Development of a Chromium-Free Consumable for Austenitic Stainless Steels—Part 1: Monel (Alloy 400) Filler Metal

Y.H. Kim,* G.S. Frankel,‡,* J.C. Lippold,** and G. Guaytima**

ABSTRACT

During fusion welding of stainless steels and other high-Cr alloys, evaporation and oxidation of Cr from the molten weld pool result in the generation of carcinogenic hexavalent chromium (Cr[VI]) in the welding fume. Stringent new exposure limits from the Occupational Safety and Health Administration (OSHA) might limit the environment in which the welding of stainless steel will be possible in the future. Therefore, a Cr-free filler metal is needed to reduce the release of Cr(VI) during the welding of stainless steel. From the galvanic series, the corrosion potential of the Ni-Cu alloy K400 (UNS N04400) is located in the same potential range as Type 304 (UNS S30400) and Type 316 (UNS S31600) stainless steels. In this study, the applicability of the Monel-type filler metals for the welding of austenitic stainless steel is examined. Type 304L (UNS S30403) stainless steel plate was successfully welded with Monel filler wire, resulting in high-quality welds with no cracks. The welds survived long-term exposure to mildly aggressive environments like 0.1 M sodium chloride (NaCl) with no evidence of corrosion. However, Cu-rich regions in the weld were the weak spots for corrosion susceptibility.

KEY WORDS: galvanic corrosion, Ni-Cu alloys, nickel, Monel, open-circuit potential, stainless steel, welding
localized corrosion, dealloying effects during long-term exposure, solution flow effects, and environmental cracking.

If stainless steel is to be welded with a filler metal that is different in composition from the base metal, then the corrosion of the welded structure will be controlled by the phenomena of galvanic corrosion and localized corrosion. Localized corrosion in the form of pits and crevices will initiate above a characteristic breakdown potential in a given environment, and one design criterion for preventing localized corrosion is to require that the corrosion potential stay lower than the breakdown potential. However, localized corrosion can propagate at potentials lower than the breakdown potential, but not below a characteristic repassivation potential. Therefore, a more conservative design criterion is that the corrosion potential must stay below the repassivation potential.

One key aspect in galvanic coupling is the area ratio of the two metals, which determines the galvanic potential. If one area is significantly larger than the other, then the galvanic potential of the couple is usually equal to the uncoupled corrosion potential of the larger metal. For a welded stainless steel structure, the area of the weld metal is typically much smaller than the area of the substrate being welded, which means that the potential of the weld metal will be equal to the corrosion potential of the stainless steel in the particular environment. If the weld metal is less noble than the stainless steel, the galvanic coupling will result in an increase in the potential of the weld. This can result in aggressive attack of the weld if the stainless steel corrosion potential is above the breakdown potential of the weld, or if the less noble weld metal does not passivate and dissolves actively. However, if the weld metal is noble relative to the stainless steel, then the galvanic coupling will result in cathodic protection of the weld metal by the stainless steel. It is possible to use the fundamental principles outlined above to develop design criteria for a new weld metal for stainless steel:

—The breakdown and repassivation potentials of the weld metal should be higher than the corrosion potential of the stainless steel base metal to prevent localized attack of the weld metal.

—The corrosion potential of the weld metal should be slightly higher than that of the stainless steel base metal so that the weld metal is cathodically protected.

Guidance on galvanic interactions can be obtained from the galvanic series. The open-circuit potential (OCP) of Monel® Alloy 400 (UNS N04400) is in the range similar to those of the austenitic stainless steels in seawater, distilled water, potable water, hydrochloric acid (HCl), and sulfuric acid (H₂SO₄). Alloy 400, commonly known as Monel, contains 31% Cu (typical value), and maximum concentrations of 2.5% Fe, 2% Mn, 0.5% Si, 0.3% C, and 0.024% S. Monel has good corrosion, erosion, and cavitation resistance in seawater and is widely used in seawater under conditions of high flow velocity such as propellers, shafts, condenser tubes, and heat exchangers. Also, Ni-Cu alloys do not generate deep pits during long-term exposure in chloride environments, but instead form shallow attack. Therefore, Monel was chosen as the starting point for this study.

In this report, the behavior of stainless steel welded with Monel and the effect of Cu on the passivity of Ni-Cu alloys are presented. A subsequent paper will present work leading to an optimized consumable composition.

