

Corrosion of Weldments

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WELDMENTS exhibit special microstructural features that need to be recognized and understood in order to predict acceptable corrosion service life of welded structures (Ref 1). This article describes some of the general characteristics associated with the corrosion of weldments. The role of macrocompositional and microcompositional variations, a feature common to weldments, is emphasized in this article to bring out differences that need to be realized in comparing corrosion of weldments to that of wrought materials. A more extensive presentation, with data for specific alloys, is given in Volume 13 of the *ASM Handbook* (Ref 2).

Weldments inherently possess compositional and microstructural heterogeneities, which can be classified by dimensional scale. On the largest scale, a weldment consists of a transition from wrought base metal through a heat-affected zone and into solidified weld metal and includes five microstructurally distinct regions normally identified (Ref 3) as the fusion zone, the unmixed region, the partially melted region, the heat-affected zone, and the base metal. This microstructural transition is illustrated in Fig. 1. The unmixed region is part of the fusion zone, and the partially melted region is part of the heat-affected zone, as described below. Not all five zones are present in any given weldment. For example, autogenous (that is, no filler metal) welds do not have an unmixed zone.

The **fusion zone** is the result of melting which fuses the base metal and filler metal to produce a zone with a composition that is most

often different from that of the base metal. This compositional difference produces a galvanic couple, which can influence the corrosion process in the vicinity of the weld. This dissimilar-metal couple can produce macroscopic galvanic corrosion.

The fusion zone itself offers a microscopic galvanic effect due to microstructural segregation resulting from solidification (Ref 4). The fusion zone also has a thin region adjacent to the fusion line, known as the unmixed (chilled) region, where the base metal is melted and then quickly solidified to produce a composition similar to the base metal (Ref 5). For example, when type 304 stainless steel is welded using a filler metal with high chromium-nickel content, steep concentration gradients of chromium and nickel are found in the fusion zone, whereas the unmixed zone has a composition similar to the base metal (Fig. 2).

Heat-Affected Zone. Every position in the heat-affected zone relative to the fusion line experiences a unique thermal experience during welding, in terms of both maximum temperature and cooling rate. Thus, each position has its own microstructural features and corrosion susceptibility.

The partially melted region is usually one or two grains into the heat-affected zone relative to the fusion line. It is characterized by grain boundary liquation, which may result in liquation cracking. These cracks, which are found in the grain boundaries one or two grains below the

fusion line, have been identified as potential initiation sites for hydrogen-promoted underbead cracking in high-strength steel.

Microstructural Gradients. On a fine scale, microstructural gradients exist within the heat-affected zone due to different time-temperature cycles experienced by each element of material. Gradients on a similar scale exist within solidified multi-pass weld metal due to bead-to-bead variations in thermal experience. Compositional gradients on the scale of a few microns, referred to as microsegregation, exist within individual weld beads due to segregation of major and trace elements during solidification (Ref 4).

Forms of Weld Corrosion

Weldments can experience all the classical forms of corrosion, but they are particularly susceptible to those affected by variations in microstructure and composition. Specifically, galvanic corrosion, pitting, stress corrosion, intergranular corrosion, and hydrogen cracking must be considered when designing welded structures.

Galvanic Couples. Although some alloys can be autogenously welded, filler metals are more commonly used. The use of filler metals with compositions different from the base material may produce an electrochemical potential difference that makes some regions of the weldment more active. For example, Fig. 3 depicts weld metal deposits that have different corrosion behavior from the base metal in three aluminum alloys (Ref 6).

For the majority of aluminum alloys, the weld metal and the heat-affected zone become more noble relative to the base metal, as demonstrated in Fig. 3(a) and (b) for a saltwater environment (Ref 6). Certain aluminum alloys, however, form narrow anodic regions in the heat-affected zone and are prone to localized attack. Alloys 7005 and 7039 are particularly susceptible to this problem (Fig. 3c).

