. Consequently, more metal needs to be melted all at the same time. However,
in multipass welding this is divided into “n” passes, which need much less material to be melted; in other words, multipass welding needs lower heat input, which in this particular case is related with hot cracking. Therefore, increasing the number of passes reduces also the susceptibility to cracking.

Another effect of increasing heat input is shown in Figure 4. High heat input produces a highly segregated centerline at the welding bead, which is favorably oriented to the highest restraint. This causes a drop in the resistance to the cracking phenomenon. When the weld pool has an elliptical shape the segregation is distributed more homogeneously, therefore elliptical shape is preferred rather than teardrop shape. This is referred to local strain concentration.

Figure 3: Comparison of restraint in two welding geometries [Ref. 24].
2.2.5. Influence of Liquid Films:

It was mentioned previously that the presence of liquid film at the grain boundaries is an essential element for WSC to occur. The nature of these liquid films is controlled by [Ref. 24]:

- Amount of liquid
- Grain boundary area
- Wetting characteristics
2.2.5.1. Amount of Liquid:

The amount of liquid has a particular influence on cracking susceptibility in the sense that if the amount of liquid is very low, then the susceptibility is also low. In the same way, if the amount of liquid is very high, then the susceptibility drops. However, when an intermediate volume fraction of liquid is present the susceptibility is maximum (Figure 5).

The final cracks that can be seen in a component exhibiting hot cracks are simply the union of small cracks that were previously highly segregated zones, where some liquid films were present, and then they failed under the effect of restraint. Hot cracks may start in one of those small zones and then, once the first crack is created, the stress concentration at the tip of this small crack may induce some neighbor zones containing liquid film to fail. In that way, the small crack joins other crack and it becomes larger. Then, the crack propagation process starts taking place.

If the amount of liquid is very low (left region of Figure 5), then the zones containing liquid film are very far from each other. A very high restraint will be necessary to produce that a small crack can induce the failure to the far neighbor zones containing liquid films. Consequently, the susceptibility is low. If the amount of liquid in those zones containing liquid film is very high, then a small crack can be created in one of those zones, but eventually it will be healed by the remnant liquid (cracking healing). However, in an intermediate case there
is not enough liquid to cause cracking healing. At the same time, the zones with liquid film are close to each other, causing the cracking susceptibility to increase. This kind of behavior is more common in alloys with eutectic reactions (e.g. Aluminum alloys). Nevertheless, the general idea of this is applicable to other alloys.

2.2.5.2. Grain Boundary Area:

The grain boundary area affects the cracking susceptibility in the sense that the zones containing liquid films are located at the grain boundary.

The amount of segregation, (and eventually the amount of liquid) is dictated by the phase diagram. In other words, in theory it is independent of the grain size. Consequently, the smaller is the grain size (i.e. more grain boundary area), the higher the amount of regions containing those liquid film is. Therefore, there is less chance that those zones can be close enough each other to cause cracking propagation.
2.2.5.3. Wetting characteristics:

The wetting characteristics depend on both the solid and the liquid in contact with it. The solid-solid interfacial energy ($\gamma_{ss}$) and the liquid-solid interfacial energy ($\gamma_{SL}$) of the boundaries are related with the wetting (or dihedral) angle as is indicted in the Figure 6. The lower is the angle, the easier the liquid wets the solid.
Figure 6: Liquid Film Wetting. When the dihedral angle is high the liquid does not wet the solid. On the other hand, when the angle is low the liquid tends to completely wet [Ref. 24].
2.3. Hot Cracking in Austenitic Materials

In general, some austenitic materials such as 300 series stainless steel or nickel and its alloys, usually exhibit low resistance to hot cracking [Ref. 24]. This is due to some metallurgical and physical factors that lead this cracking phenomenon to occur. This section will explain, in a general way, all the factors related to hot cracking.

2.3.1. Introduction:

In austenitic materials, austenite (γ) is not necessarily the first phase to solidify. In fact, many austenitic stainless steels such as AISI 304 solidify primarily as ferrite (δ), transforming later on to γ. The origin of the weld microstructure can be illustrated by using a phase diagram. If we take the example mentioned above, the Fe-Ni-Cr pseudo-binary phase diagram can explain what happens (Figure 7). For alloys with composition on the left of the peritectic/eutectic (point A) the material solidifies as primary austenite (solidification Type A or AF), while for those on the right the material solidifies as primary ferrite (solidification type FA). In both cases, the solidified metal structure is very different. Figure 8 represents the different solidification morphologies that can be observed in this kind of material.
The fact that the material solidifies as a primary ferrite has a tremendous effect not only on the solidified microstructure, but also on the hot cracking resistance of austenitic materials.

Depending on the chemical composition of the austenitic stainless steel, ferrite can be formed with high volume fraction at first when the material starts to solidify, and then eventually it can transform to austenite (stable phase). Since welding solidification involves high solidification rates, the reaction or transformation taking place are non equilibrium reactions. Therefore, even though ferrite is a non equilibrium phase at room temperature, some vestiges may remain at room temperature due to the rapid solidification and cooling rate.

The amount of ferrite at room temperature (ferrite number) can give us an idea of the amount of ferrite during solidification. In the practice, there are some tools that can help us to predict the amount of ferrite during solidification, thus they give us an idea of the hot cracking susceptibility. In general, those tools include empirical equations and charts (constitutional diagrams) that are based on the chemical composition of the alloy and can give as an output the ferrite number (FN). Figure 9 shows an example of a constitutional diagram that is extensively used in welding austenitic stainless steels. From experience people know that a FN<3 means that the alloy solidifies with austenitic microstructure type, and very little, or no ferrite is involved during solidification (solidification mode type AF and A respectively), thus the cracking susceptibility is very high. On the other hand for $3 < FN < 20$ higher amount of
ferrite forms during solidification (solidification mode type FA), therefore the crack susceptibility drops. It is very uncommon having a FN higher than 20 in austenitic stainless steels, except in the case of dissimilar welding of austenitic and ferritic (or duplex) stainless steels.

Figure 7: Fe-Cr-Ni Pseudo Phase Diagram. The point A and the dashed line indicate the eutectic/peritectic composition [Ref. 28].
Figure 8: Schematic of solidification behavior as function of the Cr/Ni equivalent [Ref. 29].

Figure 9: Constitutional phase diagrams. WRC 1992 [Ref. 24].
2.3.2. $\gamma$-$\gamma$ Boundaries and WSC

There are a number of reasons that explain the fact of poor hot cracking resistance of $\gamma$-$\gamma$ boundary over the beneficial effect of having certain amount of $\delta$ ferrite during solidification. These factors are based on physical and metallurgical effects, and they can be described as follow:

Impurity partition: this factor addresses to solubility of harmful impurities, indicating that it is higher in ferrite than in austenite; this result in stronger segregation in materials that solidify as primary austenite (solidification Type AF). The impurities tend to segregate locally at high concentration levels, which results in liquid film formation and eventually under sufficient stress it causes weld cracking.

Wetting characteristic: It refers to the fact that $\delta$-$\gamma$ boundary is not wetted so easily as $\delta$/\delta or $\gamma$/$\gamma$ boundaries are. When the material solidifies as primary austenite, the strong segregation at the boundaries causes the formation of certain amount of liquid films. Even though if a small amount of liquid is formed at $\gamma$/$\gamma$ boundaries, it can spread easily all along the boundary, which causes the formation of fissures.

Tortuosity: The morphology of the solidified metal has a sensitive influence in crack arresting (Figure 15). The grain boundaries of materials solidified as primary ferrite has a very irregular shape, while for the case of
materials solidifying as primary austenite the grain boundaries are smooth and straight. When hot cracks start propagating in the weld metal, they are arrested by the difficulty of propagation along an irregular path in $\delta+\gamma$ boundaries. However, hot cracks have a much easier propagation path along the smooth and straight $\gamma-\gamma$ boundaries.

In the following sections, some of the evidence related with each factor is presented and discussed. Most of this evidence is based on austenitic stainless steel; however, the concepts can be applied in general for all austenitic materials.

2.3.2.1. Impurities Partitioning:

In the solidification microstructure with primary austenite, the solubility of phosphorous and sulfur is lower than that in ferrite [Ref. 30]. Figure 10 compares the solubility of S for solidification type FA (AISI 304) and solidification type A (AISI 310). The figure does the same with the tendency of forming sulfur precipitates as a result of the low solubility of it. In solidification type A, the amount of sulfides increases proportionally with the increment in S. In the same way, solidification type FA (AISI 304) presents a similar tendency, but the amount of sulfide is significantly lower than that in solidification type A (AISI 310) [Ref. 31]. Sulfur is segregated along the primary austenite solidification grain boundaries (SGB's) and solidification sub grain boundaries (SSGB's). In
general, these sulphide particles are rich in Ti, Mn, Cr, Fe and Ni, depending of
the chemical composition of the austenitic material.

The solubility of phosphorus in the core of the dendrites for the
same materials listed above is shown in Figure 11. In the case of the material with
primary ferrite (AISI 304), P does not precipitate at the GB, except at very high P
contents. In contrast, AISI 310 presents the same precipitation tendency that S
does. A strong precipitation takes place at SSGB’s and SGB’s, where phosphides
rich in Cr, and Ni are formed.

In general, those highly segregated zones containing S and P tend
to form eutectic liquid with solidification temperature lower than that for the non
segregated material. Thus, the presence of those impurities may reduce sensitively
the hot cracking resistance of the material. Figure 12 shows a phosphide in a
microstructure of cast ingot of AISI 310 at room temperature (a) and at 1100 °C
(b). Notice that the melting temperature for austenitic stainless steels is typically
around 1300 °C. However, this particle starts dissolving at a lower temperature. It
can be seen in the picture that the phosphide wets along the boundary. The
eutectic melting point of an actual weld of AISI 310 containing from about 0.05
to 0.24 % P was observed to occur at about 1060 to 1100 °C as well as in the case
of the cast ingot showed in the figure 5 [Ref. 32]. In the same way†, the eutectic
melting temperature of the sulphide was observed to occur at about 1280 to 1310
°C. The effect of the segregation on an austenitic material can be illustrated by
ductility curves, which basically are ductility (strain) versus temperature plots based on a mechanical test (e.g. Varestraint Test). A point in the curve represents the minimum ductility for the given temperature. The ductility of AISI 310 (type A solidification mode) is presented in Figure 13. The relationship between the impurity content (P) and the solidification behavior can be seen in the pictures. Notice that P has a negligible effect in the AISI 304; only the brittle temperature range (BTR) is widened, but the minimum value in ductility curve (E_{min}) is still high. In contrast, for the case of AISI 310, P extremely widens the BTR, and lowers the E_{min}. The eutectic melting temperature of phosphide mentioned above coincides with the lowest temperature of the BTR in the ductility curve. This shows the detrimental effect in solidification cracking of P in weld metals that solidify as primary austenite.

\[ \text{[The technique used was the hot stage microscopy.]} \]
Figure 10: Solubility of S in the center of the dendrite for a material solidifying as austenite (310) and as ferrite (304) [Ref. 32].

Figure 11: Solubility of P in the center of the dendrite for a material solidifying as austenite (310) and as ferrite (304) [Ref. 32].
Figure 12: Phosphide in AISI 310 cast ingot at room temperature (a) in solid state, and at 1100 °C (b) in liquid state [Ref. 31].