**EXPERIMENTAL PROCEDURES**

Welds were made using a 6.35-mm-thick Type 304L (UNS S30403) base metal plate and 1.14-mm-diameter commercial Monel (AWS ERCuNi [UNS C71581]) or standard Type 308L (AWS ER308L [UNS S30883]) stainless steel filler wire. The compositions of these materials are given in Table 1. Also shown in Table 1 are the calculated values of weld metal composition for 15% and 40% dilution for the case of Type 304L base metal and Monel filler metal. This represents a typical range for most arc welding processes. Note that dilution is defined as dilution of the filler metal by the base metal. Gas tungsten arc welding (GTAW) was the welding process used in this study because it is easier to automate and control than SMAW, which is the most common process for manual welding of stainless steel. Details of the GTAW process are given in Table 2.

Corrosion testing was performed on welded samples and on buttons prepared by electric-arc melting of pure elemental mixtures. Five Ni-Cu alloys were manufactured, having a Cu composition in the range of 25 wt% to 45 wt%. The buttons were then cold-rolled with a thickness reduction ratio of 75%. Finally, they were solutionized at 1,100°C for 1 h to result in homogenized microstructures.

The specimens for electrochemical testing were mounted in epoxy, polished to 600-grit paper, degreased in acetone (CH₃COCH₃), and then rinsed with distilled water. The edge between the specimen and epoxy mold was sealed with lacquer to reduce the likelihood of crevice corrosion.

For electrochemical tests, a computer-controlled potentiostat system was used with a saturated calomel electrode (SCE) reference electrode and a carbon rod counter electrode. Air or Ar was bubbled through the solutions for aerated or deaerated conditions, respectively. Artificial seawater was produced according
to ASTM D1141-98. The pH was fixed at 8.3. For corrosion testing, samples were extracted from the welds so that the heat-affected zone (HAZ), the weld interface, and base metal were exposed. Cyclic potentiodynamic polarization was performed at a scan rate of 10 mV/min in air-bubbled 0.1 M sodium chloride (NaCl) and artificial seawater at room temperature.

Long-time exposure (LTE) testing was performed on the Ni-Cu alloys and welds in aerated artificial seawater and 0.1 M NaCl solution. The samples were polished to 600-grit paper and then spot-welded with Pt wires to allow them to be hung in the solutions and for making periodic electrochemical measurements. After degreasing in acetone, the bare Pt wire was coated with lacquer. For samples exposed in artificial seawater, the Pt/sample joint was not coated with lacquer to prevent any possibility of crevice corrosion between the lacquer layer and specimen. However, for samples exposed in 0.1 M NaCl solution, this joint was masked with black wax to prevent galvanic corrosion between the Pt wire and the sample. During the exposure, the corrosion potential and polarization resistance of each sample were periodically measured. After the exposure, the surfaces of the specimens were optically inspected and the corroded sites were analyzed with scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). All tests were carried out at room temperature.

The welds were analyzed using optical microscopy on polished sections that were electrolytically etched in 5 vol% H₂SO₄ and then in 50 vol% nitric acid (HNO₃). Weld ductility was tested by bending over a 3/4-in. (19.05-mm) mandrel, resulting in 15% tensile strain in the outer fibers. Vickers microhardness scans were performed across the welds.

### RESULTS AND DISCUSSION

#### Weldability of Monel Electrode

Welds were made with Type 304L plate and Monel filler wire using a range of conditions. Solidification cracks were observed in high-dilution welds, but not if the weld dilution was kept below about 30%. The use of 100% Ar shielding gas resulted in surface slagging and welds of unsatisfactory quality (Figure 1[a]). This slagging was worse at high heat inputs and seemed to be related to the presence of Ti in the Monel weld wire. The effect was eliminated by the use of Ar-5%H₂ shielding gas and control of weld heat input (Figure 1[b]). The weld metal was found to be fully austenitic with perhaps some second-phase formation in the interdendritic regions.

EDS line profiles from the base metal into the weld nugget of a particular Monel/304L weld indicated that there were about 10% Fe and a few percent of Cr in the weld nugget as a result of dilution (Figure 2). Also evident was a transition zone in which the composition gradually changed from the base metal to the weld metal.

A Monel/304L weld was tested by bending over a 1.9-cm mandrel. The sample passed this test with no evidence of cracking. Micro-hardness profiling was performed along the weld cross section. The hardness of the Monel/304L weld metal was slightly below that of a weld made with Type 308L filler metal (Figure 3). Transverse tensile tests were performed on Monel/304L welds at nominally 25% dilution. All failures occurred in the weld metal. The average mechanical properties were as follows: 80 ksi tensile strength, 44 ksi yield strength, and 40% elongation. In summary, the Monel weld showed good ductility and strength as long as solidification cracking was prevented by controlling the heat input.

