Development of Welding Wire for High-Purity Austenitic Stainless Steels

Welds produced with the developed filler metal possess equivalent corrosion and mechanical properties to high-purity stainless steel, in addition to good weldability

BY H. Y. HAN AND Z. SUN

ABSTRACT. High-purity austenitic stainless steels have been developed for nuclear fuel reprocessing applications. To produce nuclear fuel reprocessing facilities, i.e., process vessels and pipeworks, welded joints are necessary, thus stimulating a need for filler metals. This paper discusses the development of a high-purity welding wire. As filler metal, such welding wire should provide not only good weldability, but should also be able to produce weldments having mechanical and corrosion properties equivalent to those of the base metal. According to these criteria, potential filler metals were evaluated. Based on this investigation, a high-purity austenitic stainless steel welding wire was developed that can be used to produce satisfactory weldments in terms of weldability, mechanical properties and, most importantly, corrosion properties.

Introduction

Since its discovery and development in 1910, stainless steel has played an important role in industrial development — particularly in the last few decades (Refs. 1–5). A variety of stainless steel grades have been developed to meet various design and operating requirements (Refs. 5–12). The special features of stainless steel are good corrosion resistance and mechanical properties. As new process environments become more corrosive, increased corrosion resistance of the materials is required. With new classes of stainless steel continuously being developed to improve corrosion resistance of specific equipment in severe corrosive environments, development of welding filler metals for stainless steels remains an important issue.

Since nuclear fuel reprocessing facilities are generally operated with highly concentrated nitric acid solutions at elevated temperatures, stainless steels are the predominant materials used to construct these facilities. When operating conditions become severe, an upgrade of stainless steel is desirable to withstand the medium. For example, in the 1960s, Type 304L and 316L stainless steels were satisfactorily used for nuclear fuel reprocessing. Subsequently, Type 310LNb stainless steel was used in the ’70s and early ’80s. In all stages, welding filler metals (wires and electrodes) have been developed to meet operating requirements (Refs. 12, 13). Recently, in modern nuclear fuel processing facilities, stainless steels with improved corrosion resistance have become necessary. In such facilities, the operating mediums (which may be in the form of mixed acids) are complex. For example, they may contain not only concentrated nitric acid but also acids such as sulphuric acid with some additional corrosive ions. For this reason, a high-purity stainless steel (000Cr25Ni20) with excellent corrosion resistance has been developed (Ref. 14). The compositions of the base material are given in Table 1. Note that carbon, phosphorus and sulphur contents of the steels are lower than 0.01%, which is purer than the normal L-class stainless steels. In addition, Si content was also controlled to be less than 0.1% since Si and P were found to increase the intergranular corrosion in nonsensitized stainless steel (Refs. 14–18). This steel has particularly excellent resistance to intergranular corrosion in high-oxidizing environments. For practical industry use, new steel needs a suitable welding filler material because fabrication of most equipment requires some type of joint. In such cases, weldability of the material and properties of the joint become critical factors in controlling the range of application. As such, development of welding filler materials is imperative. The object of this research was to develop a welding wire that produced crack-free welds and matched the mechanical and corrosion properties of high-purity stainless steels.

Methodology

Two principles are normally applied to develop new corrosion-resistant stainless steels: 1) to use additional alloying elements to obtain desirable corrosion properties, and 2) to maintain a high level of purity in the steel by reducing impurity contents (i.e., carbon, sulphur and phosphorus) to achieve the enhanced corrosion properties. In this case, the new high-purity austenitic stainless steels were developed based mainly on the second principle. When welding high-purity austenitic stainless steels, a fully austenitic weld metal is desirable to match the base metal’s enhanced corrosion properties. Although a small amount of ferrite in the weld metal is of benefit in avoiding solidification cracking when welding austenitic stainless steels (Refs. 19–21), in this case, it is not recom-

