6

CORROSION

6.1 INTRODUCTION

Corrosion is often associated with welded structures, since the microstructure, properties, and composition of the weld metal and HAZ may be quite different than those of the base metal. Corrosion takes a number of forms, as described in the following section, and may result in general (uniform), localized, or microstructure-specific attack.

Often, the corrosion rate associated with welds is much higher than the base metal. The reason for this is usually a combination of the effect of microstructure and residual stress. Highly stressed regions surrounding welds may result in accelerated corrosion relative to the base metal. For example, the spot welds in automotive steels are normally the first place where corrosion attack takes place in car bodies.

There are a number of standardized tests that have been developed to quantify susceptibility to corrosion in different environments. Many of these are accelerated tests that allow long-term corrosion behavior to be estimated using short-term laboratory tests. Most of these tests can be conducted using welded samples. Corrosion control of welded structures is often the critical factor in determining the ultimate life, or fitness for service, of a structure.

6.2 FORMS OF CORROSION

Corrosion of engineering alloys is manifested in a variety of forms, most of which are macroscopic (visible with the naked eye) and others require microscopic examination. Fontana and Green [1] defined eight forms of corrosion, many of which can be linked to degradation and eventual failure of welded structures, as listed below. This classification was based on the visual appearance of the corrosion. A ninth form of corrosion that has been determined to be distinct from these other forms is termed microbiologically induced corrosion (MIC):

1. General
2. Galvanic
3. Crevice
4. Selective leaching
5. Erosion
6. Pitting
7. Intergranular
8. Stress assisted
9. Microbiologically induced

The general characteristics of the first five of these corrosion forms are briefly reviewed in the following sections. Corrosion resulting from pitting, intergranular attack (IGA), and stress-assisted mechanism are covered in more detail since these forms are most pertinent to welded structures.

6.2.1 General Corrosion

This is the most common form of corrosion encountered and is by far the most costly (over 10 billion dollars a year is spent in the United States alone to repair or prevent uniform attack). Uniform attack, or general corrosion, is characterized by a chemical or electrochemical reaction at the metal surface that results in the uniform formation of a corrosion product. In steels, this corrosion product is manifested as "rust," the oxidation of iron to form Fe_2O_3 (hematite) and Fe_3O_4 (magnetite).

General corrosion is primarily a function of composition, rather than microstructure. In cases where the weld metal and base metal compositions are similar (such as with autogenous and homogenous welds), the welds may be only slightly more susceptible to general corrosion than the surrounding base material. Increased corrosion rates in welded structures are often associated with residual stresses that may accelerate attack in certain environments.

General corrosion rates vary widely among materials. Much general corrosion data has been gathered in a variety of environments, including atmospheric, soil, and more aggressive solutions. For example, there is considerable general corrosion data available for chloride-bearing environments such as seawater. A comparison of atmospheric corrosion rates for different materials is provided in Table 6.1 [2].

TABLE 6.1   General corrosion rates of metals and alloys[a]

Material	Rate, mils/year (mm/year)
Aluminum	0.032 (0.0008)
Copper	0.047 (0.0012)
Lead	0.017 (0.0004)
Tin	0.047 (0.0012)
Nickel	0.128 (0.0032)
Monel (70N–30Cu)	0.053 (0.0013)
Zinc	0.202 (0.0051)
AISI 1020 steel	0.48 (0.0120)
Low-alloy steel (1% Cr)	0.09 (0.0023)
Type 304 stainless steel	Nil

[a]From Ref. [2].

Damage resulting from general atmospheric corrosion is usually prevented by the use of coatings or inhibitors (such as paint) or the selection of corrosion-resistant materials (such as aluminum alloys, stainless steels, and Ni-base alloys for resistance under normal atmospheric conditions).
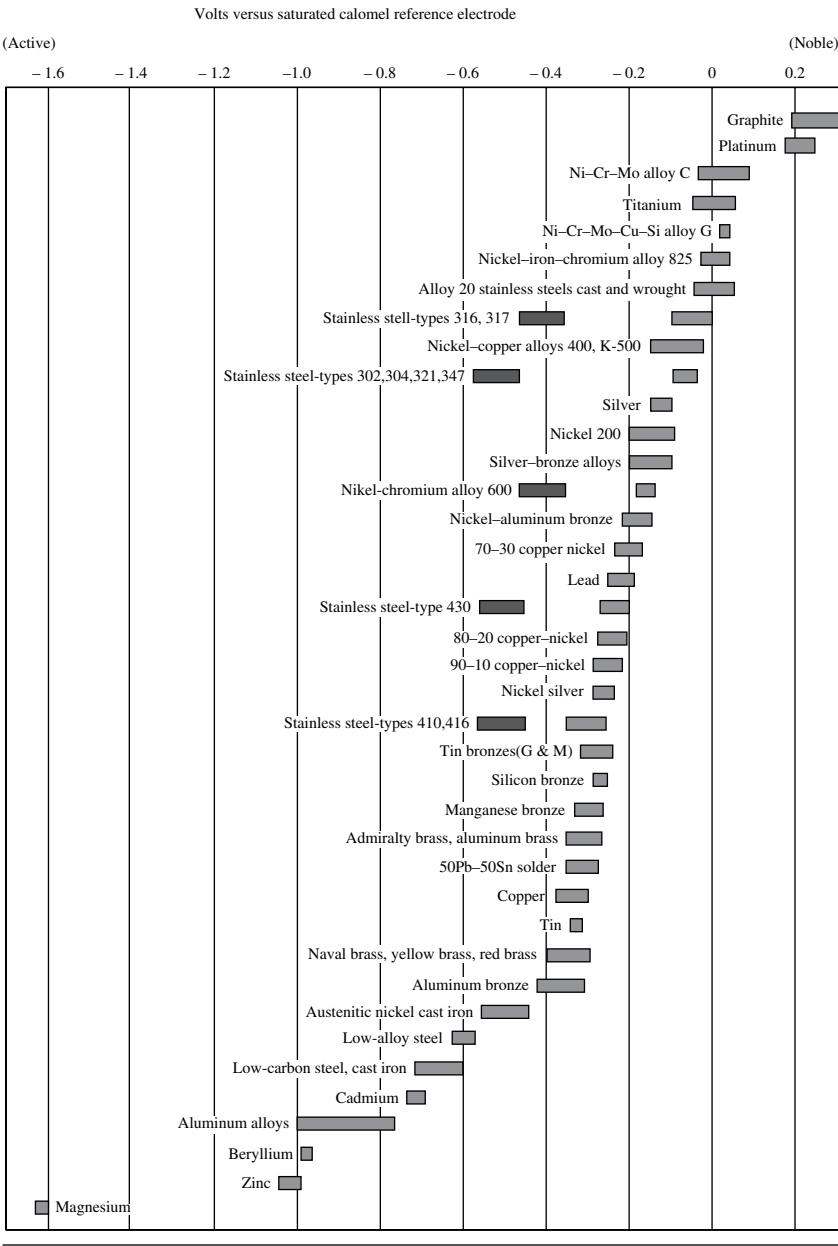
6.2.2   Galvanic Corrosion

A chemical potential difference exists between dissimilar metals when they are both in contact with a corrosive and/or conductive medium. If these metals are, in turn, in electrical contact in the presence of this same medium, the potential difference results in a flow of current between the two. By convention, the material in which a corrosion reaction (oxidation) occurs is defined as the *anode* and the material where reduction occurs is defined as the *cathode*. When two materials are connected electrically in a corrosive environment, corrosion occurs in the anodic material.

A galvanic series of some commercial alloys and pure metals in seawater is provided in Table 6.2. Metals that are anodic (active) will corrode preferentially when in contact with those that are cathodic (noble) in a corrosive medium. This medium may range from pure water (or steam) to highly corrosive acids. The rate of attack of a cathodic material relative to the anode is related to the difference in potential and the area that is exposed to the environment. Thus, from this table, magnesium would corrode rapidly if coupled to steel in seawater, while little attack would be expected in a cupronickel coupled to an austenitic stainless steel (18Cr–8Ni).

The galvanic effect can be used to provide "cathodic protection" in certain environments. For example, steel ship hulls are often cathodically protected by coupling to a massive magnesium block, which will corrode preferentially and protect the ship hull during seawater exposure.