There are a number of other common weld deposit/base metal combinations that are known to form galvanic couples. It is common practice to use austenitic stainless steel welding consumables for field repair of heavy machinery, particularly those fabricated from high-strength low-

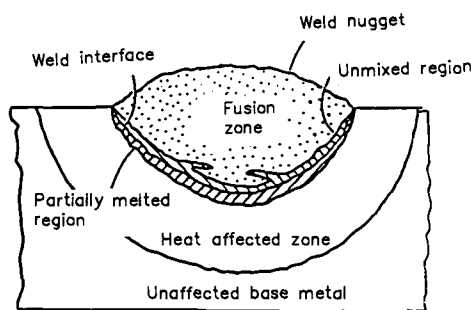


Fig. 1 Schematic showing the regions of a heterogeneous weld. Source: Ref 3

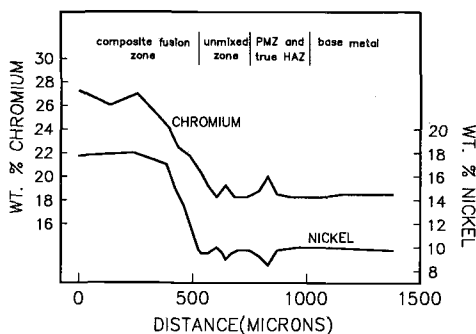


Fig. 2 Concentration profile of chromium and nickel across the weld fusion boundary region of type 304 stainless steel. Source: Ref 5

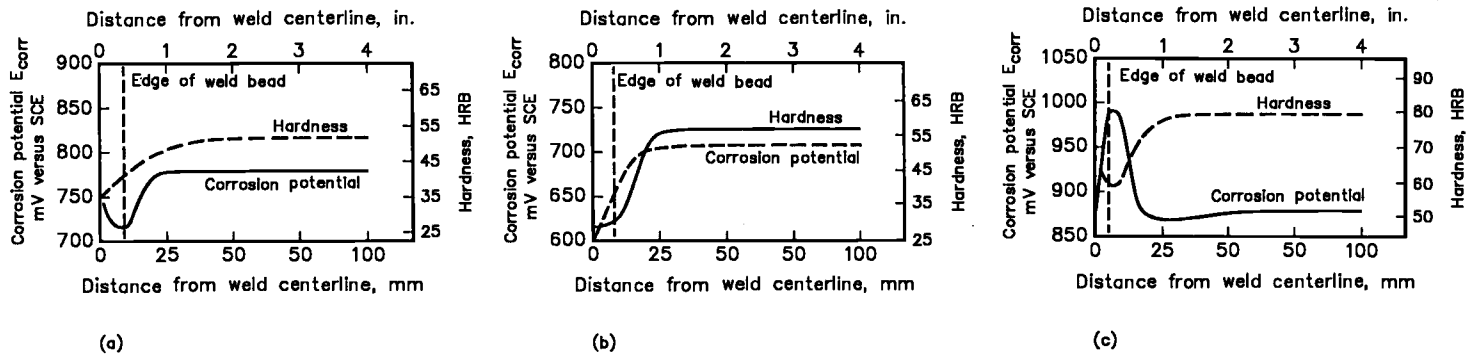


Fig. 3 Effect of welding heat on microstructure, hardness, and corrosion potential of three aluminum alloy welded assemblies. (a) Alloy 5456-H321 base metal with alloy 5556 filler. (b) Alloy 2219-T87 base metal with alloy 2319 filler. (c) Alloy 7039-T651 base metal with alloy 5183 filler. Source: Ref 6

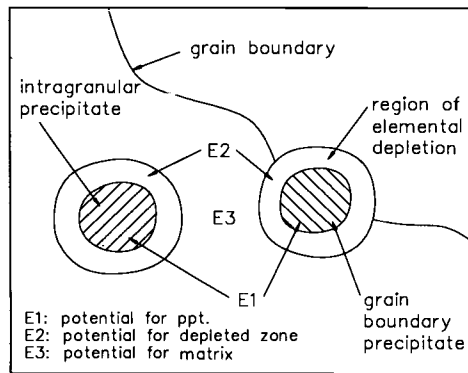


Fig. 4 Depleted regions adjacent to precipitates. These regions cause an electrochemical potential (E) difference that can promote localized corrosion at the microstructural level.

alloy steel. This practice leaves a cathodic stainless steel weld deposit in electrical contact with the steel. In the presence of corrosive environments, hydrogen is generated at the austenitic weld metal cathode, which is capable of maintaining a high hydrogen content without cracking. However, the cathodic behavior of the austenitic weld deposit may increase the susceptibility for stress-corrosion cracking in the heat-affected zone of the high-strength steel. A 40% thermal expansion mismatch between the austenitic stainless steel and ferritic base metal produces a significant residual stress field in the weldment; this residual stress field also contributes to cracking susceptibility. A similar, but more localized, behavior may explain the correlation between stress-corrosion cracking susceptibility and the presence of retained austenite in high-strength steel weld deposits.