Figure 13: Ductility vs. Temperature plot. Effect of P on high temperature range for an austenitic stainless steel (AISI 310) [Ref. 32].
2.3.2.2. Wetting Characteristic

It is experimentally noticed that the energy of the interface between two different crystal lattices in metallic phases is almost invariably lower than the energy of grain boundaries between two crystal lattices of the same phase differing only in the relative orientation. Hull [Ref. 28] states that $\delta$-$\gamma$ grain boundaries in iron have lower interface energy than either $\gamma$-$\gamma$ or $\delta$-$\delta$ grain boundaries.

Additionally, this author indicates that for the cracking behavior of fully austenitic alloys it can be assumed that:

$$\tau = \frac{\gamma_{SL}}{\gamma_{SS}} = \frac{1}{2 \cdot \cos \left( \frac{\theta}{2} \right)}$$

if we take in account the wetting of a $\gamma$-$\gamma$ boundary, and considering that for this case it can be assumed that

$$\gamma_{\Delta A} = \frac{1}{2} \gamma_{AL}$$

(approximately), then

$$\tau = \frac{\gamma_{AL}}{\gamma_{AA}} = \frac{1}{2}$$

Consequently, \( \theta \) tends to be zero, In other words, it tends to wet the boundary.

Where:
\( \gamma_{AA} \) is the surface energy in austenite-austenite boundary
\( \gamma_{LA} \) is the surface energy in liquid-austenite boundary
\( \Theta \) is the dihedral angle
Remember that the wetting characteristic can be explained simply describing the dihedral angle. The lower this angle is, the better the liquid wets the solid (refer to section 2.2.5.3, page 22).

Therefore, from this simple assumption it can be seen that the austenite-austenite boundary reduces the dihedral angle, and consequently reduces the hot cracking resistance.

Some experimental evidence is shown in Figure 14. Notice that phosphides tend to completely wet the boundary, which confirms the fact that P may have a very harmful effect on hot cracking resistance austenitic materials.

Figure 14: Hot stage microscopy micrograph of a phosphide at the \( \gamma-\gamma \)-grain boundary (1100 °C) [Ref. 31].
2.3.2.3. Crack Arrest

The effect of primary ferrite is the generation of a substantial area of interphase boundary between ferrite and austenite in addition to the $\gamma-\gamma$ boundaries. The new interphase has a very irregular shape as it is shown in Figure 15. Thus the crack path is much more tortuous than that in a single phase boundaries. Consequently, the propagation of the crack is more difficult. Figure 16 shows a TEM micrograph of a sample with some primary ferrite. A boundary appears to be incorporated along the skeletal ferrite. For a crack to propagate along the boundary, it must either tear the ferrite, which is more difficult than boundary cracking, or propagate around the long path of the secondary ferrite arms.

Hull [Ref. 28] and Brooks [Ref. 30] have shown that for material containing ferrite, cracks propagate almost entirely along the ferrite-free grain boundaries and, when they encounter ferrite within the boundaries, the cracks are arrested. The picture in Figure 17 shows a crack propagating along the $\gamma-\gamma$ a boundary until some ferrite at the G.B arrested it.
Figure 15: Morphology for austenitic material solidifying as primary austenite (a) and ferrite (b) [Ref. 30].

Figure 16: TEM micrograph showing the tortuous character of the boundary [Ref. 30].
Figure 17: Crack propagation arresting. The crack propagating along a $\gamma$-$\gamma$ interphase is arrested by the ferrite (\(\delta\)) at the grain boundary [Ref. 28].
2.4. Preventing Weld Solidification Cracking

The methods for eliminating or reducing susceptibility to solidification cracking in austenitic materials are based on controlling the solidification microstructure or solidification mode, being more desirable (when possible) the solidification mode type FA. This mode assures that ferrite will be the first solid phase to transform. Therefore, during the first stage of the solidification when WSC takes place; there is a lower amount of liquid film, which has poor wetting characteristics. These two factors end up in a lower cracking susceptibility. This objective is reach by selecting the correct consumable, which assures a FN between three and twenty.

Low impurity levels can also contribute to reducing cracking susceptibility in cases such as Monel which exhibits solidification type A. Restraint can be controlled through joint design and weld procedure. In general, lower heat input and smaller weld size reduces susceptibility. The base metal strength has influence on the solidification shrinkage. Therefore in the case that materials strengthen by precipitation hardening lower base metal strength can help in reducing the restraint.
2.5. Weldability issues in Monel/type 304 Dissimilar Welding

2.5.1. Introduction

The most important issues related to the weldability of Monel are the following: weld solidification cracking (WSC), lack of fusion, low penetration and porosity [Ref. 13, 16, 17, 23, 33, 34, 35, 36]. Regarding the first issue, Monel solidifies as primary austenite even when it is joined with mild steel or stainless steel [Ref. 33, 36]. Therefore, the hot cracking resistance is inherently low. The exact mechanism of WSC in Monel is not well understood; however, there are certain factors that are always present, including: strong segregations, and eutectic liquids. In the particular case of Monel–stainless steel dissimilar welding, the failure is always related with intergranular cracking, interdendritic zones with segregation of copper and depletion of Ni and Fe, and phases of low melting temperature [Ref. 33].

Lack of fusion and low penetration are common issues not only in Monel weld metal, but also in high Nickel alloy welds. They are related to the fluid characteristics of the molten metal [Ref. 18]. Porosity in Monel weld metal is related to the absorption in solution of gases such as nitrogen, hydrogen and oxygen, which are present in the shielding atmosphere during welding [Ref. 37].
2.5.2. Weld Solidification Cracking in Monel – Stainless Steel Dissimilar Welding.

2.5.2.1. Effect of Cr and Fe.

When Monel is joined to stainless steel, dilution of Cr and Fe have been related to hot cracking [Ref. 13, 15, 16, 17, 23, 33]. Monel weld metal can dissolve certain amount of Chromium (Cr) and Iron (Fe). After those limits are surpassed, hot cracking takes place. Those threshold values are given in the literature (around 3% for Cr, and 15% for Fe) [Ref. 13, 14, 15, 16, 17]. In terms of dilution by AISI 304, that means 44% and 20% respectively. Those values change depending on the welding process [Ref. 16, 35, 38]. For example, in order to avoid hot cracking when Monel is being welded with submerged arc welding process (SAW), iron dilution can be up to 22%, while for Gas Tungsten Arc Welding (GTAW) that value can reach 15% [Ref. 16].

The effect of Cr and Fe dilution can be illustrated using a ternary Schaeffler diagram (Figure 18). Basically, the diagram has three axes: Iron, Nickel, and Cooper content. It is similar to a ternary phase diagram; the main difference is that it has two different zones (cracking and no-cracking) instead of different phases. Note that the diagram was made for plain iron; therefore, the effect of Cr was not considered [Ref. 16]. However, if we suppose that: a) Monel weld metal has a constant content of Cr, and b) Fe content can vary due to dilution, then it is possible to infer that the Schaeffler diagram will look like Figure 19. Since Monel
has 70% nickel and 30% cooper (approximately), the starting point is on the Cu-
Ni side of the diagram (Figure 19). During the welding process, iron content
increases due to the dilution of the stainless steel. Therefore, the composition will
change following the path described by the dashed arrow in the illustration. As
dilution increases, the actual composition of the weld metal approaches to the
cracking threshold value. In this example the dilution threshold value is about
17% (dashed line on the right of Figure 19-b). When dilution surpasses this value
hot cracking phenomenon starts to operate. Finally, after certain period of time
dilution reaches the final value. For example, for GTAW process a typical value
for dilution is 25 %. Thus, taking this value the diagram predicts the presence of
hot cracks in the weld metal (Figure 19-b).

Note that Cr content may change the shape of the cracking zone in
the ternary Shaefller diagram (it may make the cracking zone increase).
Therefore, hot cracking may start to operate at a lower dilution value [Ref. 16] .
The effect of chromium on the weld metal cracking mechanism in Monel is
shown in Figure 20. Notice that when weld cracking occurs, Cr is higher than the
threshold value (3 % ) and it is depleted at the cracked zone [Ref. 17].
Figure 18: Hot Cracking in Monel-Stainless Steel weld metal. Ternary Shaefller Diagram [Ref. 16].

Figure 19: Illustration of Ternary Shaefller Diagram for Monel weld metal assuming constant content of Cr (a). Zoom-in of the zone where the changes during the welding process occur b)
Figure 20: Electron-probe microanalysis of cracked and crack-free samples in AISI 304-Monel dissimilar welding. Notice that in the zone having cracks Cr is higher than 3 %, and it is depleted at the zone where the crack is [Ref. 17].
2.5.2.2. Effect of Ti and Al

Chromium and iron are not the only elements related with hot cracking in Monel weld metal. In fact, titanium and Aluminum in solution have also a deleterious effect on the weld solidification cracking resistance of Monel [Ref. 25, 35]. Those elements widen the solidification temperature range (STR) of the weld metal ‡, increasing the cracking susceptibility [Ref. 39]. They also have been related with the formation of eutectic liquids that have very low melting temperature [Ref. 40].

Ti and Al can be added either to the filler metal core or to the flux (if it is applicable) with the objective of reducing porosity in the weld metal (see section 2.5.4). The reactions among Titanium, Aluminum, Nitrogen and Oxygen may influence the total amount of Ti and Al in solution [Ref. 25]. Figure 21 shows how the absorption Ti +Al in solution varies as function of the weld metal type (Monel and a Nickel). The absorption of those elements into the weld pool during welding has a certain influence on the hot cracking resistance. Figure 22 shows the results of FISCO cracking test for Monel and nickel weld metals. Notice that there is a direct relationship between the amount of Ti + Al and the hot cracking susceptibility. If the amount of Ti + Al exceeds 2.5 wt %, hot cracking starts to take place [Ref. 34].

‡ For a given composition, STR is the temperature range where the alloy is in the L+S zone in the phase diagram.
The WSC mechanism in Monel is related to strong segregation during solidification and the formation of eutectic liquid [Ref. 35]. Takeuchi [Ref. 40] showed that Titanium forms eutectic liquids either in the Cu-Ni-Ti and Cu-Fe-Ti ternary systems, lowering considerably the melting temperature (around 900 °C) (Figure 23). Monel weld metal has a natural tendency of segregating solute. In particular, Cu is strongly segregated during the solidification of the weld metal [Ref. 37]. Figure 24 shows a concentration curve across a dendrite in Monel weld metal containing some diluted Fe. Notice that Fe and Ni are depleted at the inter-dendritic zone, while Cu is segregated at those zones. This strong segregation can be explained by the coefficient of partition (k). Table 4 shows the value of k for Ni, Cu, and Fe. As it can be seen in this table, Cu has the highest value, which indicates that it will be rejected during solidification from the matrix (or core of the dendrite) to the boundaries (or inter-dendritic zone). There is not available data for k of titanium. However, the author estimates that there is certain segregation of Ti during solidification that in combination with the strong segregation of Cu can form eutectic liquids of very low melting temperature (as it is indicated in Figure 23).
Figure 21: Absorption of Ti and Al in Monel and Nickel weld metal as a function of the amount of Ti + Al in the welding flux [Ref. 25].