Controlling the relative differences in solution potential among the base metal, HAZ, and weld metal is the key to avoiding galvanic attack, as illustrated in Figure 6.1.

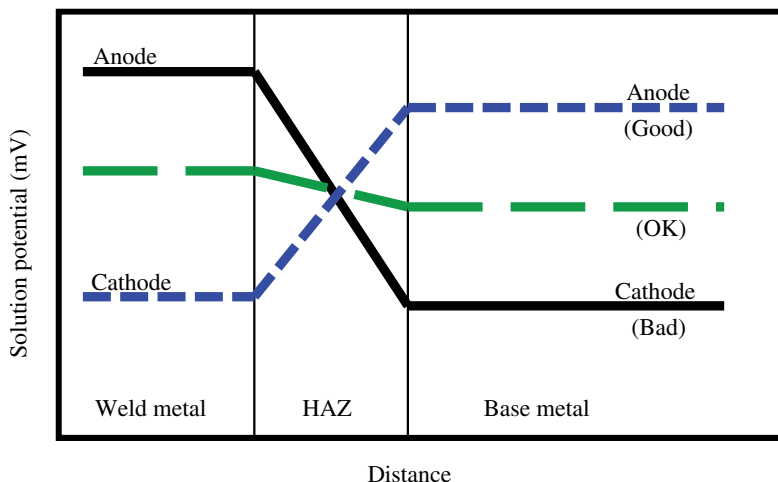**TABLE 6.2   Galvanic series for metals in seawater**

Volts versus saturated calomel reference electrode

(Active)   (Noble)

| − 1.6 | − 1.4 | − 1.2 | −1.0 | − 0.8 | − 0.6 | − 0.4 | − 0.2 | 0 | 0.2 |

Graphite
Platinum
Ni–Cr–Mo alloy C
Titanium
Ni–Cr–Mo–Cu–Si alloy G
Nickel–iron–chromium alloy 825
Alloy 20 stainless steels cast and wrought
Stainless stell-types 316, 317
Nickel–copper alloys 400, K-500
Stainless steel-types 302,304,321,347
Silver
Nickel 200
Silver–bronze alloys
Nikel-chromium alloy 600
Nickel–aluminum bronze
70–30 copper nickel
Lead
Stainless steel-type 430
80–20 copper–nickel
90–10 copper–nickel
Nickel silver
Stainless steel-types 410,416
Tin bronzes(G & M)
Silicon bronze
Manganese bronze
Admiralty brass, aluminum brass
50Pb–50Sn solder
Copper
Tin
Naval brass, yellow brass, red brass
Aluminum bronze
Austenitic nickel cast iron
Low-alloy steel
Low-carbon steel, cast iron
Cadmium
Aluminum alloys
Beryllium
Zinc
Magnesium

FIGURE 6.1 Galvanic couples and solution potentials.

In the galvanic couple, the anode (active metal) will corrode preferentially to the cathode (noble metal). If the anode area is small relative to the cathode, this attack can be quite rapid. Thus, in environments where corrosion is a concern, it is important to insure that the base metal is anodic to the weld metal and HAZ.

In the case where the weld metal is anodic and the differential in solution potential is large, very rapid attack of the weld metal is possible. For most filler metal/base metal combinations, this is not a problem since the difference in potential is usually small. However, when selecting filler metals for dissimilar combinations or when the filler metal is of significantly different composition than the base metal, it is recommended that the relative potentials of the materials are determined. This is particularly important when the welded structure is exposed to aqueous environments. The filler metals used for many common aluminum alloys are often very different in composition than the base metal and may require special attention to galvanic effects in certain environments.

6.2.3 Crevice Corrosion

Intense localized corrosion can occur at crevices and notches on metal surfaces. Crevice corrosion is usually associated with mechanical fasteners such as bolts or rivets but has resulted from the presence of weld discontinuities. Such crevices can result from lack of penetration defects, slag intrusions (e.g., at the weld toe), and cracks, which are open to the surface of the weld.

To function as a crevice corrosion site, the crevice must be wide enough to permit entry of the liquid corrosive medium but narrow enough to allow a stagnant concentration to form within the crevice. As a result, defects that are only open a few thousandths of an inch at the surface are the most susceptible. The austenitic stainless steels tend to be particularly susceptible to crevice corrosion in seawater.

6.2.4 Selective Leaching

Selective leaching is the removal of one element from an alloy by corrosion processes. The most common example of this is the selective removal of zinc from brass alloys, commonly known as dezincification. Weld regions do not appear to be any more susceptible than the base material to this form of corrosive attack.

6.2.5 Erosion Corrosion

This form of attack is basically general corrosion that is accelerated by the relative motion of the corrosive medium. Most metals and alloys are susceptible to this form of corrosive attack. Metals that are relatively soft and readily damaged or worn by mechanical abrasion, such as copper, are usually the most susceptible to erosion corrosion. The weld region in many materials may be more susceptible to this form of attack than the base material due to the softening (annealing) of the structure resulting from the weld thermal cycle. This effect is usually quite subtle.

Erosion corrosion has been observed in power generation applications where fluids or steam are being pumped at high velocities using rotors or impellers. Both the rotors and piping systems may be susceptible to erosion corrosion.

In some situations, welding can be used to mitigate erosion corrosion. For example, the application of "hard-facing" filler metals can locally increase hardness and reduce or eliminate erosion associated with softer materials. In other cases, the use of filler metals with higher corrosion resistance can have a similar effect.

6.2.6 Pitting

Pitting is an extremely localized attack that is manifested by holes, or pits, in the metal surface. Pitting is a particularly insidious form of corrosion since it is difficult to detect until the structure has been severely attacked. Pits usually grow in the direction of gravity, only rarely forming on vertical surfaces or growing upward from the bottom of horizontal surfaces. As shown in Figure 6.2, there may be little observable damage on the surface of the structure, while in the subsurface the corrosion attack may be substantial. Pitting is an autocatalytic process whereby anodic metal dissolution occurs within the pit, creating a local corrosion cell. For pitting in seawater, this anodic reaction results in formation of an acidic (pH 1.5–2.0) solution at the bottom of the pit that results in rapid dissolution of the metal.

In general, damage by pitting can be avoided by proper alloy selection. For instance, plain-carbon steel is more resistant to pitting in some environments than stainless steel (18Cr–8Ni). In situations where corrosion-resistant (general corrosion) materials are necessary, the selection of Mo-bearing stainless steels (Type 316), duplex stainless steels, or nickel-base alloys is recommended (e.g., Hastelloy).

Pitting is influenced primarily by the composition of the metal and does not appear to prefer weld regions over the surrounding base metal unless segregation of critical alloying elements has occurred. Elemental partitioning during weld solidification may enhance localized pitting attack (due to microscopic inhomogeneity).
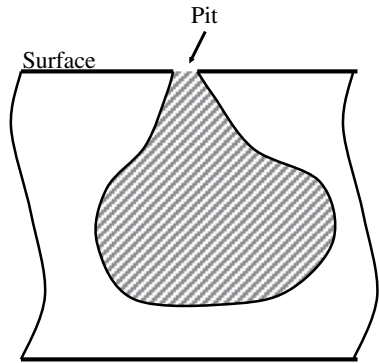
FIGURE 6.2   Illustration of pitting attack.

TABLE 6.3   Effect of alloying and impurity elements on pitting corrosion of stainless steels

Element	Effect on resistance
Chromium	Increases
Nickel	Increases
Molybdenum	Increases
Tungsten	Increases
Silicon	Decreases, except with Mo
Titanium and niobium	Decreases
Sulfur	Decreases
Carbon	Decreases, especially when sensitized
Nitrogen	Increases

As a class of materials, the stainless steels and aluminum alloys tend to be the most susceptible to damage by pitting. For the stainless steels, resistance to pitting can be influenced by variation in alloying additions. Table 6.3 lists the effect of various alloying and impurity elements on the pitting corrosion resistance of stainless steels.