### TABLE 1

Composition in wt% of Monel Filler Metal and Type 304L Base Metal Composition Range for Type 308L SS Filler Metal. Calculated Weld Metal Composition for Type 304L/Monel Welds at Two Different Dilutions are Also Given

<table>
<thead>
<tr>
<th>Element</th>
<th>Monel Wire</th>
<th>Type 304L SS</th>
<th>Type 308L SS</th>
<th>15% Dilution Calculated</th>
<th>40% Dilution Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>63.99</td>
<td>8.08</td>
<td>9 to 11</td>
<td>55.60</td>
<td>41.63</td>
</tr>
<tr>
<td>Cu</td>
<td>28.81</td>
<td>—</td>
<td>0.75 max.</td>
<td>24.49</td>
<td>17.29</td>
</tr>
<tr>
<td>Fe</td>
<td>0.76</td>
<td>72.10</td>
<td>65</td>
<td>11.46</td>
<td>29.30</td>
</tr>
<tr>
<td>Cr</td>
<td>—</td>
<td>18.09</td>
<td>19.5 to 22.0</td>
<td>2.71</td>
<td>7.24</td>
</tr>
<tr>
<td>Mn</td>
<td>3.49</td>
<td>1.24</td>
<td>1.0 to 2.5</td>
<td>3.15</td>
<td>2.59</td>
</tr>
<tr>
<td>Ti</td>
<td>1.99</td>
<td>—</td>
<td>1.69</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.90</td>
<td>0.37</td>
<td>0.3 to 0.65</td>
<td>0.82</td>
<td>0.69</td>
</tr>
<tr>
<td>N</td>
<td>—</td>
<td>0.06</td>
<td>0.06</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>C</td>
<td>0.05</td>
<td>0.03</td>
<td>.08 max.</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>Others</td>
<td>0.01</td>
<td>0.03</td>
<td>—</td>
<td>0.01</td>
<td>0.02</td>
</tr>
</tbody>
</table>

### TABLE 2

Details of GTAW Procedure

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>150 A</td>
</tr>
<tr>
<td>Voltage</td>
<td>12 V</td>
</tr>
<tr>
<td>Travel speed</td>
<td>5 in/min</td>
</tr>
<tr>
<td>Heat input</td>
<td>21.6 kJ/in (0.85 kJ/mm)</td>
</tr>
<tr>
<td>Wire feed speed</td>
<td>45 in/min</td>
</tr>
<tr>
<td>Shielding gas</td>
<td>Argon + 5% H₂</td>
</tr>
<tr>
<td>Shielding gas flow rate</td>
<td>30 ft³/min</td>
</tr>
<tr>
<td>Joint design</td>
<td>V-groove 90°, gap: 0.118 in</td>
</tr>
</tbody>
</table>
Most of the welds exhibited three zones near the welding interface: partial liquation zone in the base metal, epitaxial growth zone in weld metal, and columnar structure in the weld metal (Figure 4). The grain boundaries in the epitaxial growth zone were well matched with those in the base metal. The epitaxial growth zone was a little wider in high-dilution samples than in low-dilution samples. This might cause large micro-segregation in high-dilution samples.

Around the welding interface, the range of compositional dilution is very wide, as shown in Figure 2. Even for a low-dilution weld, the interface is composed of the full range of dilution. To connect the
composition measurements to the microstructure, EDS spot analysis was performed near the weld interface (Figure 5). The analysis at Point A in the stainless steel base metal showed no change in composition. However, at Point B in the HAZ near the weld, there was a slight increase in Cu and Ni and a slight decrease in Cr. It is not expected that the HAZ will have a significant difference in the corrosion resistance than the base metal. The epitaxial growth region, Point C, was a highly diluted zone with Fe and Cr. The initial columnar region, Point D, showed a medium dilution level and the inner columnar region, Point E, a low-dilution level.

**Long-Time Exposure Tests**

LTE tests were carried out in artificial seawater for up to 50 days. The corrosion potentials were measured for 500 h. All samples exhibited ennoblement in the corrosion potential with time (Figure 6). The five binary Ni-Cu alloys containing 25% to 45% Cu behaved similarly and exhibited corrosion potentials within about 0.05 V of each other. In the initial stage, the corrosion potential of Ni-45Cu was the highest of the five, but Ni-25Cu exhibited the highest potential in the later stages of exposure. The ennoblement of Type 304L stainless steel was the highest of all the specimens. A polished Monel/304L weld sample also exhibited ennoblement in the early stages of immersion but it became active after 2 days of immersion.

