The Eight Forms of Corrosion[(1)]

*M. G. FONTANA**

It is convenient to classify corrosion by the forms in which it manifests itself, the basis for this classification being the appearance of the corroded metal. Each form can be identified by mere visual observation. In most cases the naked eye is sufficient, but sometimes magnification is helpful or required. Valuable information for the solution of a corrosion problem can often be obtained through careful observation of the corroded test specimens or failed equipment. Examination *before* cleaning is particularly desirable.

Some of the eight forms of corrosion are unique, but all of them are more or less interrelated. The eight forms are: (1) uniform, or general attack, (2) galvanic, or two-metal corrosion, (3) crevice corrosion, (4) pitting, (5) intergranular corrosion, (6) selective leaching, (7) erosion corrosion, and (8) stress corrosion. This listing is arbitrary but covers practically all corrosion failures and problems. The forms are not listed in any particular order of importance.

Below, the eight forms of corrosion are discussed in terms of their characteristics, mechanisms, and preventive measures. Hydrogen damage, although not a form of corrosion, often occurs indirectly as a result of corrosive attack, and is therefore included.

Uniform Attack

Uniform attack is the most common form of corrosion. It is normally characterized by a chemical or electrochemical reaction which proceeds uniformly over the entire exposed surface or over a large area. The metal becomes thinner and eventually fails. For example, a piece of steel or zinc immersed in dilute sulfuric acid will normally dissolve at a uniform rate over its entire surface. A sheet iron roof will show essentially the same degree of rusting over its entire outside surface. Figure 1 shows a steel tank in an abandoned gold-smelting plant. The circular section near the center of the photograph was thicker than the rest of the tank. This section is now supported by a *lace curtain* of tank bottom metal.

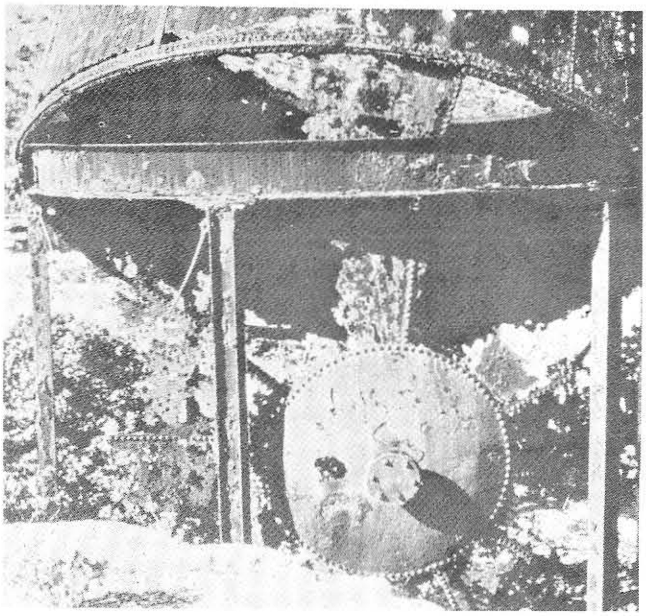


FIGURE 1 – Rusting of abandoned steel tank.

Uniform attack, or general overall corrosion, represents the greatest destruction of metal on a tonnage basis. This form of corrosion, however, is not of too great concern from the technical standpoint, because the life of equipment can be accurately estimated on the basis of comparatively simple tests. Merely immersing specimens in the fluid involved is often sufficient. Uniform attack can be prevented or reduced by (1) proper materials, including coatings, (2) inhibitors, or (3) cathodic protection.

Most of the other forms of corrosion are insidious in nature and are considerably more difficult to predict. They are also localized; attack is limited to specific areas or parts of a structure. As a result, they tend to cause unexpected or premature failures of plants, machines, or tools.

Galvanic or Two-Metal Corrosion

A potential difference usually exists between two dissimilar metals when they are immersed in a corrosive or conductive solution. If these metals are placed in contact (or otherwise electrically connected), this potential difference produces electron flow between them. Corrosion of the less corrosion-resistant metal is usually increased and attack of the more resistant material is decreased, as compared with the behavior of these metals when they are not in contact. The less resistant metal becomes anodic and the more resistant metal cathodic. Usually the cathode or cathodic metal corrodes very little or not at all in this type of couple. Because of the electric currents and dissimilar metals involved, this form of corrosion is called galvanic, or two metal corrosion. It is electrochemical corrosion, but we shall restrict the term galvanic to dissimilar-metal effects for purposes of clarity.

The driving force for current and corrosion is the potential developed between the two metals. The so-called dry-cell battery depicted in Figure 2 is a good example of this point. The carbon electrode acts as a noble or corrosion-resistant metal (the cathode), and the zinc as the anode which corrodes. The moist paste between the electrodes is the conductive (and corrosive) environment

---

(1) From Corrosion Engineering by Fontana and Greene. Copyright 1967 by McGraw-Hill Book Company. Used with permission of McGraw-Hill Book Company.

*Ohio State University, Columbus, Ohio.

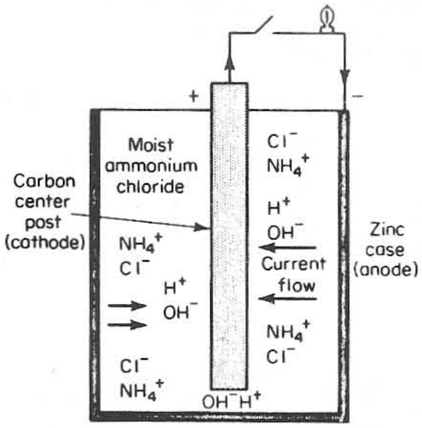


FIGURE 2 – Section of dry-cell battery.

TABLE 1 – Standard EMF Series of Metals

	Metal-Metal Ion Equilibrium (Unit Activity)	Electrode Potential vs Normal Hydrogen Electrode at 25 C, Volts
	$Au\text{-}Au^{+3}$	+1.498
	$Pt\text{-}Pt^{+2}$	+1.200
Noble or cathodic	$Pd\text{-}Pd^{+2}$	+0.987
	$Ag\text{-}Ag^{+}$	+0.799
	$Hg\text{-}Hg_2^{+2}$	+0.788
	$Cu\text{-}Cu^{+2}$	+0.337
	$H_2\text{-}H^{+}$	0.000
	$Pb\text{-}Pb^{+2}$	-0.126
	$Sn\text{-}Sn^{+2}$	-0.136
	$Ni\text{-}Ni^{+2}$	-0.250
	$Co\text{-}Co^{+2}$	-0.277
	$Cd\text{-}Cd^{+2}$	-0.403
	$Fe\text{-}Fe^{+2}$	-0.440
	$Cr\text{-}Cr^{+3}$	-0.744
	$Zn\text{-}Zn^{+2}$	-0.763
Active or anodic	$Al\text{-}Al^{+3}$	-1.662
	$Mg\text{-}Mg^{+2}$	-2.363
	$Na\text{-}Na^{+}$	-2.714
	$K\text{-}K^{+}$	-2.925

Source: A. J. De Bethune and N. A. S. Loud. Standard Aqueous Electrode Potentials and Temperature Coefficients at 25 C, Clifford A. Hampel, Skokie, Ill. (1964).

that carries the current. Magnesium may also be used as the anodic material or outer case.

EMF and Galvanic Series

The potential differences between metals under reversible, or noncorroding conditions form the basis for predicting corrosion tendencies. Briefly, the potential between metals exposed to solutions containing approximately one gram atomic weight of their respective ions (unit activity) are precisely measured at a constant temperature. Table 1 presents such a tabulation, often termed the electromotive force or emf series. For simplicity, all potentials are referenced against the hydrogen electrode (H_2/H^+), which is arbitrarily defined as zero. Potentials between metals are determined by taking the absolute differences between their standard emf potentials. For example, there is a potential of 0.462 volt between reversible copper and silver electrodes and 1.1 volt potential between copper and zinc. It is not possible to establish a reversible potential for alloys containing two or more reactive components, so only pure metals are listed in Table 1.

TABLE 2 – Galvanic Series of Some Commercial Metals and Alloys in Sea Water Commercial Metals and Alloys in Sea Water

↑	Platinum
	Gold
Noble or cathodic	Graphite
	Titanium
	Silver
	Chlorimet 3 (62 Ni, 18 Cr, 18 Mo) Hastelloy C (62 Ni, 17 Cr, 15 Mo)
	18-8 Mo stainless steel (passive) 18-8 stainless steel (passive)
	Chromium stainless steel 11-30% Cr (passive) Inconel (passive)
	Silver Solder
	Monel (70 Ni, 30 Cu) Cupronickels (60-90 Cu, 40-10 Ni) Bronzes (Cu-Sn) Copper Brasses (Cu-Zn)
	Chlorimet 2 (66 Ni, 32 Mo, 1 Fe) Hastelloy B (60 Ni, 30 Mo, 6 Fe, 1 Mn)
	Inconel (active) Nickel (active)
	Tin
	Lead
	lead-tin solders
	18-8 Mo stainless steel (active) 18-8 stainless steel (active)
	Ni-Resist (high Ni cast iron)
	Chromium stainless steel, 13% Cr (active)
	Cast iron Steel or iron
	2024 aluminum (4.5 Cu, 1.5 Mg, 0.6 Mn)
Active or anodic	Cadmium
	Commercially pure aluminum (1100)
↓	Zinc
	Magnesium and magnesium alloys

In actual corrosion problems, galvanic coupling between metals in equilibrium with their ions rarely occurs. As noted above, most galvanic corrosion effects result from the electrical connection of two corroding metals. Also, since most engineering materials are alloys, galvanic couples usually include one (or two) metallic alloys. Under these conditions, the galvanic series listed in Table 2 yields a more accurate prediction of galvanic relationships than the emf series. Table 2 is based on potential measurements and galvanic corrosion tests in unpolluted seawater conducted by The International Company at Harbor Island, N.C. Because of variations between tests, the relative positions of metals, rather than their potentials, are indicated. Ideally, similar series for metals and alloys in all environments at various temperatures are needed, but this would require an almost infinite number of tests.

In general, the positions of metals and alloys in the galvanic series agree closely with their constituent elements in the emf series. Passivity influences galvanic corrosion behavior; note in Table 2 the more noble position assumed by the stainless steels in the passive state as compared with the lower position of these materials when in the active condition. Similar behavior is exhibited by Inconel, which can be considered as a stainless nickel.

Another interesting feature of the galvanic series is the brackets shown in Table 2. The alloys grouped in these brackets are somewhat similar in base composition, for example, copper and copper alloys. The brackets indicate that in most practical applications there is a little danger of galvanic corrosion if metals in a given bracket are coupled or in contact with each other. This is because these materials are close together in the series and the potential generated by these couples is not great. The farther apart in the series, the greater the potential generated.

In the absence of actual tests in a given environment, the galvanic series gives us a good indication of possible galvanic effects. Consider some actual failures in view of the data shown in Table 2. A yacht with a Monel hull and steel rivets became unseaworthy because of rapid corrosion of the rivets. Severe attack occurred on aluminum tubing connected to brass return bends. Domestic hot-water tanks made of steel fail where copper tubing is connected to the tank. Pump shafts and valve stems made of steel or more corrosion resistant materials fail because of contact with graphite packing.

Galvanic corrosion sometimes occurs in unexpected places. For example, corrosion was noted on the leading edges of inlet cowlings on jet engines. This attack was caused by the fabric used on the engine inlet duct plugs. This was a canvas fabric treated with a copper salt to prevent mildew. Treatment of fabric is common practice for preventing mildew, flameproofing, and for other reasons. The copper salt deposited copper on the alloy steel, resulting in galvanic attack of the steel. This problem was solved by using a vinyl-coated nylon, which contained no metal.

These examples emphasize the fact that the design engineer should be particularly aware of the possibilities of galvanic corrosion, since he specifies the detailed materials to be used in equipment. It is sometimes economical to use dissimilar materials in contact, for example, water heaters with copper tubes and cast iron or steel tube sheets. If galvanic corrosion occurs, it accelerates attack on the heavy tube sheet (instead of the thin copper tubes), and long life is obtained because of the thickness of the tube sheets. Accordingly, expensive bronze tube sheets are not required. For more severe corrosion conditions, such as dilute acidic solutions, the bronze tube sheets would be necessary.

The potential generated by a galvanic cell consisting of dissimilar metals can change with time. The potential generated causes a flow of current and corrosion to occur at the anodic electrode. As corrosion progresses, reaction products or corrosion products may accumulate at either the anode or cathode or both. This reduces the speed at which corrosion proceeds.

In galvanic corrosion, polarization of the reduction reaction (cathodic polarization) usually predominates. Since the degree of cathodic polarization and its effectiveness varies with different metals and alloys, it is necessary to know something about their polarization characteristics before predicting the extent or degree of galvanic corrosion for a given couple. For example, titanium is very noble (shows excellent resistance) in sea water, yet galvanic corrosion on less resistant metals when coupled to titanium, is usually not accelerated very much or is much less than would be anticipated. The reason is that titanium cathodically polarizes readily in sea water.

Summarizing, the galvanic series is a more accurate representation of actual galvanic corrosion characteristics than the emf series. However, there are exceptions to the galvanic series, as will be discussed later, so corrosion tests should be performed whenever possible.

TABLE 3 — Change in Weight of Coupled and Uncoupled Steel and Zinc, g and Uncoupled Steel and Zinc, g

	Uncoupled		Coupled	
Environment	Zinc	Steel	Zinc	Steel
0.05M $MgSO_4$	0.00	-0.04	-0.05	+0.02
0.05M Na_2SO_4	-0.17	-0.15	-0.48	+0.01
0.05M NaCl	-0.15	-0.15	-0.44	+0.01
0.005M NaCl	-0.06	-0.10	-0.13	+0.02

Environmental Effects

The nature and aggressiveness of the environment determine to a large extent the degree of two-metal corrosion. Usually the metal with lesser resistance to the given environment becomes the anodic member of the couple. Sometimes the potential reverses for a given couple in different environments. Table 3 shows the more or less typical behavior of steel and zinc in aqueous environments. Usually both steel and zinc corrode by themselves, but when they are coupled, the zinc corrodes and the steel is protected. In the exceptional case, such as some domestic waters at temperatures over 82 C (180 F), the couple reverses and the steel becomes anodic. Apparently the corrosion products on the zinc, in this case, make it act as a surface noble to steel.

Tantalum is a very corrosion-resistant metal. It is anodic to platinum and carbon, but the cell is active only at high temperatures. For example, in the tantalum-platinum couple current does not begin to flow until 110 C (230 F) is reached and 100 ma/ft^2 flows at 265 C (509 F). Tantalum is cathodic to clean high-silicon iron in strong sulfuric acid, but the current drops rapidly to zero. Above 145 C (293 F) the polarity of the cell is reversed. Tantalum should not be used in contact with anodic metals, because it absorbs cathodic hydrogen and becomes brittle.

Galvanic corrosion also occurs in the atmosphere. The severity depends largely on the type and amount of moisture present. For example, corrosion is greater near the seashore than in a dry rural atmosphere. Condensate near a seashore contains salt, and therefore, is more conductive (and corrosive) and a better electrolyte than condensate in an inland location, even under equal humidity and temperature conditions. Atmospheric exposure tests in different parts of the country have shown zinc to be anodic to steel in all cases, aluminum varied, and tin and nickel always cathodic. Galvanic corrosion does not occur when the metals are completely dry, since there is no electrolyte to carry the current between the two electrode areas.

Distance Effect

Accelerated corrosion due to galvanic effects is usually greatest near the junction, with attack decreasing with increasing distance from that point. The distance affected depends on the conductivity of the solution. This becomes obvious when the path of the current flow and the resistance of the circuits are considered. In high-resistance, or quite pure, water the attack may be a sharp groove. Two-metal corrosion is readily recognized by the localized attack near the junction.

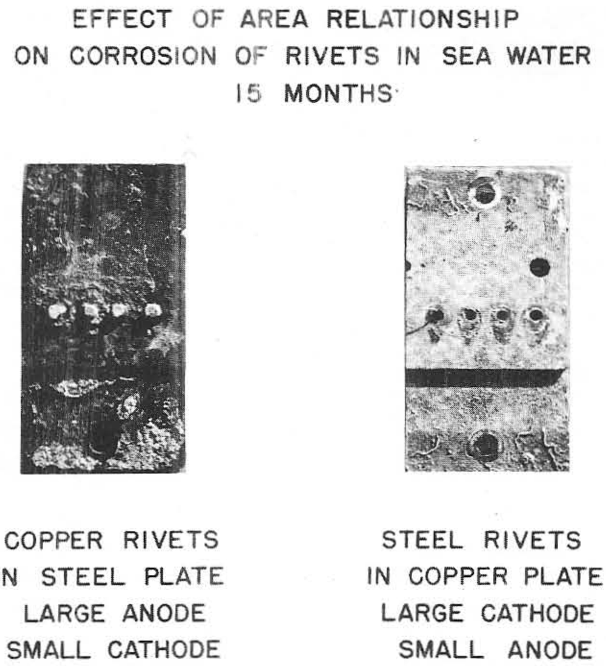


FIGURE 3 – Area effect on steel-copper couple (International Nickel Company).

Area Effect

Another important factor in galvanic corrosion is the area effect, or the ratio of the cathodic to anodic areas. An unfavorable area ratio consists of a large cathode and a small anode. For a given current flow in the cell, the current density is greater for a small electrode than for a larger one. The greater the current density at an anodic area, the greater the corrosion rate. Corrosion of the anodic area may be 100 or 1000 times greater than if the anodic and cathodic areas were equal in size. Figure 3 shows two good examples of the area effect. The specimens are riveted plates of copper and steel both exposed in the ocean for 15 months at the same time. On the left are steel plates with copper rivets; on the right, copper plates with steel rivets. Copper is the more noble, or more resistant, material to seawater. The steel plates in the left specimen are somewhat corroded, but a strong joint still exists. The specimen on the right has an unfavorable area ratio, and the steel rivets are completely corroded. The rate or intensity of attack is obviously much greater on the specimen (the steel rivets) coupled to the large copper cathodic area.

Violation of the above simple principle often results in costly failures. For example, a plant installed several hundred large tanks in a major expansion program. Most of the older tanks were made of ordinary steel and completely coated on the inside with a baked phenolic paint. The solutions handled were only mildly corrosive to steel, but contamination of the product was a major consideration. The coating on the floor was damaged also because of mechanical abuse, and some maintenance was required. To overcome this situation, the bottoms of the new tanks were made of mild steel clad with 18-8 stainless steel. The tops and sides were of steel, with the sides welded to the stainless clad bottoms as illustrated by Figure 4. The steel was coated with the same phenolic paint, with the coating covering only a small portion of the stainless steel below the weld.

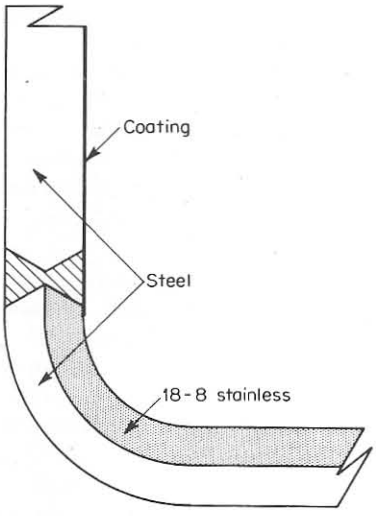


FIGURE 4 – Detail of welded steel and stainless clad tank construction.

A few months after start-up of the new plant, the tanks started failing because of perforation of the side walls. Most of the holes were located within a 2 inch band above the weld shown in Figure 4. Some of the all-steel tanks had given essentially trouble-free life for periods as long as 10 to 20 years as far as side-wall corrosion was concerned.

The explanation for the above failure is as follows. In general, all paint coatings are permeable and may contain some defects. For example, this baked phenolic coating would fail in double-distilled water service. Failure of the new tanks resulted from the unfavorable area effect. A small anode developed on the mild steel side plates. This area was in good electrical contact with the large stainless steel bottom surface. The area ratio of cathode to anode was almost infinitely large, causing very high corrosion rates in the order of 1000 mpy.

An interesting sidelight was the plant's claim that the tanks failed because of a poor coating job near the welds. They demanded recoating by the applicator; this would have cost more than the original job because of the need for sandblasting to remove the adherent phenolic coating instead of sandblasting a rusted surface. But failure would still occur at a rapid rate.

The plant *proved* that galvanic corrosion was not an important factor by conduction corrosion tests on specimens of equal area in boiling solutions. The solutions were boiled to accelerate the test, but boiling removed dissolved gases and actually decreased the aggressiveness of the environment. This problem was solved by coating the stainless steel tank bottoms, which reduced the exposed cathode area.