For the stainless steels, resistance to pitting can be quantified using the pitting resistance equivalent (PRE) based on the content of Cr, Mo, W, and N:

$$PRE = Cr + 3.3(Mo + 0.5W) + 16N$$

Note the potent effect of nitrogen with regard to increasing resistance to pitting. Nitrogen is intentionally added to duplex stainless steels to improve pitting corrosion resistance as well as to promote a balanced austenite + ferrite (duplex) microstructure. The PRE values of some austenitic and duplex stainless steels are provided in Table 6.4. Materials with a PRE greater than 32 are resistant to pitting in seawater, while resistance to hydrogen sulfide (H_2S) requires a PRE above 40.

The critical pitting temperature (CPT) can also be used to quantify pitting resistance. Figure 6.3 shows the effect of Mo additions to stainless steel on the CPT [3].

TABLE 6.4   Pitting resistance equivalent (PRE) values for stainless steels

Alloy	UNS	Alloy type	PRE_N
304L	S30403	Austenitic	20
316L	S31603	Austenitic	25
317L	S31703	Austenitic	31
254SMO	S31254	Superaustenitic	41
AL-6XN	N08367	Superaustenitic	46
2205	S32205	Duplex	36
2507	S32750	Superduplex	43
2707	S32707	Hyperduplex	49
3207	S33207	Hyperduplex	52

$$PRE_N = Cr + 3.3(Mo + 0.5W) + 16N$$
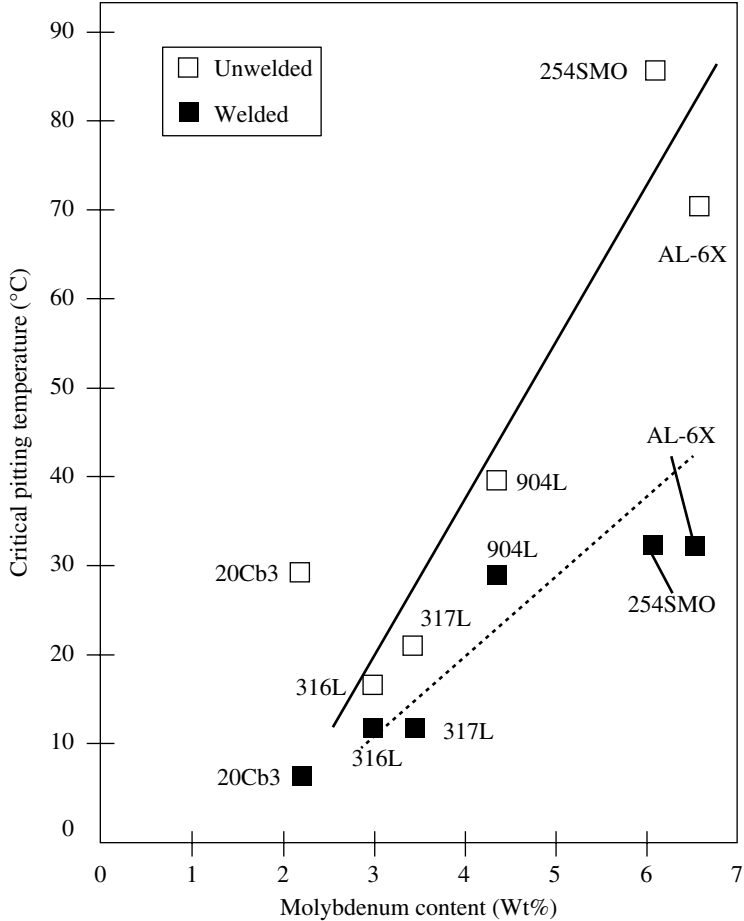
FIGURE 6.3   Critical pitting temperature (CPT) of commercial high-Mo austenitic stainless steels and their weld fusion zones. Open symbols are base metal values, and filled symbols are autogenous welds. The solid line represents the average base metal behavior, and the dotted line the weld metal behavior (Redrawn from Ref. [3]. © AWS).
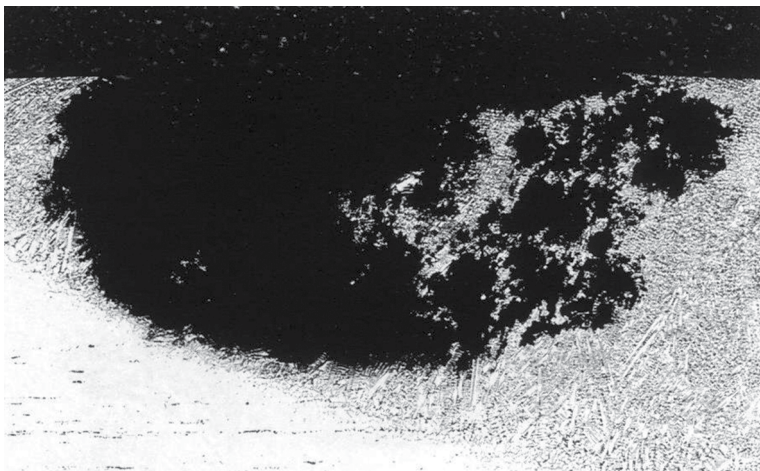
FIGURE 6.4   Severe pitting attack in superaustenitic stainless steel AL-6XN weld metal (© TWI).

A high CPT indicates good resistance to pitting. Note that the addition of Mo from 2 to over 6 wt% in austenitic stainless steels results in a significant increase in the pitting resistance of the base metal but that the weld metal response is not as large. This is primarily due to the partitioning of Mo during solidification. Since the partition coefficient (k) for Mo in stainless steel is on the order of 0.5, the core of the cells and dendrites will have Mo contents well below the average composition. For a 6% Mo alloy, the dendrite core would only achieve about 3 wt% Mo.

As a result of this, severe pitting corrosion attack can occur in the weld metal relative to the base metal, as shown in the cross section of the superaustenitic stainless steel AL-6XN weld in Figure 6.4. This situation can potentially be avoided by using a higher Mo filler metal to maintain the dendrite core composition above 5 wt%. It should be recognized, however, that the formation on an unmixed zone (UMZ) at the fusion boundary may negate this effect. The micrograph in Figure 6.5 shows such a UMZ in a weld on AL-6XN made using a high-Mo, Ni-base filler metal. Although the weld metal is now immune from pitting attack, the narrow UMZ is subject to local pitting.

Another alloying option to prevent pitting in stainless steels is to add tungsten (W) as a substitute for, or in addition to, Mo. Tungsten does not partition significantly during weld solidification, thereby preventing the reduction in pitting resistance at the dendrite core.

6.2.7   Intergranular Corrosion

Localized attack at, or adjacent to, grain boundaries with little or no attack of the grain interiors is appropriately called intergranular corrosion (IGC). This localized corrosion can be caused by impurities at the grain boundaries, an enrichment of an
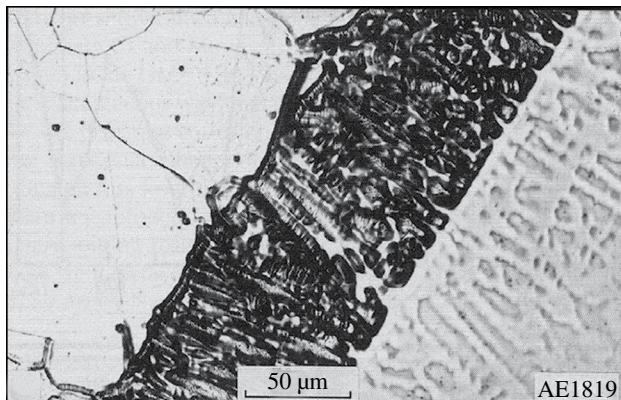
FIGURE 6.5   Unmixed zone (dark etching) that forms at AL-6XN fusion boundary when welded with a Ni-base filler metal (© AWS).

alloying element at the boundary, or, conversely, a depletion of an alloying element. Enrichment of aluminum alloy grain boundaries with iron can cause IGC in these materials. On the other hand, the depletion of chromium along grain boundaries in austenitic stainless steels results in IGC or intergranular attack (IGA). This phenomenon has been studied extensively in these alloys because of its potential for reducing the service life of components used in the power generation industry. A brief overview of IGC in austenitic stainless steels is included here.