Figure 22: FISCO cracking Test for Monel and Nickel weld metal [Ref. 25].
Figure 23: Ni-Cu-Ti (a) and Cu-Fe-Ti (b) ternary phase diagram. Notice that in both cases low melting temperature eutectics are formed [Ref. 40].
Figure 24: Segregation of Cu at the inter-dendritic zones in Monel weld metal containing some diluted iron on it [Ref. 37].

<table>
<thead>
<tr>
<th>Content of element in the alloy, %</th>
<th>Concentration of element, %</th>
<th>Coefficient of zonal liqation, ( k = \frac{C_{\text{max}}}{C_{\text{min}}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>68.0Ni</td>
<td>75.0</td>
<td>50.0</td>
</tr>
<tr>
<td>28.5Cu</td>
<td>35.0</td>
<td>15.0</td>
</tr>
<tr>
<td>2.85Fe</td>
<td>3.4</td>
<td>2.2</td>
</tr>
<tr>
<td>1.26Mn</td>
<td>2.2</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 4: Coefficient of partition \( (k) \) in Monel weld metal containing some diluted iron [Ref. 37].
2.5.2.3. Effect of other Elements on Cracking

Other elements such as S and Ce may also alter the cracking susceptibility of Monel weld metal. Sulfur is one the most harmful impurities, causing weld solidification cracking when nickel base alioys and stainless steels are welded [Ref. 34]. It is believed that S forms low-melting sulfides and eutectic phases, which produce liquid film at the grain boundaries during solidification. Therefore, those boundaries containing liquid films eventually fail upon restraint, causing cracking. If a large amount of S is present in the weld metal, Monel welds can exhibit a drop in ductility at high temperature (at the temperature range where WSC operates) [Ref. 34]. Figure 25 shows the results of tensile test at the temperature range where WSC takes place. The figure exhibits the results for samples containing high and low sulfur content for Monel and high nickel weld metals. The drop in strength for Monel containing important amount of sulfur is more important than that for Nickel weld metal. This is due to the formation of hot cracks in Monel weld metal.

Figure 25: Effect of sulfur on the reduction of ductility in Monel ( high ○, low △) and Nickel weld metal (high O, low ▲) [Ref. 34].
2.5.2.4. Effect of Fe on Mechanical Properties

Fout and Wamsley [Ref. 41] have studied the weld strength for Nickel/steel and Monel/steel welds as a function of iron content (Figure 26). Tensile test specimens of different iron content were tested to obtain strength and ductility measurements for each weld composition. For Nickel/steel welds, the obtained data indicated that for iron contents less than 20% the weld fails at the weld interface due to a lack of fusion. Between 20% and 35% iron, the highest iron dilution that could be achieved in a nickel weld, the welds were stronger than the steel base metal. This indicates that a minimum amount of iron dilution (20%) is necessary for optimum strength and avoiding lack of fusion. On the other hand for Monel/steel welds, the test results showed that the welds had good strength and integrity between 10% and 27% iron in the weld. Above 35% iron, the welds have less strength and were more brittle. The 35% iron content also corresponded to the iron dilution in Monel welds that has been shown to produce an increase in corrosion rate (the media in this particular work was ClF₃). The authors indicate that the iron dilution in Monel welds should be kept below 35% iron to maximize both the strength and corrosion resistance.
2.5.3. Lack of Fusion and Low Penetration

The results in Figure 26 illustrate not only the effect of Fe on hot cracking of Monel, but also other important weldability issues related with high nickel alloys such as lack of fusion and low penetration. In this context, it is necessary to remark that the molten metal of high nickel alloys is viscous, sluggish and it has poor wetting properties [Ref. 18]. These characteristics usually make welders increase heat input, producing just a slight increase in the
penetration and at the same time, it causes other undesirable consequences such as hot cracking due to the excessive dilution level. On the other hand, when the heat input is reduced the difficulties of flowing out to the side of the joint may cause lack of fusion, especially if the weaving technique is not used during welding. For that reason, special joint designs and optimum heat input have to be used to avoid or reduce the chances of having lack of fusion or low penetration [Ref. 16, 18].

2.5.4. Porosity in Monel weld Metal

Porosity in Monel weld metal is an issue that is usually solved by alloying addition [Ref. 23, 37, 42]. This weld metal is particularly susceptible to gas-shrinkage porosity. This phenomenon is caused by the combination of shrinkage in the liquid + solid zone with the liberation of dissolved gas (e.g. oxygen, nitrogen and hydrogen). The most active role in the formation of the pores is played by hydrogen [Ref. 37]. The addition of hydrogen to the shielding gas in GTAW welding can increase penetration, and consequently it increases productivity also [Ref. 43]. However, precautions have to be taken with regards to the potential porosity problem that hydrogen may cause.

When solving this issue, the dominant variable to control is the solidification range temperature (SRT); that is, the actual temperature range that the weld metal is in the Liquids + Solid zone during solidification. The alloying
The addition of Mn has the greatest effect on narrowing the solidification range, and consequently, it causes the greatest reduction in porosity [Ref. 37].

Other alloying elements such as titanium, aluminum, and silicon are also added to the welding consumables to reduce porosity in the weld metal. Those elements have a strong affinity for oxygen and nitrogen, especially at high temperature. Thus, they tie those gases in solution in the weld pool, reducing porosity [Ref. 23].

There is a relationship between the morphology of solidification in the weld metal and the porosity. Porosity is more likely to occur in the side of the welding bead where a directional solidification structure is present, rather than in the center of the bead where equiaxed structure is formed [Ref. 37].

The actual Monel welding consumables already contain Mn, Ti and Al, in order to reduce the chances of having porosity. Thus, this is not an important issue in nowadays, but it could take place if certain consideration such as welding cleanliness or good shielding are not taken [Ref. 18].
2.6. Description of the practical welding issues.

2.6.1. Introduction

When a new welding procedure is being developed, there are some basic roles to follow which basically what they do is to assure the quality of the weld (with certain limitations). Those rules came from different areas such as metallurgy, welding process, experience and others. Almost all of rules are contained in welding codes such as AWS codes. They are technical guide not only for welding engineers and welders, but also for inspectors. One of these basic roles is regarding the protection that the shielding gas has to provide in GTAW or any other gas shielded process. In some types of alloys such as Nickel Base alloys, the shielding protection has a very important influence on the mechanical properties [Ref. 44]. Bad protection may be generated by many factors such as inadequate gas flow rate, air leak, gas contamination and others.

Bad shielding gas protection is not the only factor that causes a contaminated or unclean weld. Sometimes, this defect is produced by some contaminants on the base metal surface such as oil, grease, shop dirt, paint etc. Also, the filler metal could be a contamination source when some impurities remain on the filler metal's surface after manufacturing. In addition, some
unusual level of certain elements in the filler metal chemical composition may be the key to find the source of the contamination.

The Monel filler 60 has around 2% Titanium (Ti). This alloying is added to pick up nitrogen (N₂) and oxygen (O₂) gases, which may produce porosity in the weld. Therefore, Ti may be forming oxide particles type TiₓNᵧ or TiₓOₓ. However, due to the strong reaction of Ti with those gases it may produce some weld pool protection problems. For that reason, in order to keep the weld pool protected and free of O₂ and N₂, it is strongly recommended to use very careful procedures such as a large gas nozzle (size 3), or addition of up to 10% of hydrogen to the Argon shielding gas [Ref. 43]. The presence of N₂ and O₂ gases in the plasma gas may produce undesirable effects such as electrode erosion or contamination [Ref. 12].

For all the reasons presented above, when welding Monel to stainless steel, not only dilution level is important, but also the weld pool protection. Therefore, variables that usually neglected such as air movement, angle of the filler metal with respect to the base material, and others became more important.
2.7. Welding Fumes

Since the 80's a lot of work has been focused on welding fume due to its influence on welder's health. More restricted regulation, standards and Laws have been proposed based on this extensive information in the literature. The objective of this section is to introduce welding fumes to the reader and to provide some background.

2.7.1. Introduction:

Welding fume generation is a very complex phenomenon that takes place in any fusion welding process. Its complexity is based on many chemical reactions taking place at the same time and at very high temperatures at the plasma arc. Fumes have a complex variety of constituents, some of them are gases (e.g. H₂, CO₂), while others are small particles or cluster of particles with different shapes and sizes.

Fume generation is measured in two different ways. The first is called Fume Generation Rate (FGR), which is defined as the amount of material present in the fumes per time unit (e.g. grams/hr). The second is named Relative Fume Formation Rate (RFFR), which is defined as the quantity of emission produced when certain mass of consumable electrode is melted (e.g. grams fume/grams consumed electrode). Usually, measurement of fume emission rates of arc
welding is based on gravimetric method, which depends on the weight of a filter used to trap certain amount of fumes[Ref. 9].

There are four major factors that influence the level of fumes and level of risk to the welder’s health:

- The welding variables (e.g. welding process type, current, base metal). This will affect the amount of fumes, their composition and the particle size distribution.

- The duration of exposure to fumes and environmental aspects.

- The use of personal protective equipment and safety engineering

- Personal work characteristics such as posture, and speed of work.

### 2.7.2. Effect of the Chromium in Welding fumes on Health

The fumes generated during welding stainless steel may contain compounds of chromium (including hexavalent chromium). The immediate effects of over-exposure to fumes containing Cr are similar to those produced by other metals. That is, it may cause symptoms such as nausea, headaches,
dizziness, and respiratory irritation. Additionally, some persons may develop sensitivity to Cr which can result in dermatitis or skin rash [Ref. 1].

Long term effects of exposure to fumes containing Cr are not definitely determined. Nevertheless, the National Institute for Occupational Safety and Health (NIOSH) implies that some forms of hexavalent Cr and its compounds should be considered occupational carcinogens[Ref. 45]. Contrarily, the International Association of Research on Cancer (IARC) implies that for the carcinogenicity of welding fumes there is limited evidence in humans, and there is inadequate evidence in experimental animals[Ref. 5].

2.7.3. Welding Fumes and Welding process Variables:

FGR depends on the nature of the welding process. For example, Gas Tungsten Arc Welding (GTAW) presents the lowest rate, while Shielding Metal Arc Welding (SMAW) exhibits the highest. This is logical because in SMAW not only the vapor coming from the filler and the base metal are present in the fume, but also the electrode coating. This coating can be made from different materials such as cellulose that can produce a large amount of fumes. On the other hand, in GTAW vaporization of metal involves only filler and base metal. In this context, the base metal can also influence the FGR. For example, Gas Metal Arc Welding (GMAW) of Aluminum has a very high FGR compare with that of GMAW of steel [Ref. 10].
The chemical composition of the coating in SMAW electrodes can have influence on the Cr (VI) emission. For example, sodium and potassium compounds in the electrode coating are associated with the release of Cr (VI)[Ref. 10]. For SMAW, FGR increases when the welding current and voltage increase. Additionally, raising the welding current has a greater effect on FGR for acid or basic coated electrodes than on that for rutile-coated electrodes. Other factors such as polarity and arc length may alter FGR as well [Ref. 7].

2.7.4. Classification of Welding Fumes Particles:

There is certain concern about the particle size of the welding fumes with regards to respirability of those particles. In general, particle with size greater than 5 μm are trapped by the respiratory system, so they are considerable no respirable. If the particle size is in the range of 0.1 - 5 μm, then they are considered as in the respirable range. Finally, if the particle size is lower than 0.1 μm the particles are removed during expiration. Thus the do not represent any hazard for welder’s health. The literature indicates most welding fume particle sizes are in the respirable range [Ref. 7].