In another plant using similar solutions, failure of the coating was accelerated because of uncoated bronze manhole doors. Bronze doors had been substituted from cast steel ones because delivery time for the former was better! In this plant, comparative tests were made on two large tanks side by side in actual service, with the only known variable consisting of bronze doors, one coated and one not coated. This test showed clearly the acceleration of failure because of the bronze.

These examples demonstrate an axiom relating to coatings. If one of two dissimilar metals in contact is to be coated, the more noble or more corrosion resistant metal should be coated. This may sound like painting the lily to

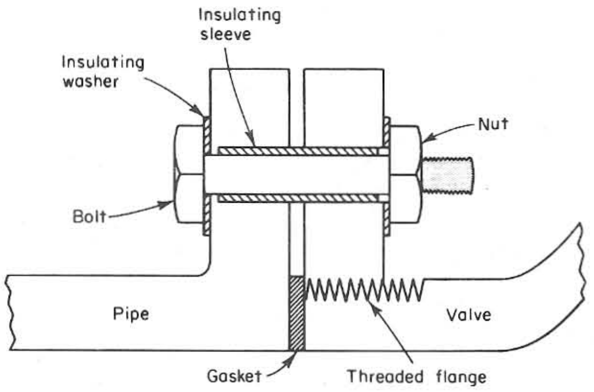


FIGURE 5 – Proper insulation of a flanged joint.

the uninitiated, but the above information should clarify this point.

Prevention

A number of procedures or practices can be used for combating or minimizing galvanic corrosion. Sometimes one is sufficient, but a combination of one or more may be required. These practices are as follows:

1. Select combinations of metals as close together as possible in the galvanic series.

2. Avoid the unfavorable area effect of a small anode and large cathode. Small parts such as fasteners sometimes work well for holding less resistant materials.

3. Insulate dissimilar metals wherever practicable. It is important to insulate completely if possible. A common error in this regard concerns bolted joints such as two flanges, like a pipe to a valve, where the pipe might be steel or lead and the valve a different material. Bakelite washers under the bolt heads and nuts are assumed to insulate the two parts, yet the shank of the bolt touches both flanges! This problem is solved by putting plastic tubes over the bolt shanks, plus the washers, so the bolts are isolated completely from the flanges. Figure 3 shows proper insulation for a bolted joint. Tape and paint to increase resistance of the circuit are alternatives.

4. Apply coatings with caution. Avoid situations similar to that described in connection with Figure 4. Keep the coatings in good repair, particularly the one on the anodic member.

5. Add inhibitors, if possible, to decrease the aggressiveness of the environment.

6. Avoid threaded joints for materials far apart in the series. As shown in Figure 5, much of the effective wall thickness of the metal is cut away during the threading operation. In addition, spilled liquid or condensed moisture can collect and remain in the thread grooves. Brazed joints are preferred, using a brasing alloy more noble than at least one of the metals to be joined. Welded joints using welds of the same alloy are even better.

7. Design for the use of readily replaceable anodic parts or make them thicker for longer life.

8. Install a third metal which is anodic to both metals in the galvanic contact.

Beneficial Applications

Galvanic corrosion has several beneficial or desirable applications. As noted before, dry cells and other primary batteries derive their electric power by galvanic corrosion of an electrode. It is interesting to note that if such a battery is used to the point where the zinc case is perforated and leakage of the corrosive electrolyte occurs, it becomes a galvanic corrosion problem! Some other beneficial applications are briefly described below:

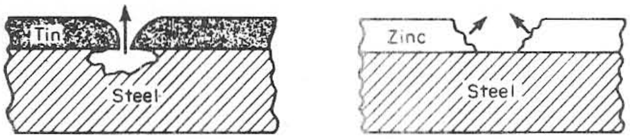


FIGURE 6 – Galvanic corrosion at perforation in tin and zinc-coated steel. Arrows indicate corrosive attack.

Cathodic Protection. The concept of cathodic protection is introduced at this point because it often utilizes the principles of galvanic corrosion. Cathodic protection is simply the protection of a metal structure by making it the cathode of a galvanic cell. Galvanized (zinc coating) is put on the steel, not because it is corrosion resistant, but because it is not. The zinc corrodes preferentially and protects the steel, as shown by Table 3 and Figure 6. Zinc acts as a sacrificial anode. In contrast, tin, which is more corrosion resistant than zinc, is sometimes undesirable as a coating because it is usually cathodic to steel. At perforations in the tin coating, the corrosion of the steel is accelerated by galvanic action. Magnesium is often connected to underground steel pipes to suppress their corrosion (the magnesium preferentially corrodes). Cathodic protection is also obtained by impressing a current from an external power source through an inert anode.

Cleaning Silver. Another useful application concerns the use of galvanic corrosion for cleaning silverware in the home. Most household silver is cleaned by rubbing with an abrasive. This removes silver and is particularly bad for silver plate because the plating is eventually removed. Many of the stains on silverware are due to silver sulfide. A simple electrochemical cleaning method consists of placing the silver in an aluminum pan containing water and baking soda (do not use sodium chloride). The current generated by the contact between silver and aluminum causes the silver sulfide to be reduced back to silver. No silver is actually removed. The silver is then rinsed and washed in warm soapy water. It does not look quite as nice as a polished surface but it saves wear and tear on the silver and also on the husband or wife (or child) who has to do the job. Simultaneous use of ultrasonic cleaning is faster and better, but this equipment is not generally available.

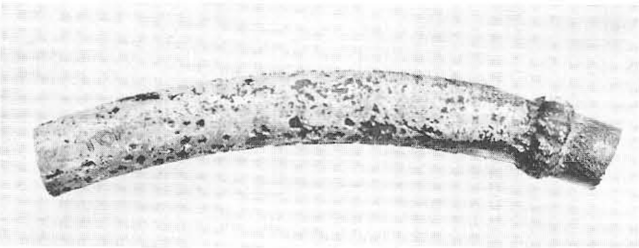
One will sometimes see for sale a piece of *magic metal* which will do the same thing. The directions call for placing it in an enameled pan. The so called magic metal is usually a piece of magnesium or aluminum.

Crevice Corrosion

Intense localized corrosion frequently occurs within crevices and other shielded areas on metal surfaces exposed to corrosives. This type of attack is usually associated with small volumes of stagnant solution caused by holes, gasket surfaces, lap joints, surface deposits, and crevices under bolt and rivet heats. As a result, this form of corrosion is called crevice corrosion or, sometimes, deposit or gasket corrosion.

Environmental Factors

Examples of deposits which may produce crevice corrosion (or deposit attack) are sand, dirt, corrosion products, and other solids. The deposit acts as a shield and



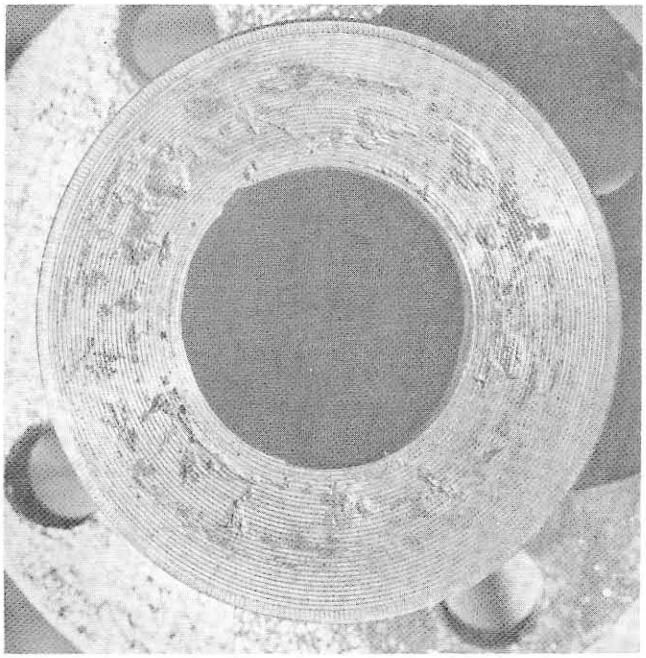


FIGURE 8 – Gasket (crevice) corrosion on a large stainless steel pipe flange (E. V. Kunkel).

creates a stagnant condition there under. The deposit could also be a permeable corrosion product. Figure 7 shows crevice corrosion of a pure-silver heating coil after a few hours of operation. Solids in suspension or solution tend to deposit on a heating surface. This happened in this case, causing the corrosion shown. The silver lining in the tank containing this coil showed no attack because no deposit formed there.

Contact between metal and nonmetallic surfaces can cause crevice corrosion as in the case of a gasket. Wood, plastics, rubber, glass, concrete, asbestos, wax, and fabrics are examples of materials that can cause this type of corrosion. Figure 8 is a good example of crevice corrosion at a gasket-stainless steel interface. The inside of the pipe is negligibly corroded. Stainless steels are particularly susceptible to crevice attack. For example, a sheet of 18-8 stainless steel can be cut by placing a stretched rubber band around it and then immersing it in seawater. Crevice attack begins and progresses in the area where the metal and rubber are in contact.

To function as a corrosion site, a crevice must be wide enough to permit liquid entry, but sufficiently narrow to maintain a stagnant zone. For this reason, crevice corrosion usually occurs at openings a few thousandths of an inch or less in width. It rarely occurs within wide (e.g., 1/8 inch) grooves or slots. Fibrous gaskets, which have a wick action, form a completely stagnant solution in contact with the flange face; this condition forms as almost ideal crevice-corrosion site.

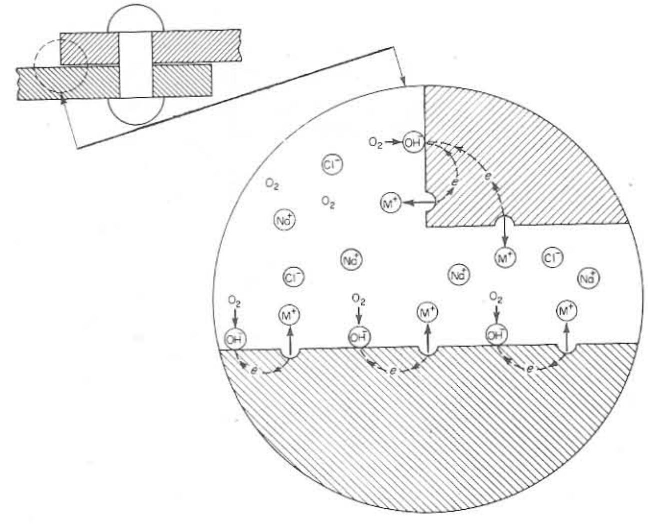


FIGURE 9 – Crevice corrosion, initial stage.

Mechanism

Until recently, it was believed that crevice corrosion resulted simply from differences in metal ion or oxygen concentration between the crevice and its surroundings. Consequently, the term *concentration cell corrosion* has been used to describe this form of attack. More recent studies[1] have shown that although metal-ion and oxygen-concentration differences do exist during crevice corrosion, these are not basic causes.

To illustrate the basic mechanism of crevice corrosion, consider a riveted plate section of metal M (e.g., iron or steel) immersed in aerated sea water (pH 7) as shown in Figure 9. The overall reaction involves the dissolution of metal M and the reduction of oxygen to hydroxide ions. Thus:

$$\textbf{Oxidation} \quad M \rightarrow M^+ + e \qquad (1)$$

$$\textbf{Reduction} \quad O_2 + 2H_2O + 4e \rightarrow 4OH^- \qquad (2)$$

Initially, these reactions occur uniformly over the entire surface, including the interior of the crevice. Change conservation is maintained in both the metal and solution. Every electron produced during the formation of a metal ion is immediately consumed by the oxygen reduction reaction. Also, one hydroxyl ion is produced for every metal ion in the solution. After a short interval, the oxygen within the crevice is depleted because of the restricted convection, so oxygen reduction ceases in this area. This, by itself, does not cause any change in corrosion behavior. Since the area within a crevice is usually very small compared with the external area, the overall rate of oxygen reduction remains almost unchanged. Therefore, the rate of corrosion within and without the crevice remains equal.

Oxygen depletion has an important indirect influence, which becomes more pronounced with increasing exposure. After oxygen is depleted, no further oxygen reduction occurs, although the dissolution of metal M continues as shown in Figure 10. This tends to produce an excess of

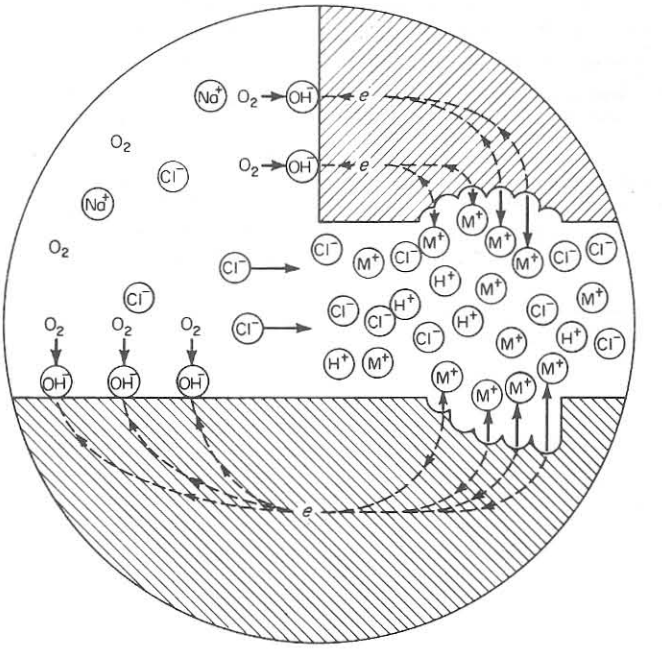


FIGURE 10 – Crevice corrosion, later stage.

positive charge in the solution (M^+) which is necessarily balanced by the migration of chloride ions into the crevice.(2) This results in an increased concentration of metal chloride within the crevice. Except for the alkali metals (e.g., sodium and potassium), metal salts, including chlorides and sulfates, hydrolize in water:

$$M^+Cl^- + H_2O = MOH\downarrow + H^+Cl^- \qquad (3)$$

Equation (3) shows that an aqueous solution of a typical metal chloride dissociates into an insoluble hydroxide and a free acid. For reasons which are not yet understood, both chloride and hydrogen ions accelerate the dissolution rates Equation (1) of most metals and alloys. These are both present in the crevice as a result of migration and hydrolysis, consequently the dissolution increases migration, and the result is a rapidly accelerating, or autocatalytic, process. The fluid within crevices exposed to neutral dilute sodium chloride possess a pH of 2 to 3. As the corrosion within the crevice increases, the rate of oxygen reduction on adjacent surfaces also increases as shown in Figure 10. This cathodically protects the external surfaces. Thus, during crevice corrosion the attack is localized within shielded areas, while the remaining surface suffers little or no damage.

The above mechanism is consistent with the observed characteristics of crevice corrosion. This type of attack occurs in many mediums, although it is usually most intense in ones containing chloride. There is often a long incubation period associated with crevice attack. Six months to a year or more is sometimes required before attack commences. However, once started, it proceeds at an ever increasing rate.

Metals or alloys which depend on oxide films or passive layers for corrosion resistance are particularly susceptible to crevice corrosion. These films are destroyed by high concentrations of chloride or hydrogen ions, and dissolution rate markedly increases. A striking example of this has been reported concerning a hot saline water solution in a stainless steel (18-8) tank in a dyeing plant. A stainless steel bolt had fallen into the bottom of the stainless tank. Rapid attack with red rust developed under the bolt after a brief period. Aluminum is also susceptible because of the Al_2O_3 film required for corrosion protection.

Combating Crevice Corrosion

Methods and procedures for combating or minimizing crevice corrosion are as follows:

1. Use welded butt joints instead of riveted or bolted joints in new equipment. Sound welds and complete penetration are necessary to avoid porosity and crevices on the inside (if welded only from one side).
2. Close crevices in existing lap joints by continuous welding, caulking, or soldering.
3. Design vessels for complete drainage; avoid sharp corners and stagnant areas. Complete draining facilitates washing and cleaning and tends to prevent solids from settling on the bottom of the vessel.
4. Inspect equipment and remove deposits frequently.
5. Remove solids in suspension early in the process of plant flow sheet, if possible.
6. Remove wet packing materials during long shutdowns.
7. Provide uniform environment, if possible, as in the case of backfilling a pipeline trench.
8. Use *solid*, nonabsorbent gaskets, such as Teflon, wherever possible.
9. Weld instead of rolling in tubes in tube sheets.

Filiform Corrosion

Although not immediately apparent, *filiform corrosion* (filamentary corrosion occurring on metal surfaces) is a special type of crevice corrosion. In most instances, it occurs under protective films, and for this reason is often referred to as underfilm corrosion. This type of corrosion is quite common; the most frequent example is the attack of enameled or lacquered surfaces of food and beverage cans which have been exposed to the atmosphere. The red-brown corrosion filaments are readily visible.

Filiform corrosion has been observed on steel, magnesium, and aluminum surfaces covered by tin, silver, gold, phosphate, enamel, and lacquer coatings. It has also been observed on paper-backed aluminum foil, with corrosion occurring at the paper-aluminum interface.

Filiform corrosion is an unusual type of attack, since it does not weaken or destroy metallic components but only affects surface appearance. Appearance is very important in food packaging, and this peculiar form of corrosion is a major problem in the canning industry. Although filiform attack on the exterior of a food can does not affect its contents, it does affect the sale of such cans.

Under transparent surface films, the attack appears as a network of corrosion product trails. The filaments consist of an active head and a red-brown corrosion product tail as illustrated in Figure 11. The filaments are 1/10 inch or less wide, and corrosion occurs only in the filament head. The blue-green color of the active heat is the characteristic color of ferrous ions, and the red-brown coloration of the inactive tail is due to the presence of ferric oxide or hydrated ferric oxide.

Interaction between corrosion filaments is most interesting (Figure 12). Corrosion filaments are initiated at edges

---

(2) Hydroxide ions also migrate from the outside, but they are less mobile than chloride, and consequently, migrate more slowly.

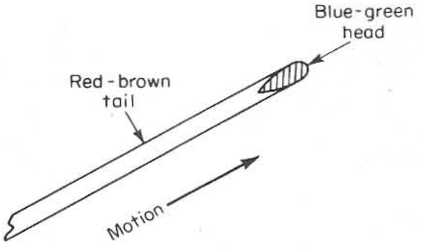


FIGURE 11 – Schematic diagram of a corrosion filament growing on an iron surface (magnified).

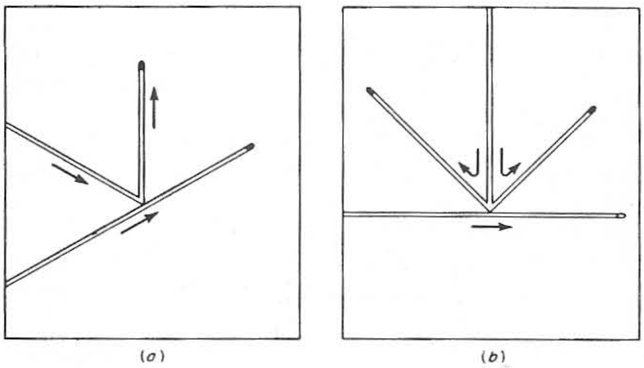


FIGURE 12 – Schematic diagrams illustrating the interaction between corrosion filaments. (a) Reflection of a corrosion filament, (b) splitting of a corrosion filament, (c) joining of corrosion filaments, and (d) "death trap".

and tend to move in straight lines. Filaments do not cross inactive tails of other filaments. As is illustrated in A, a corrosion filament upon striking the inactive tail of another filament is reflected. The angle of incidence is usually equal to the angle of reflection. If an actively growing filament strikes the inactive tail of another filament at a 90 degree angle, it may become inactive or, more frequently, it splits into two new filaments, each being reflected at an angle of approximately 45 degrees as shown in B. The active heads of two filaments may join, forming a single new filament if they approach each other obliquely (C). Perhaps the most interesting interaction is the *death trap* illustrated in D. Since growing filaments cannot cross inactive tails, they frequently become trapped and *die* as available space is decreased. Examples of *death traps* are easily found on the surface of discarded can lids, which have been exposed to moist atmospheres.

Environmental Factors. The most important environmental variable in filiform corrosion is the relative humidity of the atmosphere. Table 4 shows that filiform corrosion occurs primarily between 65 and 99% relative humidity. If relative humidity is lower than 65%, the metal is unaffected; at more than 90% humidity corrosion primarily appears as blistering. Corrosion blisters are, of course, as undesirable as filiform corrosion. Experimental studies have shown that the type of protective coating on a metal surface is relatively unimportant since filiform corrosion has been observed under enamel, lacquer, and metallic coatings. However, coatings with low water permeability suppress filiform corrosion.