IGC in 300-series austenitic stainless steels is of particular concern since it occurs in environments where the alloys would normally be expected to exhibit excellent corrosion resistance. The IGC in these alloys is particularly prevalent in the weld HAZ. Susceptibility to IGC results from the local depletion of chromium adjacent to the grain boundary due to chromium carbide (Cr-rich, $M_{23}C_6$) precipitation along the boundary. When the local chromium content drops below approximately 12 wt%, the region is no longer "stainless" and accelerated attack can occur. This phenomenon is also referred to as sensitization, since the material is made "sensitive" to IGA.

The schematic in Figure 6.6 represents the appearance of an austenitic stainless steel weld that has undergone IGA in the HAZ. On the surface of the weld exposed to the corrosive environment, there is often a linear area of attack roughly parallel to the fusion boundary. These are sometimes called "wagon tracks" because they are symmetric and parallel on either side of the weld. In cross section, severe attack (or weld "decay") can be observed along a "sensitized" band in the HAZ. Note that this band is at some distance from the fusion boundary. This is due to the fact that the carbide precipitation that leads to "sensitization" occurs in the temperature range from about 600 to 850°C (1110–1560°F). Above this temperature range, carbides go back into solution, and thus, the HAZ region adjacent to the fusion boundary that has been heated to higher temperatures is relatively free of carbides (assuming cooling rates are rapid enough to suppress carbide precipitation).
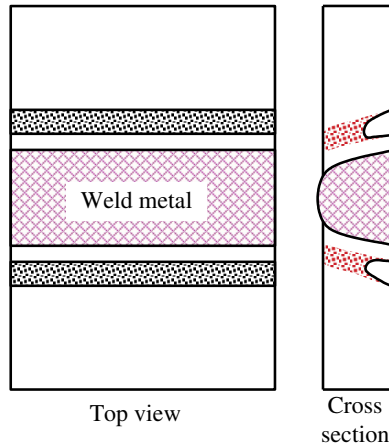
FIGURE 6.6   Illustration of intergranular attack in the HAZ of an austenitic stainless steel.
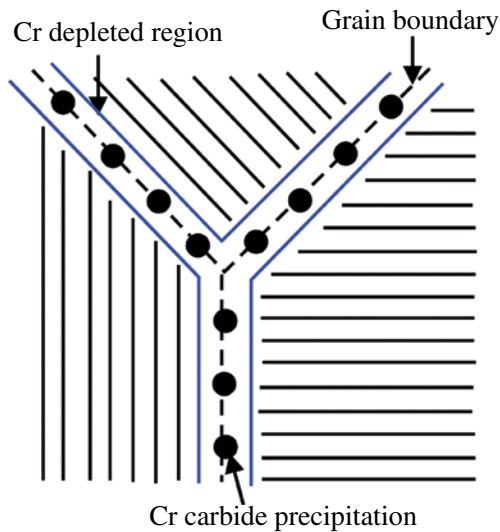

FIGURE 6.7   Schematic of grain boundary carbide precipitation and associated grain boundary chromium depletion.

In most austenitic stainless steels, Cr-rich, $M_{23}C_6$ carbides form preferentially along grain boundaries, as shown in the schematic in Figure 6.7. This precipitation requires short-range diffusion of Cr from the adjacent matrix and produces a Cr-depleted region surrounding the precipitate, as shown in Figure 6.8a. This reduces the local corrosion resistance of the microstructure and promotes rapid attack of the grain boundary region. This may be due, in part, to local galvanic attack where the Cr-depleted grain boundary is anodic to the surrounding matrix. The very
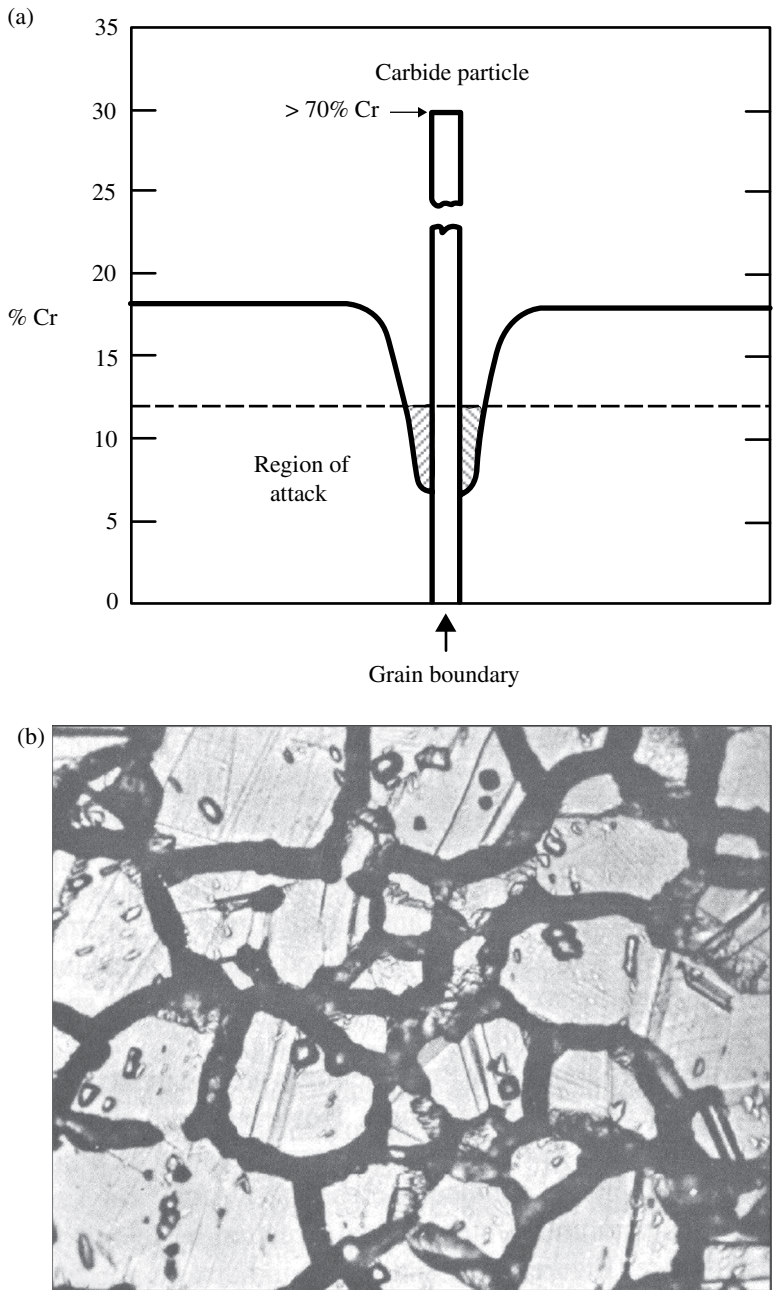
FIGURE 6.8 Intergranular corrosion. (a) Schematic of Cr depletion adjacent to the grain boundary carbide and (b) grain boundary attack in the HAZ of Type 304 (C = 0.06 wt%) (Courtesy of M.C. Juhas).
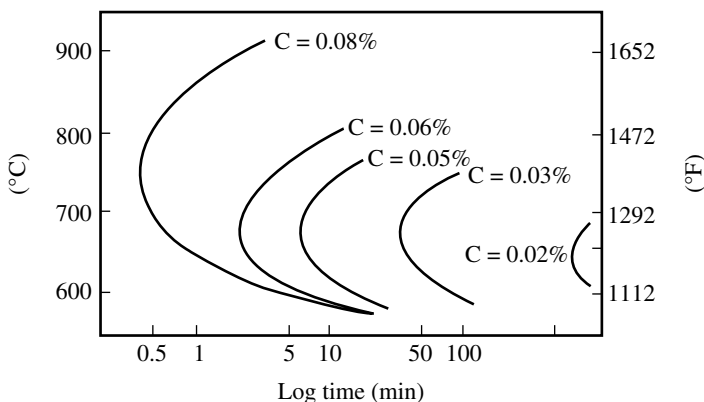
FIGURE 6.9 $M_{23}C_6$ time–temperature–precipitation curves for 18Cr–8Ni alloys with variable carbon content (From Ref. [4]. © McGraw-Hill).

small area of the grain boundary causes rapid attack, appearing as local "ditching" at the grain boundary, as shown in the metallographic section in Figure 6.8b. In extreme cases, the grains will actually drop out of the structure because of complete grain boundary attack and dissolution. This gives rise to the wagon track effect shown in Figure 6.6.

