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## Part 2: Corrosion Mechanisms

*[This is the second of a three-part series of articles on the use of stainless steel and nickel alloys in the fluid control industry. Part I covered the types of stainless steel and their classification. Part II discusses the corrosion mechanisms that affect performance, and Part III the proper selection of stainless steels.]*

**I**n part I of this series, we established the basic criterion for stainless steel, namely that the steel must contain a minimum of 10.5 percent chromium to impart resistance to rusting or oxidation. Other alloying elements are added to enhance the corrosion resistance or mechanical properties. In this article, we will discuss the corrosion mechanisms, and some of the reasons certain alloys exist. All metals are prone to corrosion. There is not one that will not corrode in some environment. Fortunately, not all metals are subject to corrosion in the same environment. Thus, we have a choice in determining the proper material for each environment.

What is corrosion? Technically, it is the tendency of any metal to return to its most stable thermodynamic state. Namely, that with the most negative free energy of formation. More simply stated, it is a chemical reaction of the metal with the environment to form an oxide, carbonate, sulfate or other stable compound. Corrosion is expensive, costing more than \$3 billion a year. Corrosion affects every facet of life, from the delays on the interstate because of replacement of rusting bridges or rebar; to spoiled food from perforated cans; to grounded aircraft because of failed rivets; to derated power stations because of leaking condenser or feedwater heater tubes; to leaking nuclear fuel canisters. In most of these cases, using a different alloy, material, proper coating or impressed current could have prevented the problems.

When a metal part fails in service, it is essential to determine the cause of the failure, so that the replacement part can be manufactured from the proper alloy to prevent future failure. Many times, a failed part is replaced with the same alloy. For example, if a control valve is made from Type 304L stainless steel and it fails by chloride stress corrosion cracking, replacing with the same alloy will assure failure within the same time frame. If a change of alloy is made, say to a six-percent Mo stainless steel, the control valve may last for the lifetime of the system.

Corrosion can be broadly classified in two forms: chemical dissolution of the metal, and galvanic, or electrically driven. Abrasion, fretting or erosion sometimes is classified as a corrosion mechanism, but, technically, they are a mechanical metal removal process, as compared to a chemical removal process. Chemical action may be associated with the mechanical removal process to speed up the dissolution, but the chemical reaction will fit into the two basic forms. Within these two basic classifications there are five types of corrosion: general or uniform corrosion; intergranular corrosion; galvanic corrosion, including pitting and crevice corrosion; stress corrosion cracking and or microbiologically-induced corrosion (MIC). Many times, a metal starts to corrode by one mechanism, for example, pitting corrosion, then fails by a second mechanism, stress corrosion cracking.

### BASIC CORROSION RESISTANCE

A metal derives its corrosion resistance by forming a protective oxide on the surface. Metals may

Metal	Volts	Corresponding alloy
Corroded end (anodic or least noble)		
Magnesium	-1.55	Magnesium
Aluminum	-1.33	Aluminum
Zinc	-0.76	Zinc
Iron	-0.44	Steel, iron, stainless steel (active), Alloy C (alloy)
Nickel	-0.23	Nickel (active), Alloy 600 (active), Alloy B-2
Hydrogen	0.00	
Copper	+0.34	Brass, copper, Monel, nickel (passive), Alloy 600 (passive), stainless steel (passive)
Silver	+0.80	Silver
Gold	+1.36	Gold
Protected end (cathodic or most noble)		

Table I: A Simplified Galvanic Series of Metals and Alloys

be classified in two categories, depending on the nature of the oxide film: active and passive. With active film metals, the oxide film continuously grows, until it reaches a limiting thickness, then sloughs off, continues to grow, then sloughs off until the metal is completely consumed. Examples of metals with active oxides are iron, copper and zinc. Passive film metals form an extremely thin oxide layer, in the order of 30 to 300 atoms thick, then stop growing. This film remains stable, until something upsets the equilibrium. Examples of passive film metals are stainless steel, titanium, gold, platinum and silver.