TABLE 4 – Effect of Humidity on Filiform Corrosion of Enameled Steel

Relative Humidity, %	Appearance
0-65	No corrosion
65-80	Very thin filaments
80-90	Wide corrosion filaments
93	Very wide filaments
95	Mostly blisters, scattered filiform
100	Blisters

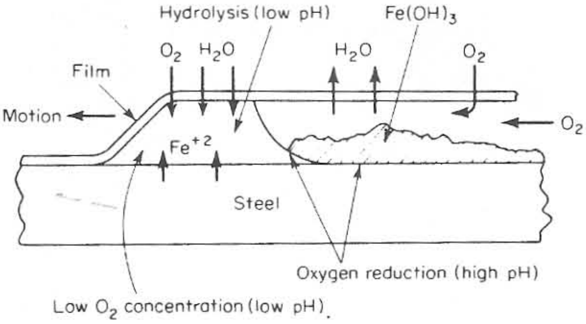


FIGURE 13 – Cross section of a corrosion filament on a steel surface.

Microscopic studies have shown that there is little or no correlation between corrosion filaments and metallurgical structure. Filaments tend to follow grinding marks and polishing direction.

The addition of corrosion inhibitors to enamel or lacquer coatings has relatively little influence on the nature and extent of corrosion filaments. Because of the wormlike appearance of corrosion filaments, and their unusual interactions, early investigators suspected the presence of microbiological activity. However, filaments have been observed to grow in the presence of toxic reagents, so the presence of biological organisms can be eliminated as a contributing factor.

Mechanism.^{2} The mechanism of filiform corrosion is not completely understood. The basic mechanism appears to be a special case of crevice corrosion as is illustrated in Figure 13. During growth, the head of the filament is supplied with water from the surrounding atmosphere by osmotic action due to the high concentration of dissolved ferrous ions. Osmosis tends to remove water from the inactive tail, because of the low concentration of soluble salts (iron has precipitated as ferric hydroxide). Thus, as shown in Figure 13, atmospheric water continuously diffuses into the active head and out of the inactive tail. Although oxygen diffuses through the film at all points, the concentration of oxygen at the interface between the tail and the head is high because of lateral diffusion. Corrosion is restricted to the heat where hydrolysis of the corrosion products produces an acidic environment. Thus, filiform corrosion can be viewed as a self-propagating crevice. Although Figure 13 adaquately explains the basic corrosion mechanism, the unusual growth characteristics (i.e., lack of spreading) and interactions between filaments are not understood.

Prevention. There is no completely satisfactory way to prevent filiform corrosion. An obvious method is to score coated metal surfaces in low humidity environments. Although this technique can be used in some instances, it is not always practical for long-time storage. Another preventive measure which has been employed consists of coating with brittle films. If a corrosion filament begins growing under a brittle coating, the film cracks at the growing head. Oxygen is then admitted to the head, and the differential oxygen concentration originally present is removed and corrosion ceases. However as noted above, corrosion filaments usually start at edges. Hence, a new corrosion filament begins at the point of rupture. Although brittle films suppress the growth rate of corrosion filaments, they do not offer much advantage since articles coated with such film must be handled very carefully to prevent damage. Recent developments with films of very low water permeability hold some promise in preventing filiform corrosion.

Pitting

Pitting is a form of extremely localized attack that results in holes in the metal. These holes may be small or large in diameter, but in most cases are relatively small. Pits are sometimes isolated or so close together that they look like a rough surface. Generally a pit may be described as a cavity or hole with the surface diameter about the same as or less than the depth.

Pitting is one of the most destructive and insidious forms of corrosion. It causes equipment to fail because of perforation with only a small percent weight loss of the entire structure. It is often difficult to detect pits because of their small size, and because the pits are often covered with corrosion products. In addition, it is difficult to measure quantitatively and compare the extent of pitting because of the varying depths and number of pits that may occur under identical conditions. Pitting is also difficult to predict by laboratory tests. Sometimes the pits require a long time (several months or a year) to show up in actual service. Pitting is particularly vicious because it is a localized and intense form of corrosion, and failures often occur with extreme suddenness.

Pit Shape and Growth

Figure 14 is an example of pitting of 18-8 stainless steel by sulfuric acid containing ferric chloride. Note the sharply defined holes and the lack of attack on most of the metal surface. This attack developed in a few days. However, this is an extreme example, since pitting usually requires months or years to perforate a metal section. Figure 15 shows a copper pipe that handled potable water and failed after several years' service. Numerous pits are visible, together with a surface deposit.

Pits usually grow in the direction of gravity. Most pits develop and grow downward from horizontal surfaces. Lesser numbers start on vertical surfaces, and only rarely do pits grow upward from the bottom of horizontal surfaces.

Pitting usually requires an extended initiation period before visible pits appear. This period ranges from months to years, depending on both the specific metal and the corrosive. Once started, however, a pit penetrates the metal at an ever-increasing rate. In addition, pits tend to undermine or undercut the surface as they grow. This aspect, illustrated in Figure 16, shows a magnified section of a 16% Cr stainless steel (Type 430) tube which failed because of small pinhole leaks. The tube contained circulating water for cooling nitric acid in a plant making this acid. The outside of the tube (bottom) was exposed to the process side, or nitric acid side, and no measurable corrosion occurred on this surface. The cooling water contained a small amount of chlorides. Pitting started on the inside (upper) surface and progressed outwards. The hole in the bottom surface is the actual leak. The tendency of pits to undercut the surface makes their detection much more difficult. Subsurface damage is usually much more severe than is indicated by surface appearance.

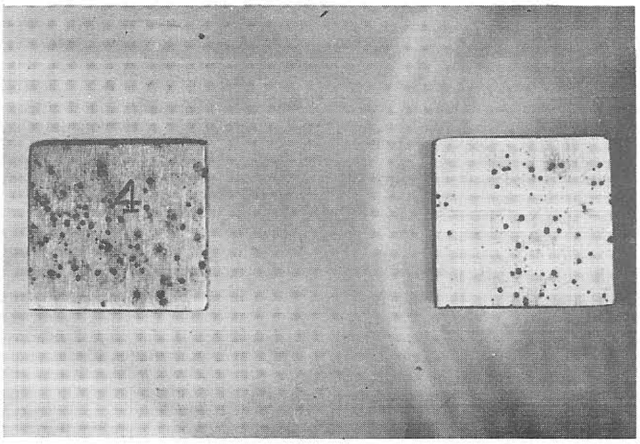


FIGURE 14 – Pitting of 18-8 stainless steel by acid-chloride solution.

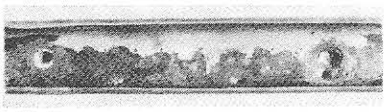


FIGURE 15 – Pitting of a copper pipe used for drinking water.

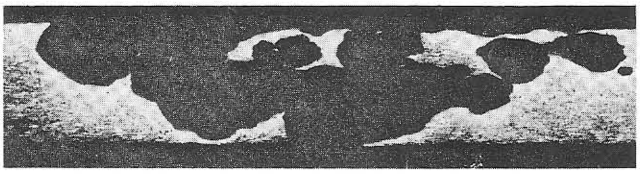


FIGURE 16 – Pitting of stainless steel condenser tube.

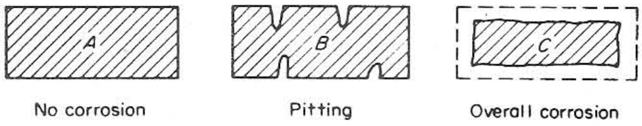
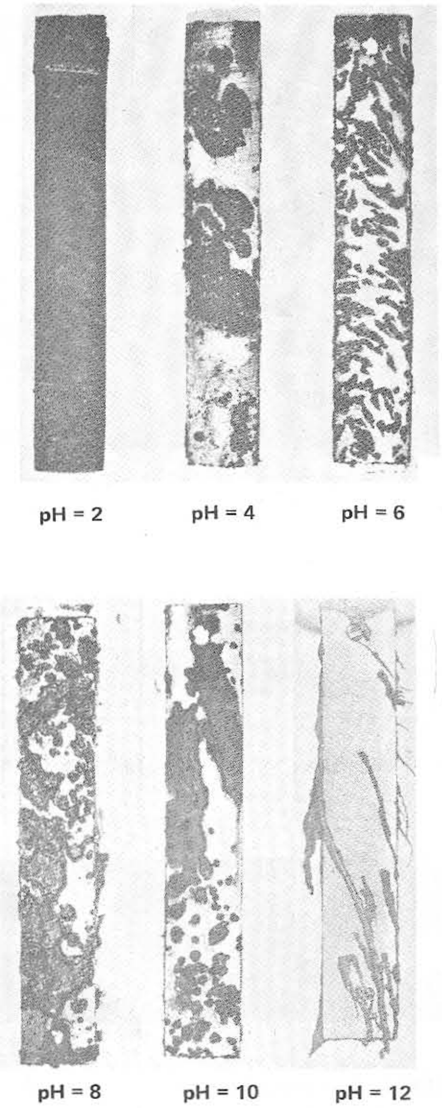


FIGURE 17 – Diagrammatic representation of pitting corrosion as an intermediate stage.

Pitting may be considered as the intermediate stage between general overall corrosion and complete corrosion resistance. This is shown diagramatically in Figure 17. Specimen A shows no attack whatsoever. Specimen C has



pH = 2 pH = 4 pH = 6

pH = 8 pH = 10 pH = 12

FIGURE 18 – Corrosion of steel after 24 hours in 5% NaCl and 500 lb/in.^{2} oxygen pressure (Continental Oil Co.).

metal removed or dissolved uniformly over the entire exposed surface. Intense pitting occurred on specimen B at the points of breakthrough. This situation can be readily demonstrated by exposing three identical specimens of 18-8 stainless steel to ferric chloride and increasing the concentration and/or the temperature as we move to the right in Figure 17. Very dilute, cold, ferric chloride produces no attack (in a short time) on A, but strong hot ferric chloride dissolves specimen C. Riggs, Sudbury, and Hutchinson[3] have observed a striking example of this during a study of the effects of high oxygen pressure and pH on the corrosion of steel by a 5% NaCl brine. Figure 18 shows that as pH is increased, the corrosion progresses from general corrosion to highly localized pitting. Beginning at pH 4, the pits are covered by a cap of corrosion products. At pH 12, the corrosion products assume an unusual tubular shape and corrosion rates are 17,000 mpy at the bottom of the tubes! The mechanism of this effect is discussed in the following section.

Autocatalytic Nature of Pitting

A corrosion pit is a unique type of anodic reaction. It is an autocatalytic process. That is, the corrosion processes within a pit produce conditions which are both simulating and necessary for the continuing activity of the pit. This is illustrated schematically in Figure 19. Here a metal M is being pitted by an aerated sodium chloride solution. Rapid dissolution occurs within the pit, while oxygen reduction takes place on adjacent surfaces. This process is self-stimulating and self-propagating. The rapid dissolution of metal within the pit tends to produce an excess of positive charge in this area, resulting in the migration of chloride ions to maintain electro-neutrality. Thus, in the pit there is a high concentration of MCl and, as a result of hydrolysis [See Equation (3)], a high concentration of hydrogen ions. Both hydrogen and chloride ions stimulate the dissolution of most metals and alloys, and the entire process accelerates with time. Since the solubility of oxygen is virtually zero in concentrated solutions, no oxygen reduction occurs within a pit. The cathodic oxygen reduction on the surfaces adjacent to pits tends to suppress corrosion. In a sense, pits cathodically protect the rest of the metal surface.

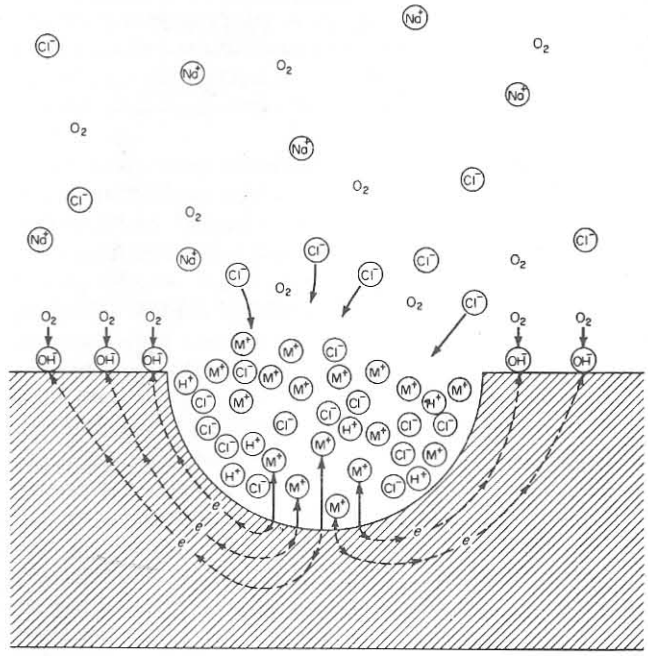


FIGURE 19 – Autocatalytic processes occurring in a corrosion pit.

Although Figure 19 indicates how a pit grows through self-stimulation, it does not immediately suggest how this process is initiated. Evans[4] has indicated how it could lead to the start of pitting. Consider a piece of metal M devoid of holes or pits, immersed in aerated sodium chloride solution. If, for any reason the rate of metal dissolution is momentarily high at one particular point, chloride ions will migrate to this point. Since chloride stimulates metal dissolution, this change tends to produce conditions which are favorable to further rapid dissolution at this point. Locally, dissolution may be momentarily high because of a surface scratch, an emerging dislocation or other defect, or random variations in solution composition. It is apparent that during the initiation or early growth stages of a pit, conditions are rather unstable. The locally high concentration of chloride and hydrogen ions may be swept away by stray convection currents in the solution since a protective pit cavity does not exist. The authors have observed that new pits are indeed unstable, since many become inactive

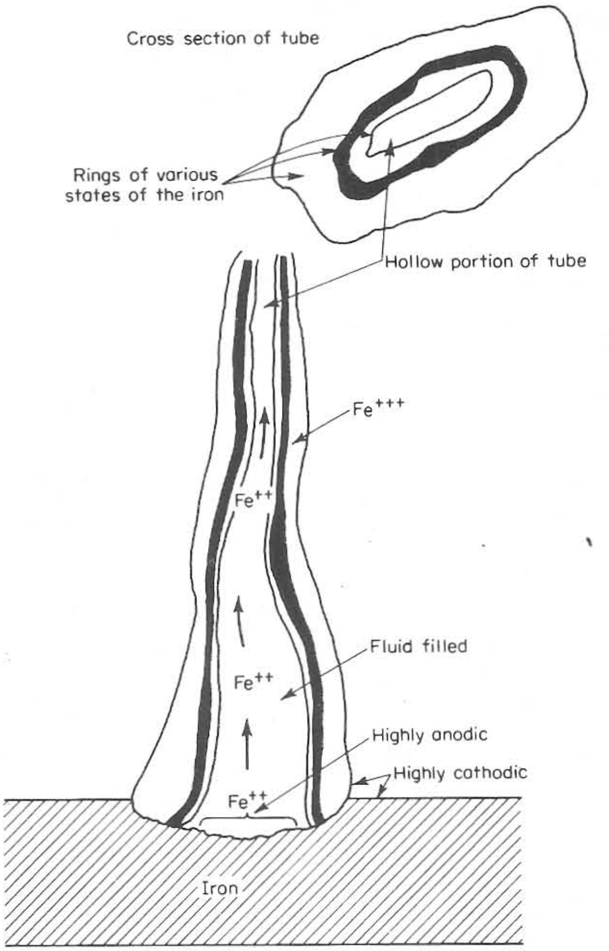


FIGURE 20 – Corrosion tube growth mechanism (Continental Oil Co.).

after a few minutes' growth.

The gravity effect mentioned before is a direct result of the autocatalytic nature of pitting. Since the dense, concentrated solution within a pit is necessary for its continuing activity, pits are most stable when growing in the direction of gravity. Also, pits are generally initiated on the upper surfaces of specimens because chloride ions are more easily retained under these conditions.

The pits with tabular corrosion products shown in Figure 18 grow by a mechanism similar to that described above. Figure 20 indicates the mechanism proposed by Riggs, Sudbury, and Hutchinson. At the interface between the pit and the adjacent surface, iron hydroxide forms due to interaction between the OH^- produced by the cathodic reaction and the pit-corrosion product. This is further oxidized by the dissolved oxygen in the solution to $Fe(OH)_3$, Fe_3O_4, Fe_2O_3, and other oxides. This *rust* rim grows in the form of a tube as shown in Figure 20. The oxides forming the tube were identified by X-ray diffraction.

Comparison of Figures 20, 19, and 10 shows that the mechanism of pit growth is virtually identical to that of crevice corrosion. This similarity has prompted some investigators to conclude that pitting is in reality only a special case of crevice corrosion. This view has some merit, since all systems which show pitting attack are particularly susceptible to crevice corrosion (e.g., stainless steels in sea water or ferric chloride). However, the reverse is not always correct: many systems which show crevice attack do not suffer pitting on freely exposed surfaces. It appears to us that pitting, although quite similar to crevice corrosion, deserves special consideration since it is a self-initiating form of crevice corrosion. Simply, it does not require a crevice, it creates its own.

Solution Composition

From a practical standpoint, most pitting failures are caused by chloride and chlorine-containing ions. Chlorides are present in varying degrees in most waters and solutions made with water. Much equipment operates in sea water and brackish waters. Hypochlorites (bleaches) are difficult to handle because of their strong pitting tendencies. Mechanisms for pitting by chlorides are controversial and not well established. Perhaps the best explanation is the acid-forming tendency of chloride salts and the high strength of its free acid (HCl). Most pitting is associated with halide ions, with chlorides, bromides, and hypochlorites being the most prevalent. Fluorides and iodides have comparatively little pitting tendencies.

Oxidizing metal ions with chlorides are aggressive pitters. Cupric, ferric, and mercuric halides are extremely aggressive. Even our most corrosion-resistant alloys can be pitted by $CuCl_2$ and $FeCl_3$. Halides of the nonoxidizing metal ions (e.g., NaCl, $CaCl_2$) cause pitting but to a much lesser degree of aggressiveness.

Cupric and ferric chlorides do not require the presence of oxygen to promote attack because their cations can be cathodically reduced. These ions are reducible as follows:

$$Cu^{++} + 2e \rightarrow Cu \qquad (4)$$

$$Fe^{+++} + e \rightarrow Fe^{++} \qquad (5)$$

In other words, they are electron acceptors. This is one reason ferric chloride is widely used in pitting studies. The reactions are not appreciably affected by the presence or absence of oxygen.

Pitting can be prevented or reduced in many instances by the presence of hydroxide, chromate, or silicate salts. However, these substances tend to accelerate pitting when present in small concentrations.

Velocity

Pitting is usually associated with stagnant conditions such as a liquid in a tank or liquid trapped in a low part of an inactive pipe system. Velocity, or increasing velocity, often decreases pitting attack. For example, a stainless steel pump would give good service handling seawater if it were run continuously but would pit if it were shut down for extended periods. Figure 21 demonstrates this point. The material is Type 316 stainless steel, and the environment an acid-ferric chloride mixture at elevated temperature. This test was run for 18 hours at the same time and in the same solution. Specimen C was exposed to high velocity flow (about 40 ft/sec) and specimen A to a few feet per second, while specimen B was in a quiet or completely static solution. All specimens show pitting, but the depth of penetration in C is relatively small. Pitting is more intense on A, and B has deep and large *worm holes*.

Metallurgical Variables

As a class, the stainless steel alloys are more susceptible to damage by pitting corrosion than are any other group of

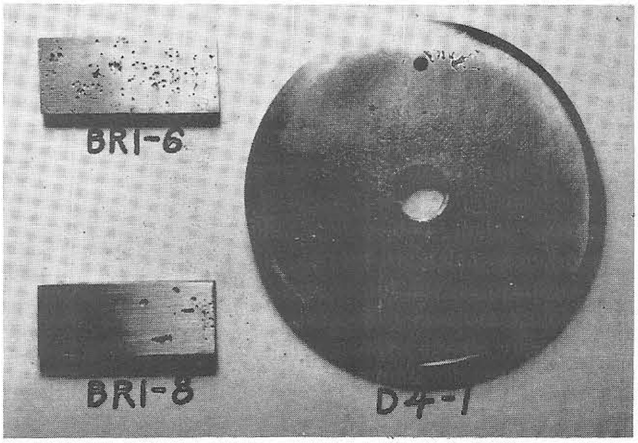


FIGURE 21 – Effect of velocity on pitting of stainless steel.

metals or alloys. As a result, numerous alloy studies have been devoted to improving the pitting resistance of stainless steels. The results are summarized in Table 5.

Holding Types 304 and 316 stainless steel in the sensitizing temperature range [950 to 1450 F (510 to 788 C)] decreases their pitting resistance. Austenitic stainless steels exhibit the greatest pitting resistance when solution-quenched above 982 C (1800 F).