In general, the particle shape is spherical, but some agglomerates or chains can form. In the particular case of stainless steel welding fumes, the particles do not tend to form agglomerates and the particle average size is the range of 0.05 - 0.4 μm [Ref. 7].
For a given consumable, the chemical composition of the fumes does not vary among the different welding arc processes. What it is different is the oxidation state of chromium (trivalent and hexavalent). For example, in SMAW the fraction of hexavalent Chromium (Cr\textsuperscript{6+}) in the surface of the particle is in the range 60-100 %, while in the case of GMAW the fraction does not surpass 15%. Another very important characteristic of fumes containing Cr is the solubility of Cr\textsuperscript{6+}. This characteristic may affect the carcinogenesis in aqueous media. In the case of GMAW most of the Cr(VI) is insoluble, while in the case of SMAW almost all is soluble[Ref. 7].
CHAPTER 3

OBJECTIVES

- Develop a gas tungsten arc welding (GTAW) procedure with Monel 60 filler metal and Type 304L base metal.

- Produce GTA welds in the dilution level from 15% to 45%.

- Characterize the microstructure of the welds in this dilution range.

- Evaluate the weld solidification cracking susceptibility of the Monel/304L combination.

- Determine the mechanical properties of optimal welds.

- Determine the relative chromium levels in welding fume of Monel and 308L SMA welds.

- Provide welded samples for corrosion testing at the Fontana Corrosion Center (OSU).
CHAPTER 4

EXPERIMENTAL PROCEDURE

4.1. Material

The studies were based on plates of AISI 304L ¼" thickness, Monel filler 60 (0.045 in diameter), and ENR308L filler metal (0.045 in diameter). The chemical composition of the material is presented in

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<tr>
<th>Type 304L</th>
<th>Element</th>
<th>Content [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
</tr>
<tr>
<td>S</td>
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<td></td>
</tr>
<tr>
<td>P</td>
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<td></td>
</tr>
<tr>
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<td>Cu</td>
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<table>
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<th>Content [wt%]</th>
</tr>
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<td></td>
</tr>
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<td>Cu</td>
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<tr>
<td>Other</td>
<td>&lt;0.5</td>
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</table>

Table 5: Actual composition of the used filler and base metal

63
4.2. Welding Procedure

Almost all the tests in this investigation used three different levels of dilution. The welding parameters were adjusted previous to the actual weld, looking for the best performance. The welding quality parameters were set based on having good protection, desirable amount of dilution, good penetration, avoiding weld solidification cracking, and minimizing distortion.

4.2.1. Tensile Test Sample Preparation

The sample were prepared using a double V- groove 90° 2.5 mm gap welding design, starting from two 3 x 12 in AISI 304L plates. The sample dimensions are schematically shown in Figure 27. The plates were clamped to a thick aluminum table and two GTAW spot welds were made in the ends to keep the gap constant during welding. The weld was completed using GTAW and after the first pass, the plates were flipped over and the second pass was performed. Details of the welding parameters are presented in Table 6.
Figure 27: Tensile test specimen dimensions.

<table>
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<th></th>
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<td>175</td>
<td>2.11</td>
<td>27.51</td>
<td>15</td>
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<tr>
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<td>150</td>
<td>2.11</td>
<td>19.05</td>
<td>15</td>
</tr>
<tr>
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<td>120</td>
<td>2.11</td>
<td>42.33</td>
<td>10</td>
</tr>
<tr>
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<td>14</td>
<td>120</td>
<td>2.11</td>
<td>12.70</td>
<td>10</td>
</tr>
<tr>
<td>Low</td>
<td>ER308L</td>
<td>12</td>
<td>150</td>
<td>2.96</td>
<td>29.63</td>
<td>13</td>
</tr>
</tbody>
</table>

Table 6: GTAW Welding Parameter for AISI 304L-Monel Dissimilar welding

The plates were kept on the aluminum welding table until they cooled down, in order to reduce distortion. After that, the samples were cut from the plate using Water-Jet cutting and a manual machining with a file was performed to make the edge round and reduce stress concentration. The samples
were polished also with abrasive paper up to 400 grit in order to reduce the roughness. The test was run at a extension rate of 0.84 mm/sec (0.0333 in/sec) in a regular tensile test machine.

4.2.2. Bend Test Samples

The samples were prepared starting from two 1/4 in thick plates with dimension 3 x 12 inches under specification of the AWS Structural Welding Code-Stainless Steel [ref]. Figure 31 shows the experimental set up. The welding configuration was again single V-groove 90°, 2 mm gap. The welding parameters were similar to those used in tensile test preparation. After welding, the reinforcement was grounded, and polished with abrasive paper up to 400 grit in order to reduce the roughness. A wrap-around bending machine was used to perform the test. The strain was calculated based on the diameter of the die, thickness of the plate and the nomogram in Figure 29. The actual sample dimensions are specified in Figure 30. The test was performed using a wrap-around bend machine as showed in Figure 31.
Notes:
1. Radius A shall be as specified, or as determined from the nomogram in Figure 4.9. Dimensions not shown are the option of the designer, except that the minimum width of the components shall be 2 in. (50 mm).
2. It is essential to have adequate rigidity so that the jig will not deflect during testing. The specimen shall be firmly clamped on one end so that it does not slide during the bending operation.
3. Test specimens shall be removed from the jig when the outer roll has traversed 180° from the starting point.

Figure 28: Scheme of the wrap-around bend testing [Ref. 46].
Figure 29: Nomogram for calculating strain in bending test. The dashed line (---) indicates how the strain is calculated as a function of the radius of the shoulder [Ref. 46].

Figure 30: Bend Test sample dimensions
Figure 31: Experimental set-up for bend testing. At the beginning, the straight sample is placed between the shoulder and the arm. Then, the arm is rotate in the clock wise direction, bending the sample around the shoulder.

4.2.3. Microhardness

The same metallographic samples were re-used for this test (see page 77). The samples were re-polished and used in the as-polished condition (1 μm final polishing). A LECO® micro-Vickers testing machine was used to perform this test. This instrument has the capability of measuring microhardness in a wide range of values (Figure 32).
Figure 32: Microhardness tester [Ref. 47].
4.3. Fume Analysis

The objective of these experiments was to measure the total amount of chromium in the fume generated by Monel 60 filler metal and AISi 308L filler metal. The welding process used in this case was shielding metal arc welding (SMAW). For the identification of each element present in the samples Electron Dispersion Spectroscopy (EDS) was used.

4.3.1. Fume Collection

The collection of fume was performed using an ELFI real time particle size distribution and concentration measurement system. The welding fume containing the particles is first sampled through a unipolar corona charger. The charged particles then pass into a low pressure impactor with electrically isolated collection stages. A precisely known charge given to particles in the charger is measured in real time with highly sensitive multichannel electrometers as the particles impact each impactor stage. The 12 different groups or stages are housed in a single compact unit (Figure 33). The machine can separate the particle by size. Starting with the largest particle size group (stage 12), which average diameter is equal to 10.52 μm, and ending with the smallest one (stage 1), which average diameter is equal to 0.03 μm.
The system is based in a simple principle. In every stage the heavier particles cannot turn and impact in the collection plate (Figure 34). Since the particles are electrically charged, they are bonded to the surface, which is a very thin Aluminum film (Figure 35) [Ref. 48].
Figure 33: Scheme of ELPI real-time particle size distribution and concentration measurement systems [Ref. 48].
Figure 34: Sketch of the fume collection equipment. The fumes are sucked from the welding and introduced in the input of the machine. The tortuous path makes the heavier particles to impact in a earlier stage (---→), while the light one can pass down stream and impact several stages ahead (→).

Figure 35: Typical impactor of the system. The Aluminum foil in the center is the place where the heavier particles impact, while the lighter continue down stream through the gap [Ref. 48].
4.3.2. Welding Parameter during fume collection

Identical Welding parameters and experimental set-up were used in all the experiments.

Following, the experimental variables are presented:

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Monel</td>
<td>1</td>
<td>71</td>
<td>20</td>
<td>3 1/8</td>
<td>27</td>
<td>40</td>
</tr>
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<td></td>
<td>2</td>
<td>71</td>
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<tr>
<td></td>
<td>3</td>
<td>71</td>
<td>20</td>
<td>4.5</td>
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<tr>
<td></td>
<td>4</td>
<td>71</td>
<td>20</td>
<td>5.5</td>
<td>47</td>
<td>40</td>
</tr>
<tr>
<td>308L</td>
<td>1</td>
<td>71</td>
<td>20</td>
<td>5.5</td>
<td>47</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>71</td>
<td>20</td>
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<tr>
<td></td>
<td>3</td>
<td>71</td>
<td>20</td>
<td>5.5</td>
<td>47</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>71</td>
<td>20</td>
<td>5 3/4</td>
<td>51</td>
<td>13</td>
</tr>
</tbody>
</table>

Table 7: Welding Parameters during fume collection

4.3.3. SEM sample preparation:

The SEM/EDS samples were prepared taking the foil used in each stage containing the particles and sticking it to a holder by using a silver paint. The use of the paint was for providing electric conduction during the measuring in the SEM/EDS.

The samples were coated with a very fine carbon layer to avoid charging electrically the particles. Additionally, an acceleration voltage of 20KeV was used in order to analyze chromium more accurately.
Figure 36: SEM fume sample from two different stages. Notice that the one on the right has less amount of material (spots) because it comes from a later stage.
4.4. Characterization Techniques

4.4.1. Metallography

4.4.1.1. Sample Preparation. Polishing

The polishing of this dissimilar welding may be difficult because the presence of very hard titanium nitrate (TiN) particles. In general, those particles have an average size of 10-15 μm, thus for fine polishing that may be a problem if those particles are mechanically removed during polishing.

Caution must be taken in order to keep those hard particles in the metal matrix and avoid scratching and contamination of the polishing cloth. With that objective, a hard polishing cloth and high pressure on the sample should be used to produce a quick and homogeneous polishing.

Aluminum oxide polishing powder produces a quick over polishing of this microstructure, thus it is not recommended.
The procedure used was the following:

Grinding:

- Three stages of SiC abrasive (240-400-600 grit)

Polishing:

- Diamond paste 9 μm, hard cloth, medium- hard pressure, 15-30 sec

Fine Polishing:

- Water-based Diamond 1 μm, soft cloth, medium pressure, and low pressure at the end. 3-4 minutes.
- Vibromet, 0.05 μm silica-gel, no extra weight, 20-30 minutes

4.4.1.2. Sample Preparation. Etching:

Sometimes etching dissimilar welding could be a difficult job because the etchants that work for the base metal or filler metal may not work when the metal is a mix between both, that is a dissimilar weld metal. Unfortunately, that was the case for this dissimilar weld. The etchants that the literature recommends for Monel or for AISI 304 do not work very well in this dissimilar welding. Some of them may attack one zone in particular (e.g. grain boundaries), and produce a light etching to the rest. Sometimes a double etching technique may be used, in which basically the sample is etched in two different stages, attacking selectively some zones in the microstructure, and then the rest. This technique sometimes is difficult to apply, since during the second stage the zones that were attacked previously still react during the second stages and partial over-etching may occur.
Local segregation may sensitize the metal and produce a higher etching rate with respect to the rest of the material, resulting in a local over-etching. In other words, the etchant aggressively attacks the sensitized zones and for the rest of the material it attacks in a normal rate. If the sensitized zones are enough small, this effect may be acceptable. However, if those areas are big for the magnification that is being used, then this attack is not acceptable.