## GENERAL OR UNIFORM CORROSION

Uniform corrosion occurs over large areas of the metal surface. This is the most common form of corrosion with steel and copper. It is the easiest form of corrosion to measure, and service lifetime is easy to calculate. This is the only form of corrosion that may be accurately calculated for failure lifetime. This type of corrosion is measured by corrosion rate, usually reported as mpy (mils per year); mm/y (millimeters per year); ipm (inches per month) or mg/sdm/yr (milligrams per square decimeter per year). This type of corrosion may be minimized in the active metals by painting the surface, and unexpected failures can be avoided by periodic inspections.

Stainless steel is subject to general corrosion in many acids and some salt solutions. They are not subject to general corrosion in water, therefore no data is available.

## GALVANIC CORROSION

Galvanic corrosion occurs whenever two electrically different metals are connected in a circuit and are in an electrically conductive solution. This type of corrosion requires three elements: two metals that differ in the galvanic or electromotive series; an electrically conductive path between the metals and both metals submerged in a conductive solution. A variation of this can occur with passive film metals that have lost the passive film in one spot and the metal becomes active in that area. Thus, the metal has both passive and active sites on the same surface. This is the mechanism for pitting and crevice corrosion. Table I, on page 35, is a list of materials and their relative position in the galvanic series.

- **Pitting corrosion** is a form of galvanic corrosion, wherein the chromium in the passive layer is dissolved, leaving only the corrosion prone iron and an active site. The voltage difference between the passive and active layer on an austenitic stainless steel is 0.78 volts. Acid chlorides are the most common cause of pitting with stainless steel. Chlorides are deadly to stainless because they form chromium chloride ( $\text{CrCl}_2$ ), which is very soluble in water. This allows the chromium to be removed from the passive layer, leaving only the active iron oxide. As the chromium is dissolved, the electrically driven chlorides

bore into the stainless steel, creating a spherical, smooth wall pit. The residual solution in the pit is ferric chloride,  $\text{FeCl}_3$ , which is very corrosive to stainless steel. This is the reason ferric chloride is used in so many of the corrosion tests for stainless steel. When molybdenum and/or nitrogen is used as an alloying element in stainless steel, the pitting corrosion resistance improves. In an attempt to quantify the effect of alloying elements, a relationship of the various elements responsible for corrosion resistance was developed. The resulting equation is called the pitting resistance equivalent number, or PREN. It has a number of different coefficients; the most commonly used form is:

$$\text{PREN} = \% \text{Cr} + 3.3(\% \text{Mo}) + 16(\% \text{N})$$

A PREN of 32 is considered the minimal for seawater pitting resistance.

Higher temperature and lower pH influence pitting, and conversely, at lower temperatures and a higher pH, the alloy may be immune to pitting. There is a threshold below which pitting corrosion will not take place, and the higher above the threshold, the more rapidly pitting occurs. Pitting can occur rather rapidly once it starts. For example, under the right conditions of chloride content, pH and temperature, a Type 304 tube with a 0.035-inch (0.89 mm.) wall will pit through in less than eight hours.

- **Crevice corrosion** is another form of galvanic corrosion, wherein the corroding metal is in close contact with another metal, a piece of plastic, paint, rubber gasket, rubber band, masking tape or any other material that makes a tight crevice. Like pitting, a conductive solution must be present, and the presence of chlorides makes the reaction proceed at a faster rate. Crevice corrosion is temperature dependent, and will not occur below the critical crevice corrosion temperature (CCCT), but will above. The greater the temperature difference between the CCCT and the environmental temperature, the more rapid the corrosion rate. There is a relationship between the PREN and the CCCT, with the higher the PREN, the higher the CCCT. Also, there is a relationship between the tightness of the crevice, and the onset time and severity of corrosion. For example, one should never wrap stainless steel pipe with Neoprene, then tightly clamp in a pipe hanger if the pipe is in a marine or other environment where airborne chlorides are present. The pipe will crevice corrode under the Neoprene.