Severe cold-working increases the pitting attack of 18-8 stainless steels in ferric chloride. Preferential edge pitting is usually observed on most wrought stainless products.

Surface finish often has a marked effect on pitting resistance. Pitting and localized corrosion are less likely to occur on polished than on etched or ground surfaces. Generally, the pits that form on a polished surface are larger and penetrate more rapidly than those on rough surfaces.

Ordinary steel is more resistant to pitting than stainless steel alloys. For example, the pitting of stainless steel condenser tubing exposed to brackish water or sea water often can be alleviated by the substitution of steel tubes. Although the general corrosion of steel is much greater than that of stainless steel, rapid perforation due to pitting does not occur.

Evaluation of Pitting Damage

Since pitting is a localized form of corrosion, conventional weight-loss cannot be used for evaluation or comparison purposes. Metal loss is very small and does not indicate the depth of penetration. Measurements of pit depth are complicated by the fact that there is a statistical variation in the depths of pits on an exposed specimen as shown in Figure 22. Note that the average pit depth is a poor way to estimate pit damage, since it is the deepest pit which causes failure.

Examination of Figure 22 suggests that a measurement of maximum pit depth would be a more reliable way of expressing pitting corrosion. This is correct, but such measurements should never be used to predict equipment life since pit depth is also a function of sample size. This is shown in Figure 23, which shows the relative probability of finding a pit of a given depth as a function of exposed area. For example, there is a probability of 0.2 (20%) of a pit with a depth of *d* occurring on a sample with an area of 1. On a specimen four times larger, it is a virtual certainty (probability = 1.0) that a pit of this depth will occur, and a 90% chance that a pit twice as deep will also occur. This clearly indicates that attempts to predict the life of a large plant on the basis of tests conducted on small laboratory specimens would be unwise. However, for laboratory comparisons of pitting resistance, maximum-pit-depth measurements are reasonably accurate.

TABLE 5 – Effects of Alloying on Pitting Resistance of Stainless Steel Alloys

Element	Effect on Pitting Resistance
Chromium	Increases
Nickel	Increases
Molybdenum	Increases
Silicon	Decreases; increases when present with molybdenum
Titanium and columbium	Decreases resistance in $FeCl_3$; other mediums no effect
Sulfur and selenium	Decreases
Carbon	Decreases, especially in sensitized condition
Nitrogen	Increases

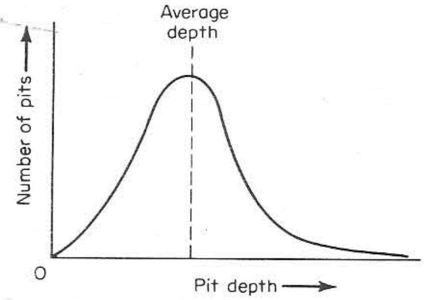


FIGURE 22 – Relationship between pit depth and the number of pits appearing on a corroded surface.

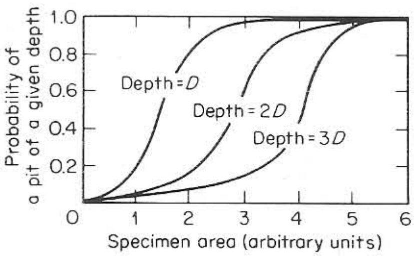


FIGURE 23 – Pit depth as a function of exposed area.

Prevention

The methods suggested for combating crevice corrosion generally apply also for pitting. Materials that show pitting, or tendencies to pit, during corrosion tests should not be used to build the plant or equipment under consideration. Some materials are more resistant to pitting than others. For example, the addition of 2% molybdenum to 18-8S (Type 304) to produce 18-8S Mo (Type 316) results in a very large increase in resistance to pitting. The addition apparently results in a more protective or more stable passive surface. These two materials behave so differently that one is considered unsuitable for sea water service, but the other is sometimes recommended. The best procedure is to use materials that are known not to pit in the environment under consideration. As a general guide, the following list of metals and alloys may be used as a qualitative guide to suitable materials. However, tests should be conducted before final selection is made.

Increasing pitting resistance ↓	Type 304 stainless steel
	Type 316 stainless steel
	Hastelloy F, Nionel, or Durimet 20
	Hastelloy C or Chlorimet 3
	Titanium

Adding inhibitors is sometimes helpful, but this may be a dangerous procedure unless attack is stopped *completely*. If it is not, the intensity of the pitting may be increased.[5]

Intergranular Corrosion

Grain-boundary effects are of little or no consequence in most applications or uses of metals. If a metal corrodes, uniform attack results since grain boundaries are usually only slightly more reactive than the matrix. However, under certain conditions, grain interfaces are very reactive and intergranular corrosion results. Localized attack at and adjacent to grain boundaries, with relatively little corrosion of the grains, is *intergranular corrosion*. The alloy disintegrates (grains fall out) and/or loses its strength.

Intergranular corrosion can be caused by impurities at the grain boundaries, enrichment of one of the alloying elements, or depletion of one of these elements in the grain-boundary areas. Small amounts of iron in aluminum, wherein the solubility of iron is low, have been shown to segregate in the grain boundaries and cause intergranular corrosion. It has been shown that based on surface-tension considerations, the zinc content of a brass is higher at the grain boundaries. Depletion of chromium in the grain-boundary regions results in intergranular corrosion of stainless steels.

Austenitic Stainless Steels

Numerous failures of 18-8 stainless steels have occurred because of intergranular corrosion. These happen in environments where the alloy should exhibit excellent corrosion resistance. When these steels are heated in approximately the temperature range 510 to 788 C, they become sensitized or susceptible to intergranular corrosion. For example, a procedure to sensitize intentionally is to heat at 649 C (1200 F) for 1 hour.

The almost universally accepted theory for intergranular corrosion is based on impoverishment or depletion of chromium in the grain-boundary areas. The addition of chromium to ordinary steel imparts corrosion resistance to the steel in many environments. Generally more than 10% chromium is needed to make a stainless steel. If the chromium is effectively lowered, the relatively poor corrosion resistance of ordinary steel is approached.

In the temperature range indicated, $Cr_{23}C_6$ (and carbon) is virtually insoluble and precipitates out of solid solution if carbon content is about 0.02% or higher. The chromium is thereby removed from solid solution, and the result is metal with lowered chromium content in the area adjacent to the grain boundaries. The chromium carbide in the grain boundary is not attacked. The chromium depleted zone near the grain boundary is corroded because it does not contain sufficient corrosion resistance to resist attack in many corrosive environments. The common 18-8 stainless steel (Type 304) usually contains from 0.06 to 0.08% carbon, so excess carbon is available for combining with the chromium to precipitate the carbide. This situation is shown schematically in Figure 24. Carbon diffuses towards the grain boundary quite readily at sensitizing temperatures, but chromium is much less mobile. The surface already available at the grain boundary facilitates the formation of a new surface, namely that of the chromium carbide.

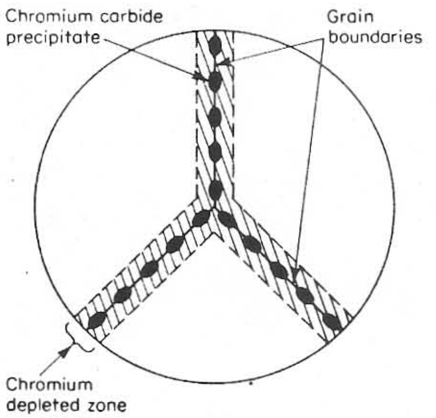


FIGURE 24 – Diagrammatic representation of a grain boundary in sensitized Type 304 stainless steel.

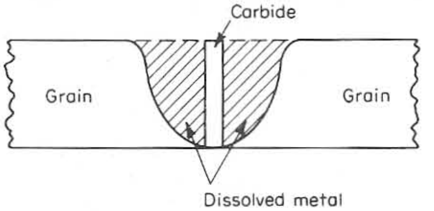


FIGURE 25 – Cross section of area shown in Figure 24.

There is some evidence to indicate that the chromium content at the boundary may be reduced to a very low level or zero. Assume that the chromium content is reduced to 2%. Corrosion resistance is lowered, two dissimilar metal compositions are in contact, and a large unfavorable area ratio is present. The depleted area protects the grains. The net effect is rapid attack in the impoverished area, with little or no attack on the grains.

If the alloy were cut into a thin sheet and a cross section of the grain boundary area made, it would look something like Figure 25. The corroded area would appear as a deep, narrow trench when observed at low magnifications such as 10 diameters.

Chromium carbide precipitates have been described for many years as particles because they are too small for detailed examination by the light microscope. Mahla and Nielsen of DuPont, using the electron microscope, have shown that the carbide forms as a film or envelope around the grains in a leaf-like structure. Figure 26, which is from their work, shows the residue after the metallic portions of the alloy were dissolved in strong hydrochloric acid. This emphasizes the point, indicated by Figure 25, that the carbides themselves are not attacked: the adjacent metal depleted in chromium is dissolved. In fact, this acid rapidly corrodes all of the 18-8 type alloys regardless of heat treatment.

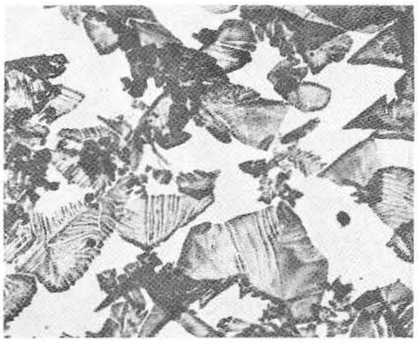


FIGURE 26 – Electron photomicrograph of carbides isolated from sensitized Type 304 stainless steel.

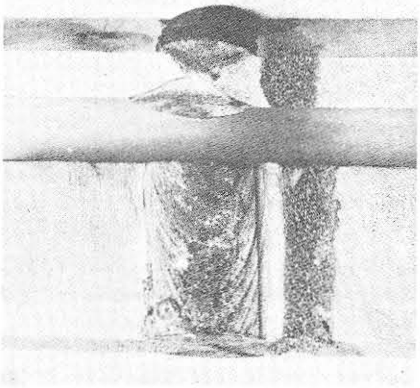


FIGURE 27 – Intergranular corrosion in weld decay zone. Right, Type 304, and left, stabilized with titanium.

Weld Decay

Many failures of 18-8 occurred in the early history of this material until the mechanism of intergranular corrosion was understood. Failures still occur when this effect is not considered. These are associated with welded structures, and the material attacked intergranularly is called *weld decay*. The weld-decay zone is usually a band in the parent plate somewhat removed from the weld. Such a zone is shown in Figure 27 to the right of the weld. The *sugary* appearance is due to the small protruding grains that are about to drop off. This specimen was exposed to boiling nitric acid after welding. The absence of weld decay to the left of the weld if explained under *Control for Austenitic Stainless Steels*.

The metal in the weld-decay zone must have been heated in the sensitizing range. Figure 28[6] is a *tablecloth analogy* of heat flow and temperatures associated with welding. Visualize a mountain-like block being moved on a table under an elastic striped tablecloth. This moving block represents the weld being made along the plate. The rise and fall of each stripe represents the rise and fall of temperature in the welded plate. The dark center line in Figure 28 is the center of the weld, which is the hottest (above the melting point). The lines with the *x's* represent temperatures in the sensitizing zone. These *x* lines correspond to the weld-decay zone in Figure 28.

Figure 29[6] depicts in different form essentially the same picture. Thermocouples were placed at points A, B, C, and D, and temperatures and times recorded during welding. The metal at points B and C (and between these points) is in the sensitizing temperature range for some time. Time and temperature relationships vary with the size or thickness of the material welded, the time to make the weld, and the type of welding. For example, thin sheet is rapidly welded, whereas heavy plate may take several weld passes. For sheet 1/8 inch thick or less, time in the sensitizing range is sufficiently short so as not to cause intergranular corrosion in environments not particularly selective or aggressive to stainless steels. Cross welds would essentially double the time in this range, and appreciable carbide precipitation may occur.

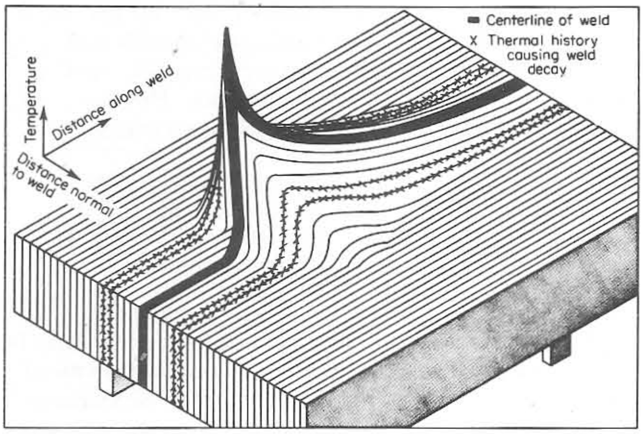
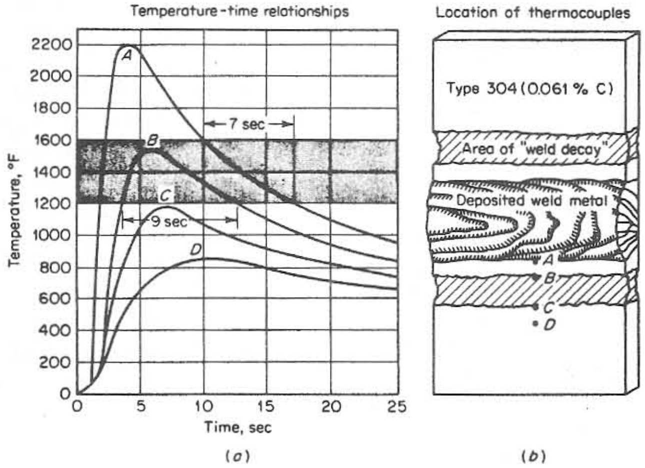


FIGURE 28 – Table cloth analogy of heat flow and temperatures during welding. Visualize a mountainlike block being moved beneath an elastic striped tablecloth. The rise and fall of each stripe represents the rise and fall of temperature in a welded plate (DuPont Co.).



(a) (b)

FIGURE 29 – Temperatures during electric-arc welding of Type 304 stainless steel (DuPont Co.).

Time and temperature effects provide one reason why electric arc welding is used more than gas welding for stainless steels. The former produces higher and more intense heating in shorter times. The latter would keep a wider zone of metal in the sensitizing range for a longer time, which means greater carbide precipitation.

It should be emphasized that sensitized stainless steels do not fail in all corrosive environments, because these steels are often used where the full corrosion resistance of the alloy is not required or where selective corrosion is not a problem. Examples are food equipment, kitchen sinks,

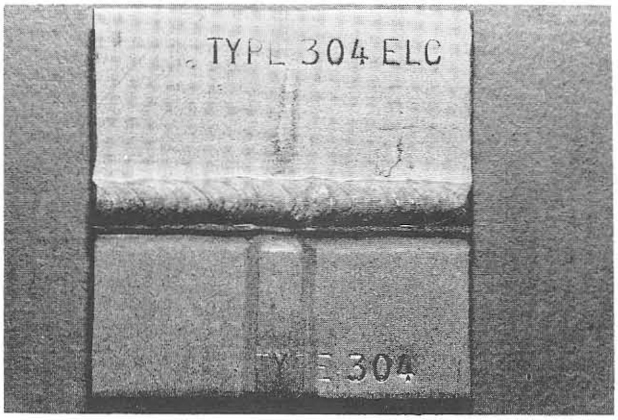


FIGURE 30 – Elimination of weld decay by Type 304L.

automobile trim, and facings on buildings. However, it is desirable to have all of the metal in the condition of its best corrosion resistance for the more severely corrosive applications.

Control for Austenitic Stainless Steels

Three methods are used to control or minimize intergranular corrosion of the austenitic stainless steels: (1) employing high-temperature solution heat treatment, commonly termed *quench-annealing* or *solution-quenching*, (2) adding elements that are strong carbide formers (called stabilizers), and (3) lowering the carbon content to below 0.03%.

Commercial solution-quenching treatments consist of heating from 1066 to 1121 C (1950 to 2050 F) followed by water-quenching. Chromium carbide is dissolved at these temperatures, and a more homogeneous alloy is obtained. Most of the austenitic stainless steels are supplied in this condition. If welding is used during fabrication, the equipment must be quench-annealed to eliminate susceptibility to weld decay. This poses an expensive problem for large equipment and, in fact furnaces are not available for heat-treating very large vessels. In addition, welding is sometimes necessary in the customer's plant to make repairs or, for example, to attach a nozzle to a vessel.

Quenching, or rapid cooling from the solution temperature, is very important. If cooling is slow, the entire structure would be susceptible to intergranular corrosion.

The strong carbide formers or stabilizing elements, columbium (or columbium plus tantalum) and titanium, are used to produce Types 347 and 321 stainless steels, respectively. These elements have a much greater affinity for carbon than does chromium and are added in sufficient quantity to combine with all of the carbon in the steel. The stabilized steels eliminate the economic and other objections of solution-quenching the unstabilized steels after fabrication or weld repair. The left plate in Figure 27 does not show weld decay, because it is Type 321. The same picture would be obtained if it were Type 347.

Lowering the carbon to below 0.03% (Type 304L) does not permit sufficient carbide to form to cause intergranular attack in most applications. One producer calls these the extra-low-carbon (ELC) steels. Figure 30 shows a situation similar to Figure 27, except that here weld decay is absent in the low-carbon plate. The vertical trenches are due to a weld bead deposited on the back surface of the specimen.

The original 18-8 steels contained approximately 0.20% carbon, but this was quickly reduced to 0.08% because of rapid and serious weld-decay failures. Lowering the carbon content much below 0.08% was not possible until it was discovered that it was possible to blow oxygen through the melt to burn out carbon and until low-carbon ferrochrome was developed.

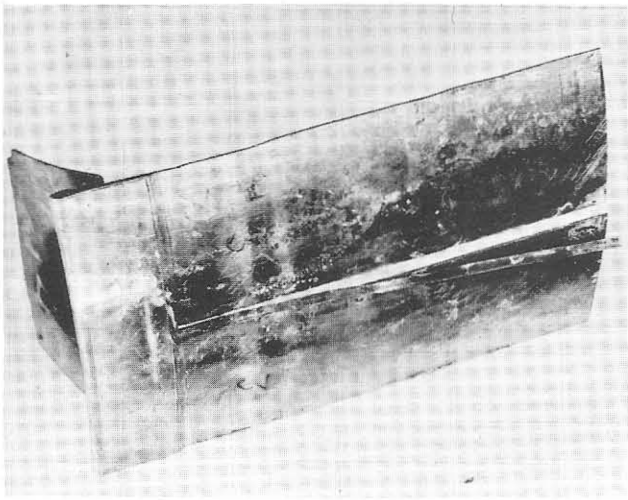


FIGURE 31 – Knife-line attack on Type 347 stainless steel.

These stainless steel have a high solubility for carbon when in the molten state and therefore have a tremendous propensity for picking up carbon. For example, the intent of the low-carbon grades is obviated when the welder carefully cleans the beveled plate with an oily or greasy rag before welding!

A few isolated carbides that may appear in Type 304L are not destructive for many applications in which a continuous network of carbides would be catastrophic. In fact, the susceptibility to intergranular corrosion of the austenitic stainless steels can be reduced by severely cold-working the alloy. Cold-working produces smaller grains and many slip lines, which provide a much larger surface for carbide precipitation. This is not, however, a recommended or practical procedure.

KLA

Knife-line Attack

The stabilized austenitic stainless steels are attached intergranularly, under certain conditions, because of chromium carbide precipitation. Columbium or titanium fail to combine with the carbon. Figure 31 shows a section of a Type 347 (18-8 + Cb) drum which contained fuming nitric acid. Severe intergranular attack occurred in a narrow bank, a few grains wide, on both sides of the weld and immediately adjacent to it. Practically no corrosion is observable on the remainder of the container. This phenomenon was studied at Ohio State University and the basic mechanism for failure established.[7] It was christened knife-line attack because of its distinctive appearance.

Knife-line attack (KLA) is similar to weld decay in that they both result from intergranular corrosion and both are associated with welding. The two major differences are (1) KLA occurs in a narrow band in the parent metal immediately adjacent to the weld, whereas weld decay develops at an appreciable distance from the weld, (2) KLA occurs in the stabilized steels, and (3) the thermal history of the metal is different.

The mechanism for the failure of this drum is based on the solubility of columbium in the stainless steel. Colum-

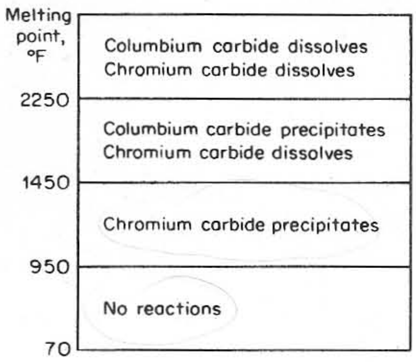


FIGURE 32 – Schematic chart showing solution and precipitation reactions in Types 304 and 347.

bium and columbium carbides dissolve in the metal when it is heated to a very high temperature and they remain in solution when cooled rapidly from this temperature. The columbium stays in solution when the metal is then heated in the chromium carbide precipitation range; columbium carbide does not form, and the metal behaves (sensitizes) as though it were 18-8 without columbium.