This is the case when we used both optical and scanning electronic microscopy (SEM). Local over-etching may be acceptable for optical microscopy, but at the higher magnification in SEM zones look just like holes and no further information may be obtained from them. The best etchant was the ferri-cloride (see Appendix for details). It attacks very uniformly low and medium dilution samples, however it may over etch the highly segregated zone is the time is too long.

4.4.2. Dilution Measurement:

Dilution was measure by cutting a cross section of the weld bead, polishing and etching the weld metal to develop the weldment profile. After that, pictures of the cross section were taken and analyzed using Pax-it®, special software for optical microscopy with features like live capture image, area measuring and others.
To measure the dilution two different pictures were taken: one previous and one after welding. Then dilution was estimated with the simple formula showed in Equation 1.

\[ D\% = \frac{(A - A_0)}{A} \times 100 \]

Equation 1: calculation for dilution level in a dissimilar weld, where \( A \) is the area after the weld, and \( A_0 \) is the initial area.

Figure 37: Example of the technique to measure dilution. Picture before (a), and after welding (b).

### 4.4.3. Microscopy:

Optical and Scanning Electron Microscopy (SEM) techniques were used to characterize the microstructure. The Electron Dispersive Spectroscopy (EDS) technique was used to study the distribution of elements in the interdendritic zones and characterize the different parts of the microstructure including TiN particles.
4.4.4. **Weld Quality Control Techniques:**

Three techniques were used for weld quality control: visual inspection, penetrant liquids and x-rays. Visual inspection and penetrant technique were assisted by optical stereoscopy.
CHAPTER 5

RESULTS AND DISCUSSIONS

5.1. Microstructure Studies

Metallography samples were prepared for optical and scanning electron microscopy (SEM). Three dilution levels were used in this study. The results show that four different zones can be distinguished: Base Metal (BM), which has basically 304L microstructure; Heat Affected Zone (HAZ); Transition zone (TZ) within the fusion zone where a chemical profile between Monel and 304L exists; finally there is a Fusion Zone (WZ) or weld metal, which has a typical “as welded” microstructure (Figure 38).
Figure 38: Typical weld microstructure of AISI 304L-Monel dissimilar welding. Four zones are distinguished: Base Metal (BM), Heat Affected Zone (HAZ), Transition Zone (TZ) and Weld Metal (WM).

5.1.1. Transition zone (TZ):

In general, the width of TZ varies with the level of dilution, but in average it is around 30 µm (Figure 39). This value coincides with the one reported in the literature [Ref. 49]. The microstructure in the TZ is different from the rest of the zones due to the chemical profile across it, which is shown in Figure 39. Of course, this profile will depend on the dilution level and the mixing that takes place during welding. Since both base metal and weld metal are austenitic the
type of boundary is type I; that means there is epitaxial growing during weld solidification. Figure 40 shows how the solidification starts at the fusion line continue to growing from the grains at the BM into the WM. That is evidenced by the continue grain boundaries that cross over the fusion line.

Titanium nitrides are present in the TZ also. Figure 41 presents a SEM micrograph where some precipitates can be observed. As it can be seen from the micrograph, there is a tendency to have more precipitates at the TZ, probably due to the drag effect during the welding when the molten metal is stirred. In any case, the nitrides do not tend to be at the grain boundary. They are randomly distributed along the grains. Notice also that the precipitates at the TZ are smaller than those in the WM, probably due to the drag effect also.

Since the transition zone is a critical zone across which the chemical composition varies across it, any source of flaws such as cracks or disbanding can be expected. However, no cracks were observed in any case. Figure 42 shows a high magnification micrograph of TZ, where the microstructure can be seen more in detail. As it can be seen in Figure 43, there is certain diffusion of elements into the HAZ. Since the diffusion is quite higher at the grain boundaries, it seems that there is a more accentuated chemical profile at the grain boundaries of HAZ. Figure 44 shows this fact; similar etched lines at the TZ cross over the fusion line into the HAZ. This effect is stronger when the heat input is increased. Of course, the higher is the heat input, the faster the diffusion is. Another effect that takes place when the heat input is increased is the
increment of the TZ size. Some other effects related with lack of mixing at the bottom of the welding bead may cause an anomalous very wide TZ. Figure 45 shows a sample that exhibit a small part of the BM dissolving in the middle of the TZ. The content in this part of the weld metal may contain high concentration of Fe and Cr.

![Figure 39: Typical structure of transition zone. The dashed line on the right is the fusion boundary (FB), which divides the TZ from HAZ. Notice that the size of TZ is about 25 μm wide](image)
Figure 40: Epitaxial Growth at the fusion boundary (FB). Notice how the grain boundaries continue into the Transition zone (TZ).
Figure 41: Precipitates at Transition zone. The small and square white spots at the TZ are TiN precipitates. Notice that these precipitates are smaller than the ones at the WM.

Figure 42: High magnification Electron Back Scattering micrograph of transition zone.
Figure 43: Chemical composition across the fusion line. From EDS data.

Figure 44: TZ and HAZ interpenetration. Elements diffuse mainly via grain boundaries.
Figure 45: Effect of increasing heat input on size of TZ.
5.1.2. Fusion Zone (FZ):

Since the cracking phenomenon takes place in the fusion zone, a lot of effort was focus in this particular region of the welds. The study was focus on the highly segregated zones, analyzing the chemical composition in order to know which elements are segregated the most. The main objective of this study was to find the mechanism that operates in the Monel/type 304L dissimilar weld. For that reason, the study included metallography, optical microscopy, electronic micrography, EDS and EDS mapping. The last technique is very helpful analyzing element distribution. The interpretation of the results of this technique is easy: the bright zones indicate high concentration of each element, while darker spots represent low concentration of the element.

FZ has a typical dendritic microstructure with highly segregated material in the inter-dendritic zones. The weld also present some precipitates mainly titanium precipitate, but they will be discuss later on in section 5.1.4. The degree of segregation of solute depends upon the dilution level (segregation is a function of the coefficient of partition k). In other words, the higher is the dilution, the higher the segregation is. Figure 46 a and b) show a low and a high dilution samples respectively. There is a notable difference between both samples: high dilution level tends to produce more segregation in the interdendritic zones. This fact is illustrated in the micrographs by the effect of the etchant. In this welds, the highly segregates zones are more sensitive to the etchant, so they are
more attacked than the rest of the material. Figure 46 shows darker spots, revealing the location of the highly segregated zones.

In welding, segregation during solidification always occurs; the degree of segregation depends on the solubility and amount of solute the alloys has. Thus, the solute is rejected from the solid during solidification causing a liquid richer in solute and with lower melting temperature (k<1). Figure 47 presents an EDS map of a low heat input sample lightly etched. The segregated solute was mainly Cu (Figure 47-b); while Ni, Fe and Cr seemed to be depleted from the segregated zone where Cu is (Figure 47-a, -c, -d respectively). On the other hand, Ti and Mn segregation showed to be more homogenous (Figure 47-e, -f respectively). Notice that in this kind of welds Ti forms some nitrides, so the particles look very bright in Figure 47-f (for more detail about this precipitates see section 5.1.4). Experimental data for the coefficient of partition (k) for Cr, Ni and Cu are presented in Table 4 (page 49)\textsuperscript{8}, where k for Cu is the highest in this table (k= 2.33). This data can explain why Cu is more segregated than Fe in Figure 47.

Depending on the level of dilution, after certain point the enriched liquid can reach the composition that causes other phase to precipitate (e.g. eutectic). That can be shown by the effect of an etchant; since it attacks mainly base on chemical composition, the presence of other phase richer in solute will be etched differently from the rest. Focusing on the area inside the square in Figure 48-a, it can be noticed that there was a strong segregation taking place there.
During solidification, the new formed solid rejected solute into the surrounding liquid. As the time passed by, this liquid pool was getting smaller and richer in solute. After a certain point, the segregation was high enough to cause another phases to precipitate (darker spot).

The enrichment of these areas can be shown by back scattering electron microscopy (BSE), which basically shows an image with contrast based on the atomic number of the atoms present; thus, different chemical composition areas have different colors. Figure 48-b exhibits a BSE micrograph of a sample with high dilution in the as-polished condition; since the high segregated zones have a very different chemical composition, then they look white, while the rest look darker.

Figure 50 shows also a BSE micrograph of a high dilution sample in the as-polished condition. There a high segregated zone on the left of the figure (point A), in the middle of the micrograph is the core of the dendrite (point B), and on the right there is crack which still containing some segregation (C).

The chemical composition of the point A, B and C is listed in Table 8. Notice that Fe, Cr and Ni are depleted from the high segregated zone, while Cu is highly segregated. This table also shows that the liquid which caused the failure and then solidified around the crack has very similar chemical composition than the highly segregated zone in Figure 50. Consequently, it can be assumed that the liquid that

---

5 This data is for Monel weld metal with some diluted Fe.
participates in the cracking is coming from these highly segregated zones.

Therefore, the highly etched zones in Figure 48-a, which coincide with the white spots in Figure 48-b, are enriched mainly in Cu. This fact is supported by Figure 50, which exhibits an EDS mapping of the area showed in Figure 48-b. This segregation is more intense than that in Figure 47, which makes sense with what is shown in Figure 46 and it coincides with what is described in Table 8.

The results of this study revealed that other elements always related with hot cracking in high nickel alloys such as S and P were not present in the highly segregated zones. Al, Si and C were detected in very low concentration and homogenously distributed.
Figure 46: Typical FZ microstructure of a low diluted (a) high diluted weld (b).
Figure 47: EDS Mapping Technique of a low diluted weld. Maps for Ni (a), Cu (b), Fe (c), Cr (d), Mn (e), Ti (f), corresponding to a free-crack zone (g). The bright spots mean high concentration of the element, while dark spots mean low concentration of the element.
Figure 48: Segregation during solidification. (a) Notice that the etching develops the interdendritic zone as a valley where there is high segregation, but there is another region inside that has different chemical composition, so the etching attacks differently. (b) Back Scattering microscopy of a high dilution sample exhibiting cracks in the as-polished condition. Notice that the
Figure 49: BSE micrograph of a high dilution sample in as-polished condition. Measurement of chemical composition in a high segregated zone (A), middle dendrite (B), and in a crack (C).

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration [%wt]</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>SiK</td>
<td>0.56</td>
</tr>
<tr>
<td>TiK</td>
<td>0.01</td>
</tr>
<tr>
<td>CrK</td>
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</tr>
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<td>MnK</td>
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</tr>
<tr>
<td>FeK</td>
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</tr>
<tr>
<td>NiK</td>
<td>18.66</td>
</tr>
<tr>
<td>CuK</td>
<td>62.01</td>
</tr>
</tbody>
</table>

Table 8: Chemical composition in Figure 49 for a high segregated zone (A), middle dendrite (B), and in a crack (C).
Figure 50: EDS Element Mapping Technique of a high segregated zone for Cu (a), Ni (b), Fe (c), Mn (d), Ti (e), Cr (f), P (h) from a crack area of Figure 49 (i).
5.1.3. Hot cracking Mechanism in Monel/type 304L dissimilar welding

The analysis of the mechanism operating in Monel/type 304 dissimilar welding is based on the results of the previous section. The highly segregated zones that were described previously are related with the hot cracking mechanism. Figure 51 shows the microstructure of a high dilution level sample. In the center of the micrograph there is a crack propagating from the right to the left via grain boundary. The arrow indicates some evidence liquid at the grain boundary around a crack. The micrograph suggests that during solidification this region of the weld was in the liquid state, while the rest of the material already had been solidified. At that time, the restraint was high enough to open a crack on the boundary. Since in the tip of the big crack (right side of the micrograph) there was high stress concentration, which caused the highly segregated zones containing liquid (left side of the micrograph) to failure. In this way, the big crack propagates by joining small cracks.

