Localised corrosion susceptibility of AISI 316L stainless steel welded joints in high temperature alkaline environments

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ABSTRACT: Susceptibility of Type 316L austenitic stainless steel welded joints to localized pitting corrosion in alkaline solutions (sodium hydroxide [NaOH] and potassium hydroxide [KOH]) has been investigated in this paper. The study compared the pitting resistance of welded joints (produced by Shielded Metal Arc Welding [SMAW] and Metal Inert Gas welding [MIG]) in high temperature (125°C) NaOH and KOH solutions with causticity of 50%. All the studies were by immersion method. The weldments (Base Metal [BM], Weld Metal [WM] and Heat Affected Zone [HAZ]) of both SMAW and MIG manifested low corrosion resistance potentials in both environments. The near-high power density of MIG process succeeded in creating a narrow HAZ, however pitting corrosion occurred in the HAZ thus confirming the depletion of Cr. This sensitization-induced Cr depletion leads to grain boundary segregations and concentration modifications at the grain boundaries. Mo and Cr elements dissolution was established and the dissolution mechanism is explained by comparative “weak bond energy” of these elements with the other elements in the matrix. The depth of de-alloying or internal penetration varied from surface roughening, cracks and intergranular attack. Since the stainless steels resistance to corrosion in hot alkali becomes unstable at approximately 93°C, it is very likely that de-alloying commences at lower temperature. This negatively shifted the pitting potential of the welded joints of both weld processes. The high temperature is responsible for Caustic Stress Corrosion Cracking (CSCC) observed.

Key words: 316L Stainless steel, high temperature alkaline, SMAW, MIG, intergranular corrosion, pitting corrosion.

INTRODUCTION

High temperature caustic or strong alkaline (NaOH or KOH solution) environments containing over 50% of alkalis) are present in several industries, from nuclear power generation, pulp and paper industries, textile industries, soap and detergent industries, iron and steel industries, oil refineries to food processing plants. Caustic media refer usually to highly concentrated solutions of sodium hydroxide (caustic soda), potassium hydroxide (caustic potash) and calcium hydroxide (caustic lime). Corrosion by caustic solutions at all concentrations is easily handled at room temperature (and up to approximately 80°C) with a variety of metals and alloys, including carbon steels. It becomes increasingly more corrosive with increasing service temperature and causticity of the solution. The useful safe limit
of carbon steel is approximately 65°C, both with regard to general and localized corrosion (Clarke, 2000). Stainless steels are more resistant to general corrosion compared with carbon steel; however, their resistance becomes unstable at approximately 120°C. As a general rule, the resistance to caustic solutions increases with increasing nickel content in the alloy and the susceptibility to both general and localized corrosion is dependent on several variables, including alloy content, caustic concentration, service temperature and stress level. As with other mechanisms, there is a threshold concentration level where corrosion will not occur; unfortunately, the threshold level for stainless steel (SS) welded joints in high temperature caustic solution environment has not been determined specifically (Crook et al., 2006).

Failures of American Iron and Steel Institute (AISI) type 316L SS in high temperature caustic environments especially the welded joints (weldments) have been reported severally in the pulp and paper industries, textile, soap and detergent as well as food processing industries (Dillon, 1994; Crook et al. 2006).

Stainless steel alloys, the same as other alloys, may suffer two main types of corrosion: uniform corrosion and localized corrosion. Uniform corrosion may happen under reducing state in the active region of potentials and also under oxidizing state in the form of a slow passive dissolution. Localized corrosion such as pitting and crevice corrosion generally occurs under oxidizing conditions. Pitting corrosion is commenced by the presence of chlorides and aggravated by increasing temperatures. Inter-crystalline or intergranular corrosion primarily affects the grain boundaries of a polycrystalline metal. The most important basis for inter-crystalline corrosion is the material itself or the material composition. Major examples of materials prone to this type of corrosion are the highly alloyed austenitic chromium-nickel and ferritic chromium steels. When austenitic steel is exposed for a time in the temperature range of approximately 550°C to 750°C, or when the steel is heated to higher temperature and allowed to cool slowly through that temperature range, the chromium and carbon in the steel matrix combine to form chromium carbide particles with the formula Cr23C6 along the grain boundaries (Clerke et al., 2006).