The temperature of the weld metal is high enough to melt the alloy during welding, say, 1650 C (3000 F). The metal adjacent to the weld is also at a high temperature because it is in contact with molten metal. The unmelted sheet is therefore just below the melting point, which is around 1427 to 1483 C (2600 to 2700 F). A sharp thermal gradient exists in the metal because of the relatively poor termal conductivity of 18-8 and because the welding operation on this thin (1/16 inch) sheet is rapid (to avoid *burning through*). The thin sheet cools rapidly after welding).

This situation can be better explained by means of the chart shown as Figure 32. The stainless steel as received from the steel mill contains columbium carbides and essentially no chromium carbides because it was heat treated by water-quenching from 1066 C. Focus attention now on the narrow band of metal adjacent to the weld. This was heated to around 1427 C and cooled rapidly. According to the chart this band of metal has everything in solution (no precipitation of either carbide). If this metal is not heated in the sensitizing range of about 510 to 760 C (950 to 1400 F) as the drum was to relieve stress, only chromium carbide precipitates, because the temperature is not high enough to form columbium carbide. If the drums were not heated after welding, failure would not have occurred, because no carbides would have been present.

A simple experiment proves the mechanism. Take a sample of 18-8 + Cb, heat to 1260 C (2300 F), and quench in water. Now heat it for 1/2 hour at 649 C and cool. The entire sample sensitizes essentially the same as 18-8 (no Cb).

The obvious remedy to avoid knife-line attack is to heat the completed structure (after welding) to around 1066 C. According to the chart, chromium carbide dissolves and columbium carbide forms, which is the desired situation. The rate of cooling after the 1066 C treatment is not important.

Titanium-stabilized stainless steel (Type 321) is also subject to knife-line attack under conditions similar to Type 347. Type 304L steels have been given superior performance in cases where the stabilized steels exhibited knife-line attack.

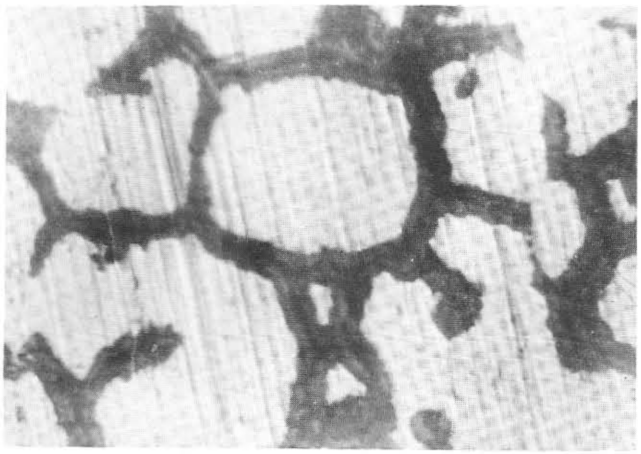


FIGURE 33 – Intergranular corrosion of ancient Greek bronze.

Intergranular Corrosion of Other Alloys

High-strength aluminum alloys depend on precipitated phases for strengthening and are susceptible to intergranular corrosion. For example, the Duraluminum-type alloys (Al-Cu) are strong because of precipitation of the compound $CuAl_2$. Substantial potential differences between the copper-depleted areas and adjacent material have been demonstrated. When these alloys are solution-quenched, to keep the copper in solution, their susceptibility to intergranular corrosion is very small but they possess low strength. Other precipitates, such as $FeAl_3$, Mg_5Al_8, Mg_2Si, $MgZn_2$, and $MnAl_6$, along grain boundaries or slip lines in other aluminum-alloy systems show somewhat similar characteristics, but perhaps less drastic. Some magnesium and copper base alloys are in the same category.

Die-cast zinc alloys containing aluminum exhibit intergranular corrosion by steam and marine atmospheres.

Intergranular attack can be rapid or slow. Figure 33 shows an ancient Greek bronze, circa 500 B.C.

Selective Leaching

Selective leaching is the removal of one element from a solid alloy by corrosion processes. The most common example is the selective removal of zinc in brass alloy (dezincification). Similar processes occur in other alloy systems in which aluminum, iron, cobalt, chromium, and other elements are removed. Selective leaching is the general term to describe these processes, and its use precludes the creation of terms such as *dealuminumification*, *decobaltification,* etc. *Parting* is a metallurgical term that is sometimes applied, but selective leaching is preferred.

Dezincification: Characteristics

Common yellow brass consists of approximately 30% zinc and 70% copper. Dezincification is readily observed with the naked eye, because the alloy assumes a red or copper color contrasting with the original yellow. There are two general types of dezincification, and both are readily recognizable. One is uniform, or layer-type, and the other is localized, or plug-type, dezincification. Figure 34 shows an example of uniform attack. The dark inner layer is the dezincified portion, and the outer layer is the unaffected yellow brass. Penetration of about 50% of the pipe wall occurred after several years in potable-water service.

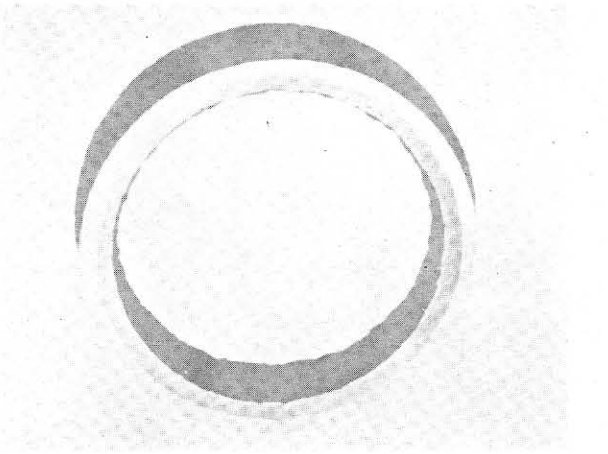


FIGURE 34 – Uniform dezincification of brass pipe.

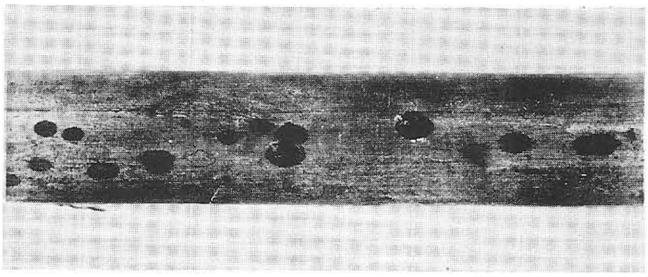


FIGURE 35 – Plug-type dezincification.

Figure 35 is a good example of plug-type dezincification. The dark areas are the dezincified plugs. The remainder of the tube is not corroded to any appreciable extent. This tube was removed from a powerhouse heat exchanger with boiler water on one side and fuel combustion gases on the outside. Figure 36 is a section through one of the plugs. Attack started on the water side of the tubing. Addition of zinc to copper lowers the corrosion resistance of the copper. If the dezincified area were good solid copper, the corrosion resistance of the brass would be improved. Unfortunately, the dezincified portion is weak, permeable, and porous as indicated in Figure 36. The material is brittle and possesses little aggregate strength. This tube failed because of holes caused by some of the plugs being blown out by the water pressure (darkest areas in Figure 35).

Overall dimensions do not change appreciably when dezincification occurs. If a piece of equipment is covered with dirt or deposits, or not inspected closely, sudden unexpected failure may occur because of the poor strength of dezincified material.

Uniform, or layer-type, dezincification seems to favor the high brasses (high zinc content) and definitely acid environments. The plug types seem to occur more often in the low brasses (lower zinc content) and neutral, alkaline, or slightly acidic conditions. These are general statements, and many exceptions occur. Stagnant conditions usually favor dezincification because of scale formation or foreign deposits settling on the metal surface. This can result in crevice corrosion and/or higher temperatures because of the insulating effect of the deposit (if a heat exchanger is involved).

Metal structure and composition are important. Some brasses contain over 35% zinc. In these cases, a zinc-rich beta phase forms (duplex structure) and localized corrosion may occur. Sometimes the beta phase is attacked first, and then dezincification spreads to the alpha matrix.

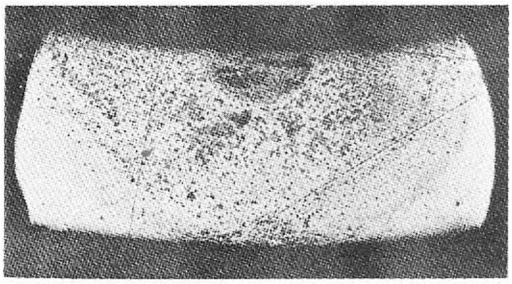


FIGURE 36 – Section of one of the plugs shown in Figure 35.

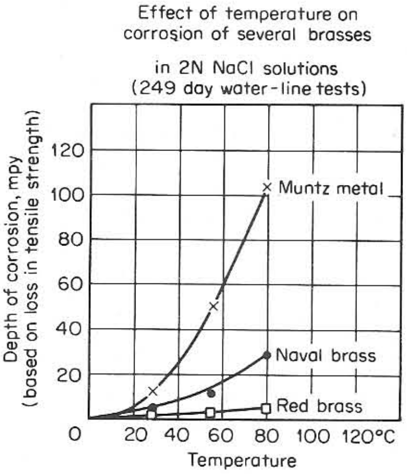


FIGURE 37 – Effect of temperature on corrosion of three brasses.

Figure 37 shows the effect of temperature on corrosion of three brasses by a 2N sodium chloride solution. Red brass contains 15% zinc, naval brass about 37% zinc, and Muntz metal 40% zinc. The data are based on loss in tensile strength of the test specimens. This is a good measure because in dezincified portions of the alloy exhibit practically no strength.

Dezincification: Mechanism

Two theories have been proposed from dezincification. One states that zinc is dissolved leaving vacant sites in the brass lattice structure. This theory is not proven. A strong argument against it is that dezincification to appreciable depths would be impossible or extremely slow because of difficulty of diffusion of solution and ions through a labyrinth of small vacant sites.

The commonly accepted mechanism consists of three steps as follows: (1) the brass dissolves, (2) the zinc ions stay in solution, and (3) the copper plates back on. Zinc is quite reactive, while copper is more noble. Zinc can corrode slowly in pure water by the cathodic ion reduction of H_2O into hydrogen gas and hydroxide ions. For this reason dezincification can proceed in the absence of oxygen. Oxygen also enters into the cathodic reaction and hence increases the rate of attack when it is present. Analyses of dezincified areas show 90 to 95% copper with some of it present as copper oxide. The amount of copper oxide is related to oxygen content of the environment. The porous nature of the deposit permits each contact between the solution and the brass.

Dezincification: Prevention

Dezincification can be minimized by reducing the aggressiveness of the environment (i.e., oxygen removal) or by cathodic protection, but in most cases these methods are not economical. Usually a less susceptible alloy is used. For example, red brass (15% Zn) is almost immune. Its improved performance is illustrated in Figure 37.

One of the first steps in the development of better brasses was the addition of 1% tin to a 70-30 brass (Admiralty Metal). Further improvement was obtained by adding small amounts of arsenic, antimony, or phosphorus as *inhibitors*. For example, arsenical Admiralty Metal contains about 70% Cu, 29% Zn, 1% Sn, and 0.04% As. Apparently these inhibiting elements are redeposited on the alloy as a film and thereby hinder deposition of copper. Arsenic is also added to aluminum (2% Al) brasses.

For severely corrosive environments where dezincification occurs, or for critical parts, cupronickels (70 to 90% Cu, 30 to 10% Ni) are utilized.

Graphitization

Gray cast iron sometimes shows the effects of selective leaching particularly in relatively mild environments. The cast iron appears to become *graphitized* in that the surface layer has the appearance of graphite and can be easily cut with a penknife. Based on this appearance and behavior, this phenomenon was christened *graphitization*. This is a misnomer because the graphite is present in the gray iron before corrosion occurs. It is also called *graphitic corrosion*.

What acutally happens is selective leaching of the iron or steel matrix leaving the graphite network. The graphite is cathodic to iron, and an excellent galvanic cell exists. The iron is dissolved leaving a porous mass consisting of graphite, voids, and rust. The cast iron loses strength and its metallic properties. Dimensional changes do not occur, and dangerous situations may develop without detection. The surface usually shows rusting that appears superficial, but the metal has lost its strength. The degree of loss depends on the depth of the attack. Graphitization is usually a slow process. If the case iron is in an environment which corrodes this metal rapidly, all of the surface is usually removed and more-or-less uniform corrosion occurs.

Graphitization does not occur in nodular or malleable cast irons because the graphite network is not present to hold together the residue. White cast iron has essentially no free carbon and is not subject to graphitization.

Other Alloy Systems

Selective leaching by aqueous environments occurs in other alloy systems under appropriate conditions, especially in acids. Selective removal of aluminum in aluminum bronzes has been observed in hydrofluoric and other acids. A two-phase or duplex structure is more susceptible. Massive effects were observed in crevices on aluminum bronze where the solution contained some chloride ions.

Selective leaching has been observed in connection with removal of silicon from silicon bronzes (Cu-Si) and also removal of cobalt from a Co-W-Cr alloy. It should be emphasized that these are rate cases and not as well known as dezincification.

Sometimes selective corrosion of one element in an alloy may be beneficial. Enrichment of silicon observed in the oxide film on stainless steels resultes in better passivity and resistance to pitting.

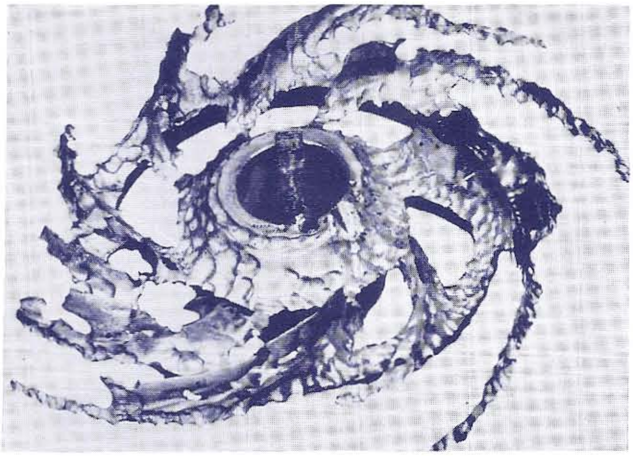


FIGURE 38 – Erosion corrosion of stainless alloy pump impeller.

High Temperatures

The senior author's early work on high-temperature oxidation of stainless steels showed selective oxidation of chromiumWhen there is competion for oxygen, the elements with higher free energies for their oxide formation (higher affinity for oxygen) are oxidized to a greater degree. In the case of stainless steels, this results in a more protective scale. However, the remaining or substrate metal will be deficient in chromium. This phenomenon was clearly demonstrated by Trax and Holzwarth.[8] Pitting of Type 430 (17% Cr) trim on automobiles was attributed to depletion of chromium during bright-annealing operations. Chromium contents as low at 11% were determined at and near the surface of the steel. Another unusual case showed the selective corrosion of chromium and iron from Inconel (75% Ni, 15% Cr, 9% Fe) by potassium-sodium-fluoride-chloride salt baths at about 802 C. The alloy was destroyed by conversion to a spongy mass.

Erosion Corrosion

Erosion corrosion is the acceleration or increase in rate of deterioration or attack on a metal because of relative movement between a corrosive fluid and the metal surface. Generally, this movement is quite rapid, and mechanical wear effects or abrasion are involved. Metal is removed from the surface as dissolved ions, or it forms solid corrosion products which are mechanically swept from the metal surface. Sometimes movement of the environment decreases corrosion, particularly when localized attack occurs under stagnant conditions, but this is not erosion corrosion because deterioration is not increased.

Erosion corrosion is characterized in appearance by grooves, gullies, waves, rounded holes, and valleys and usually exhibits a directional pattern. Figure 38 shows a typical wavy appearance of an erosion-corrosion failure. This pump impeller was taken out of service after 3 weeks of operation. Figure 39 is a sketch representing erosion corrosion of a heat-exchanger tube handling water. In many cases, failures because of erosion corrosion occur in a relatively short time, and they are unexpected largely because evaluation corrosion tests were run under static conditions or because the erosion effects were not considered.

Most metals and alloys are susceptible to erosion-corro-

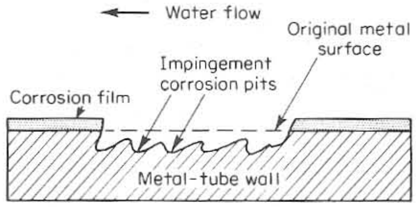


FIGURE 39 – Erosion corrosion of condenser tube wall.

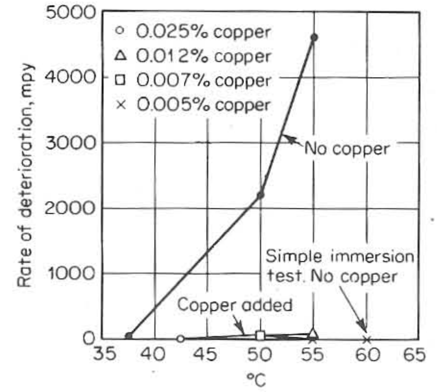


FIGURE 40 – Effect of temperature and copper-ion addition on erosion corrosion of Type 316 by sulfuric acid slurry (velocity, 39 ft/sec.).

sion damage. Many depend upon the development of a surface film of some sort (passivity) for resistance to corrosion. Examples are aluminum, lead, and stainless steels. Erosion corrosion results when these protective surfaces are damaged or worn and the metal and alloy are attacked at a rapid rate. Metals that are soft and readily damaged or worn mechanically, such as copper and lead, are quite susceptible to erosion corrosion.

Many types of corrosive mediums could cause erosion corrosion. These include gases, aqueous solutions, organic systems, and liquid metals. For example, hot gases may oxidize a metal and then at high velocity blow off an otherwise protective scale. Solids in suspension in liquids (slurries) are particularly destructive from the standpoint of erosion corrosion.

All types of equipment exposed to moving fluids are subject to erosion corrosion. Some of these are piping systems, particularly bends, elbows, and tees; valves; pumps; blowers; centrifugals; propellers; impellers; agitators; agitated vessels; heat-exchanger tubing such as heaters and condensers; measuring devices such as an orifice; turbine blades; nozzles; ducts and vapor lines; scrapers; cutters; wear plates; grinders; mills; baffles; and equipment subject to spray.

Since corrosion is involved in the erosion-corrosion process, all of the factors that affect corrosion should be considered. However, only the factors directly pertinent to erosion corrosion are discussed here.

Surface Films

The nature and properties of the protective films that form on some metals or alloys are very important from the standpoint of resistance to erosion corrosion. The ability of these films to protect the metal depends on the speed or ease with which they form when originally exposed to the environment, their resistance to mechanical damage or wear, and their rate of reforming when destroyed or damaged. A hard, dense, adherent, and continuous film would provide better protection than one that is easily removed by mechanical means or worn off. A brittle film that cracks or spalls under stress may not be protective. Sometimes the nature of the protective film that forms on a given metal depends upon the specific environment to which it is exposed, and this determines its resistance to erosion corrosion by the fluid.

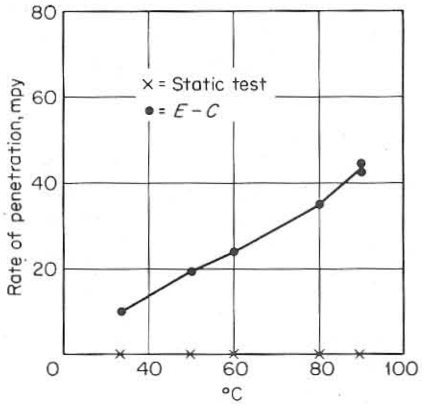


FIGURE 41 – Erosion corrosion of hard lead by 10% sulfuric acid (velocity 39 ft/sec.).

Stainless steels depend on passivity for resistance to corrosion. Consequently these materials are vulnerable to erosion corrosion. Figure 40 shows rapid attack of Type 316 stainless steel by a sulfuric acid-ferrous sulfate slurry moving at high velocity. The rate of deterioration is about 4500 mpy at 55 C (131 F). This material showed no weight loss and was completely passive under stagnant conditions as shown by the x on the abscissa at 60 C (140 F). The impeller shown in Figure 38 gave approximately 2 years' life, which was reduced to 3 weeks when the solution pumped was made more strongly reducing, thus destroying the passive film.