## INTERGRANULAR CORROSION

All metals are composed of small grains that normally are oriented in a random fashion. These grains each are composed of orderly arrays of atoms, with the same spacing between the atoms in every grain. Because of the random orientation of the grains, there is a mismatch between the atomic layers where the grains meet. This mismatch is called a grain boundary. In a typical stainless steel product, there are about 1,000 grain boundaries that intersect a one-inch or 25-mm. line drawn on the surface.

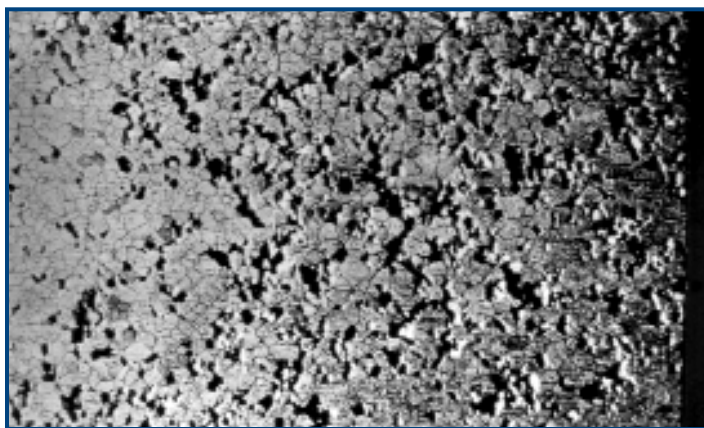


Figure 1  
Appearance of the surface of stainless steel (magnification, 50X) that has undergone intergranular corrosion. This surface is sometimes called "sugared".

Grain boundaries are regions of high-energy concentration. Therefore, chemical or metallurgical reactions usually occur at grain boundaries before they occur within the grains. The most common reaction is formation of chromium carbide in the heat-affected zone (HAZ) during welding. These carbides form along the grain boundaries. Because the carbides require more chromium than is locally available, the carbon pulls chromium from the area around the carbon. This leaves a grain boundary zone, low in chromium, creating a new, low chromium alloy in that region. Now, there is a mismatch in galvanic potential between the base metal and the grain boundary, so galvanic corrosion begins. The grain boundaries corrode, allowing the central grain and the chromium carbides to drop out as so many particles of rusty sand. The surface of the metal develops a “sugary” appearance, as illustrated in Figure 1 (on page 36). When a piece of metal with intergranular corrosion is dropped, it gives off a “thud,” rather than a metallic ring.

Chromium carbide is not the only compound that can cause intergranular corrosion. Other compounds are sigma phase, a chromium-iron compound; chi phase, a chromium-iron-molybdenum compound and several other less often observed compounds. Note these are compounds, not a random mixture or alloy.

These compounds, usually are formed when some type of heating occurs, such as welding, heat treatment or metal fabrication. Understanding how they form makes it relatively easy to control their formation. For example, always use a low carbon grade of stainless steel when welding is to be done. These grades are very common today, ever since the invention of argon – oxygen – decarburization (AOD) refining about 25 years ago. Almost all stainless steel is made by this method, since it allows very precise control of the alloying elements, and it is possible to obtain routinely carbon levels in the range of 0.025 percent, a level at which no chromium carbide particles form in the HAZ during welding. These grades normally are designated as “L” grades, like Types 304L, 316L or 317L. Always use the “L” grades if there is any chance that the system will be welded. Another way of controlling the formation of chromium carbide is to use a stabilizing element addition to the stainless steel. These are titanium and niobium (columbium). The Type 304 equivalent with titanium is Type 321, and the Type 304 equivalent with niobium is Type 347. Stabilized grades should be used whenever the steel is held for long periods in the temperature range of 800 to 1500°F (425 to 800°C). Sigma or chi phase may be minimized by avoiding the temperature range where they form, or by using alloys high in nickel and nitrogen.