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KEY WORDS

High-Purity Stainless Steel
Corrosion Resistance
Welding Wire
Solidification Cracking
Mechanical Properties
GTAW
Filler Metal
mended for high-purity austenitic stainless steel. Although ferrite may not be detrimental to corrosion resistance in nitric acid, it may lead to selective corrosion in mediums such as sulphuric acid. In addition, the possible reduction of ductility and toughness of duplex weld metal is also a concern. Therefore, the object of this research was to develop a welding wire capable of producing fully austenitic weld metal. When developing filler materials for high-purity stainless steels, two major problems should be solved: solidification cracking and corrosion resistance. The methodologies used to solve these problems were based on adjusting alloying elements and/or reducing impurity levels.

**Corrosion Properties**

To increase corrosion resistance, a low level of impurity elements such as C, Si, S and P is desirable (Ref. 14). Therefore, the methodology was to develop a welding wire with low levels of impurities, i.e., the P and S content was controlled at least as low as the base metal. Carbon content was also controlled to a level lower than 0.01%.

**Solidification Cracking**

The tendency to solidification cracking in stainless steels, particularly Type 310L, has long been recognized (Refs. 19–43). Austenitic stainless steels are usually susceptible to solidification cracking, due to their inherent characteristics. First, large deformation and tensile residual stresses can form in austenitic stainless steel weld metals during the local welding heat effect, due to the small thermal conductivity and large thermal expansion coefficient, as compared to other steels. Second, microstructure in the weld metal tends to be dendritic, with strong directionality that facilitates the segregation of impurities and formation of low-melting liquid films. Third, the complex composition of austenitic stainless steels facilitates the formation of low-melting phases from both impurities and some alloying elements, due to the limitation of solubility. In general, two measures can be used to reduce the hot-cracking sensitivity of austenitic stainless steels:

1) Reduce the level of impurities such as C, S and P. (This method can be widely used today due to advanced steelmaking technology.)

2) Add some useful alloy elements to reduce hot crack sensitivity, such as Mn, Mo, N, etc. The beneficial effect of Mn is to suppress the harmful effect of P and/or S by forming the high-melting compound MnS. In this way, it can prevent the formation of low-melting NiS-Ni eutectic and become the nucleus of solidification, thus speeding up weld solidification and reducing the brittleness temperature range (BTR) (Refs. 25, 33, 45). Molybdenum has a large solubility in Fe, Cr and Ni, which forms a solid solution with a melting temperature near that of the weld metal. Therefore, it can reduce BTR and become more crack resistant (Ref. 44). The methodology adopted in this research was to reduce the level of impurities while concurrently adding some useful alloy elements (such as Mn and Mo) in the filler metal, to avoid the occurrence of cracking in the weld metal.

**Experimental Procedures**

**Materials**

**Base Material**

High-purity austenitic stainless steels were melted via the vacuum induction furnace. The ingot was then forged and hot rolled into 6- and 12-mm-thick plates. The plates were subsequently solution heat-treated at 1050°C (1922°F) for 30 min, followed by water quenching. Sensitization treatment was carried out at 650°C (1202°F) x 1 h, followed by air cooling. The chemical compositions of the steels are given in Table 1.

**Welding Wires**

The filler metals were produced by melting the high-purity raw materials with a low level of C, S, P and Si content in a 25-kg vacuum induction furnace. The ingot was first heated to 1140–1170°C (2084–2138°F) for 1 h and then forged into blocks. The blocks were rolled into 6.5-mm-diameter wire rods, which were then drawn into 1.6-mm-diameter wires through a few repeated steps (including solution treatment at