Another common dissimilar metal combination involves the use of high-nickel alloys for weld repair of cast iron. Fe-55Ni welding electrodes are used to make weld deposits that can hold in solid solution many of the alloying elements common to cast iron. Furthermore, weld deposits made with Fe-55Ni welding consumables have an acceptable thermal expansion match to the cast iron. Because cast iron is anodic to the high-nickel weld deposit, corrosive attack occurs in the cast iron adjacent to the weld

deposit. It is suggested that cast iron welds made with high-nickel deposits be coated (painted) to reduce the susceptibility to selective corrosion attack.

Plain carbon steel weldments can also exhibit galvanic attack. For example, the E6013 welding electrode is known to be highly anodic to A285 base metal in a seawater environment (Ref 7). It is important to select a suitable filler metal when an application involves a harsh environment.

Weld Decay of Stainless Steel. During welding of stainless steels, local sensitized zones (i.e., regions susceptible to corrosion) often develop. Sensitization is due to the formation of chromium carbide along grain boundaries, resulting in depletion of chromium in the region adjacent to the grain boundary (Ref 8-14). This chromium depletion produces very localized galvanic cells (Fig. 4). If this depletion drops the chromium content below the necessary 12 wt% that is required to maintain a protective passive film, the region will become sensitized to corrosion, resulting in intergranular attack. This type of corrosion most often occurs in the heat-affected zone. Intergranular corrosion causes a loss of metal in a region that parallels the weld deposit (Fig. 5). This corrosion behavior is called weld decay (Ref 13).

The formation of sufficient chromium carbide to cause sensitization can be described by the C-shaped curves on the continuous cooling diagram illustrated in Fig. 6. The figure shows susceptibility to sensitization as a function of temperature, time, and carbon content (Ref 15). If the cooling rate is sufficiently great (curve A in Fig. 6), the cooling curve will not intersect the given C-shaped curve for chromium carbide and the stainless steel will not be sensitized. By decreasing the cooling rate, the cooling curve (curve B) eventually intersects the C-shape nucleation curve, indicating that sensitization may occur. At very low cooling rates, the formation of chromium carbide occurs at higher temperature and allows for more nucleation and growth, resulting in a more extensive chromium-depleted region.

The minimum time required for sensitization as a function of carbon content in a typical stainless steel alloy is depicted in Fig. 7. Because the

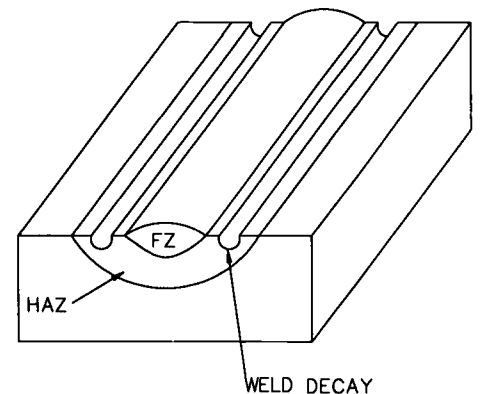


Fig. 5 Intergranular corrosion (weld decay) of stainless steel weldments. FZ, fusion zone

normal welding thermal cycle is completed in approximately two minutes, for this example the carbon content must not exceed 0.07 wt% to avoid sensitization. Notice that the carbide nucleation curves of Fig. 6 move down and to longer times with decreasing carbon content, making it more difficult to form carbides for a given cooling rate.