AISI type 316L austenitic SS is known for its better weldability and superior corrosion resistance quality due mainly to its low carbon content. This enables the making of high quality weldments with improved corrosion resistance in hot (> 100°C) caustic soda or potash bearing media and to sensitization especially in the HAZ. SMAW is the common conventional welding process in Nigeria. This work sets out to determine the corrosion resistance stability of Type 316L weldments (produced with SMAW and MIG) in hot (125°C) NaOH and KOH solutions with 50% causticity.

**MATERIALS AND METHODS**

Commercial grade AISI type 316L material of 7.75 mm thickness was obtained and the chemical composition analysis is presented in Table 1. The material was prepared (cut) into 40 pieces of 50 x 50 x 7.75 mm each. The pieces were paired into abutting single V-groove joints and welded: 10 pairs were welded with shielded metal arc welding process and the other 10 pairs were welded with metal inert gas welding process. Each of the two processes was done with welding electrodes containing 0.03% carbon by mass, compatible with that of base metal. American Welding Society (AWS) B2.1: Standard for Welding Procedure and
Performance Qualification is the reference standard for welding procedure specifications used in this study. All welded specimens were cleaned in 10% HCl-methanol mixture to remove slag particles trapped in the weldments. Each welded specimen had a 5 mm hole bored through it at a suitable point at one of the square corners (to enable tie a marine rope to the specimen). The specimens were then ground and polished to fine diamond grade after which they were pickled and rinsed with de-mineralized water. This was done to remove fully the oxide and chromium-depleted layers in the specimens. Due care was taken to avoid stain or inadvertent corrosion on the surfaces. (Fang and Stahele, 1999). Components that have been correctly ground, pickled and rinsed will normally have better corrosion resistance than surfaces that were ordinarily brushed or machined. (McIlree and Michels, 1977).

**Corrosion Studies**

From each welded process, five specimens each were separately immersed into different solution chambers of caustic soda (50% concentration), and another set of five specimens in caustic potash (50% concentration) in a life process plant (Soap and Detergent Plant). The service temperature of the chambers ranged from 123°C to 127°C (averaged 125°C). Specimens were allowed in the immersed state for 120 days. Care was taken to avoid galvanic contacts between the specimens and also between specimens and chamber material. This was to avoid corrosion induced by galvanic action. The long immersion duration is to allow enough time to grow the pits (if any) for shape studies. At the end of the duration for both media, the specimens were retrieved, etched in 10% ammonium persulphate, cleaned and dried. To study the initiation sites of the pits, the pitted weld metal specimens were first observed visually and later examined in an optical microscope. Metallographical studies with Villela’s reagent was done to analyse the microstructure of sites of pits initiation and growth (ISO 11130:1999, ASTM G31:2004 and ASTM G52:2004).

**RESULTS AND DISCUSSION**

**Microstructures**

The microstructure of Base Metal (BM) before the weld is mainly austenitic with some retained ferrite, the microstructure of HAZ of specimens welded by SMAW process is heterogeneous. This is as a result of the gentle heat gradient induced by the weld process. It is not ferrite-free however, there are still strings of ferrites present. The therodynamic impacts have reduced the quantity of austenite in the matrix. The microstructure (Fig. 1) of HAZ from MIG is close to that of the BM. This is viewed as related to the near-high energy welding density of the MIG process which generated a steep heat slope within the HAZ. The Weld Metal (WM) in the MIG specimens solidified very fast, the microstructure of this WM is that of “quenched” austenite; the delta-ferrite was transformed in a measure to other secondary phases. The fast cooling of the WM, though beneficial in “preserving” the integrity of the microstructure, introduced thermal strain in the WM structure matrix. Cr in this state is expected to remain in solution to combine with oxygen to form passivating oxide when exposed to intense corrosive medium (Kovach and Redmond, 2000). Some researchers (Rodriguez et al., 1999), concluded that retained ferrite has no effect on pitting corrosion susceptibility, but it is equally widely held that retained ferrite phase promotes
the dissolution of carbon and progressive formation of carbide precipitates (Le and Ghali, 1993). This phenomenon increases the available sites for pit initiation/enlargement. Significant amounts of Cr seem to be beneficial for caustic service; it contributes in increasing the overall corrosion resistance of SS due to the higher chromium oxide which potentially may be formed by it.