## STRESS CORROSION CRACKING

Stress corrosion cracking (SCC) has three components: alloy composition, environment and the presence of tensile stress. All metals are susceptible to stress corrosion cracking, as Table II (page 37) indicates. Nickel containing stainless steel is especially susceptible to

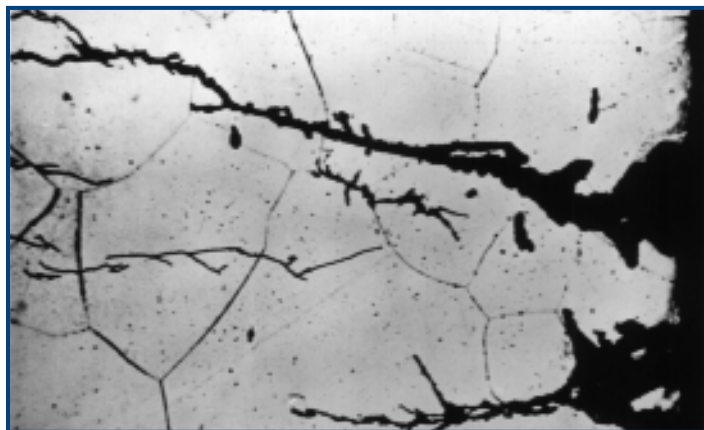


Figure 2 Polished and etched cross-section of stress corrosion cracked stainless steel (magnification 250X) showing the transgranular cracks and feathery appearance of crack tips.

Alloy	Environment
Aluminum alloys	Air Seawater Salt and chemical combinations
Magnesium alloys	Nitric acid Caustic Salts Coastal atmospheres
Copper alloys	Ammonia and ammonium hydroxide Amines Mercury
Carbon steel and iron	Caustic Anhydrous ammonia Nitrate solutions
Martensitic & precipitation hardening stainless steel	Seawater Chlorides Hydrogen sulfide
Austenitic stainless steel	Chlorides, both organic and inorganic Caustic solutions Sulfurous and polythionic acid
Nickel alloys	Caustic above 600°F (315°C) Fused caustic Hydrofluoric acid
Titanium alloys	Seawater Salt atmospheres Fused salt

Table II: Alloy Systems Subject to Stress Corrosion Cracking

chloride-induced SCC. The maximum susceptibility is in the nickel range of about five to 35 percent. The pure ferritics, such as Types 430, 439 and 440 are immune. The point of maximum susceptibility occurs between seven and 20 percent nickel. This makes Types 304/304L, 316/316L, 321, 347, etc., very prone to such failure.

It does not take much chloride to cause failure, a few parts per million will do the job, providing that the pH is low, and oxygen is present. Temperature is important, and there is a threshold temperature below which the steel will not crack. This is related to the critical pitting temperature. Therefore, the threshold temperature increases as the molybdenum content increases. Type 304 may SCC at room temperature, whereas the six percent Mo alloys have a threshold temperature in the range of 450°F (239°C).

The stress component is more subtle. First, the stress must be tensile, and it must exceed the yield strength of the component. On the surface, this sounds simple enough. However, anytime a component is bent, or straightened, the material exceeds the yield strength by definition, since the yield strength must be exceeded to place the material in a fixed shape. Now we add the complication of stress multiplication factors. If a pit or other sharp notch is present, then the residual stress is multiplied by several times, resulting in a stress far in excess of the tensile yield strength. Thus, SCC usually starts with pitting or crevice corrosion as a precursor to forming a stress concentrator.

When the cracks form, they usually are transgranular as illustrated in Figure 2 (on page 37). That is, they crack through the grain. Cracking occurs rapidly, and progresses through the grain, terminating in a feathery cluster of small cracks. This is a characteristic that distinguishes SCC from other types of cracking. Using microprobe analysis, or electron dispersive spectroscopy (EDS), on the crack surface to look for the presence of chlorine, gives conclusive evidence that SCC has occurred.