### Table 2 — Compositions of the Filler Metals (wt-%)*

<table>
<thead>
<tr>
<th>#</th>
<th>Filler Metal</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>P</th>
<th>S</th>
<th>Mo</th>
<th>N</th>
<th>P</th>
<th>S</th>
<th>Mo</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>000C/25Ni22Mn4Mo2</td>
<td>0.008</td>
<td>0.22</td>
<td>4.47</td>
<td>24.83</td>
<td>22.17</td>
<td>0.067</td>
<td>0.07</td>
<td>2.17</td>
<td>0.05</td>
<td>0.006</td>
<td>0.006</td>
<td>2.18</td>
<td>0.12</td>
</tr>
<tr>
<td>#2</td>
<td>000C/25Ni22MnMo2N</td>
<td>0.003</td>
<td>0.21</td>
<td>1.99</td>
<td>24.87</td>
<td>22.42</td>
<td>0.003</td>
<td>0.003</td>
<td>2.18</td>
<td>0.12</td>
<td>0.006</td>
<td>0.006</td>
<td>2.38</td>
<td>0.12</td>
</tr>
<tr>
<td>#3</td>
<td>000C/25Ni22MnMo2</td>
<td>0.006</td>
<td>0.22</td>
<td>4.4</td>
<td>25.08</td>
<td>22.30</td>
<td>0.008</td>
<td>0.006</td>
<td>2.8</td>
<td>0.05</td>
<td>0.006</td>
<td>0.006</td>
<td>2.8</td>
<td>0.05</td>
</tr>
<tr>
<td>#4</td>
<td>000C/25Ni22MnMo2N</td>
<td>0.006</td>
<td>0.14</td>
<td>3.79</td>
<td>24.66</td>
<td>21.81</td>
<td>0.005</td>
<td>0.006</td>
<td>2.38</td>
<td>0.12</td>
<td>0.006</td>
<td>0.006</td>
<td>2.38</td>
<td>0.12</td>
</tr>
<tr>
<td>#5</td>
<td>000C/25Ni22MnMo2N</td>
<td>0.023</td>
<td>0.14</td>
<td>4.8</td>
<td>24.99</td>
<td>21.99</td>
<td>0.005</td>
<td>0.006</td>
<td>2.5</td>
<td>0.12</td>
<td>0.006</td>
<td>0.006</td>
<td>2.5</td>
<td>0.12</td>
</tr>
</tbody>
</table>

*#5 is a commercially available wire.*
1050°C and pickling). To determine the effect of these elements, filler metals with several compositions were produced. The chemical analyses of the filler metals are given in Table 2. For comparison, in some tests, a commercial filler metal #5 was also used.

**Corrosion Testing**

Two types of welding samples were prepared for corrosion testing: welded joints and weld deposits — Fig. 1. The sizes and orientations of corrosion testing specimens are also shown in Fig. 1. The welding conditions used are given in Table 3. The corrosion specimens were prepared by machining the welded joints and weld deposits to the surface finish required by the testing specification (surface roughness Ra around 0.8 µm). The specimens were completely immersed in the corrosive solutions. Two specimens were used for each test; the corrosion rate is the average of the two specimens. The corrosion testing was arranged in two stages. First, initial selection of welding wires was conducted by corrosion testing in a boiling nitric acid containing hexavalent chromium ions (HNO₃ + Cr⁶⁺). In the second stage, a selected wire with good corrosion resistance from the first stage was tested in simulated corrosion environments, such as evaporators and dissolvers, to determine corrosion matchability between the base metal and the filler metal. The major compositions of such corrosion mediums, which contain nitric acid and certain amounts of other corrosive elements, are given in Tables 7–9. Details about the corrosion testing mediums are given in (Ref. 14).

**Weldability Tests**

Since hot cracking was the major concern, two types of tests were used to examine the cracking sensitivity of the welding wires: 1) plate deposition test and 2) FISCO test (Refs. 46, 47). In the plate deposition test, filler metal was deposited onto a rigid plate by gas tungsten arc welding (GTAW). The size of the deposited weld was 150 x 30 x 10 mm — Fig. 2. Dye penetrant was used to check the surface crack in each pass, with the interpass temperature kept below 150°C (302°F). The deposit sample was then sectioned transversely to the welding direction for micro-examination at a magnification of 100X. When checking cracks in the deposit samples, both solidification cracks in the weld metal and liquation cracks in the reheated weld metal were included.