Table 1: Chemical Composition of AISI 316L Stainless Steel Material and Welding Electrodes

<table>
<thead>
<tr>
<th>Element</th>
<th>AISI 316L Stainless Steel Material (% by weight)</th>
<th>SMAW Weld Filler Material (% by weight)</th>
<th>MIG Weld Filler Material (% by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (C)</td>
<td>0.03</td>
<td>0.031</td>
<td>0.031</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>17.50</td>
<td>18.00</td>
<td>18.20</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>12.50</td>
<td>12.00</td>
<td>11.95</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>1.80</td>
<td>1.90</td>
<td>1.90</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>0.85</td>
<td>1.00</td>
<td>0.95</td>
</tr>
<tr>
<td>Molybdenum (Mo)</td>
<td>2.30</td>
<td>2.05</td>
<td>2.15</td>
</tr>
<tr>
<td>Phosphorus (P)</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Sulphur (S)</td>
<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>64.95</td>
<td>64.969</td>
<td>64.769</td>
</tr>
</tbody>
</table>

Fig. 1: HAZ microstructure of 316L SS welded by MIG

De-alloying of Stainless Steels in Hot Caustic Solutions

It is known that stainless steels undergo alloy loss in high temperature caustic solutions (Kearns and Johnson, 2009). Photomicrographs of specimens (Figs. 2 and 3) retrieved from both NaOH and KOH media revealed preferential dissolution of Mo and Cr, leaving dark Ni in the matrix. Figure 4 shows typical uniform surface alloy depletion in the BM. It must be remarked that this is different from Cr depletion occasioned by carbon combination with chromium to form the complex chromium carbide. This carbide formation commonly occurs in the HAZ due to heat sensitization and the kinetics of elemental diffusion in the matrix “pushes” this mechanism into loss of Cr along the grain boundaries. Preferentially, these grain boundaries become “hot spots” for corrosion initiation, including pitting. The mechanism of Mo and Cr dissolution is explained by comparative “weak bond energy” of these elements with the other elements in the matrix. At high temperatures, Cr$_2$O$_3$ passivating film is not stable (Nelson, 1987). The reason of including Mo is to harden (strengthen) the Cr$_2$O$_3$ film and slow down its breakdown. The bond energy attaching Mo to Cr$_2$O$_3$ is weak, Mo thus easily moves or attaches or is attracted to higher bonding energy sites with other elements or compounds. Another explanation, going by Huijbrechts, (1983) is hinged on the structural attachment of the elements in the matrix. The oxidizing effects of the hydroxides find strong affinity to Mo and Cr in the matrix and they
become the first to react or “combine” with the oxides and leave their host. A number of researches have provided details of the mechanism(s) of dissolution but conflicting experimental results make it difficult to settle on any (Clarke, 2000; Deakin et al., 2004). What is clear is that such dissolution takes place. The depth of de-alloying or internal penetration varied from alloy to alloy. For some alloys, surface roughening, cracks, fissures and intergranular attack have been reported. For some others, internal penetration was de-alloying, intergranular attack and some roughening (Rebak and Chambers, 2001).

Published results (Deakin et al., 2004) show that de-alloying mainly occurred to alloys that had a high proportion of Mo and the depth of attack increased as the media temperature increased. Since the stability of stainless steels resistance to corrosion in hot caustics becomes unstable at approximately 93°C, it is very likely that de-alloying commences at about 90°C.

**Caustic soda solution environment**

**SMAW WM and HAZ:** The specimens retrieved from the caustic soda solution environment indicated noticeable pits, not only in the welded joints but included the BM. Detailed
metallography (Fig. 5) performed showed the corrosion pit “start point” was foremost in the HAZ. There are more pits in the HAZ, then a drop in “quantity” of pits in the WM followed by another drop in the BM. Clearly, the SS and its weldments are not resistant to uniform and localized pitting corrosion in this medium; the strength to resistance is least in the HAZ. This confirms the depletion of Cr in the HAZ zone. Due to weld heat sensitization of the HAZ, combination of Cr and carbon to form Cr$_{17}$C$_6$ mainly at the grain boundaries is encouraged; this leads to Cr depletion. The sensitization-induced Cr depletion leads to grain boundary segregations and concentration modifications at the grain boundaries. This Cr depletion is different from the general alloy loss in hot caustic alkaline media which has already been discussed in this paper. Transformation of delta-ferrite to other secondary phases like the brittle sigma takes place in the WM; the area of austenite / delta-ferrite interface is reduced and this brought about a reduction in the corrosion-prone locations in WM compared to the HAZ.