Carbon content has the most profound influence on susceptibility to IGC in austenitic stainless steels. The use of low-carbon ("L"-grade) alloys minimizes the risk of sensitization by slowing down the carbide precipitation reaction. The time–temperature–precipitation curves shown in Figure 6.9 demonstrate the effect of carbon content on the time to precipitation [4]. Note that with low carbon contents (C < 0.04 wt%), the nose of the curve is beyond 1 h, while for carbon levels from 0.06 to 0.08 wt%, the time for precipitation may be less than a minute. This difference demonstrates the benefit of the low-carbon austenitic stainless steel grades (so-called L grades such as 304L and 316L) for reducing or eliminating HAZ grain boundary sensitization during welding. The presence of residual stresses in the HAZ may also serve to accelerate the precipitation reaction.

In most cases, sensitization and subsequent IGC occur in the HAZ as a direct result of the weld thermal cycle. It should be noted, however, that the stress relief temperature range for most austenitic stainless steels overlaps the carbide precipitation range. Care must be taken not to sensitize the entire structure during PWHT. This is a particular concern with alloys containing more than 0.04 wt% C.

6.2.7.1 *Preventing Sensitization* It is possible to minimize or eliminate IGC in austenitic stainless steel welds by the following methods:

- Select base and filler metals with as low a carbon content as possible (L grades such as 304L and 316L).
- Use alloys that are "stabilized" by additions of niobium (Nb) and titanium (Ti). These elements are more potent carbide formers than chromium and, thus, tie up
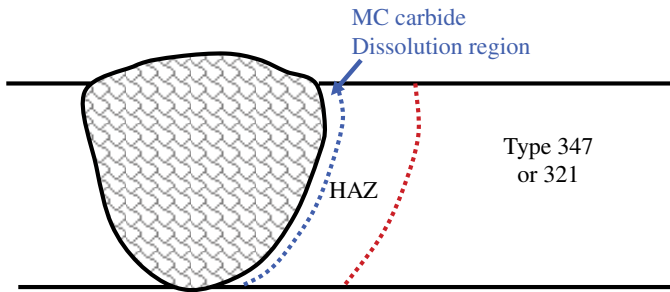
FIGURE 6.10 Location of knifeline attack that occurs in stabilized grades of austenitic stainless steels.

the carbon, minimizing the formation of Cr-rich, grain boundary carbides. They are also quite stable and resist dissolution during the weld thermal cycle.

- Use annealed material or anneal prior to welding to remove any prior cold work (cold work accelerates carbide precipitation).
- Use low weld heat input and low interpass temperature to increase weld cooling rates, thereby minimizing the time in the sensitization temperature range.
- In pipe welding, water cool the inside of the pipe after the root pass. This will help to eliminate sensitization of the ID resulting from subsequent passes.
- Solution heat treatment after welding. Heating the structure into the temperature range from 900 to 1100°C dissolves any carbides that may have formed along grain boundaries in the HAZ. The structure is then quenched (or rapidly cooled) from this temperature to prevent carbide precipitation during cooling. Note, however, that there are a number of practical considerations that tend to limit the usefulness of this latter approach. Distortion during quenching is a serious problem for many structures. Inability to quench complex pipe weldments is also a limiting factor.

6.2.7.2 Knifeline Attack IGC can also occur in certain situations in the stabilized grades, such as Types 347 and 321. This attack, shown schematically in Figure 6.10, may occur in a very narrow region just adjacent to the fusion boundary. It is called "knifeline" attack because the weld appears as if it was cut out with a knife. This type of attack occurs when the stabilizing carbides (NbC or TiC) dissolve at elevated temperatures in the region just adjacent to the fusion zone. Upon cooling, Cr-rich carbides will form faster than NbC or TiC, resulting in a narrow sensitized region. Farther from the fusion boundary, NbC and TiC do not dissolve and sensitization does not occur. Knifeline attack is associated with high heat input welds where the HAZ thermal cycle allows sufficient time for MC-type carbides to dissolve. This form of localized attack can usually be prevented by control of the welding procedure.

6.2.7.3 Low-Temperature Sensitization It has been observed that sensitization can actually occur after long exposures at low temperatures (<300°C) following an
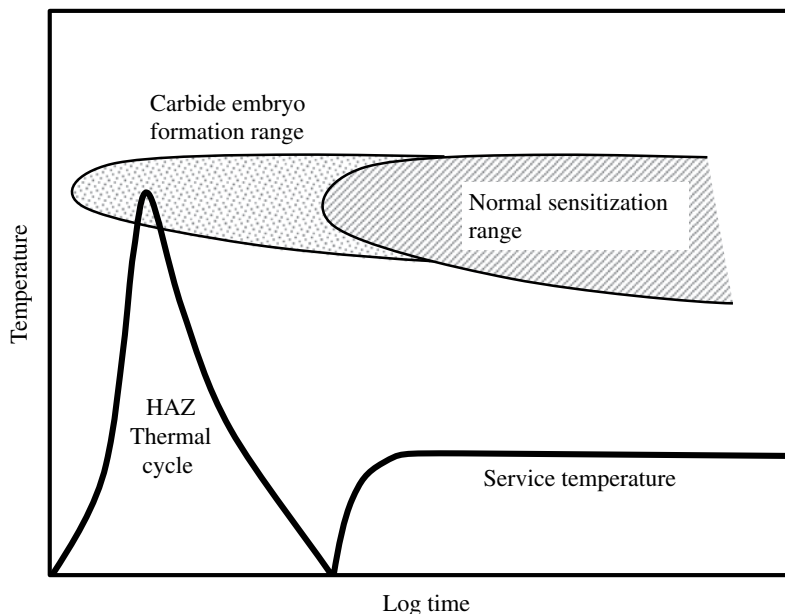
FIGURE 6.11 Thermal history associated with low-temperature sensitization in low-carbon austenitic stainless steels.

initial high-temperature thermal cycle, such as that experienced in the HAZ. This has come to be known as low-temperature sensitization (LTS) and has been a problem with stainless steel piping used in the power generation industry [5, 6]. LTS occurs because carbide "embryos" form in the HAZ during the original welding process and then grow to form carbide precipitates at low temperature. Figure 6.11 shows this phenomenon schematically. The long-term effect is the sensitization of the grain boundaries and the potential for IGC or intergranular stress corrosion cracking (IGSCC), even though the C curve for sensitization under normal conditions does not predict carbide precipitation during the thermal history of the weldment. This phenomenon has occurred in L-grade alloys, but does not seem to be a problem with stabilized grades such as Type 347.

6.2.8 Stress Corrosion Cracking

Stress corrosion cracking (SCC) refers to localized cracking resulting from the simultaneous presence of a tensile stress and a specific corrosive medium. Virtually all structural metals are susceptible to SCC given the appropriate combination of environment and stress, as indicated in Table 6.5. One of the earliest reports of SCC was "season cracking" of brass cartridge artillery shells. During periods of heavy rainfall or high humidity, cracks were often observed in brass cartridge cases at the point where the cartridge was crimped to the shell.

TABLE 6.5   Materials and environments leading to stress corrosion cracking

| Alloy or alloy system	Environment
Aluminum alloys	NaCl solutions, seawater
Copper alloys	Ammonia vapors and solutions
Gold alloys	$FeCl_3$ solutions, acetic acid–salt solutions
Inconel	Caustic soda solutions
Lead	Lead acetate solutions
Magnesium alloys	Distilled water
Monel	Fused caustic soda, hydrofluoric acid
Nickel	Fused caustic soda
Carbon and low-alloy steels	Multiple
Stainless steel (austenitic)	Multiple, including seawater and H_2S
Titanium alloys	Fuming nitric acid, seawater, N_2O_4
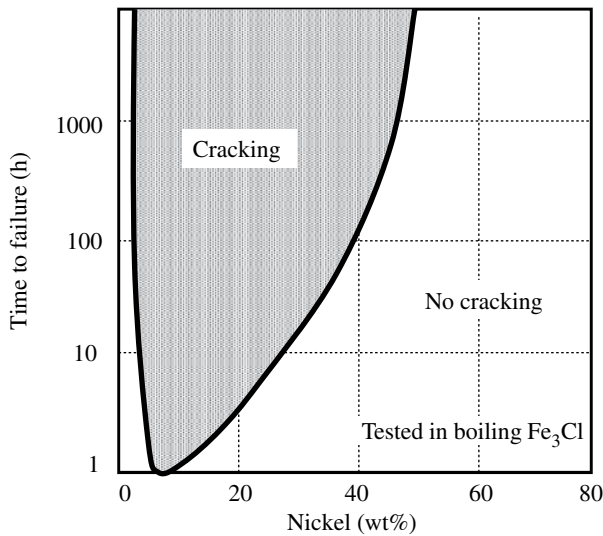
FIGURE 6.12   The Copson curve for predicting SCC susceptibility in stainless steels (Redrawn from Ref. [7]).