The control of stainless steel sensitization may be achieved by using:

- A postweld high-temperature anneal and quench to redissolve the chromium at grain boundaries, and hinder chromium carbide formation on cooling
- A low-carbon grade of stainless steel (e.g., 304L or 316L) to avoid carbide formation
- A stabilized grade of stainless steel containing titanium (alloy 321) or niobium (alloy 327), which preferentially form carbides and leave chromium in solution. (There is the possibility of knife-line attack in stabilized grades of stainless steel.)
- A high-chromium alloy (e.g., alloy 310)

Role of Delta Ferrite in Stainless Steel Weld Deposits. Austenitic weld deposits are frequently used to join various ferrous alloys. It has been well established that it is necessary to have austenitic weld deposits solidify as primary ferrite, also known as a δ ferrite, if hot cracking is to be minimized (Ref 16, 17). The amount and

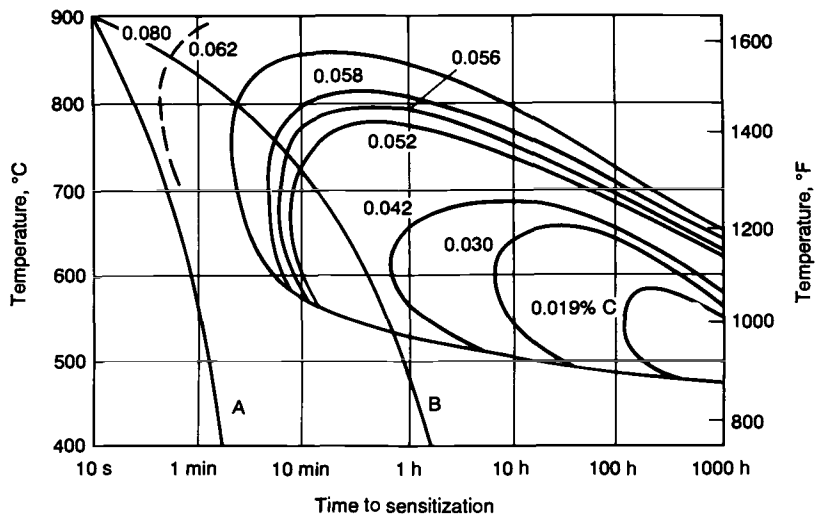


Fig. 6 Time-temperature-sensitization curves for type 304 stainless steel in a mixture of CuSO_4 and H_2SO_4 containing copper. Source: Ref 15. Curves A and B indicate high and medium cooling rates, respectively.

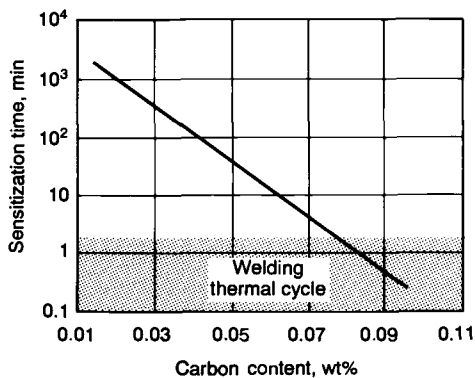


Fig. 7 Minimum sensitization time from a time-temperature-sensitization diagram as a function of carbon content for a typical 300-series stainless steel alloy. Source: Ref 15

form of ferrite in the weld metal can be controlled by selecting a filler metal with the appropriate chromium and nickel equivalent. A high chromium/nickel ratio favors primary ferrite formation, whereas a low ratio promotes primary austenite (Fig. 8). An optimum condition can be attained for ferrite contents between 3 and 8 vol% in the weld deposit. Ferrite contents above 3 vol% usually guarantee primary ferrite formation and thus reduce hot cracking susceptibility. However, ferrite above 10 vol% can degrade mechanical properties at low- or high-temperature service. At low temperatures, excess ferrite can promote crack paths when the temperature is below the ductile-brittle transition temperature. At high temperatures, continuous brittle sigma phase may form at the interface between the austenite and the ferrite. The ferrite content can be confirmed using magnetic measuring equipment (Ref 16, 17).