After immersion for 50 days, no corrosion was found on the binary Ni-Cu alloys samples containing 35% Cu or less, but pits were observed on the 40% and 45% Cu samples. Several pits were observed on the Monel sample, and they exhibited blue corrosion products that were likely Cu-rich. However, since the Ni-30Cu binary alloy, which has the same Cu content as Monel, did not exhibit any corrosion, it is possible that the attack on Monel was caused by heterogeneities in the commercial rod product. Some contamination was generated on the surface of the stainless steel sample during LTE testing, but it was not corrosion product because it was easily removed by brushing. The polished weld also exhibited different forms of corrosion (Figure 7). Pits were found in the weld metal near the interface. Some of the pits were quite large, with diameters more than 100 µm, but they were not deep. Intergranular corrosion was found inside these pits (Figure 7[e]) and at some locations on the interface of the weld metal and base metal (Figure 7[f]). Some regions of heavy corrosion product were also found along the interface (Figure 7[f]).

In 0.1 M NaCl solution, the corrosion potentials of the various samples were measured for 172 h. The corrosion potential of the Ni-25 Cu and Ni-30Cu binary alloys increased with time and reached a plateau of about 50 mV_{SCE} (Figure 8[a]). The corrosion potentials for the other samples were lower, in the range of ~50 mV_{SCE} to ~100 mV_{SCE}. After 172 h, the weld potential was the lowest. These results were similar to the data in artificial seawater except that the Type 304L sample did not exhibit the highest corrosion potential in 0.1 M NaCl as it did in seawater. For most of the exposure period, the corrosion potential of the polished weld was between that of the Ni-30Cu alloy and Type 304L stainless steel. Polarization resistance ($R_p$) measurements found that the $R_p$ of the Ni-Cu alloys initially increased with time and then decreased (Figure 8[b]). After 7 days, the $R_p$ of stainless steel and pure Ni were the highest, while that of Ni-45Cu alloy was the lowest. The $R_p$ of the polished weld was between those of Type 304L stainless steel and Ni-30Cu alloy.

After 14 days of immersion in 0.1 M NaCl, potentiodynamic polarization tests were performed on three Ni-Cu alloys, pure Ni, Type 304L stainless steel, and a polished Monel/304L weld sample. As shown in Figure 9, all of the Ni-Cu alloys exhibited a higher
OCP than Type 304L stainless steel. One of the important results is that the weld still maintained a passive state after the 14-day LTE test. The OCP and breakdown potentials are summarized in Figure 10. For some of the Ni-Cu alloys, a sharp breakdown potential was not observed and the breakdown potential was taken to be the potential at the current density of 100 µA/cm². For all samples, the OCP was lower than the breakdown potential, indicating the stability of passivity. Ni-30Cu had the widest gap and therefore the most stable passivity among the Ni-Cu alloys. The weld also exhibited a stable passivity range of 0.1 V. The breakdown potential of the weld was almost the same as that of Ni-45Cu.

Attack in the form of localized breakdown was observed after polarization to high potentials (up to a current density of 100 µA/cm²) above the breakdown potential. On these samples, most of the attack occurred in the weld metal (Figure 11). The attack was interdendritic in nature and looked similar to the columnar and dendrite microstructure found after etching the sample (Figure 4). The Ni-Cu binary system forms an ideal solid solution, and Cu has a higher melting point, so Cu is enriched interdendritically in the liquid phase during solidification and is then finally segregated along the columnar and dendrite boundaries.25-26 Also, as the heat input rate in welding process increases, the level of the segregation at the boundary will increase because of the slow cooling rate.

Therefore, it is likely that the Cu enrichment at the boundary will be higher for high-dilution welds.

**Effect of Cu**

The long-term exposure tests on the Type 304L/Monel welds indicated that they have good corrosion resistance to dilute chloride solutions open to air. No attack was observed after exposure to 0.1 M NaCl. However, the purposeful attack of the weld by polarization in chloride solution to high potentials indicated that the most susceptible region of the weld is the Cu-rich interdendritic microstructure. Therefore, it is of interest to understand better the effects of Cu on the corrosion properties.

Potentiodynamic polarization measurements were made on polished samples in artificial seawater. The corrosion potential in aerated artificial seawater was found to increase with increasing Cu content of the binary alloys (Figure 12[a]). Monel Alloy 400 had a similar corrosion potential as Ni-30Cu. The corrosion potentials of the Monel/304L weld and Type 304L were slightly higher than the binary alloys in this solution. In deaerated artificial seawater, there was little effect of Cu on the corrosion potential for the binary alloys. However, Monel and the weld exhibited much lower values.