The way that the crack is formed seems to be via Cu-rich liquid present in the boundaries, or sometimes provided by a highly segregated zones. Figure 52 shows a BSE micrograph of a high dilution sample containing cracks. In the middle of the micrograph there is a highly segregated zone, which in this micrograph has a different color due to the difference in chemical composition respect to the rest of the material. As indicated in the previous section, these highly segregated zones are enriched in Cu. At high temperature and after the rest
of the material solidified, the highly segregated zone containing this enriched low melting liquid seems to be the source of liquid that caused the formation of the cracks showed in the micrograph.

There is a strong influence of dilution level on hot cracking susceptibility. Low dilution welds do not contain any cracks. On the other hand, high dilution levels can cause a significant drop in crack resistance as showed in Figure 53, which illustrates the case of a weld metal presenting very high cracking susceptibility. On the top of the micrograph a hot crack started at the FZ and could propagate even into the HAZ.

Hot cracks may be also linked with crack at the MGB (Figure 54). This may be related with other cracking mechanism operating at lower temperature range such as ductility dip cracking [Ref. 24, 50].

Crack healing also was observed in this dissimilar welding. This phenomenon may occur when enough liquid at the grain boundaries is present; as a result, the crack can be filled out by the liquid that solidifies later on closing finally the crack (Figure 55).

With the information obtained with this study, the characterization of the enriched liquid causing cracking could not be gone beyond the following statements: the liquid associated with weld solidification cracking in Monel/Type 304L welds is rich in Cu, and it is formed in the interdendritic zones. In order to study the mechanism in more detail thermodynamic information is necessary (for
more detail about the information used in this section see Appendix). The easiest way to start the analysis is to study the Cu-Fe binary phase diagram (Figure 56). This diagram does not show any eutectic reaction at the Cu-rich portion of the diagram; however, it has a broad S+L field. As it was mentioned in chapter 1, this is the field where weld solidification cracking mechanism operates. The wider is this field, the higher the probability of having hot cracks is [Ref. 24]. In fact, hot cracking has been reported in the welding of mild steel and copper alloys [Ref. 51]. Ni-Cu and Ni-Fe systems do not present eutectic reactions also and they have a very narrow L+S field [Ref. 52], so this logic is not applicable in these cases.

The next step is to study more complex systems that tend to be closer to describe the behavior of the real welds. In this context, the Ni-Cu-Fe ternary system does not present any eutectic reaction [Ref. 53]. No further information was found about this system. In particular, about the width of the L+S field. Increasing the complexity of the phase diagram, Monel can be represented by the Ni-Cu-Fe-Mn quaternary system, which is characterized by the unlimited solubility of the component in the liquid and solid state [Ref. 37]. Again, no further information was found about this system. Eutectic reactions have been reported in the Ni-Cu-Ti and Fe-Cu-Ti systems [Ref. 40]. However, the information of these diagrams is limited to 50 % Cu; thus, it does not cover the range of chemical composition that the results of this work show. Of course that for a complete study Cr should be included also; thus, the complexity of the system raises so much that computer analysis such as Thermocal® is needed.
Unfortunately, the limited thermodynamic data about Ni-Cu system did not make possible any study using this software.

Consequently, with the limited thermodynamic information at this point no claim about the details of the cracking mechanism in Monel/type 304L dissimilar welds can be stated. However, the evidence of having no eutectic in all the systems presented above may suggest that the mechanism could be similar to that in mild steel-copper alloy dissimilar welds. This particular mechanism is based on a wide L+S field, which produces a drop in the cracking resistance at intermediate copper contents. The weld has low susceptibility at low Cu content, while crack healing is observed at high Cu contents [Ref. 51]. In this context, during the present investigation evidence of crack healing at high dilution level have been observed in the Monel/type 304L (Figure 55). On the other hand, at low dilution levels the welds are crack-free. Further investigation needs to be done in order to reveal the details of the cracking mechanism operating in the studied dissimilar welds.
Figure 51: Hot crack propagation. Notice how the crack is propagating from the right to the left. The crack propagates joining small crack that lay in front of it.

Figure 52: BSE micrograph of high dilution sample having cracks. In the middle od the micrograph there is a highly segregated zone that at high temperature seems to provide liquid to the cracks on the right and on the left.
Figure 53: Hot cracking in high diluted welds. The cracking susceptibility is so high the crack can propagate even into the HAZ.

Figure 54: Link between a hot crack and a crack at the MGB.
Figure 55: Crack healing. Notice that there was a crack all along the distance showed by the picture, but there is some evidence of liquid healing on the left, which apparently partially closes the crack.
Figure 56: Fe-Cu phase diagram [Ref. 51].
5.1.4. Precipitates in AISI 304L-Monel dissimilar welds

There are some different types of precipitates that can be observed in this dissimilar welding. Figure 57 illustrates some of them and it shows how they look in an actual weld.

Figure 57: Different precipitates in AISI 304L-Monel dissimilar Welding
5.1.4.1. Titanium Nitrides:

Another characteristic of this microstructure is the presence of small and square particles. The metallography (Figure 58) and EDS (Figure 59) studies revealed that those particles are Titanium nitrides. They are already in the filler metal before the welding process. During the fusion, some particles remain in the weld metal with a certain distribution pattern. In general, they are homogenously distributed in the FZ. However, there are fewer and smaller particles in the TZ (see section 5.1.1). At this point, there is no evidence that these particles can affect any mechanical property. Nevertheless, these particles can interact with grain boundaries presenting a locking effect on the motion of the boundaries (Figure 60).
Figure 58: Typical Titanium nitride (TiN).
Figure 59: Spectrum obtain from the particle in Figure 58 using EDS

Figure 60: Locking effect of TiN and intergranular precipitates on MGB's. The square particle is a TiN particle that locked the MGB so it has to curve in order to keep going.
5.1.4.2. Titanium carbides:

These particles are present the whole studied range of dilution. Their morphology is shown in Figure 61. Usually they are in the interdendritic zone in the high segregate zones. They have different shape with respect to the TiN, which tends to be square and bigger than TiC. They may form during solidification via bulk diffusion, or via eutectic reaction (Figure 60) or via grain boundary diffusion (Figure 61). An EDS study revealed the presence of TiC in Figure 63. Since the size of the particle is small, and this technique excites at least 1 μm$^3$ of the material, other elements appear in the spectrum. An important peak in C shows up in this spectrum; however, the content of C in matrix is very low as it was indicated in section 5.1.2 (page 90). That indicates that this particle is rich in carbon. Additional evidence is present in Figure 64, where EDS mapping shows that the main elements present in the particle are Ti and C.
Figure 61: Typical TiC. Notice that they have irregular shape and are connected to the boundary.

Figure 62: Formation of the TiC. Notice that there two particles inside of the rectangle in the figure. One is a TiN which is square and usually bigger than TiC, which lays just on the right of the first one on a high segregated zone.
Figure 63: EDS spectrum for a TiC particle. (Since the particles are small part of the matrix was excited during the measurement, thus other elements show up).
Figure 64: Titanium Carbide particle (d). EDS element mapping for C(a), Ti (b), and Ni (c). The Cu content in this particular study was low.
5.1.4.3. Intergranular precipitates:

In the WZ there are some small particles that precipitate at the grain boundaries. Its morphology can be described as rectangular shape particles with sizes around 1 μm long and less than 0.5 μm width (Figure 65). The presence of these precipitates may be important even at low dilution levels. Obviously, they have a locking effect for the motion of MGB’s (Figure 60). Due to the small size of these particle it was not possible to measure the chemical composition by using EDS technique.

Figure 65: Intergranular precipitates
5.1.4.4. Titanium-Aluminum Nitrides:

Titanium aluminum nitrides were observed in high dilution samples with similar morphology as titanium nitrides. Figure 67 shows the EDS spectrum for this particle. In the center of this particle there is another small one. It seems that this particle nucleated in other particle that was formed previously (probably TiN).

Figure 66: Titanium Aluminum Nitrides.
Figure 67: EDS spectrum of Ti-Al-N particle
5.1.4.5. Titanium Sulfide:

Sulfur combines with titanium to form precipitates also at high segregated zones. Again, since these particles are so small some indication from the metal matrix is obtained during EDS analysis (Figure 69).

![Titanium sulfide in the weld metal](image)

**Figure 68: Titanium sulfide in the weld metal**
Figure 69: EDS spectrum of TiS particle
5.1.5. Shielding Problems:

The constant problem of protection at medium and high dilution levels led to a study of this problem in more detail. The study included SEM, EDS, optical microscopy, and visual observation during the welding process. The main objective of this study was to determine the nature of the “slag” formed under bad protection of the weld pool. From the chemical composition analysis of sample in the “as welded” condition it was determined that the “slag” is rich in Ti. Optical and electronic microscopy showed that this “slag” has a porous structure, like it is showed in the picture. It is obvious that it is not metallic, but ceramic (Figure 70). In this figure a Back Scattered Electron (BSE) micrograph is showed. It exhibits the presence of square particles rich in a heavy element (Ti), and surrounding by lighter elements (probably N and O)**. Figure 70 shows also how porous this structure is. The EDS spectrum of this “slag” is shown in Figure 71; there is a clear peak in Ti. However, there are not other elements other than the weld metal constituents.

** Due to technical problems in the EDS equipment, it was not possible to measure the amount of oxygen and nitrogen.
Figure 70: SEM micrograph of the top of an unprotected weld. The slag forming a irregular surface on the top of the bead (a); Back scattering Image reveals how porous is the slag, and the presence of Ti, O, and Ti, N (b).

Figure 71: EDS Spectrum of slag on the top of the weld bead.
5.2. Mechanical Testing

5.2.1. Tensile Tests

The results of tensile tests for Monel-AISI 304L dissimilar welding show similar tensile properties to AISI 304L-ER308L filler metal (Table 3). Figure 72 shows a typical curve obtained from tensile test, indicating a strong weldment (crultim = 80 Ksi), and a very good ductility (46 %).

A total of five samples were run in this test. The results and some statistic information are presented in Table 9.
Figure 72: Tensile test. Typical Stress vs. Strain curve for Monel- AISI 304L dissimilar welding.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Ultimate Stress [Ksi]</th>
<th>Yield Stress [Ksi]</th>
<th>Elogation [%]</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>81.24</td>
<td>42.5</td>
<td>47</td>
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<tr>
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<td>81.93</td>
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</tr>
<tr>
<td>5</td>
<td>80.06</td>
<td>44.5</td>
<td>40.5</td>
</tr>
<tr>
<td>Average</td>
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</tr>
<tr>
<td>Standard deviation</td>
<td>1.40</td>
<td>1.44</td>
<td>2.77</td>
</tr>
</tbody>
</table>

Table 9: Tensile Test for Monel-304L, at 13 % dilution. Results for each tested sample and some statistic information for this experiment.
5.2.2. Microhardness

Microhardness tests were performed on several welds, with different dilution levels (13-35%). Different loads were used in order to have small mark and measure the hardness in the Transition Zone and Heat Affect Zone. Welds using ER 308L and Monel filler 60 were tested under the same conditions. The results are shown in the Figure 73. Notice that in the Monel 60 welds are softer, but they are in the range of 175-190 HV, which is very close to the 308L weld range.