Figure 8 can be used to predict the type of ferrite (primary or eutectic) and the ferrite content when a difference exists between the stainless steels being joined, such as when welding

type 304 to type 310 stainless steel (Ref 18). This diagram shows the compositional range for the desirable primary solidification mode. The dotted lines on the diagram indicate the various transitions in the primary solidification phase. Because not all ferrite is primary ferrite (i.e., some is a phase component of a ferrite-austenite eutectic), this diagram can be used to ensure that ferrite is the first solid (primary) phase to form. This condition occurs when the weld deposit has a composition in the range labeled FA in Fig. 8. Because primary ferrite is the preferable microstructure, use of this diagram should reduce problems of hot cracking during welding. Also, the corrosion behavior of stainless steel weld deposits and castings is measurably different depending on whether the stainless steel has a microstructure generated with primary ferrite or primary austenite (Ref 19-25). Thus, knowledge of the weld metal ferrite content and form is necessary in order to be able to properly characterize and predict corrosion behavior.

Pitting is a form of localized attack caused by a breakdown in the thin passive oxide film that protects material from the corrosion process. Pits are commonly the result of a concentration cell established by a variation in solution composition that is in contact with the alloy material. Such compositional variations result when the solution at a surface irregularity is different from that of the bulk solution composition. Once a pit has formed, it acts as an anode supported by relatively large cathodic regions. Pitting has a delay time prior to nucleation and growth, and nucleation is very site-selective and microstructure-dependent. Pits are often initiated at specific microstructural features in the weld deposit (Ref 26). Pitting occurs when the material/solution combination achieves a potential that exceeds a critical value, known as the pitting potential. The tendency for a given alloy/solution combination to pit can often be characterized by critical potentials for pitting and

repassivation determined by a cyclic potentiodynamic polarization technique.

Pits develop more readily in metallurgically heterogeneous materials. For example, when austenitic stainless steel is heated to temperatures where sensitization takes place (Ref 26, 27), the resulting chromium-depleted region is subject to pitting. Pits may also initiate at the austenite-ferrite interfaces in stainless steel weld metal.

Although weld metal has a higher probability of being locally attacked because of microsegregation in the dendritic structure, filler metals are now available that have better pitting resistance than their respective base metals; information about these filler metals can be obtained from consumable suppliers. However, even when the proper filler metal is used, pitting may still occur in the unmixed zone.

Duplex stainless steels, with ferrite contents in the range of 40 to 50 vol%, are often used to decrease the tendency of stress-corrosion cracking in chromium-nickel high-alloy steels. The welding practice for duplex stainless steels must be given special attention (Ref 20-22, 24, 25, 27) to avoid reduction in corrosion resistance. The combination of a low carbon content and a carefully specified nitrogen addition have been reported to improve resistance to pitting corrosion, stress-corrosion cracking, and intergranular corrosion in the as-welded condition. The low carbon content helps avoid sensitization, while the addition of nitrogen slows the precipitation kinetics associated with the segregation of chromium and molybdenum during the welding process (Ref 1). On rapid cooling from high temperature, nitrogen also has been reported to form deleterious precipitates (for example, Cr_2N) in the ferrite, thus reducing the corrosion resistance (Ref 28). Nitrogen also increases the formation of austenite in the heat-affected zone and weld metal during cooling. A minimum pitting corrosion rate is achieved at a ferrite content of about 50 vol%.

Stress-Corrosion Cracking. Weldments can be susceptible to stress-corrosion cracking under specific environmental conditions. This cracking requires the proper combination of corrosive media, susceptible microstructure, and tensile stress. Welds are often loaded in tension (due to residual stress) to a level approaching the yield strength of the base metal. A weld, with its various heterogeneous microstructural features, thus becomes an excellent candidate for stress-corrosion cracking.

Stress-corrosion cracks have an anodic crack tip and often leave apparent corrosion products along the fracture. Cracking is often characterized by crack branching and usually has a delay time prior to crack initiation, with initiation occurring at corrosion pits. Increasing the ferrite content in stainless steel weld metal reduces stress-corrosion cracking susceptibility. Approximately 50 vol% ferrite gives optimum stress-corrosion cracking resistance.