The breakdown potentials measured in both aerated and deaerated artificial seawater decreased with increasing Cu content for the binary alloys (Figure 12[b]). Monel Alloy 400 exhibited a lower breakdown potential than Ni-30Cu and the Monel/304L weld exhibited similar breakdown potentials as Ni-45Cu. The breakdown potential of Type 304L stainless steel was the highest.

The significant result from this analysis is that the corrosion potential of Type 304L stainless steel is lower than the breakdown potential of the weld in both 0.1 M NaCl and artificial seawater. From these
data, it can be predicted that the weld will not corrode from the mechanism of galvanic corrosion. Furthermore, as the Cu concentration in Ni-Cu alloys with composition near Monel increases, the resistance to localized corrosion decreases. This finding is in line with the observation of the intergranular attack at the welds during long-time exposure to artificial seawater, since the interdendritic region is likely enriched in Cu.

**FIGURE 7.** Images of the Monel/304L weld following 50 days in artificial seawater: (a) low-magnification optical image (each division in scale is 1 mm); (b) SEM image of the box marked 1 in (a). Note the large shallow pit in the weld metal (box 2) and the heavy corrosion product at the interface (box 4). (c) SEM image of the box marked 2 in (b). (d) SEM image of the box marked 4 in (b). (e) SEM image of the box marked 3 in (c). Note the intergranular corrosion in a region of the pit. (f) SEM image of the box marked 5 in (d). Note the intergranular corrosion and the heavy corrosion product.
To investigate the effect of the segregation on the corrosion properties in Ni-Cu alloys, two welds having different levels of dilution were annealed at 1,150°C for 1 h to homogenize the microstructure and then rapidly cooled. Both showed much higher breakdown potentials than as-welded samples with the same dilution (Figure 13). After annealing, the breakdown potentials of the two welds were increased by 50 mV to 80 mV. The fact that homogenization improved the breakdown behavior of the Monel/304L welds further supports the notion that micro-segregation of Cu dominates the corrosion resistance of Ni-Cu welds.

The corrosion potential of the Monel weld was lower than its breakdown potential in chloride solution, even after long-term immersion. However, some ennoblement of the corrosion potential of this weld occurred and its breakdown potential was considerably lower than that of stainless steel. For applications involving long-time exposure, this weld should have improved breakdown behavior. To develop optimized Cr-free consumables for the welding of stainless steel, it is necessary to improve further the localized corrosion properties of the weld metal. The detrimental effects of Cu on the properties of the weld suggest that...
lower Cu contents would be beneficial. However, the Cu is beneficial for increasing the corrosion potential of the weld to minimize galvanic coupling with the stainless steel base metal. A subsequent report will show that 5% to 10% Cu is sufficient to ennoble the corrosion potential of Ni, and results in minimal degradation of the localized corrosion properties. Noble element alloying is also beneficial.

CONCLUSIONS

- Good-quality GTAW welds were achieved using Monel (ERNiCu-7) filler metal and Type 304L base metal by controlling shielding gas and weld heat input.
- The strength and ductility of Monel/304L GTA welds were comparable to those of Type 308L/304L welds. Weld solidification cracking was observed at high heat inputs and dilution levels, but could be eliminated by restricting dilution below about 30%.
- Corrosion potentials generally increased during immersion in aerated chloride solutions. Polished welds exhibited this ennoblement in the early stage of immersion, but then the corrosion potential decreased, indicating some activation.
- No corrosion was observed on the weld sample or any of the alloys tested after long-term exposure to 0.1 M NaCl. However, some localized corrosion of the weld was observed after long-term exposure to artificial seawater.
- Sharp line attack was observed at the base-metal/weld-metal interface as a result of compositional dilution and accompanied microstructural heterogeneities. Large and shallow pits were found in the weld metal.
At the columnar structures in the weld metal, micro-segregation of Cu occurred. Interdendritic regions are attacked during potentiodynamic polarization to high potentials, indicating an increased susceptibility associated with high Cu content.

As the Cu content in Ni-Cu alloys increases, the corrosion potential increases but the breakdown potential decreases. The corrosion potential of the weld is lower than the breakdown potential.

Ni-Cu alloys are possible candidates for Cr-free consumables for welding Type 304L stainless steel.

ACKNOWLEDGMENTS

This work was supported by SERDP (Strategic Environmental Research and Development Program) through project PP-1346 and under the direction of C. Pellerin.

REFERENCES


FIGURE 13. Effect of the homogenization treatment on the breakdown behavior of welds with different amounts of dilution: (a) 12% dilution and (b) 24% dilution.