The FISCO testing sample was a 200 x 100 x 12-mm plate. The two base metal plates were secured in a FISCO fixture and welded using the conditions given in Table 3. Three 40–50-mm-long welds were produced with a 5-mm root opening between each. The space between the weld was 10 mm. The butt joint was removed from the fixture after cooling down to room temperature. The weld surface and weld metal were then microscopically checked to determine crack size. The heat-affected zone (HAZ) crack was also examined at the same time. Figure 3 shows a FISCO testing sample.

**Mechanical Testing**

Mechanical testing, including tensile, bending and Charpy V-notch toughness tests, were performed for the joints. Welding parameters are given in Table 3.

**Results and Discussion**

**Corrosion Properties**

Since corrosion resistance was one of the most critical criteria for determining whether the filler metal developed would match the high-purity stainless steel, the first step in this work was to select suitable wires that possessed at least similar corrosion resistance as the base metal. In this stage, 000Cr25Ni20(A) base metal was used. Table 4 lists the corrosion test results for the wires and base metals in an 8N boiling HNO₃ + 0.3gCr⁶⁺/L medium.

It was noted that the joints and deposit samples made of high-purity filler metals (#1, #2, #3) had corrosion rates similar to the high-purity base metal. Although a slight corrosion trace in the weld metal could be visually observed, no intergranular corrosion was found by microscopic observation. Figures 5 and 6 show the micrographs of samples made with #1 wire for the deposit sample and joint, respectively. The effect of carbon content in the wires on the corrosion resistance was evidenced by the test results, i.e., higher carbon content results in a higher corrosion rate (comparing #5 with #1, #2 and #3 wires in Table 4). It was also found that the deposit samples and joints with 2% Mn (#2) gave similar corrosion resistance to those with 4% Mn (#1 and #3). However, the deposit sample showed micro-cracks with low Mn wire — Fig. 7. No microcracks were found in deposit samples produced with higher Mn wire — Fig. 8. Based on these observations, a higher Mn wire is recommended to prevent cracking. Furthermore, the corrosion test results also show that there is no significant difference in corrosion resistance from wires with different N con-
The purpose of adding some nitrogen to the wire is to increase the stability of the austenite in the weld metal, although no ferrite was found in the welds. It was noted that no obvious traces of corrosion in the HAZ were observed for the samples from joints.

Table 5 lists the corrosion test results in a boiling 8N HNO₃ + 0.6g Cr⁶/L medium having higher Cr⁶ content than that in Table 4. In this test, 00Cr25Ni20(B) steel, in both solution-treated and sensitized states, was included for comparison. It can be seen that the corrosion rate increased in all materials due to the higher Cr⁶ content as compared to Table 4, but the corrosion tendency was the same. It can also be seen that 00Cr25Ni20(B) steel possessed better corrosion resistance than 00Cr25Ni20(A) steel, due to the purity difference. Based on the above results, a welding wire with the composition of #4 in Table 2 was proposed for further corrosion testing. This wire was modified from #1, #2, and #3 in consideration of reducing crack sensitivity and increasing the stability of austenite in the weld metal, i.e., using high Mn content and additional nitrogen in the wire. Note that no ferrite was observed in the weld metals of #1, #2, and #3 wires.

In the second stage, various simulated mediums were used to further evaluate the corrosion resistance of the selected wire. All the deposit samples and joints in this stage were produced with #4 welding wire using the 000Cr25Ni20(B) steel. Results are given in Tables 6–9 in the various corrosion mediums. Since these mediums were selected based on specific applications, they are representative of the future service environments of the steel (Ref. 14).