Welding parameters influence the amount and distribution of residual stress, because the extent of the stressed region and the amount of distor-

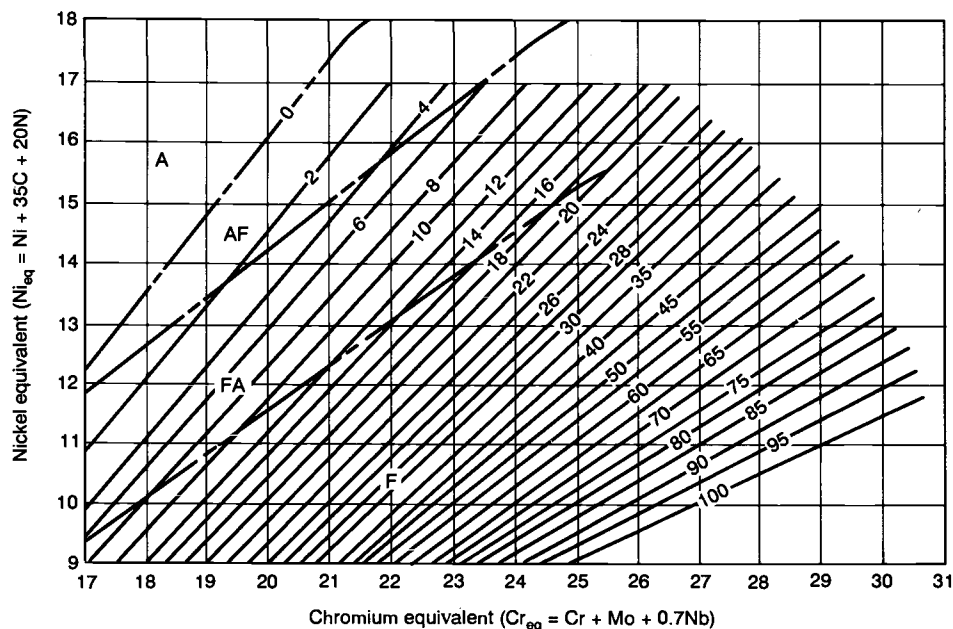


Fig. 8 Welding Research Council (WRC-1988) diagram used to predict weld metal ferrite content. Source: Ref 18

tion are directly proportional to the size of the weld deposit; this deposit is directly related to the heat input. The thermal experience of welding is often very localized, resulting in strains that can cause distortion and residual stress. These residual stresses can be important in the initiation and propagation of environmentally assisted cracking. The use of small weld deposits reduces the stress and thus reduces the susceptibility of environmentally enhanced cracking.

It is known that postweld heat treatment can reduce stress-corrosion cracking by redistributing the localized load and by reducing the magnitude of the residual tensile stress available to induce corrosion cracking (Ref 29). In a recent study on a cast austenitic stainless steel, post-solidification heat treatments were also shown to modify the local composition gradients, significantly altering the susceptibility of the solidified microstructure to stress-corrosion cracking (Ref 30).

Hydrogen damage results from the combined actions of hydrogen and stress (Ref 31); the stress can be residual or applied. The weld pool in the liquid state has a much higher solubility for hydrogen than solid metal, and during solidification the hydrogen content becomes supersaturated in the weld pool as hydrogen attempts to transport from the weld deposit. While some of the hydrogen leaves the weldment, significant amounts transport through the fusion line and into the heat-affected zone.

The fusion line region also has the highest cooling rate, which may lead in some alloys to fracture-sensitive microstructures (e.g., martensite). The combination of high hydrogen content and brittle microstructures can produce cracking. The result is underbead cracking, characterized by delayed slow propagating cracks that

travel adjacent to the fusion line in the heat-affected zone. The typical hydrogen crack travels one or two grains from the fusion line in the heat-affected zone.

Weld metal hydrogen cracking often takes the form of chevron cracks (Ref 32-34). Chevron crack formation and propagation are influenced by the combination of stress and orientation of the columnar grain boundaries. Chevron cracking occurs at high hydrogen content levels and appears to be inactive at low levels. This type of cracking appears to be sensitive to reheating during multi-pass deposition of welding beads. Chevron cracking is most likely found with flux-related welding processes.

Microbiologically Influenced Corrosion (MIC) is a phenomenon in which microorganisms play a role in the corrosion of metals. This role may be to initiate or accelerate the corrosion process. For example, water and some organic media may contain certain microorganisms that can produce a biofilm when exposed to a metal surface. The resulting nonuniform coverage may lead to a concentration cell and eventually initiate corrosion. In addition, the metabolic process of the microorganism can produce a localized acid environment that changes the corrosion behavior of the exposed metal by, for example, altering anodic and cathodic reactions, destroying protective films, or creating corrosive deposits (Ref 35).