![Image of hardness test results]

Figure 73: Microhardness Curves of 304L (base metal) using two different filler metals (Monel 60 and 308L) under similar welding conditions.
5.2.3. Bend Testing

The bend Test was performed according the American Welding Society (AWS) Structural Stainless Steel Code (AWS D1.6:1999). The tested was performed using a conventional wrap-around bending machine. The inspection was visual, according with the code, but in some cases liquid penetrant technique was used. Weld samples having low and medium dilution level were tested. The total calculated strain was approximately 15%. All the samples passed the test satisfactorily.

Figure 74: Bend Test Sample. Notice that even though the weld is under a high strain (around 15%), it does not present any crack.
5.3. Fume analysis

After the fume collection, the particle weight in each stage was measured. The weight distribution is exhibited in Table 10 and Figure 75. Notice that most of the particles are in the respirable range. The peak of the curve is 0.30 μm. During this study, it was observed that the Monel fume particles tend to form clusters. Therefore, even small particles (like in the stage 1) form big clusters larger than 1 μm, which is the minimum size that the EDS technique requires to measure chemical composition. Figure 76 shows one of those particle clusters. The formation of this cluster may occur during the collection due to the electric charge that the machine imposed to the particles, or due to a source of wing effect. Since clusters have more area, then the aerodynamic effect may cause big cluster to be deposit in earlier stages.

The data obtained from the EDS analysis of AISI 308 and Monel fume particles is shown in Figure 77 and Figure 78, respectively. For statistical purposes, up to four different samples coming from different stages in the fume collection machine were studied. Thus, different particle sizes were analyzed. The nomenclature used in Table 11 for sample identification refers first to the filler metal (308 or Monel), following by the stage number where the particles come from (i.e. particle size), and finally the number of the spot analyzed. (e.g. 308-S1-
3 means that the particles come from the AISI 308L filler metal, the particle size correspond to the stage 1 and it was the third spot analyzed).

There is an evident difference in the Chromium content between AISI 308 and Monel fume particles (Figure 77 and Figure 78). Notice that Cr is practically not detected in Monel fume particles.

<table>
<thead>
<tr>
<th>Stage</th>
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<th>Average size [um]</th>
<th>weight fraction [%]</th>
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<td>Eliminated during expiration</td>
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<tr>
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<td></td>
<td>0.59</td>
<td>2.33</td>
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<tr>
<td>4</td>
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</tr>
<tr>
<td>12</td>
<td></td>
<td>10.52</td>
<td>2.33</td>
</tr>
</tbody>
</table>

*from AWS classification [Ref. 2].

Table 10: Monel SMAW fumes. Particle weight as a function of the particle size.
Particle Weight Distribution

Figure 75: Particle weight distribution for Monel SMAW fumes.
Figure 76: SEM micrograph of a cluster of fume particles.
a) Data base on wt %

<table>
<thead>
<tr>
<th>sample</th>
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<th>308-S3</th>
<th>308-S4</th>
<th>308-S5</th>
<th>308-S6</th>
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<th>308-S9</th>
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Table 11: Chemical Composition for EDS data for Fume analysis samples for 308L (a) and Monel (b).

![Figure 77: EDS Spectrum for AISI 308 fume particles](image-url)
Figure 78: EDS Spectrum for Monel Fume particle clusters.
5.4. Welding Issues

5.4.1. Description of Welding Issues:

The main problems in this particular dissimilar weld are the following:

5.4.1.1. Bad Protection:

It is manifested by very dark layer on the bead and the surrounding zones. Typically, after welding a regular weld surface lacks undulations (Figure 79-a), but in the case of this dissimilar welding the weld bead presents a very smooth surface layer on the top of it (Figure 79-b). At first, it was thought that this layer could be some slag, similarly like in other welding processes like SMAW or GMAW. However, after passing the wire brush, it remains on the bead as a part of bead. The formation of this layer strongly depends on the heat input level, heat extraction, shielding gas flow rate. At high heat inputs, when there is poor heat extraction, or when the protection of the weld pool is not adequate, the layer tends to cover the entire bead. However, at low heat input the layer tends to be on the sides of the bead (Figure 79-a).

Electrode contamination was observed when using GTAW. Immediately after the welding process, it is observed on the tip of the electrode.
some svelte particles which lay perpendicular to the electrode. In a welding context they are called “whiskers”. Additionally, the electrode is cover with a dark layer. In general, when there is typical problem of bad protection the tip of the electrode exhibit a dark color. However, in this particular case this layer was found faraway from the tip. Figure 80 sketches what happen during the process. Some dark spots start to appear in the filler metal. They are transferred to the weld pool, and later to the welding bead. Finally, they lay at the bead side and grow more due to the fact that the metal is still very hot and more oxidation takes place. The final texture is a smooth surface, no-shiny, and not brittle.

Figure 79: Comparison of weld quality. a) Bad protected 304L-Monel weld; b) 304L weld with 308L filler under similar welding conditions. Notice the presence of "slag" and the black film on Monel bead.
5.4.1.2. **Hot Cracking:**

After the welding process was completed, visual inspection showed that some cracks were formed during the process. Numerous cracks were found in welds with high heat input. However, at low heat input no cracks were found. Figure 81 shows some evidence to proof that these cracks are formed by the Hot Cracking phenomenon. Inside the crack the dendritic structure can be observed. This evidences the fact that the material was torn when some liquid films still remained.
5.4.1.3. Penetration:

The first welding configuration used was V- on plate; it was found that in order to reach good penetration the dilution level must be increased so much, that hot cracking starts taking place. The first observation was the tendency of the weld pool to grow preferably in the transversal direction (Figure 82).
Figure 82: Effect of increasing heat input on the shape of welding bead. The first pass (top) has better penetration than the second (bottom), which was made at higher heat input. There is a clear tendency of widening the bead, rather than increasing penetration.
5.4.2. Overcoming welding issues

5.4.2.1. Bad Protection

This problem was related with the presence of Ti in the weld metal (see section 5.1.5, page 120). With those observations, a systematic study was performed. Welding parameters were varied one by one in order to find the most critical ones. Several dozen welds were made in this study by using Monel Filler 60. Additionally, to have a point of comparison some welds were made with 308L filler metal instead of Monel. All the variables were tested; voltage, current, gas nozzle cup size, shielding gas purity, gas flow rate, and others. The problem was overcome by using 5% Hydrogen in the argon shielding gas, which lowered the oxidation reactions due to its reducing characteristics.

Another critical variable was the gas nozzle size (Figure 83-a). Better results were obtained using the biggest size (size #3), or using a travel shielding gas nozzle. The reason to explain this is that for a given heat input increment, the weld pool tends to grow more in transversal and longitudinal direction than in through-thickness direction. This is due to the sluggish molten metal and the poor stirring cause by the nature of the molten metal; as a result, the weld pool tends to be larger. Therefore, for medium and high heat inputs the weld pool becomes so big that it is not efficiently covered by the shielding gas. In addition, at such heat input levels the material just behind the torch is still very
hot, making Ti able to react on the unprotected surface. In other words, even when hydrogen helps to reduce the protection problems, if the gas nozzle is not big enough to protect the weld pool efficiently during the process, bad results are obtained. As a conclusion, beside the addition of hydrogen to the shielding gas, good protection is achieved by the use of either appropriate gas nozzle size or travel shielding gas.

Some additional protection may be provided by a back shielding fixture (Figure 83-b). An actual weld obtained following the procedure described above is shown in Figure 83-c. Notice it is clean and free of any slag.
5.4.2.2. Electrode Contamination

Another problem observed in this dissimilar welding was the constant contamination of the electrode during GTAW. Notice that a kind of "crown" is formed around the tip of the electrode. This was noticed especially at medium and high heat input when bad protection and the formation of the slag on the top of the bead take place. Fortunately, this problem was overcome automatically when hydrogen was added to the shielding gas.
5.4.2.3. Controlling Dilution:

As it was mentioned previously, the hot cracking phenomenon mechanism needs three factors: susceptible microstructure and stress. For that reason, in the practice the susceptibility to this phenomenon depends on dilution and on the restraint for a given welding configuration. Therefore the selection of the correct welding design may lower the susceptibility to hot cracking. It was found that V- on plate configuration has a better performance than single and double V-groove; however, it has a very poor penetration. Obviously, this is because the section gets very sharp in the bottom of the groove, causing lack of penetration. In order to keep the dilution in a safe level the selection of the heat input is critical. Relative high current and voltage have to be used, trying to set up the travel speed in such a way that it is high enough, so just a small amount of base metal is melted. But at the same time it has to be low enough to avoid center line segregation (Figure 4). Otherwise, despite of having low dilution, the restraint will reach such a level that eventually the weld will form cracks.

Other successful technique used was to oscillate the torch in the transversal direction (with respect to the travel direction). For a given weld width, this technique allows a decrease in the heat input and it increases the filler metal feed rate, causing a considerable drop of dilution and an increase in the travel speed.
Current pulsing also has had a beneficial effect on dilution control. The alternating current peaks enhances penetration, at the same that it keeps dilution lower enough. Using this technique, the dilution level reached a lower value than that in the case of a constant current with a value equal to the peak current during pulsing.

5.4.2.4. Penetration:

The first problem in the seeking of the solution to the penetration problem was the sluggish molten metal, which is typical of nickel base alloys. The second problem was the strong influence of titanium slag on the molten metal flow (under bad weld pool protection conditions). The third problem was the welding design (V- on plate 90°). At the tip of the groove, section is a very narrow. Considering the negative factors sluggish molten metal, surface tension of the molten metal at the tip of the groove, and the low heat conduction of stainless steels, then it is easy to understand the tendency of wider weld pool over penetration (Figure 84-a). The effects of Ti on penetration are based on the fact that Ti forms a source of slag, which floats on the top of the weld pool during welding. This slag may cover a big fraction of the weld pool; consequently, it may change the fluid pattern of the molten metal. Therefore, penetration may be affected by the presence of this slag.
A change in the welding configuration was tried. A double V-groove no gap configuration was selected. At first the results were poor. Again, bad penetration did not allow the molten metal to flow in the bottom of the V-groove, in fact the weld pool tended to be very wide. The proposed solutions to this problem were: a) to increase the current and to decrease the arc length, or b) to open the gap. The first solution obviously increases the penetration, but also the dilution level. Additionally, good penetration is obtained just in the first pass. The second pass tends to widen the pool, producing a shallow penetration (Figure 84-a). Therefore, this solution was discarded. The second one has the following problems: if the gap is small (2 mm.) the penetration is good in the beginning of the weld, but after certain distance from the starting point the high thermal expansion and the poor thermal conduction of stainless close completely the gap in between the work pieces. This reduces penetration (Figure 84-c). That was observed even when good clamping system was used to keep the work pieces static. Logically, then a larger gap was used (4mm), but the problem was that the molten metal on the V-groove just drop and there was no joint between the work pieces. There was no way to avoid the dropping of the molten metal, because there is not enough accessibility in this particular design to use any backing plate.