## MICROBIOLOGICALLY INFLUENCED CORROSION

Microbiologically influenced corrosion (MIC) is a recently discovered phenomenon. Actually, it is not a separate corrosion mechanism, rather a different agent that causes corrosion of metals. It is not limited to stainless steel as Table III (page 38) indicates. Most metals are attacked by some type of bacteria. The mechanism usually is general

Organism	Action	Problem
Desulfovibro Clostridium Thiobacillus	Hydrogen sulfide producer (sulfate reducers)	Corrosive to metals Reduces chromates Destroys chlorine Precipitates zinc
Thiobacillus	Produces sulfuric acid	Corrosive to metals
Nitrobacter Nitrosomonas	Produces nitric acid	Corrosive to active film metals
Gallionella Crenothrix Spaerotilus	Converts soluble ferrous ions to insoluble ferric oxide Converts soluble manganese ions to insoluble manganese dioxide	Produces iron oxides and forms crevices Produces manganese dioxide that can form crevices, or can react with chlorine to produce hydrochloric acid

Table III: Corrosive Microorganisms

or crevice corrosion under the bacteria colonies, as seen in Figure 3 (page 38). In some cases, the metabolic byproducts react with the environmental solution to create a very corrosive media. An example is the reaction of chlorine in water, with the manganese dioxide byproduct from gallionella bacteria, on the surface of the stainless steel. This reaction generates hydrochloric acid, which causes rapid pitting of many common grades of stainless steel.

One of the most common forms of MIC is the metabolic byproduct of the sulfur fixing bacteria that produces sulfurous or sulfuric acid. These bacteria cause rapid corrosion of the lower alloy stainless steels, like Types 304L or 316L, resulting in through wall crevice corrosion under the bacteria colonies.

Other than the use of bactericides, such as chlorine or ozone, the usual solution to this type of corrosion is to use a superferritic or superaustenitic stainless steel.

## CONCLUSION

In the final article of this series, we will present a simplified method of selecting the proper stainless steel for the application. Keep in mind, that the proper selection relies heavily on knowing the corrosion mechanism, and the corrodents that are present. It is essential to know these critical factors: the composition of the solution present; its pH; the temperature; the presence of stresses; whether the solution is aerated or not and the exposure time. Corrosion is an electrochemical reaction. Therefore, it follows basic rules of electrochemistry.

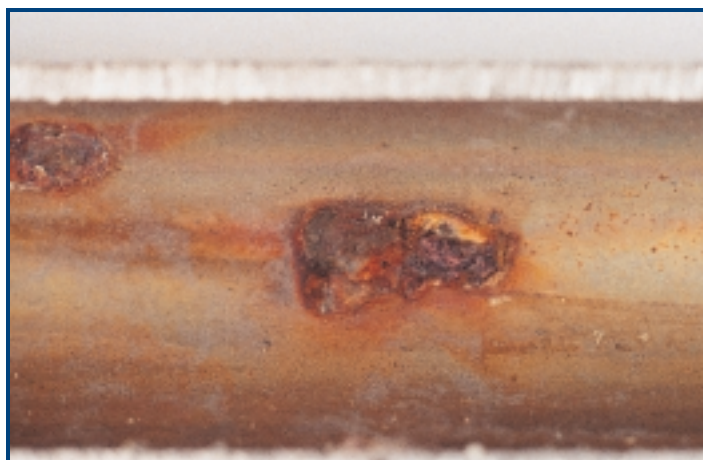


Figure 3  
Crevice corrosion under bacteria colony on the inside of a stainless steel tube (magnification 5X).

Corrosion can be controlled, but it requires application of physical limits, and the proper alloy. Type 304 stainless is not the universal alloy to be used in all applications.

### About the Author

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