The results in second-stage corrosion testing indicated that weldments produced with #4 wire showed equivalent corrosion rates to the base metal in either the solution-treated or sensitized states given in Tables 6 and 7. Therefore, the corrosion resistance of the wire is...
Table 6 — Corrosion Rate (g/m².h) in Boiling 13N HNO₃ [106°C (222.8°F)] (5 x 48 h)

<table>
<thead>
<tr>
<th>Base Metal</th>
<th>Solution Treated</th>
<th>Sensitized</th>
<th>Deposit Sample</th>
<th>Joints</th>
</tr>
</thead>
<tbody>
<tr>
<td>000Cr25Ni20(B)</td>
<td>0.0535</td>
<td>0.0540</td>
<td>0.0640</td>
<td>0.0618</td>
</tr>
</tbody>
</table>

Table 7 — Corrosion Rate (g/m².h) in Boiling 8N HNO₃ with Certain Amount of Fe⁺⁺⁺ + Na⁺ + Al⁺⁺⁺ Medium (106°C x 250 h)

<table>
<thead>
<tr>
<th>Base Metal</th>
<th>Solution Treated</th>
<th>Sensitized</th>
<th>Joints</th>
</tr>
</thead>
<tbody>
<tr>
<td>000Cr25Ni20(B)</td>
<td>0.0709</td>
<td>0.0670</td>
<td>0.0988</td>
</tr>
</tbody>
</table>

Table 8 — Corrosion Rate (g/m².h) in 1M HNO₃ with Certain Amount of Hg(NO₃)₂ + Al(NO₃)₂ Medium [100°C (212°F) x 240 h]

<table>
<thead>
<tr>
<th>Base Metal</th>
<th>Solution Treated</th>
<th>Sensitized</th>
<th>Deposits</th>
<th>Joints</th>
</tr>
</thead>
<tbody>
<tr>
<td>000Cr25Ni20(B)</td>
<td>0.00170</td>
<td>0.00240</td>
<td>0.000678</td>
<td>0.00443</td>
</tr>
</tbody>
</table>

Table 9 — Corrosion Rate (g/m².h) in 6.5M HNO₃ with Certain Amount of Hg(NO₃)₂ + Al(NO₃)₂ Medium [106°C (222°F) x 240 h]

<table>
<thead>
<tr>
<th>Base Metal</th>
<th>Solution Treated</th>
<th>Sensitized</th>
<th>Deposits</th>
<th>Joints</th>
</tr>
</thead>
<tbody>
<tr>
<td>000Cr25Ni20(B)</td>
<td>0.0140</td>
<td>0.021</td>
<td>0.0124</td>
<td>0.0155</td>
</tr>
</tbody>
</table>

Table 10 — Comparison of Hot Cracking Susceptibility of Various Austenitic Stainless Steels Using Transvarestraint Test Criteria

<table>
<thead>
<tr>
<th>Material</th>
<th>BTR °C (°F)</th>
<th>Eₘᵟᵣ (%)</th>
<th>CST (x10⁻³°C⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>000Cr25Ni20 [42]</td>
<td>70 (158)</td>
<td>0.36</td>
<td>11.4</td>
</tr>
<tr>
<td>Normal 310 [25]</td>
<td>160 (320)</td>
<td>0.08</td>
<td>0.9</td>
</tr>
<tr>
<td>Normal 321 [25]</td>
<td>70 (158)</td>
<td>0.40</td>
<td>16</td>
</tr>
<tr>
<td>Normal 304 [25]</td>
<td>60 (140)</td>
<td>0.60</td>
<td>22</td>
</tr>
</tbody>
</table>

*Composition of 000Cr25Ni20 steel (wt-%): C-0.003, Si-0.25, Mn-1.22, S-0.004, P-0.007, Cr-24.95, Ni-19.78.

considered to be satisfactory in heavy-oxidizing mediums. Although corrosion rates of deposit and joint samples were higher than the base metal in some mediums (shown in Tables 8 and 9), they were still lower than the required technical specification (<0.05 - 0.1 g/m².h) (Ref. 14). Since a low level of Si in the steel was found to be more corrosion-resistant (Refs. 14, 15, 17, 18), it may also be beneficial to improving the corrosion resistance of the weld, if the wire has less than 0.1% Si. Further investigation is needed to verify this. Nevertheless, the current level of Si in the wire can still meet the requirements. Therefore, it can be concluded that 000Cr25Ni22Mn4Mo2N (#4) wire is a suitable filler metal to the 000Cr25Ni20 high-purity austenitic stainless steel, in terms of corrosion resistance.