Stainless steels can also be susceptible to SCC, and these materials have been studied extensively because of their engineering importance. The presence of residual tensile stresses in the HAZ may accelerate corrosion attack and cracking along the sensitized grain boundaries. This is called IGSCC and may appear very similar to the IGC that was described in the previous section. Transgranular stress corrosion cracking (TGSCC) is also observed in austenitic stainless steels. This form of cracking is usually associated with Cl-bearing environments (seawater).

The Copson curve, shown in Figure 6.12, indicates the resistance of stainless steels to SCC in boiling magnesium chloride as a function of nickel content [7].
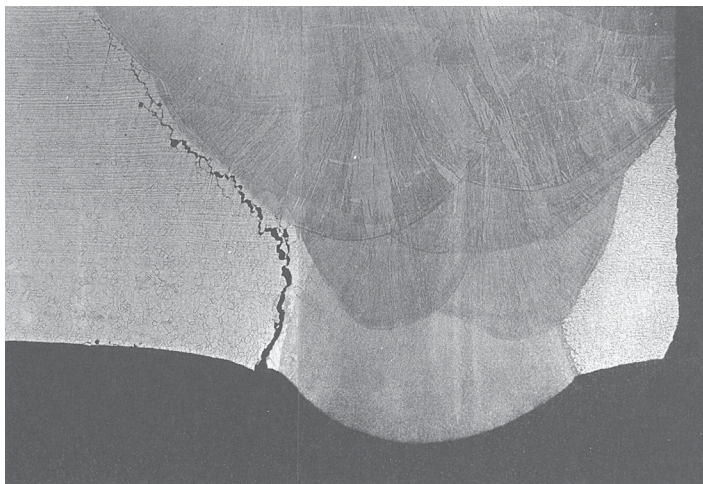
FIGURE 6.13 Intergranular SCC in the HAZ of Type 304 stainless steel (From Ref. [2]. © ASM).

The use of this aggressive environment is intended to accelerate the corrosion processes that would occur in other Cl-bearing environments (such as seawater). Note that the minimum of the resistance curve occurs in the range from 8 to 12% Ni. This is precisely the range within which many popular austenitic stainless steels alloys lie, such as Types 304 and 316.

As this figure indicates, SCC can be avoided by selecting alloys with either higher (>20%) or lower (<5%) nickel content. In the former case, the use of "super" austenitics or Ni-base alloys is common. In the low-Ni case, ferritic or duplex stainless steels are often selected. SCC has also been observed in caustic (high-pH) environments, such as in pulp and paper mills. It appears that the same rules apply in these environments as with Cl-bearing environments with respect to alloy selection to avoid caustic-induced SCC.

An example of IGSCC is shown in Figure 6.13 [2]. This is from a pipe weld in Type 304 stainless steel welded with Type 308 filler metal. Note that the cracking is specific to the region of the HAZ that has been sensitized during welding. An example of severe TGSCC in a Type 316 tubesheet after exposure to a caustic solution of sodium hydroxide in a pulp and paper mill is shown in Figure 6.14. This structure was exposed to the caustic solution for less than a year prior to failure. The residual stresses resulting from the weld in addition to imposed operating stresses led to the severe cracking seen in Figure 6.14. For this application, the Type 316 alloy was replaced with a duplex grade, Alloy 2205. This alloy has not exhibited any cracking after several years of service.

SCC is best avoided by proper alloy selection. The use of duplex and ferritic stainless steels in applications where austenitic grades would otherwise be selected can avoid SCC. Welding may exacerbate SCC in alloy systems that are otherwise resistant due to changes in microstructure and the presence of tensile residual stresses.
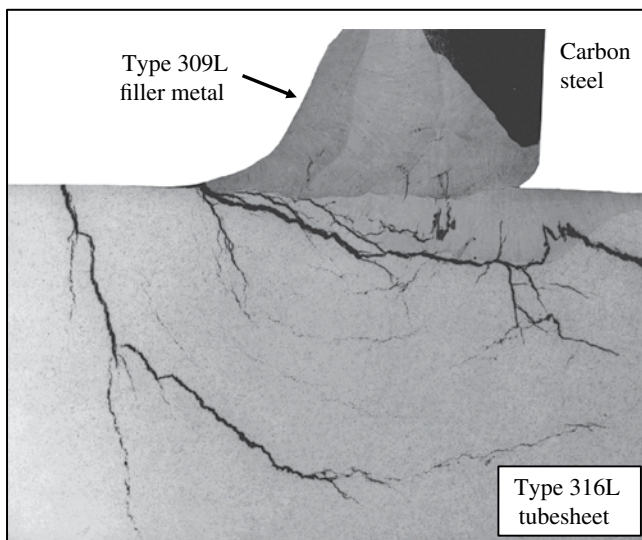
FIGURE 6.14 Transgranular SCC near the weld in Type 316L stainless steel after exposure to a caustic sodium hydroxide environment.

Sensitization can promote IGSCC in both austenitic (Fig. 6.13) and ferritic grades of stainless steel. Weld designs or conditions that generate high residual stress or create stress concentrations can also promote SCC. Postweld stress relief can sometimes be used to reduce these stresses and minimize susceptibility to SCC. But, as noted in Section 6.2.7.1, postweld stress relief needs to be done with care to avoid sensitization.

6.2.9 Microbiologically Induced Corrosion

MIC occurs in certain aqueous environments where aerobic or anaerobic bacteria literally attack the metal. MIC manifests itself as pitting, whereby the metal surface exhibits a small hole, or pit, and rapid attack occurs subsurface. In the past, MIC was probably often misinterpreted as normal pitting corrosion. However, it can be distinguished by the presence of "tubercules" of biological residue and corrosion products over the pit.

This form of corrosion has been observed in both freshwater and seawater and in many cases requires oxygenated water to support the metal dissolution reaction, as shown in Figure 6.15 [8]. In general, the presence of specific "metal-munching" bacteria, a warm-water (20–40°C) oxygenated environment, and specific materials are required to support MIC. This form of corrosion has been reported in a wide range of materials, including iron and steel, stainless steels, copper alloys, and aluminum alloys. Austenitic stainless steels seem to be particularly susceptible, and the presence of a two-phase austenite + ferrite microstructure, such as that present in many weld metals, seems to influence susceptibility. Studies have shown that MIC occurs preferentially in the ferrite phase.
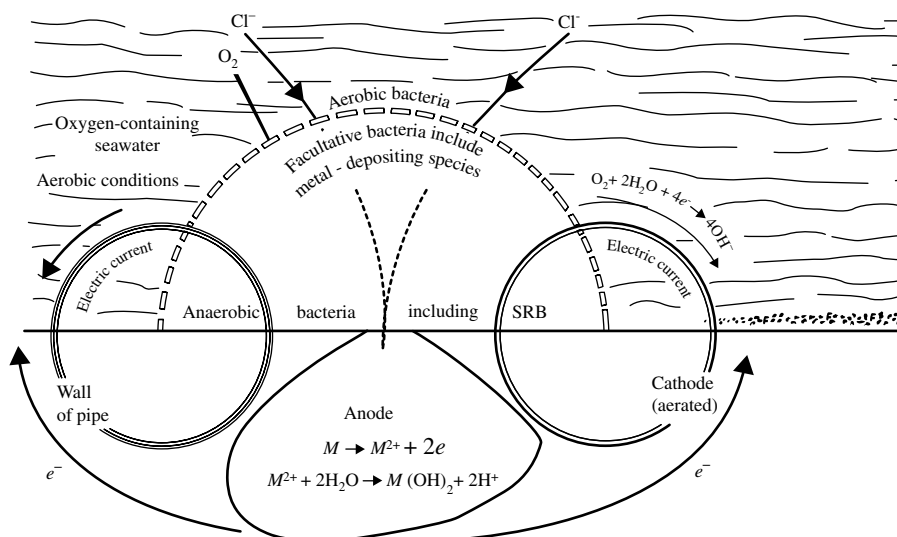
Reactions possible under tubercules created by metal depositing bacteria