Lead depends on the formation of a lead sulfate-lead oxide protective surface for long life in sulfuric acid environments, and in many cases more than 20 years' service is obtained. Lead gains weight when exposed to sulfuric acid because of the surface coating or corrosion product formed, except in strong acid wherein the lead sulfate is soluble and not protective. However, lead valves failed in less than 1 week and lead bends were rapidly attacked in a plant handling a 3% sulfuric acid solution at 90 C (194 F). As a result of these failures, erosion corrosion tests were made and the results are plotted in Figure 41. Under static conditions the lead showed no deterioration (slight gain in weight) as shown by the points on the abscissa. Under high-velocity conditions, attack increased with temperature as shown by the curve.

Variations in amount of attack on steel by water with different pH values but constant velocity are apparently due to the nature and composition of the surface scales formed. Figure 42 shows the effect of pH of distilled water at 50 C (122 F) on erosion corrosion of carbon steel. Little attack is shown for pH specimens exhibiting high rates of deterioration was granular in nature and consisted of magnetic Fe_3O_4. Below a pH of 5 the scale cracked, probably because of internal stresses, and fresh metal was exposed. In regions of low attack the corrosion products were $Fe(OH)_2$ and $Fe(OH)_3$, which are more protective

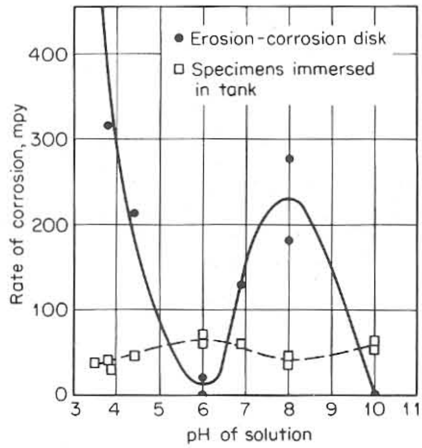


FIGURE 42 – Effect of pH of distilled water on erosion corrosion of carbon steel at 50 C (velocity 39 ft/sec).

probably because they hinder transfer of oxygen and ions. Erosion corrosion tests in boiler feedwater at 121 C (250 F) using a different type of testing equipment, and also power-plant experience, substantiate the results indicating higher attack at pH 8 as compared with slightly lower values.

Tests on copper and brass in sodium chloride solutions with and without oxygen show that copper is attacked more than brass in the oxygen-saturated solutions. The copper was covered with a black and yellow-brown film ($CuCl_2$). The brass was covered with a dark gray film (CuO). The better resistance of the brass to attack was attributed to the greater stability or protectiveness of the dark gray film. Difficulty was encountered in obtaining reproducible results until a controlled alkali cleaning and drying procedure for the specimens was adopted. This indicates that surface films formed on copper and brass because of atmospheric exposure, abrading, or other reasons can have a definite effect on erosion-corrosion performance under some conditions.

Titanium is a reactive metal but is resistant to erosion corrosion in many environments because of the stability of the TiO_2 film formed. It shows excellent resistance to sea water and chloride solutions and also to fuming nitric acid.

The behavior of steel and low-alloy-steel tubes handling oils at high temperatures in petroleum refineries depends somewhat on the sulfide films formed. When the film erodes, rapid attack occurs. For example, a normally tenacious sulfide film becomes porous and nonprotective when cyanides are present in these organic systems.

The effective use of inhibitors to decrease erosion corrosion depends, in many cases, on the nature and type of films formed on the metal as a result of reaction between the metal and the inhibitor.

Velocity

Velocity of the environment plays an important role in erosion corrosion. Velocity often strongly influences the mechanisms of the corrosion reactions. It exhibits mechanical wear effects at high values, particularly when the solution contains solids in suspension. Figure 40 and 41 show large increases in attack because of velocity. Figure 42 indicates that misleading results could be obtained when only static tests, or tests at low velocities, are made. The specimens in the tank were subjected to only a mild swirling motion. Table 6 shows the effect of velocity on a variety of metals and alloys exposed in sea water. These data show that the effect of velocity may be nil or extremely great.

TABLE 6 – Corrosion of Metals by Sea Water Moving at Different Velocities

Material	Typical corrosion rates, mdd		
	1 ft/sec(1)	4 ft/sec(2)	27 ft/sec(3)
Carbon steel	34	72	254
Cast iron	45	–	270
Silicon bronze	1	2	343
Admiralty brass	2	20	170
Hydraulic bronze	4	1	339
G bronze	7	2	280
Al bronze (10% Al)	5	–	236
Aluminum brass	2	–	105
90-10 Cu Ni (0.8% Fe)	5	–	99
70-30 Cu Ni (0.05% Fe)	2	–	199
70-30 Cu Ni (0.5% Fe)	<1	<1	39
Monel	<1	<1	4
Stainless steel type 316	1	0	<1
Hastelloy C	<1	–	3
Titanium	0	–	0

(1)Immersed in tidal current.
(2)Immersed in sea water flume.
(3)Attached to immersed rotating disk.
Source: International Nickel Co.

Increases in velocity generally result in increased attack, particularly if substantial rates of flow are involved. The effect may be nil or increase slowly until a critical velocity is reached, and then the attack may increase at a rapid rate. Table 6 lists several examples exhibiting little effect when the velocity is increased from 1 to 4 ft/sec, but destructive attack at 27 ft/sec. This high velocity is below the critical value for other materials listed at the bottom of the table.

Erosion corrosion can occur on metals and alloys that are completely resistant to a particular environment at low velocities. For example, hardened straight chromium stainless steel valve seats and plugs give excellent service in most steam applications, but grooving or so-called *wire drawing* occurs in high-pressure steam reducing or throttling valves.

Increased velocity may increase or reduce attack, depending on its effect on the corrosion mechanism involved. It may increase attack on steel by increasing the supply of oxygen, carbon dioxide, or hydrogen sulfide in contact with the metal surface, or velocity may increase diffusion or transfer of ions by reducing the thickness of the stagnant film at the surface.

Velocity can decrease attack and increase the effectiveness of inhibitors by supplying the chemical to the metal surface at a higher rate. It has been shown that less sodium nitrite is needed at high velocity to protect steel in tap water. Similar mechanisms have been postulated for other types of inhibitors.

Higher velocities may also decrease attack in some cases by preventing the deposition of silt or dirt which would cause crevice corrosion. On the other hand, solids in suspension moving at high velocity may have a scouring effect and thus destroy surface protection. This was the case in connection with Figure 40, which involved rapid erosion corrosion of Type 316 centrifugals handling a sulfuric acid slurry.

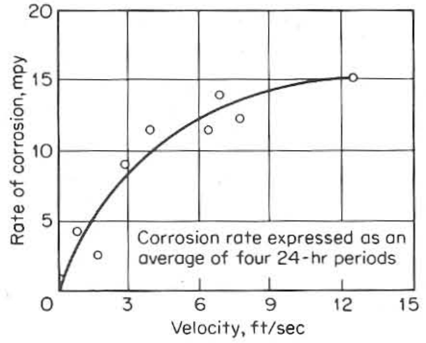


FIGURE 43 – Erosion corrosion of 3003 aluminum by white fuming nitric acid at 108 F.

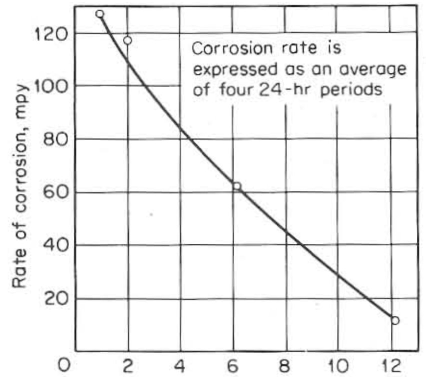


FIGURE 44 – Erosion corrosion of Type 347 stainless steel by white fuming nitric acid at 108 F.

Erosion corrosion studies of aluminum and stainless alloys in fuming nitric acid produced unusual and interesting results. Attack on aluminum increased and attack on Type 347 stainless steel decreased as velocity was increased, because of the different corrosion mechanisms involved. Figure 43 shows increasing attack on aluminum with increasing velocity. Aluminum can form films of aluminum nitrates and aluminum oxide in fuming nitric acid. Little or no attack occurs at zero or very low velocities. At intermediate velocities of 1 to 4 ft/sec, the action of the solution is sufficient to remove the nitrate film but not strong enough to destroy the more adherent oxide film. Velocities above 4 ft/sec apparently remove much of the oxide, and erosion corrosion occurs at a faster rate.

Figure 44 shows decrease in attack on Type 347 stainless steel as velocity is increased. Under stagnant conditions this steel in nitric acid is attacked autocatalytically because of formation of nitrous acid as a cathodic reaction product. Increasing velocity sweeps away the nitrous acid and thus removes one of the corrosive agents in the environment.

Many stainless steels have a strong tendency to pit and suffer crevice corrosion in sea water and other chlorides. However, some of these materials are used successfully in sea water, provided the water is kept moving at a substantial velocity. This motion prevents formation of deposits and retards the initiation of pits.

Turbulence

Many erosion-corrosion failures occur because turbulence or turbulent flow conditions exist. Turbulence results in greater agitation of the liquid at the metal surface than is the case for lamellar (straight line) flow. Turbulence results in more intimate contact between the environment and the metal. Perhaps the most frequently occuring example of this type of failure occurs in the inlet ends of tubing in condensers and similar shell-and-tube heat exchangers. It is designated as inlet-tube corrosion. The attack is usually confined to the first few inches of the tubing at the inlet end. Turbulence exists in this area because the liquid is flowing essentially from a large pipe (the exchanger head) into a small diameter pipe (the tubes). Lamellar flow develops after the liquid has progressed down the tube a relatively short distance.

FIGURE 45 – Impingement failure of elbow in steam condensate line.

The type of flow obtained depends on the rate and quantity of fluid handled and also on the geometry or design of the equipment. In addition to high velocities, ledges, crevices, deposits, sharp changes in cross section, other obstructions that disturb the lamellar flow pattern may result in erosion corrosion. Impellers and propellers are typical components operating under turbulent conditions.

Impingement

Many failures are directly attributed to impingement. Figure 45 is an example of this type of failure. The vertical and horizontal runs of pipe were relatively unaffected, but the metal failed where the water was forced to turn its direction of flow. Other examples are steam-turbine blades, particularly in the exhaust or wet-steam ends; entrainment separators; bends; tees; external components of aircraft; parts in front of inlet pipes in tanks; cyclones; and any other applications where impingement conditions exist. Solids and some times bubbles of gas in the liquid increase the impingement effect. Air bubbles are an important factor in accelerating impingement attack.

Figure 46 shows severe erosion corrosion, caused by impingement in less than 1 year of service, of a slide valve in contact with a fluidized catalyst and oil at 482 C (900 F) in a refinery. This was originally solid steel about 3 inches in diameter. Figure 47 shows two types of erosion corrosion in a thermal cracking furnace for oil. The tube on the left contained superheated steam. It cracked, and escaping steam formed the two holes shown. This steam impinged on an oil tube, shown on the right, and a leak developed. Catalytic cracking (catalyst in suspension) experience indicates that an angle of 25 degrees can cause

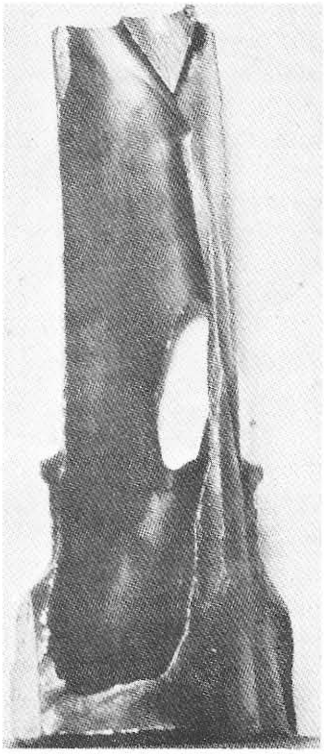


FIGURE 46 – Erosion corrosion of slide valve at 900 F in petroleum refinery.

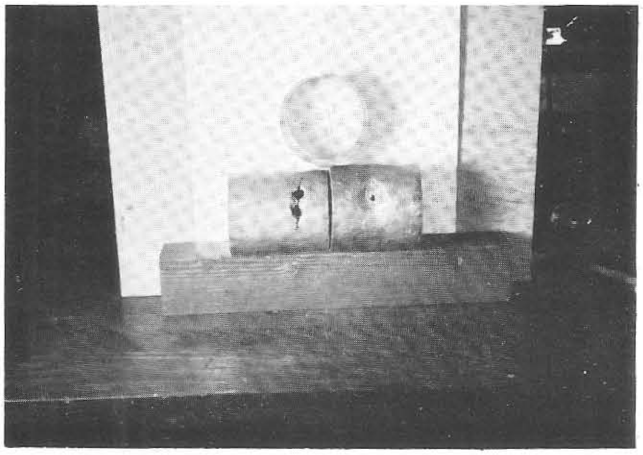


FIGURE 47 – Impingement by escaping steam from cracked tube (left).

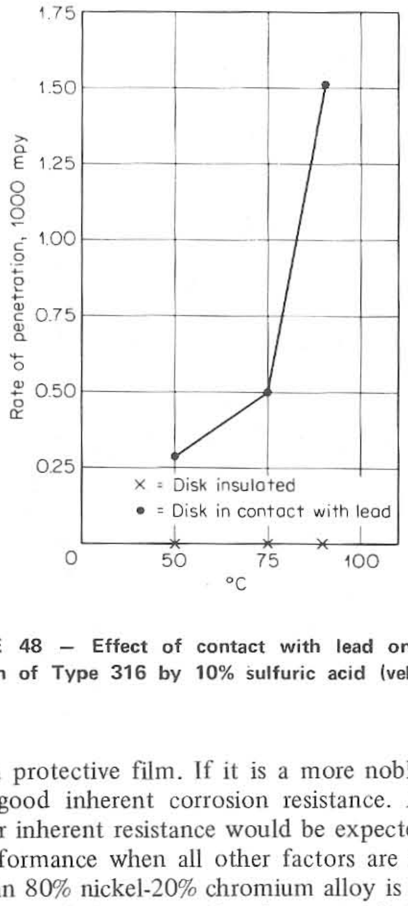


FIGURE 48 – Effect of contact with lead on erosion corrosion of Type 316 by 10% sulfuric acid (velocity 39 ft/sec.).

impingement attack.

Galvanic Effect

Galvanic, or two-metal, corrosion can influence erosion corrosion when dissimilar metals are in contact in a flowing system. The galvanic effect may be nil under static conditions but may be greatly increased when movement is present. Figure 48 shows that attack on Type 316 by itself was nil in high velocity sulfuric acid but increased to very high values when its alloy was in contact with lead. The passive film was destroyed by the combined forces of galvanic corrosion and erosion corrosion. Couples of lead and Type 316 showed no corrosion under static conditions. Cracks in the Fe_3O_4 scale formed in the lower pH ranges of Figure 42 doubtlessly contributed to increased attack because the scale is cathodic to the substrate steel by about 500 mV.

Velocity changes can produce surprising galvanic effects. In seawater at low velocity the corrosion of steel is not appreciably affected by coupling with stainless steel, copper, nickel, or titanium. At high velocities the attack on steel is much less when coupled to stainless steel and titanium than when coupled to copper or nickel. This is attributed to the more effective cathodic polarization of stainless steel and titanium at high velocities.

Nature of Metal or Alloy

The chemical composition, corrosion resistance, hardness, and metallurgical history of metals and alloys can influence the performance of these materials under erosion-corrosion conditions. The composition of the metal largely determines its corrosion resistance. If it is an active metal, or an alloy composed of active elements, its corrosion resistance is due chiefly to its ability to form and maintain a protective film. If it is a more noble metal, it possesses good inherent corrosion resistance. A material with better inherent resistance would be expected to show better performance when all other factors are equal. For example, an 80% nickel-20% chromium alloy is superior to an 80% iron 20% chromium alloy because nickel has better inherent resistance than iron. For the same reason, a nickel-copper alloy is better than one of zinc and copper.

The addition of a third element to an alloy often increases its resistance to erosion corrosion. The addition of iron to cupronickel produces a marked increase in resistance to erosion corrosion by sea water as shown in Table 6. The addition of molybdenum to 18-8 to make Type 316 makes it more resistant to corrosion and erosion corrosion. In both cases, the addition of the third element produces a more stable protective film. Aluminum brasses show better erosion corrosion resistance than straight brass.

Resistance of steel and iron-chromium alloys to acid mine waters under erosion-corrosion conditions showed a straight-line increase in resistance with increasing chromium up to 13%. At this content and above. no attack occurred. Low-alloy chromium steels show better erosion-corrosion resistance than straight carbon steels in high temperature boiler feedwater. Type 3 Ni-Resist (30% nickel, 3% chromium cast iron) showed practically no attack by sea water after 60 days under erosion-corrosion conditions, whereas ordinary cast iron was badly deteriorated.

Erosion-corrosion resistance of stainless steels and stainless alloys varies depending upon their compositions. Durimet 20 (30% Ni, 20% Cr, 3.5% Cu, 2% Mo) exhibits better performance than 18-8 steels in fuming nitric acid, sea water, and many other environments not only because of better inherent resistance, but also because of the more protective films formed.

The soft metals are more susceptible to erosion corrosion because they are more subject to mechanical wear. Hardness is a fairly good criterion for resistance to mechanical erosion or abrasion, but it is not necessarily a good criterion for predicting resistance to erosion corrosion. There are many methods for producing hard metals and alloys or for hardening them. One sure method for producing good erosion-corrosion resistance is solid-solution hardening. This involves adding one element to another to produce a solid solution that is corrosion resistant and is inherently hard. It cannot be softened or further hardened by heat treatment. The best and most familiar example is high-silicon (14.5% Si) iron. It is perhaps the most universally corrosion resistant of the nonprecious metals, and the only alloy that can be used in many severe erosion-corrosion conditions.

A good example of poor performance by a high-hardness material concerned the centrifugals and conditions discussed in connection with Figure 40. Both Type 316 and Type 329 stainless steels showed no measurable corrosion in the sulfuric acid slurry under static conditions, even when the Type 329 was age-hardened to 450 Brinell hardness. Under the erosion-corrosion conditions in the centrifugal, however, the hard Type 329 steel deteriorated more than 10 times faster than the soft (150 Brinell) Type 316.

Cast iron sometimes shows better performance than steel under erosion-corrosion conditions, particularly in hot strong sulfuric acid. The iron in the cast iron is corroded, but the remaining graphitized layer consisting of the original graphite network and corrosion products provides some protection.

Combating Erosion Corrosion

Five methods of prevention or minimization of damage due to erosion corrosion are used. In order of importance, or extent of use, they are (1) materials with better resistance to erosion corrosion, (2) design, (3) alteration of the environment, (4) coating, and (5) cathodic protection.

Better Materials. The reasons for using better materials which give better performance are obvious. This method represents the economical solution to most erosion-corrosion problems.

Design. This is an important method in that the life of presently used, or less costly materials, can be extended considerably or the attack practically eliminated. Design here involves change in shape, or geometry, and not selection of material. Erosion-corrosion damage can be reduced through better design as illustrated by the following examples. Increasing pipe diameter helps from the mechanical standpoint by decreasing velocity and also ensures lamellar flow. Increasing the thickness of material strengthens vulnerable areas. In one instance of severe erosion corrosion of lead, maintenance costs were reduced to a satisfactory level by using a sweeping bend and doubling the thickness of the pipe. The design of other equipment, such as inlets and outlets, should be streamlined to remove obstructions for the same reasons. Readily replaceable impingement plates or baffles should be inserted. Inlet pipes should be directed towards the center of a tank instead of near its wall. Tubes should be designed to extend several inches beyond the tube sheet at the inlet end. In several cases, life of tubing was practically doubled by increasing the length 4 inches. The protruding tube ends were attacked, but operation was not affected.

Ferrules, or short lengths of flared tubing, can be inserted in the inlet ends. These could be made of the same material as the tubes or of material with better resistance. Bakelite and other plastic ferrules are readily available and widely used in condensers. The end of the ferrule should be *Feathered* to blend the flow. If this is not done, erosion corrosion occurs on the tube just beyond the end of the ferrule because of the step present. Galvanic corrosion must be considered when using metallic inserts. The life of tubing in a vertical evaporator was doubled by turning the evaporator upside down when the inlet or bottom ends of the tubes became thin. The outlet ends, which were not appreciably attacked, became inlet ends. Equipment should be designed so parts can be replaced readily. Tube bundles that can be readily removed and replaced by spares can be repaired at leisure. Buckets and conveyor flights that are easily replaced on centrifugals and other conveying equipment reduce costs of erosion corrosion. Use of pumps with interchangeable parts in different alloys helps reduce costs when an unsatisfactory alloy is originally selected. In one case, some of the blades of a steam turbine were out of line and the protruding blades suffered severe erosion-corrosion damage from water droplets in the steam. Misalignment from one pipe section to the next can cause erosion corrosion in both flanged and welded joints. Good design implies proper construction and workmanship.