Crack Sensitivity Evaluation

Although, in general, austenitic stainless steels are susceptible to solidification cracking, high-purity austenitic stainless steels have better crack resistance when compared to the same grade of steels. Table 10 lists some crack sensitivity evaluation data among several grades of austenitic stainless steels by using the Transvarestraint test (Refs. 25, 42). In the Transvarestraint test, the crack susceptibility was evaluated by determining the solidification BTR, the minimum augmented strain required to cause cracking (Eₘᵟᵣ) within the BTR and the critical strain rate (CST) for a temperature drop, defined as the inclination of the tangent to the ductility curve from the liquidus temperature. The larger the BTR, the more sensitive the material is to hot cracking. In contrast, the larger the values of Eₘᵟᵣ and CST, the less sensitive the material is to hot cracking. Studies indicate that the CST index is the most reliable one among the BTR, Eₘᵟᵣ and CST (Refs. 24, 25, 42).

In this study, crack sensitivity was evaluated based on the corrosion testing results (i.e., the evaluation was made only for those filler metals that could produce weldments with acceptable corrosion resistance). Therefore, welding wires #1, #2 and #3 were evaluated using the two weldability tests discussed above. The plate deposition test was used mainly to examine the hot-cracking sensitivity in weld metals, while the FISCO test was used for both weld metals and HAZs.

The results of the two weldability tests showed that there were no cracks found in #1 and #3 welding wires. However, microscopic observation of deposit samples in the plate deposition test revealed intergranular cracks for #2 welding wire — Fig. 7. Therefore, #4 welding wire, which was developed based on weldability tests results of #1, #2 and #3 wires, was considered to be a good choice for this application, with satisfactory crack resistance. In fact, no cracks were found in welds produced with #4 welding wire.

Mechanical Properties

The mechanical testing samples were prepared by welding 000Cr25Ni20(B) steel with #4 welding wire. Results of the mechanical testing listed in Table 11 show that the weld metal and joints possessed satisfactory mechanical properties (Ref. 14). Therefore, #4 welding wire meets the specification requirements.

Welding Wire

Based on the above investigation, a wire with a composition of 000Cr25Ni22Mn4Mo2N (#4) was suc-
cessfully developed with corrosion resistance, mechanical properties and weldability. Currently, only a wire for GTAW can reach the high-purity criteria. It has been difficult to produce coated electrodes with such high purity. (The procedure for manufacturing such wire was described above.)

Conclusions

A high-purity austenitic stainless steel welding wire (000Cr25Ni22Mn4Mo2N) was developed, which can be used to produce satisfactory weldments with newly developed, 000Cr25Ni20 high-purity austenitic stainless steels in terms of weldability, mechanical properties and, most importantly, corrosion properties. Therefore, potential applications of the new high-purity austenitic stainless steels in the production of nuclear fuel reprocessing facilities (evaporators, dissolvers and waste containers) can be realized by using this filler metal.

Acknowledgments

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Fatigue of Welded Components
by John M. Barsom and Robert S. Vecchio

Fatigue failures in engineering structures occur predominantly at component connections, even in those structures that have been designed, fabricated and inspected according to “Code.”

Given the preponderance of weld-related fatigue failures, it is reasonable to expect that state-of-the-art design codes would incorporate rules or procedures for addressing the fatigue life of welded components. However, several design codes do not incorporate explicit fatigue life curves for welded components.

This bulletin examines the parameters that most affect the fatigue life of welded components and the manner in which various codes address fatigue.

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