FIGURE 6.15 Mechanism for microbiologically induced corrosion (MIC) (From Ref. [8]. © NACE).
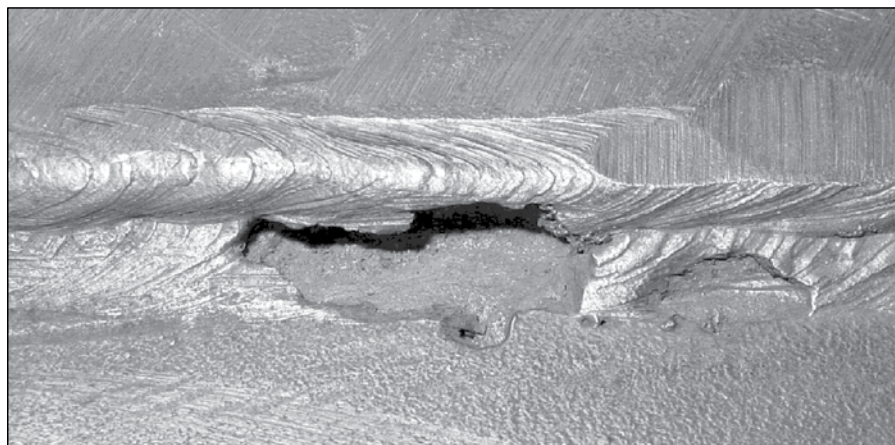

FIGURE 6.16   MIC attack in Type 308 weld metal (Courtesy of Chris Hayes).

An example of MIC that occurred during the construction of a storage tank is shown in Figure 6.16. This is a shielded metal arc weld using E308-16 and joining two Type 304 plates in a butt weld configuration. The ferrite content of the weld metal was FN 10 (~10 vol%). During construction, water was allowed to accumulate in the bottom of the tank covering the weld shown in Figure 6.16. This created the environment for MIC, as evidenced by the severe attack of the weld metal.

6.3   CORROSION TESTING

Knowledge of corrosion behavior is an important part of alloy and filler metal selection for welded construction. While there is considerable corrosion data for most base metals, sufficient corrosion data to support the selection of welding processes and filler metals to prevent corrosion attack may not be available. In many situations, corrosion may represent the most significant factor relative to the service lifetime of a welded component. There are many examples of how rapid corrosion or corrosion-related cracking has led to premature, and sometimes catastrophic, failure.

Fortunately, there are many corrosion tests that have been developed over the years that can be used to quantify susceptibility to various the forms of corrosion. Many of these have been standardized by codes such as those published by the American Society for Testing and Materials (ASTM) and the National Association of Corrosion Engineers (NACE). Most of these test methods are designed for laboratory use and accelerate the attack that might be experienced in service. These include immersion tests, where samples are simply exposed to an aggressive environment and evaluated on a periodic basis, and electrochemical tests, where an electrical potential is applied to the material. ASTM Volume 03.02: Corrosion of Metals; Wear and Erosion describes many of these test techniques. Tests for IGC in stainless steels are described in ASTM A262. Some examples of commonly used corrosion tests that are applicable to testing and qualification of welds are briefly described here.

6.3.1   Atmospheric Corrosion Tests

The standard practice for conducting atmospheric corrosion tests is described in ASTM G50. For simple exposure tests, samples are mounted on a test rack and checked periodically. To determine, general corrosion rates, samples are simply weighed and weight loss is converted to corrosion rate in terms of mils/year (or mm/year). In other cases, the sample may be simply observed or photographed to determine the onset of staining, pitting, or other surface effects. Welded samples are often exposed in a U-bend configuration where the weld is bent in a longitudinal direction to provide equal straining in the weld metal and HAZ. The procedures for stress corrosion testing of welded samples for atmospheric exposure are described in ASTM G58.

6.3.2   Immersion Tests

In order to accelerate corrosion attack, samples are often immersed in an aggressive solution. These tests are widely used to evaluate susceptibility to pitting, crevice corrosion, and IGC. Many of these are described in ASTM standards. A partial list of such standards for determining susceptibility to IGC in stainless steels, nickel-base alloys, and aluminum alloys (5xxx series) is provided in Table 6.6. Procedures for sample preparation are very important since the surface condition will influence the degree of attack. These procedures are described in ASTM G31: Standard Practice for Laboratory Immersion Corrosion Testing of Metals.

TABLE 6.6   Immersion tests for evaluation of intergranular corrosion

Alloy	UNS number	Applicable ASTM standard	Solution	Immersion time (h)
Ferritic stainless steels				
Type 430	S43000			24
Type 446	S44600	A763-X	Ferric sulfate	72
26-1	S44625			120
Austenitic stainless steels				
Type 304/316	S30400/S31600	A262-A	Oxalic acid[a]	
		A262-B	Ferric sulfate	120
Type 321/347	S32100/	A262-C	Nitric acid	240
	S34700			
Nickel-base alloys				
Alloy 625	N06625	G28-A	Ferric sulfate	120
Alloy 690	N06690	A262-C	Nitric acid	240
Hastelloy C-4	N06455	G28-A	Ferric sulfate	24
Aluminum alloys				
5xxx alloys	A95005–95657	G67	Nitric acid	24

[a]Electrolytic test etched at $1\,A/cm^2$ for 1.5 min.

Most of these tests work quite well for welded samples. For base metal samples, weight loss is a good measure of corrosion rate. For samples containing welds, the attack may be localized and periodic removal of the sample from the solution is required to determine the location of the IGA. For example, a welded Type 304 stainless steel sample may undergo IGA in the HAZ well before any attack occurs in the base metal.

In some cases, it may be possible to use thermal simulation to produce samples with a HAZ microstructure. The sample shown in Figure 6.8b is a Type 304L stainless steel that was heated to 1300°C in a Gleeble™ thermomechanical simulator and then cooled at a specific rate to allow grain boundary carbide precipitation. This sample was then subjected to ASTM A262-A (oxalic acid) to produce the grain boundary attack shown.