Alteration of the Environment. Deaeration and the addition of inhibitors are effective methods, but in many cases they are not sufficiently economical for minimizing erosion-corrosion damage. Settling and filtration are helpful in removing solids. Whenever possible, the temperature of the environment should be reduced. This has been done in many cases without appreciably affecting the process. Temperature is out worst enemy in erosion corrosion, as it is in all types of corrosion.

Coatings. Applied coatings of various kinds that produce a resilient barrier between the metal and its environment are sometimes utilized but are not always feasible for solving erosion-corrosion problems. Hard facings, or welded overlays, are sometimes helpful, provided the facing has good corrosion resistance. Repair of attacked areas by welding is often practical.

Cathodic Protection. This helps to reduce attack, but it has not found widespread use for erosion corrosion. One plant uses steel plates on condenser heads to provide cathodic protection of the inlet ends of tubes in heat exchangers handling sea water. Others use zinc plates. Zinc plugs are frequently used in water pumps.

Fortunately, all pumps, valves, lines, pipes, elbows, etc., do not fail because of erosion corrosion. However, serious trouble may develop if erosion corrosion is not considered.

Cavitation Damage

Cavitation damage is a special form of erosion corrosion which is caused by the formation and collapse of vapor bubbles in a liquid near a metal surface. Cavitation damage occurs in hydraulic turbines, ship propellers, pump impellers, and other surfaces where high-velocity liquid flow and pressure changes are encountered. Before considering cavitation damage, let us examine the phenomenon of cavitation. If the pressure on a liquid such as water is reduced sufficiently, it boils at room temperature. Consider a cylinder full of water which is fitted with a tight piston in contact with the water. If the piston is raised away from the water, pressure is reduced and the water vaporizes, forming bubbles. If the piston is now pushed toward the water, pressure is increased and bubbles condense or collapse. Repeating this process at high speed such as in the case of an operating water pump, bubbles of water vapor form and collapse rapidly. Calculations have shown that rapidly collapsing vapor bubbles produce shock waves with pressures as high as 60,000 lb/in.^{2} Forces this high can produce plastic deformation in many metals. Evidence of this is indicated by the presence of slip lines in pump parts and other equipment subjected to cavitation.

The appearance of cavitation damage is somewhat similar to pitting, except that the pitted areas are closely spaced and the surface is usually considerably roughened. Cavitation damage has been attributed to both corrosion and mechanical effects. In the former case, it is assumed that the collapsing vapor bubbles destroy protective surface films which results in increased corrosion. This mechanism is shown schematically in Figure 49. The steps are as follows: (1) a cavitation bubble forms on the protective film; (2) the bubble collapses and destroys the film; (3) the newly exposed metal surface corrodes and the film is reformed; (4) a new cavitation bubble forms at the same spot; (5) the bubble collapses and destroys the film, and (6) the exposed area corrodes and the film reforms. The repetition of this process results in deep holes.

Examination of Figure 49 shows that it is not necessary to have a protective film for cavitation damage to occur. An imploding cavitation bubble has sufficient force to tear metal particles away from the surface. Once the surface has been roughened at a point, this serves as a nucleus for new cavitation bubbles in a manner similar to that shown in Figure 49. In actual practice, it appears that cavitation damage is the result of both mechanical and chemical action.

Table 7 presents the results of some cavitation-damage tests using a high speed vibrator. These tests correlate very well with performance under actual operating conditions.

In general, cavitation damage can be prevented by the techniques used in preventing erosion corrosion outlined above. Also, there are some specific measures. Cavitation damage can be reduced by changing design to minimize hydrodynamic pressure differences in process flow streams. More corrosion resistant materials may be substituted (compare cast iron and 18-8 stainless steels in Table 7). Smooth finishes on pump impellers and propellers reduce damage since smooth surfaces do not provide sites for bubble nucleation. Coating metallic parts with resilient coatings such as rubber and plastic have also proven beneficial. It is important to use caution in applying such coatings, since bonding failures between the metal-coating interface frequently occur during operation. Cathodic protection also reduces cavitation damage. The mitigating effect of cathodic protection is apparently due to the formation of hydrogen bubbles on the metal surface which cushions the shock wave produced during cavitation.

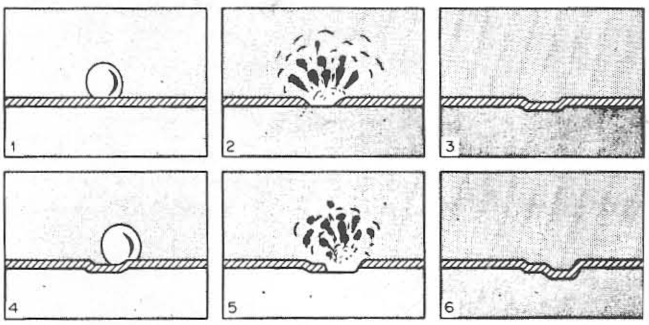


FIGURE 49 – Schematic representation of steps in cavitation (R. W. Henke).

Fretting Corrosion

Fretting describes corrosion occuring at contact areas between materials under load subjected to vibration and slip. It appears as pits or grooves in the metal surrounded by corrosion products. Fretting is also called friction oxidation, wear oxidation, chafing, and false brinelling (so names because the resulting pits are similar to the identations made by a Brinell hardness test). It has been observed in engine components, automotive parts, bolted parts, and other machinery. Essentially, fretting is a special case of erosion corrosion which occurs in the atmosphere rather than under aqueous conditions.

Fretting corrosion is very detrimental because of the destruction of metallic components and the production of oxide debris. Seizing and galling often occur, together with loss of tolerances and loosening of mating parts. Further, fretting causes fatigue fracture since the loosening of components permits excessive strain, and the pits formed by fretting act as stress raisers.

A classic case of fretting is that which occurs at bolted tie plates on railroad rails. Frequent tightening of these plates is required because the parts are not lubricated and fretting corrosion proceeds rapidly. Another common case of fretting corrosion occurs at the interface between a press-fitted ball bearing shaft as shown in Figure 50. Fretting corrosion in this area leads to loosening and subsequent failure.

The basic requirements for the occurrence of fretting corrosion are: (1) the interface must be under load; (2) vibration or repeated relative motion between the two surfaces must occur, and (3) the load and the relative motion of the interface must be sufficient to produce slip or deformation on the surfaces.

The relative motion necessary to produce fretting corrosion is extremely small; displacements as little as 10^{-8} cm cause fretting damage. Repeated relative motion is a necessary requirement for fretting corrosion. It does not occur on surfaces in continuous motion, such as axle bearings or the ball bearings shown in Figure 50, but rather on interfaces which are subject to repeated small relative displacements. This point is best illustrated by considering fretting corrosion occurring on automobile axles during long-distance shipment by rail or boat. This is caused by the load on these surfaces and the continuous vibration or jiggling which occurs during shipment. Normal operation of

TABLE 7 – Relative Resistance of Metals to Cavitation Damage by the Vibratory Test Method

		Composition, %									Weight loss at 25 C for last 60-min exposure, mg/hr	
Nonferrous	Form	Cu	Sn	Zn	Mn	Si	Ni	Fe	Pb	Al	Freshwater	Seawater
Bronze (Cu, Zn, Sn)	Rolled	60	1	39	–	–	–	–	–	–	69.5	65.2
Brass (Cu, Zn)	Rolled	60	–	40	–	–	–	–	–	–	77.8	68.7
Brass (Cu, Zn)	Rolled	85	–	15	–	–	–	–	–	–	115.2	101.3
Brass (Cu, Zn)	Rolled	90	–	10	–	–	–	–	–	–	134.9	122.8
Bronze (Cu, Al)	Cast	89	–	–	–	–	(1)	(1)	–	10	15.3	14.5
Bronze (Cu, Sn, Ni)	Cast	87.5	11	–	–	–	1.5	–	–	–	54.6	62.4
Bronze (Cu, Sn, Pb)	Cast	88	10	–	–	–	–	–	2	–	60.4	48.5
Bronze (Cu, Si)	Cast	92-94	–	(1)	–	3-4	–	(1)	–	(1)	42.6	40.4
Bronze (Cu, Si, Mn)	Cast	94	–	–	1	5	–	–	–	–	52.4	54.5
Bronze (Cu, Zn, Al, Mn)	Forged	60-70	–	20-30	–	–	–	(1)	–	(1)	19.2	19.9
Bronze (Cu, Zn, Fe, Mn)	Cast	58	–	40	–	–	–	1	–	(1)	53.0	55.4
Bronze (Cu, Sn, Zn)	Cast	88	10	2	–	–	–	–	–	–	65.8	57.4
Nickel (Cu, Fe, Si)	Cast	32-33	–	–	–	4	62-63	2	–	–	20.0	21.4
Nickel (Cu, Fe, Mn)	Drawn	29	–	–	1	–	68	1	–	–	53.3	53.2
Nickel (Cu)	Rolled	70	–	–	–	–	30	–	–	–	86.2	87.6

		Composition, %									Weight loss at 25 C for last 60-min exposure, mg/hr	
Ferrous	Form	C	Si	Cu	Mo	S	P	Mn	Cr	Ni	Freshwater	Seawater
Iron	Cast	3.1	2.3	–	–	0.12	0.07	0.75	–	–	50.1	80.9
Iron	Cast	3.4	1.3	–	–	0.08	0.25	0.75	–	–	69.8	115.3
Iron	Cast	3.4	2.3	–	–	–	–	0.59	–	–	89.7	100.2
Iron (Cu, Ni, Cr, Si)	Cast	3.0	1.9	6.0	–	–	–	–	4.0	14.4	41.6	51.4
Iron (Mo)	Cast	3.3	1.3	–	0.40	–	–	0.51	–	–	54.1	63.9
Iron (Mn, Cu, Ni, Cr)	Cast	3.0	1-2	6.0	–	0.10	0.04	1.0	1-3	12-15	85.3	95.3
Steel	Rolled	0.35	–	–	–	–	0.45	0.67	–	–	34.2	39.6
Steel	Rolled	0.27	–	–	–	0.40	0.45	0.48	–	–	68.3	77.8
Steel	Rolled	0.20	–	–	–	0.03	0.02	0.50	–	–	78.2	82.4
Steel	Cast	0.37	0.31	–	–	0.04	0.04	1.10	–	–	44.8	53.6
Steel	Cast	0.26	0.32	–	–	0.04	0.04	0.60	–	–	72.9	80.9
Steel (Ni, Cr)	Rolled	0.34	0.20	–	–	0.03	0.02	0.52	0.60	1.18	20.0	22.0
Steel (Ni)	–	0.19	–	–	–	0.02	0.02	0.60	–	2.2	61.3	64.0
Stainless steel (Cr)	Rolled	0.08	0.57	–	–	0.02	0.03	0.47	17.2	0.34	11.8	10.8
Stainless steel (Cr)	Rolled	0.09	0.38	–	–	0.02	0.02	0.43	12.2	0.32	20.6	23.0
Stainless steel (Cr, Ni)	Cast	0.15	0.50	–	–	–	–	0.50	16-20	8-12	13.5	13.4
Stainless steel (Cr, Ni)	Rolled	0.07	0.37	–	–	0.14	0.19	0.48	18.4	8.7	16.1	15.3

(1) 1.0% max. present, but not determined analytically.

Source: Trans. ASME, Vol. 59 (1937).

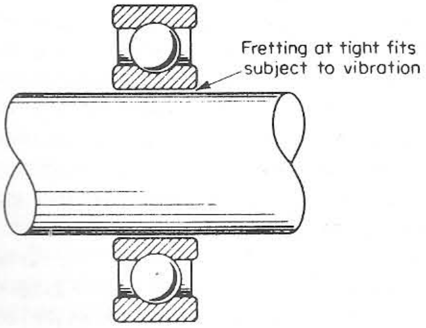


FIGURE 50 – Example of typical fretting corrosion location.

an automobile does not show this difficulty because the relative motion between the axle bearing surfaces is very large (complete revolutions).

The two major mechanisms proposed for fretting corrosion are the wear-oxidation and oxidation-wear theories, which are schematically illustrated in Figures 51 and 52, respectively. The wear-oxidation mechanism is based on the concept that cold welding or fusion occurs at the interface between metal surfaces under pressure, and during subsequent relative motion, these contact points are ruptured and fragments of metal are removed. These fragments, because of their small diameter and the heat due to friction, are immediately oxidized. This process is then repeated with the resulting loss of metal and accumulation of oxide residue. Thus, the wear-oxidation hypothesis is based on the concept that frictional wear causes the damage

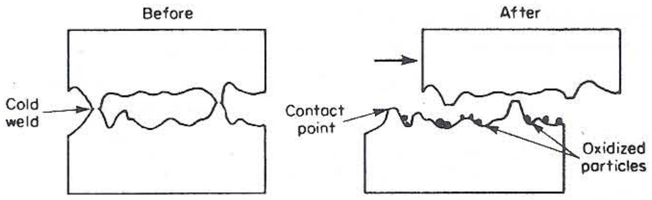


FIGURE 51 – Schematic illustration of the wear-oxidation theory of fretting corrosion.

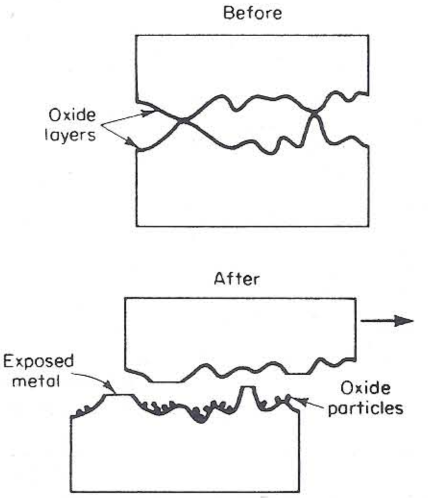


FIGURE 52 – Schematic illustration of the oxidation-wear theory of fretting corrosion.

and subsequent oxidation is a secondary effect.

The oxidation-wear concept, illustrated in Figure 52, is based on the hypothesis that most metal surfaces are protected from atmospheric oxidation by a thin adherent oxide layer. When metals are placed in contact under load and subjected to repeated relative motion, the oxide layer is ruptured at high points and results in oxide debris as shown schematically in Figure 52. It is assumed that the exposed metal reoxidizes and the process is repeated. The oxidation wear theory is essentially based on a concept of accelerated oxidation due to frictional effects.

Considering Figures 51 and 52 and the two theories outlined above, it is obvious that both theories lead to the same conclusion: namely, the production of oxide debris and destruction of metal interfaces. Recent investigations suggest that both of the above mechanisms operate during fretting corrosion. The presence of an oxide layer does not appear to be necessary in every case, since fretting damage has been observed on almost every kind of surface including the noble metals, mica, glass, and ruby. Oxygen, however, does have an effect since its presence accelerates fretting attack of many materials, especially ferrous alloys. The actual mechanism of the fretting corrosion is probably a combination of the mechanisms illustrated in Figures 51 and 52.

Fretting corrosion can be minimized or practically eliminated in many cases by applying one or more of the following preventive measures:

1. Lubricate with low-viscosity, high-tenacity oils and greases. Lubrication reduces friction between bearing surfaces and tends to exclude oxygen. Also, phosphate coatings (*Parkerizing*) are often used in conjunction with lubricants since these coatings are porous and provide oil reservoirs.

TABLE 8 – Fretting Resistance of Various Materials

Poor	Average	Good
Aluminum on cast iron	Cast iron on cast iron	Laminated plastic on gold plate
Aluminum on stainless steel	Copper on cast iron	Hard tool steel on tool steel
Magnesium on cast iron	Brass on cast iron	Cold-rolled steel on cold-rolled steel
Cast iron on chrome plate	Zinc on cast iron	Cast iron on cast iron with phosphate coating
Laminated plastic on cast iron	Cast iron on silver plate	Cast iron on cast iron with coating of rubber cement
Bakelite on cast iron	Cast iron on copper plate	Cast iron on cast iron with coating of tungsten sulfide
Hard tool steel on stainless	Cast iron on amalgamated copper plate	Cast iron on cast iron with rubber gasket
Chrome plate on chrome plate	Cast iron on cast iron with rough surface	Cast iron on cast iron with Molykote lubricant
Cast iron on tin plate	Magnesium on copper plate	Cast iron on stainless with Molykote lubricant
Cast iron on cast iron with coating of shellac	Zirconium on zirconium	

Source: J. R. McDowell, ASTM Special Technical Publication No. 144, p. 24, American Society for Testing Materials, Philadelphia (1952).

2. Increase the hardness of one or both of the contacting materials. This can be accomplished by choosing a combination of hard materials or hard alloys. Table 8 lists the relative fretting corrosion resistance of various material combinations. As shown, hard materials are more resistant than soft materials. Also, increasing surface hardness by shot-peening or cold-working increases fretting resistance.

3. Increase friction between mating parts by roughening the surface. Often, bearing surfaces which will be subjected to vibration during shipment are coated with lead to prevent fretting corrosion. When the bearing is placed in service, the lead coating is rapidly work away.

4. Use gaskets to absorb vibration and to exclude oxygen at bearing surfaces.

5. Increase load to reduce slip between mating surfaces.

6. Decrease the load at bearing surfaces. It is important to note that decreasing the load is not always successful, since very small loads are capable of producing damage.

7. If possible, increase the relative motion between parts to reduce attack.

Stress Corrosion

Stress corrosion cracking (SCC) refers to cracking caused by the simultaneous presence of tensile stress and a specific corrosive medium. Many investigators have classified all cracking failures occurring in corrosive mediums as SCC, including failures due to hydrogen embrittlement. However, these two types of cracking failures respond differently to environmental variables. To illustrate, cathodic protection is an effective method for preventing SCC, whereas it rapidly accelerates hydrogen-embrittlement effects. Hence, the importance of considering SCC and hydrogen embrittlement as separate phenomena is obvious. For this reason, the two cracking phenomena are discussed separately in this chapter.

During SCC, the metal or alloy is virtually unattacked over most of its surface, while fine cracks progress through it. This is illustrated in Figure 53. This cracking phenomenon has serious consequences since it can occur at stresses within the range of typical design stress. The stresses required for SCC are compared with the total range of strength capabilities for Type 304 stainless steel in Figure 54. Exposure to boiling $MgCl_2$ at 154 C (310 F) is

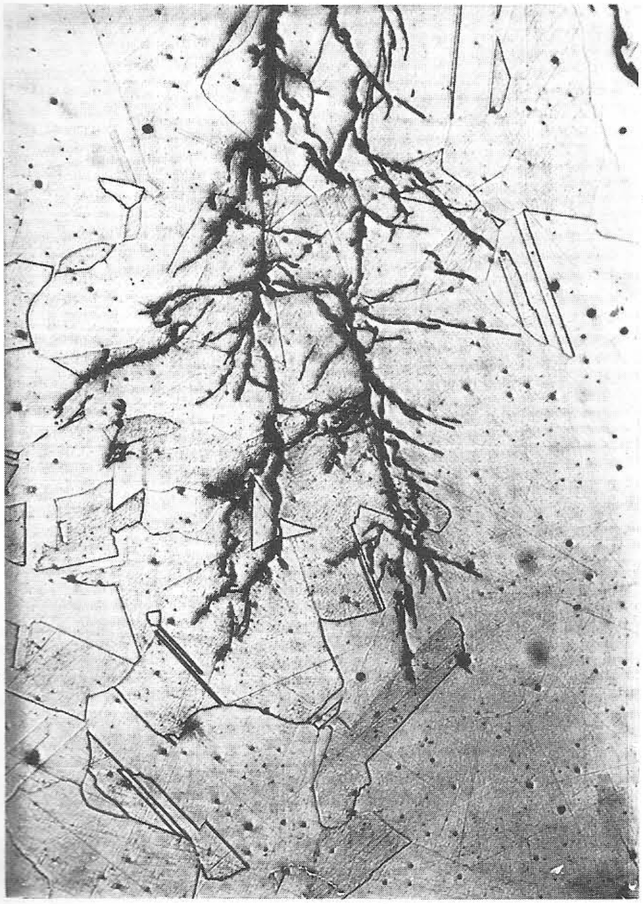


FIGURE 53 – Cross section of stress corrosion crack in stainless steel.

shown to reduce the strength capability to approximately that available at 649 C.

The two classic cases of SCC are *season cracking* of brass, and the *caustic embrittlement* of steel. Both of these obsolete terms describe the environmental conditions present which lead to SCC. Season cracking refers to the SCC failure of brass cartridge cases. During periods of heavy rainfall, expecially in the tropics, cracks were observed in the brass cartridge cases at the point where the case was crimped to the bullet. It was later found that the important environmental component in season cracking was ammonia resulting from the decomposition of organic matter. An example of this is shown in Figure 55.