Finally, a single V-groove with 3mm gap was used (Figure 84-d). In this case, the joint design allows use of a backing plate, therefore good penetration was assured by using a big gap, and the molten metal dropping was avoid by using a backing plate. However, it was noticed that if an intermediate
gap is used, then the molten metal dropping is also avoided but without using a backing plate. The explanation for this observation is that for intermediate gap, the gravity force may be compensated by the surface tension. As a result, the molten metal flows in the gap, producing full penetration, but it does not drop.

Figure 84: Penetration problems. a) Double V- groove. Uneven weld pool low penetration; b) Any increment in current increase penetration, but it produce high dilution; c) Change of the penetration as the function of the gap in Double V- groove. On the left the gap was excessive, so the material was dropped. In the center the penetration was good, but after that the gap was closed by the thermal expansion and thermal stresses; d) single V- two pass, full penetration weld.
5.4.3. Distortion

V-groove configuration seems to be the correct one; however, excessive distortion may occur. The reason for this is the fact that during cooling the weld bead tends to contract, producing an uneven stress distribution. In contrast, in double V-groove design this phenomenon is compensated when the second pass is completed.

Distortion may be reduced by using clamping forces, but some distortion always remains after the clamping force is released. Distortion is an important issue when preparing tensile test samples. Therefore, they were prepared using double-V-groove geometry.
CHAPTER 6

CONCLUSIONS

6.1. Welding Procedure Development

- Welding procedures for Gas Tungsten Arc Welding (GTAW) with Monel filler metal 60 and Type 304L base metal have been developed. Using this procedure, crack-free and slag-free welds were obtained. Three different heat inputs were selected in order to have three different dilution values within the 15-45% range.

- The shielding issue was solved by adding 5% of hydrogen to the argon shielding gas. This factor and extra protection produced slag-free welds.

- The main weldability issue was weld metal solidification cracking. Dilution of Type 304L was intimately related with cracking. Solidification cracking is avoided if dilution is kept below 25%.
6.2. Metallurgy Behavior

- Segregation of copper was related to the cracking mechanism. Cu tends to form low melting phases when dilution is high. At low dilution levels, such segregation was not observed. The cracking susceptibility is very high for dilution levels higher than 40%.

- Monel 60/Type 304L weld metal exhibits a variety of Titanium precipitates. The most abundant precipitates were Titanium nitrides (TiN), which were observed at all dilution levels. TiN particles were identified as intragranular precipitates. They were present in Monel filler metal and were transferred to the weld metal during welding.

- Titanium carbides were identified as intergranular precipitates. Partial dissolution of the particle along the grain boundary was observed.

- Abundant small intergranular particles were observed (particle size < 1μm). Identification was not possible due to the small size of the precipitates. Other Ti-rich precipitates were observed, including precipitates rich in S, Al, and C. In any case, no relationship between these precipitates and the cracking mechanism was determined.
6.3. Mechanical Properties

- Mechanical properties of Monel/Type 304L were determined. Tensile testing showed that the ultimate tensile stress, yield stress and the ductility were similar to 308L/Type 304L. Ultimate stress was 80 Ksi, yield stress was 44 Ksi, and elongation was 44%.

- Bend Testing was performed at 15% strain. All samples passed the test.

- Microhardness testing showed similar properties across the fusion boundary. The microhardness in Monel 60/Type 304L weld metal was similar to that for ER308-L/ Type 304.

6.4. Fume Generation

- Chromium content of SMA welding fumes using Monel 60 and E 308-16 was analyzed. Cr was reduced in the welding fume by a factor of 20 when comparing Monel 60 to E308-16.

- Most of the welding fume particles were in the respirable rage (0.1 μm-5μm diameter).
List of References


APPENDIX A

ETCHANTS AND ETCHING TECHNIQUES
CHEMICAL ETCHANT AND ELECTROETCHANT:

- **Oxalic**
  
  The first etchant tried was the most popular etchants for AISI 304. In particular, the 10 %wt oxalic. It produced over etching very easily in particular in the interdendritic zones. The parameters were 5 volts for 5-10 sec.

- **Phosphoric:**

  Phosphoric acid (H₃PO₄) in glycerol and water is used for both of these alloys. The current density recommendation in ASM Handbook Volume 3 Metallography and Microstructures is a little different from the one.

  The recommended solution is:

  - 37 ml H₃PO₄
  - 56 ml glycerol
  - 7 ml water

  For stainless steel, the recommendation is 0.78 A/cm² at 100-120 C for 5-10 minutes. For Monel, the recommendation is 0.9-1.0 A/cm².

  The etching must be done at 80 °C. For that reason a heater was used for heating up the etchant. The temperature was sensed constantly by using a Hg thermometer. The set up of power of the heater was done by trial and error. For this study different temperatures around 80°C were used.
The current density was estimated by measuring the exposed area of the sample and using a multimeter for measuring the current. The time was varied from 1 minute to 1.5 minutes. The results were poor. The etching was very unstable and difficult to set up. Its thermal inertial is high, so it is difficult to reach and keep the desirable temperature. Its effects depend strongly on the temperature.

- **Sodium Cyanide:**
  This immersion etching was used following the recommendations in the metal handbook (Ref.). Special care was taken, since this chemical is highly poisonous. The chemical formula used was the following:
  
  - 10% NaCN
  - 10% (NC₄)₂ S₂ O₉

  The time was varied from 30 sec up to 3 minutes. Its effect was very unstable also. Sometimes it produced a very different etching effect even when similar samples.

- **Nitric-Acetic:**
  This is a chemical etching which chemical composition is the following:

  - 50% vol. Nitric Acid
  - 50% vol. Acetic Acid

  The samples were swabbed with cotton stick for a period of time 15-30 sec. The results again were poor.
• **Nitric-Acetic-Hydrochloric:**
  Equal parts of nitric acid, acetic acid and hydrochloric acid were mixed (add nitric last). The samples were swabbed with cotton stick. For 1-1.5 minutes. It did not attack the metal.

• **Chromic:**
  This is an electroetching which formula is 10% wt of chromic acid in water. The voltage was 6 volts, and time varied from 30 sec – 2 minutes. The result were poor. It over-etches the inter-dendritic zone very easily.

• **HydroFluoric:**
  This is an electroetching which formula is the following:

  - 7.5 ml HF
  - 2.5 ml HNO₃
  - 200 ml Methanol

  The current density was set at 0.78 A/ cm². The current density was estimated by measuring the exposed area of the sample and using a multimeter for measuring the current. The time was varied up to 4 minutes without any result.

• **Sulfuric:**
  Water based electroetching with 5 % Vol. Sulfuric acid. The voltage varied 3-6 volts and the time 1 sec - 45 sec. It over-etches the inter-dendritic zone very easily.
- **Ferric-Chloride:**
  
  This etchant is usually used for Monel. It is chemical etching, and its formula is the following:

  - 8 gr. FeCl₃·3H₂O
  - 25 ml HCl
  - 100 ml water

  Mix in ultrasonic vibration bath for 30 minutes. The time varies from 5-10 seconds. This one presents the best results. An indication of the etchant is ready is the color: during mixing the color will be brown, while when the etchant is ready the color is yellow.
APPENDIX B

PHASE DIAGRAMS
[Ref. 53]
[Ref. 53]
[Ref. 52]
APPENDIX C

WELDING PRACTICES
SHIELDING IN GTAW

The shielding of Monel60/Type 304L is critical. Depending on the heat input level, poor shielding may be an important issue. At low heat input levels, shielding is not a problem at all and 100 % argon can be used. However, when the heat input is increased, the low heat conduction of the base metal, plus the high viscosity of the weld metal make the weld pool wider. In general, the protection of a given nozzle size is more effective in the central area of the protected region underneath of the nozzle. Thus, if the weld pool size increases, then the shielding is less effective. Increasing the flow rate may help, but this solution is limited because after certain flow rate the gas flows in the turbulent mode. Changing the nozzle size may help also, but the problem is that when increasing heat input the weld pool not only is wider, but also longer. It tends to form a teardrop shape. Again, this is due to the poor heat extraction. In the practice the material behind the torch that just has been melted is still very hot and able to be oxidized. Using a copper chiller underneath of the joint is very effective in reducing the weld pool size. In the same sense, when welding larger pieces the weld pool tends to be smaller compare to the welding of smaller pieces (when all other variables are the same).

The main problem with the shielding of Monel 60/Type 304L is titanium, which is present in the filler metal. Ti can react with oxygen and
nitrogen that may be present in the shielding atmosphere. The chances of having those elements in the shielding atmosphere increases when the gas flowing is more turbulent. This explain why increasing the flow rate for a given nozzle size has limited effect on the shielding quality. This reaction occurs at very high temperatures. Some experimental evidences were found during welding. At low heat input, the arc produces the typical radiation, which is observed as an orange or red color light. However, at high heat input, this light will turn green and the fume generation rate will also increase. To the author, this may be an indication that other chemical reactions, including titanium oxidation, take place at high heat input levels.

The product of these chemical reactions among N, O and Ti is what it was referred as slag. The formation of this slag starts at the tip of the filler metal. Underneath of the nozzle the filler metal is very hot due to the high temperature of the plasma; thus, it turns red and titanium can react. The shielding gas flows forming a bell shape, in such a way that the effective shielding radius will be smaller at the nozzle edge, increasing gradually until it reaches the maximum value at the surface of the work piece. In the proximity of the edge and out of the bell the shielding is poor. This make the filler metal angle an important variable: at low angle the tip of the filler metal will be more protected (it is in a larger effective shielding radius). Therefore, low angle are preferred; however, if the angle is too low, then for a given feed rate the filler metal will start touching
the weld pool edge (fusion boundary) and for instance the filler metal will be pushed out of the weld pool stopping the feeding.

Other important variable is the distance between the copper tip of the feeder. The closer the copper tip, the better the chilling effect, so the titanium reactions are reduced. Thus, a short distance is preferred. However, if the copper tip is too close to the plasma, then it will melt.

Finally, little details such as wind in the welding area may have an importance role in the shielding quality. The wind can blow the plasma and cause more turbulence. Be aware of this, and protect the welding area using shielding walls.

In summary, the best welding practice is to keep heat input as low as possible in order to avoid any shielding problem. In the case that an intermediate or high heat input is necessary, use hydrogen-argon gas mixture in combination with a large nozzle.

**Welding Using Other Welding Process**

Other welding processes may be more effective than GTAW. The change in the weld penetration may be important. SMAW has a higher hot cracking threshold value for dilution than that for GTAW. Therefore, it is more flexible than GTAW from the cracking point of view. More feed rate can be
reach, so for a given groove-section single pass can be used without the risk of having cracking.

GMAW has also a better performance than GTAW. However, argon-hydrogen mixture gas must to be used for all range of heat input. Globular transfer seemed to be more stable that spray for 95% argon – 5% hydrogen shielding gas. Penetration and deposition rate were higher than using GTAW. The tilting angle has an important relationship with penetration. Too low angles may cause bad protection and cracking. An angle between 30° - 45° is preferred. For ¼ in thickness plate better result were obtained using the following welding parameters:

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