There are also a number of immersion tests that are used to determine susceptibility to SCC. The sample types and configurations are described in ASTM G58. Two commonly used specimen types are the U-bend and C-ring configurations shown in Figure 6.17 [9]. Note that both of these use a bolt to apply the stress to the sample. This can sometimes create a problem with crevice corrosion unless precautions are taken to mask this area of the sample. Stainless steels and nickel-base alloys are often tested in boiling magnesium chloride to determine susceptibility to chloride SCC. This procedure is described in ASTM G36. Aluminum alloys of the 2XXX and 7XXX types are tested by immersion in a 3.5% NaCl solution. For the SCC immersion tests, the samples must be removed from the solution periodically to check for cracking.
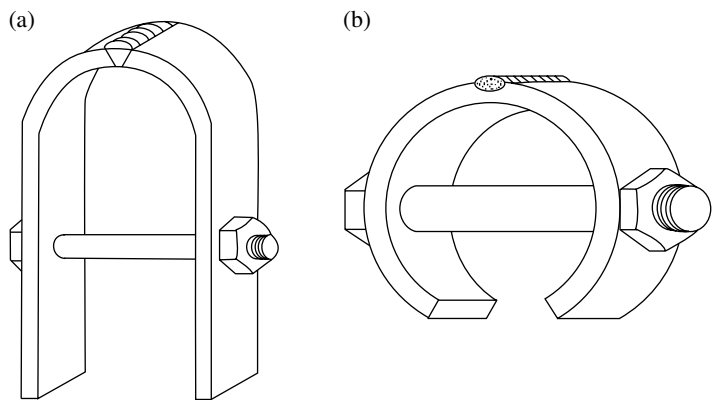
FIGURE 6.17 Welded specimen types for immersion corrosion tests. (a) U-bend and (b) C-ring (From Ref. [9]. © ASTM).
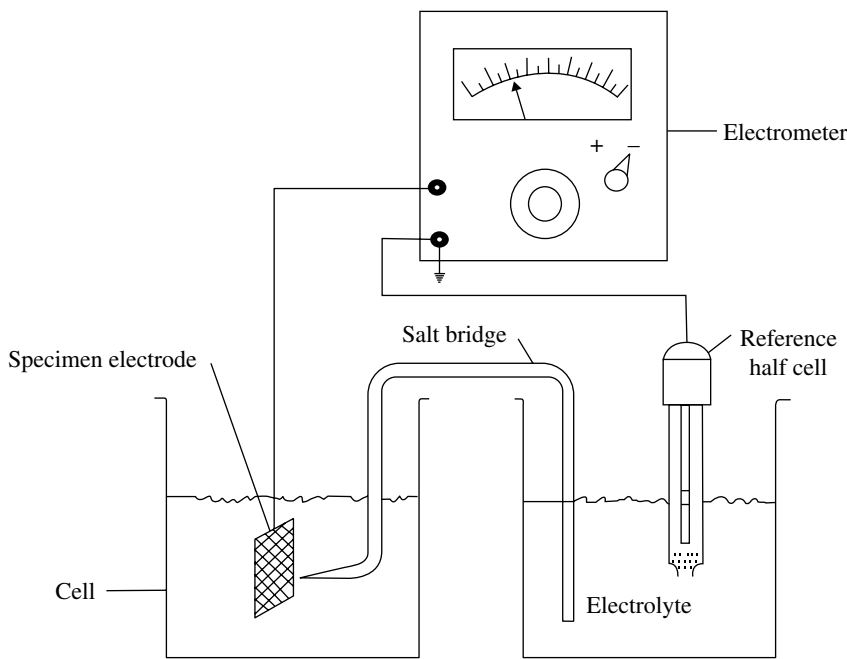

FIGURE 6.18 Configuration for performing electrochemical polarization tests (From Ref. [10]. © ASTM).

6.3.3 Electrochemical Tests

Electrochemical tests are commonly used to measure corrosion behavior in a wide range of metals. The basic procedure uses a potentiostat consisting of a reference electrode and a polarization cell as shown in Figure 6.18 [10]. The potential is
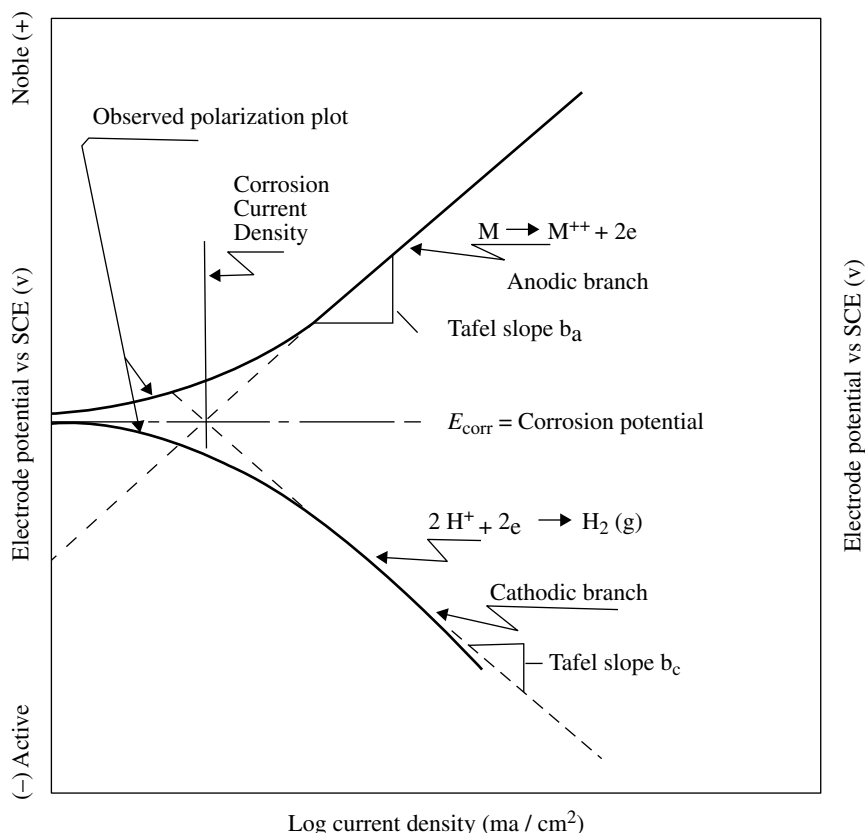
FIGURE 6.19 Tafel polarization plot from electrochemical testing (From Ref. [10]. © ASTM).

scanned from the active to passive region, and the current density in the sample is measured. An example of a polarization plot using this method is shown in Figure 6.19 [10]. Above the so-called open circuit potential of the material, the sample is anodic (active), and below this potential, it is cathodic. By measuring the slopes of these curves, a value of the corrosion current density at the open circuit potential can be determined. This value, taken from what is called the Tafel polarization plot, can be used to estimate the general corrosion behavior of a material. The procedure for estimating general corrosion rates is described in ASTM G105: Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements.

Electrochemical methods can also be used to determine susceptibility to localized corrosion, such as pitting. An example of the potentiodynamic polarization response of a material exhibiting passive anodic behavior (such as a stainless steel) is shown in Figure 6.20 [10]. From this plot, a critical pitting potential can be determined that is related to the breakdown of the passive surface film on the sample. Another test
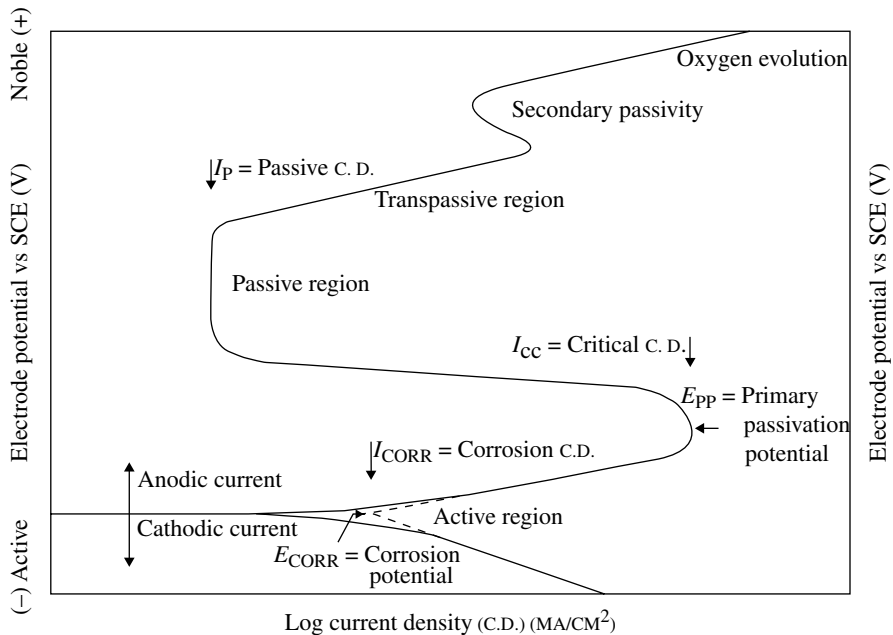
FIGURE 6.20 Hypothetical anodic and cathodic polarization plot for a material exhibiting passive anodic behavior (From Ref. [10]. © ASTM).

known as the electrochemical potentiostatic reactivation (EPR) test has been used to determine the degree of sensitization in stainless steels.

Electrochemical tests can be useful for determining the corrosion behavior of weld metals. Since the sample size is relatively small, all weld metal samples can be excised from weldments. It may also be possible to evaluate HAZ behavior, especially if a thermal simulator (such as the Gleeble) is used to generate samples of appropriate microstructure.

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