**MIG WM and HAZ:** In spite of the near-BM microstructure obtained in HAZ from MIG weld process, all the specimens retrieved from the NaOH corrosive medium indicated corrosion pits within the weldments, with the pits dominantly originating and located in the HAZ. The BM suffered uniform corrosion as well, an indication that the causticity and service temperature of this study are well above the threshold limits for corrosion immunity of the SS in this environment. The metallurgy of diffusion of elements in the WM is governed by insufficient time for complete mixing of the elements in the weld pool due to the high energy rate over a short time of the process (Franson and Grubb, 2000). The WM here, as earlier remarked, has a “quenched” austenite microstructure. After cooling, there exists tiny regions that are more highly alloyed than the bulk WM. These regions are harder and in service could be problematic with respect to stress corrosion cracking. In this case, the SS material is exposed to thermal (high temperature solution) stress. This explains the cracks observed in some of the specimens welded via MIG process (Fig. 6).

**Caustic potash solution environment**

**SMAW WM and HAZ:** The specimens retrieved from the caustic potash solution environment showed visible marks of pitting corrosion. The photomicrograph (Fig. 7) of one of the specimens showed wide and deep pits. Uniform corrosion was observed on the weldments as well as the BM. Pits appeared to originate randomly from all parts of the weldment microstructure (higher pit density) and the relatively large size of pits makes it further difficult to determine which part of the weldment the pit initiated from and

![Fig. 6: Caustic stress corrosion cracks (CSCC) near HAZ. Cracks both inter and trans granular.](image1)

![Fig. 7: Corrosion pits in one of the specimens in KOH solution.](image2)
enlarged. As in the case of caustic soda solution medium, clearly, the SS and its weldments are not resistant to uniform and localized pitting corrosion in caustic potash medium. The mechanisms discussed earlier in the caustic soda medium equally apply here. One clear point is the higher degree of pitting noticed here which lends support to the conclusions of Huijbregts, (1983); who found that NaOH showed a critical concentration of 2-3 molar while KOH shows a critical concentration of 1.5 molar. Put another way, KOH is a more corrosion aggressive alkaline medium than NaOH. Because of the higher degree of sensitization (DOS) of the HAZ, it is very likely the pits initially, preferentially, nucleated there.

**MIG WM and HAZ:** The low pitting corrosion resistance manifested by the SS in the NaOH medium also showed in KOH medium. All the specimens retrieved from the KOH medium indicated corrosion pits within the weldments, with the pits dominantly originating and located in the HAZ. The BM suffered uniform corrosion as well, though all WMs from both weld processes suffered pitting, close observations indicated that the WM produced by MIG process comparatively showed better pitting resistance than that of SMAW. The mechanisms discussed for specimens welded by MIG and retrieved from caustic soda solution apply here. Thermal stress induced cracking was also observed in the specimens retrieved from KOH environment (Fig. 8).

**CONCLUSION**

AISI 316L SS and its weldments produced by SMAW and MIG weld processes are strongly susceptible to pitting corrosion in NaOH and KOH solution media of the following specifications: Causticity: Equal or greater than 50%. Service Temperature: Equal or greater than 125°C; with KOH environment showing more aggressive corrosive attacks than NaOH environment. Under mild oxidizing conditions both Ni and Cr are important alloying elements, but Mo is a detrimental alloying element in caustic environments. The significant de-alloying suffered by Mo-bearing alloys modifies the metallurgical balance and negatively shifts the pitting resistance potential especially under mildly oxidizing conditions. MIG, compared with SMAW, produced superior weldments with respect to pitting resistance. Further studies are required to determine the causticity combined with service temperature threshold of NaOH and KOH solutions for SS 316L immunity to corrosion.

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