In austenitic stainless steel weldments, the effects of MIC are usually observed as pitting on or adjacent to welds (Ref 36, 37). MIC attacks either γ or α phases, and chlorides are sometimes found in a pit, even when the water has extremely low chloride content. Pits are found in regions of the heat-affected zone at the fusion line, and in the base metal near the weld for reasons not well understood. There is some evi-

dence that MIC takes place along with stress-corrosion cracking in weldments of austenitic stainless steel. Welding design and plant operation can minimize MIC attack, mainly by preventing an acceptable environment for microorganisms.

Heat-Tint Oxide Formation. The welding process, especially with poor gas shielding, can produce a variation in the thickness of the passivating oxide. The variation in oxidation will result in a gradient in the degree of chromium depletion adjacent to a stainless steel weld. This behavior will cause some tendency for localized corrosion (Ref 1). An indication of this problem can be seen by the heat-tint oxide formation (Ref 38).

Welding Practice to Minimize Corrosion

Several methods are available to minimize corrosion in weldments (Ref 39). The most important of these are discussed below.

Material and Welding Consumable Selection. Careful selection of materials and welding consumables can reduce the macro- and micro-compositional differences across the weldment and thus reduce the galvanic effects.

Surface Preparation. A properly selected cleaning process can reduce defects that are often sites for corrosive attack in aggressive environments. However, the cleaning process can also be a source of trouble. For example, any mechanically cleaned surface (i.e., cleaned by sand blasting or grinding) can leave impurities on the surface. The type of wire brush used can also be an important consideration (Ref 39). Stainless steel brushes are generally preferred because they do not form corrosion products capable of holding moisture.

Welding design should promote deposits that have relatively flat beads with low profiles and have minimal slag entrapment. A poor design can generate crevices that trap stagnant solutions, leading to pitting and crevice corrosion. Irregular weld deposit shapes can promote turbulent flow in a tubular product and result in erosion corrosion.

Welding Practice. Complete penetration is preferred to avoid underbead gaps. Slag should be removed after each pass with a power grinder or power chipping tool. If the welding method uses flux, the geometry of the joint must permit thorough flux removal, because many flux residues are hydrophilic and corrosive.

Weld Surface Finishing. The weld deposit should be inspected visually immediately after welding. Maximum corrosion resistance usually demands a smooth uniformly oxidized surface that is free from foreign particles and irregularities (Ref 37). Deposits normally vary in roughness and in degree of weld spatter, a concern that can be minimized by grinding. For smooth weld deposits, wire brushing may be sufficient. For stainless steel, however, brushing disturbs the existing passive film and may aggravate corrosive attack.

Surface Coating. When a variation in composition across the weld metal can cause localized attack, it may be desirable to use protective coatings. The coating needs to cover both the weldment and the parent metal and often requires special surface preparation.

Postweld Heat Treatment. A postweld heat treatment can be an effective way to reduce corrosion susceptibility. This improved corrosion resistance is accomplished through a reduction in residual stress gradients that influence stress-corrosion cracking growth. Postweld heat treatment can assist in the transport of hydrogen from the weldment and reduce susceptibility to hydrogen cracking. The treatment can also reduce compositional gradients (i.e., microsegregation) and corresponding microgalvanic cells.

Preheat and Interpass Temperature. The selection and use of proper preheat treatment and interpass temperature may prevent hydrogen cracking in carbon and low-alloy steel.

Passivation Treatment. A passivation treatment may increase the corrosion resistance of stainless steel welded components.

Avoidance of Forming Crevices. Slag that is still adhering to the weld deposit and defects such as lack of penetration and microfissures can result in crevices that can promote a localized concentration cell, resulting in crevice corrosion. Proper selection of welding consumables, proper welding practice, and thorough slag removal can alleviate this form of corrosion damage.

Removing Sources of Hydrogen. Through proper selection of welding consumables (that is, low-hydrogen shielded metal arc welding electrodes), proper drying of flux, and welding clean surfaces, the hydrogen pickup can be drastically reduced.

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