Many explosions of riveted boilers occurred in early steam-driven locomotives. Examination of these failures showed cracks or brittle failures at the rivet holes. These areas were cold-worked during riveting operations, and analysis of the whitish deposits found in these areas showed caustic, or sodium hydroxide, to be the major component. Hence, brittle fracture in the presence of caustic resulted in the term caustic embrittlement. Figure 56 shows a plate which failed by caustic embrittlement. The cracks are numerous and very fine and have been revealed by application of a penetration dye solution. While stress alone will react in ways well known in mechanical metallurgy (i.e., creep, fatigue, tensile failure) and corrosion alone will react to produce characteristic dissolution reactions; the simultaneous action of both sometimes produces the disastrous results shown above.

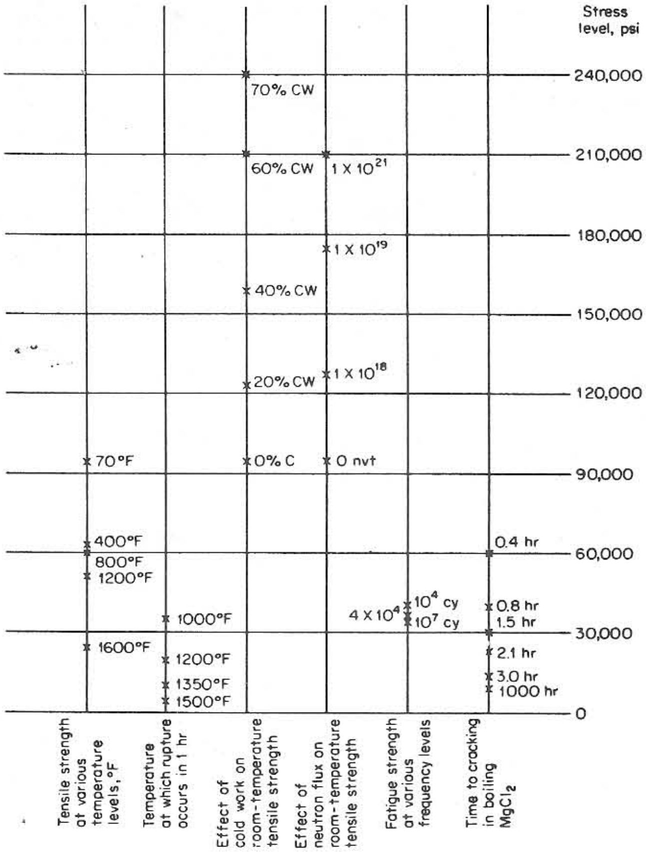


FIGURE 54 – Comparison of fracture stresses by various techniques compared with stress corrosion cracking. Material: Type 304 stainless (R. W. Staehle, Ohio State University).

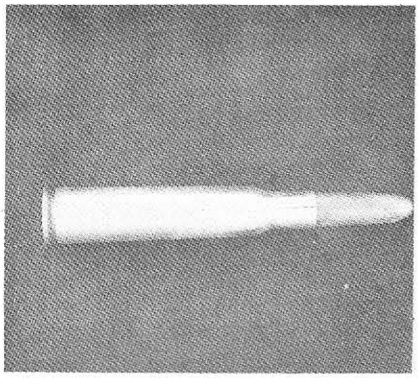


FIGURE 55 – Season cracking of German military ammunition.

Not all metal-environment combinations are susceptible to cracking. A good example is the comparison between brasses and austenitic stainless steels. Stainless steels crack in chloride environments but not in ammonia containing environments, whereas brasses crack in ammonia containing environments but not in chlorides. Further, the number of different environments in which a given alloy will crack is generally small. For example, stainless steels do not crack in sulfuric acid, nitric acid, acetic acid, or pure water, but they do crack in chloride and caustics.

The important variables affecting SCC are temperature, solution composition, metal composition, stress, and metal structure. In subsequent sections these factors will be

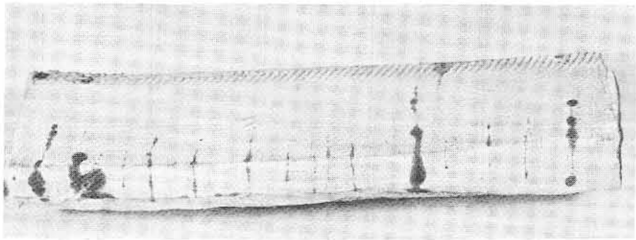


FIGURE 56 – Carbon steel plate from a caustic storage tank failed by caustic embrittlement (Imperial Oil, Limited, Ontario, Canada).

FIGURE 57 – Intergranular stress corrosion cracking of brass (E. N. Pugh).

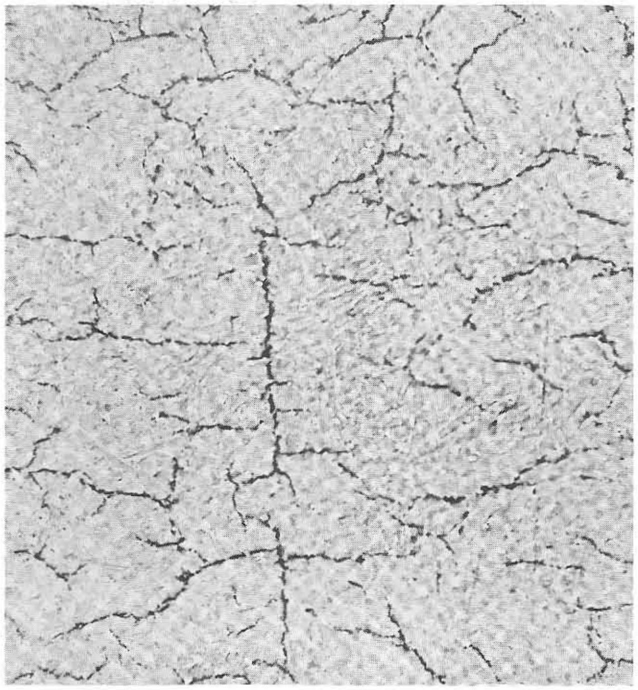


FIGURE 58 – Stress corrosion cracking of the head of a 6Al-4V-Ti alloy tank exposed to anhydrous N_2O_4.

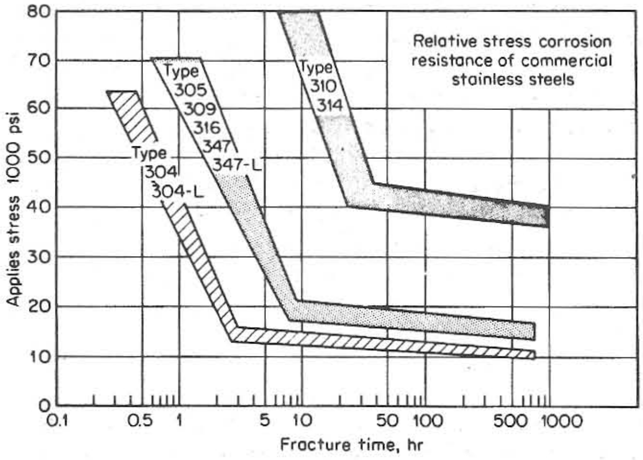


FIGURE 59 – Composite curves illustrating the relative stress corrosion cracking resistance for commercial stainless steels in boiling 42% magnesium chloride.

discussed together with comments on crack morphology, mechanisms, and methods of prevention.

Crack Morphology

Stress corrosion cracks give the appearance of a brittle mechanical fracture while, in fact, they are the result of local corrosion processes. However, even though SCC is not strictly a mechanical process, it is still convenient to label the process and general features of Figure 53 as a crack.

Both intergranular and transgranular SCC are observed. Intergranular cracking proceeds along grain boundaries, while transgranular cracking advances without apparent preference for boundaries. Figure 53 is an example of transgranular cracking, and Figure 57 shows the intergranular mode of cracking. Intergranular and transgranular cracking often occur in the same alloy, depending on the environment or the metal structure. Such transitions in crack modes are known in the high-nickel alloys, iron-chromium alloys, and brasses.

Cracking proceeds generally perpendicular to the applied stress. Cracking in Figures 53 and 57 is of this type. An interesting case is shown in Figure 58, in which the metal is subjected to uniform biaxial tensile stresses (the hemispherical head of a pressure vessel under internal pressure). The cracks appear to be randomly oriented. Cracks vary also in degree of branching. In some cases the cracks are virtually without branches (Figure 56), and in other cases they exhibit multibranched *river delta* patterns (Figure 53). Depending on the metal structure and composition and upon the environment composition, crack morphology can vary from a single crack to extreme branching.

Stress Effects

Increasing the stress decreases the time before cracking occurs, as shown in Figure 59. There is some conjecture concerning the minimum stress required to prevent cracking. This minimum stress depends on temperature, alloy composition, and environment composition. In some cases it has been observed to be as low as about 10% of the yield stress. In other cases, cracking does not occur below about 70% of the yield stress. For each alloy-environment

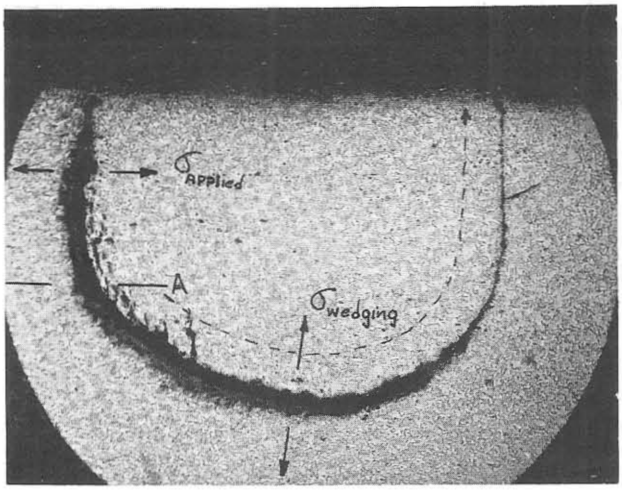


FIGURE 60 – The wedging action of corrosion products. This crack in stainless steel has proceeded in its circular path under the influence of stresses produced only by corrosion products.

combination there is probably an effective minimum, or threshold, stress. This threshold value must be used with considerable caution since environmental conditions may change during operation.

The criteria for the stresses are simply that they be tensile and of sufficient magnitude. These stresses may be due to any source: applied, residual, thermal, or welding. In fact, numerous cases of SCC have been observed in which there is no externally applied stress. As-welded steels contain residual stresses near the yield point.

Corrosion products have been shown to be another source of stress. Stresses up to 10,000 lb/in.^{2} can be generated by corrosion products in constricted regions. A stress corrosion crack which has been propagated by corrosion product stresses is shown in Figure 60. In this figure, the corrosion products appear to exert a wedging action.

Time to Cracking

The parameter of time in SCC phenomena is important since the major physical damage during SCC occurs during the later stages. As stress corrosion cracks penetrate the material, the cross-sectional area is reduced and the final cracking failure results entirely from machined action. This is illustrated in Figures 61 and 62. Figure 61 illustrates the rate of cracking as a function of crack depth for a specimen under constant tensile load. Initially, the rate of crack movement is more or less constant, but as cracking progresses the cross-sectional area of the specimen decreases and the applied tensile stress increases. As a result, the rate of crack movement increases with crack depth until rupture occurs. Immediately preceding rupture, the cross section of the material is reduced to the point where the applied stress is equal to or greater than the ultimate strength of the metal, and failure occurs by mechanical rupture. Figure 62 illustrates the relationship between the time of exposure and the extension of a specimen during SCC. The width of the crack is narrow during the early stages of cracking, and little change in extension is observed. During later stages, the crack widens. Prior to rupture, extensive plastic deformation occurs and a large change in extension is observed.

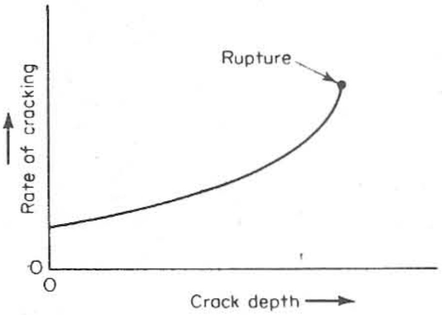


FIGURE 61 – Rate of stress corrosion crack propagation as a function of crack depth during tensile loading.

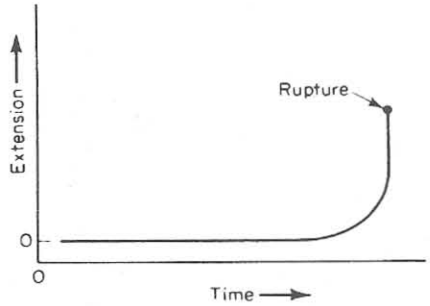


FIGURE 62 – Specimen extension as a function of time during constant-load stress corrosion cracking test.

A common and important question frequently asked concerning SCC is: How long should a SCC test be conducted? Figures 61 and 62 indicate that the test should be avoided since very little physical and mechanical evidence of cracking is apparent until it has occurred.

Environmental Factors

At present there apperas to be no general pattern to the environments which cause SCC of various alloys. SCC is well known in various aqueous mediums, but it also occurs in certain liquid metals, fused salts, and nonaqueous inorganic liquids (Figure 58).

The presence of oxidizers often has a pronounced influence on cracking tendencies. Figure 63 shows the combined effects of chloride and dissolved oxygen on the SCC of Type 304 stainless steel. In fact, the presence of dissolved oxygen or other oxidizing species is critical to the cracking of austenitic stainless steels in chloride solutions, and if the oxygen is removed, cracking will not occur.

Table 9 lists a number of environment-alloy systems in which cracking occurs. New environments which cause SCC in various alloys are constantly being found. Thus, it is always necessary to evaluate a given alloy in stress corrosion tests when the environmental composition is changed. It is usually characteristic of crack-producing environments that the alloy is negligibly attacked in the nonstressed condition. Although SCC of steel is frequently reported in hydrogen sulfide solutions and cyanide-containing solutions, as shown in Table 9, these failures are undoubtedly due to hydrogen embrittlement rather than SCC.

As is the case with most chemical reactions, SCC is accelerated by increasing temperature. In some systems, such as magnesium alloys, cracking occurs readily at room temperature. In other systems, boiling temperatures are required. Most alloys susceptible to cracking will begin

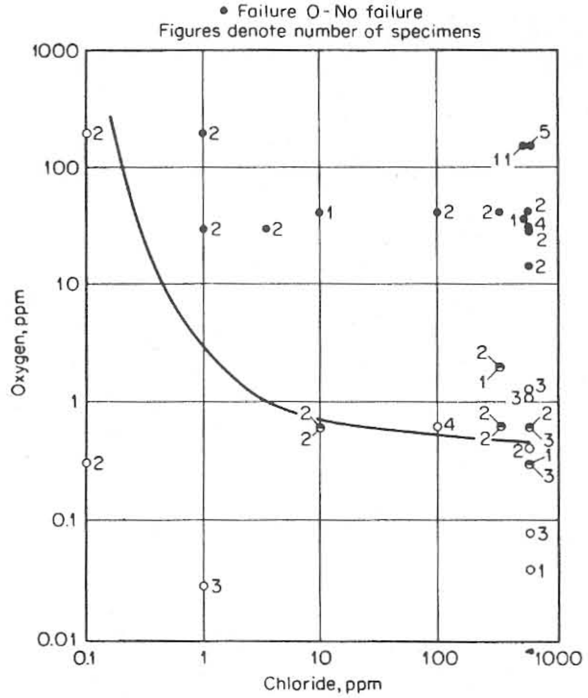


FIGURE 63 – Proposed relationship between chloride and oxygen content of alkaline phosphate-treated boiler water, and susceptible to stress corrosion cracking of austenitic stainless steel exposed to the steam phase with intermittent wetting.

TABLE 9 – Environments That May Cause Stress Corrosion of Metals and Alloys

Material	Environment	Material	Environment
Aluminum alloys	$NaCl-H_2O_2$ solutions NaCl solutions Sea water	Ordinary steels	NaOH solutions $NaOH-Na_2SiO_2$ solutions Calcium, ammonium, and sodium nitrate solutions Mixed acids ($H_2SO_4-HNO_3$) HCN solutions Acidic H_2S solutions Sea water Molten Na-Pb alloys
Copper alloys	Ammonia vapors and solutions Amines Water, water vapor		
Gold alloys	$FeCl_3$ solutions Acetic acid-salt solutions		
Inconel	Caustic soda solutions		
Lead	Lead acetate solutions	Stainless steels	Acid chloride solutions such as $MgCl_2$ and $BaCl_2$ $NaCl-H_2O_2$ solutions Sea water H_2S $NaOH-H_2S$ solutions Condensing steam from chloride waters
Magnesium alloys	$NaCl-K_2CrO_4$ solutions Rural and coastal atmospheres Distilled water		
Monel	Fused caustic soda Hydrofluoric acid Hydrofluosilicic acid		
Nickel	Fused caustic soda		
		Titanium alloys	Red fuming nitric acid, sea water, N_2O_4, methanol-HCl

cracking at least as low as 100 C (212 F). The effect of temperature in the cracking of austenitic stainless steels is shown in Figure 64. Similar data for the caustic embrittlement of as-welded steel are presented in Figure 65.

The physical state of the environment is also important. Alloys exposed to single-phase aqueous environments are sometimes less severely attacked than metals at the same temperature and stress when exposed to alternate wetting and drying conditions.

The autoclave^9 is used for stress-corrosion tests under vapor condensation conditions involving chloride-containing water at 204 C (400 F). Liquid condensing on the top of the autoclave drips on the specimen and flash-dries, thus concentrating the chloride. At these temperatures

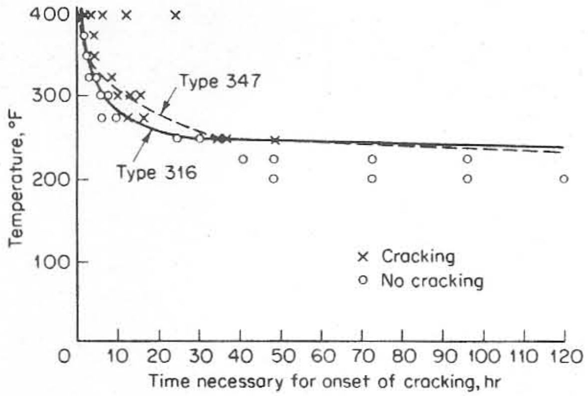


FIGURE 64 – Effect of temperature on time for crack initiation in Types 316 and 347 stainless steels in water containing 875 ppm NaCl (W. W. Kirk, F. H. Beck, and M. G. Fontana. Stress Corrosion Cracking of Austenitic Stainless Steels in High Temperature Chloride Waters, in T. Rhodin (ed.), Physical Metallurgy of Stress Corrosion Fracture, Interscience Publishers, Inc., New York (1959).

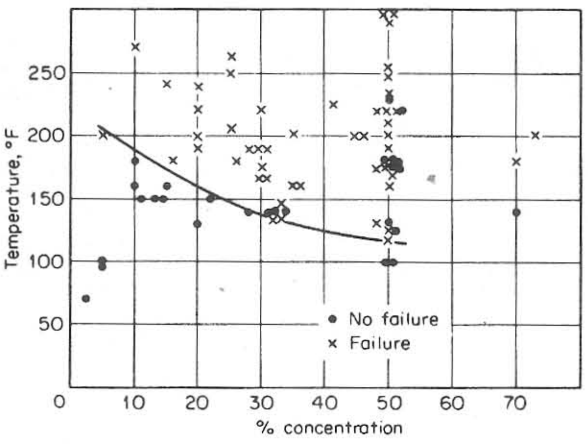


FIGURE 65 – Effects of temperature and concentration on the cracking of as-welded carbon steel in sodium hydroxide based on service experience.

sodium chloride is present in the vapor phase. Cracking of 18-8 stainless steels in 2 hours at applied stresses as low as 2000 lb/in.^{2} occurs under these conditions. The specimen immersed in the liquid requires high stresses and long times for cracking. Similar results are obtained when the specimen is alternately immersed in and removed from the water.

Good correlation is obtained between these tests and actual service failures. Figure 66 is an excellent example. This high-pressure autoclave was forged from 18-8 stainless steel with a 2 inch wall and cost $20,000. It was in operation for only a few batches with total times in hours. Dy-Chek penetrant was used to emphasize the appearance of the many cracks on the outside surface. This surface was cooled by a good grade of city water. The cooling jacket system drained after each operation. The droplets of water clinging to the autoclave surface dried and the chloride concentrated.

Figure 67 shows cracking of an 18-8 tank from the outside surface. Cracks are accentuated by dye penetrant. This vessel handled warm distilled water.

The outside was covered with an insulating material

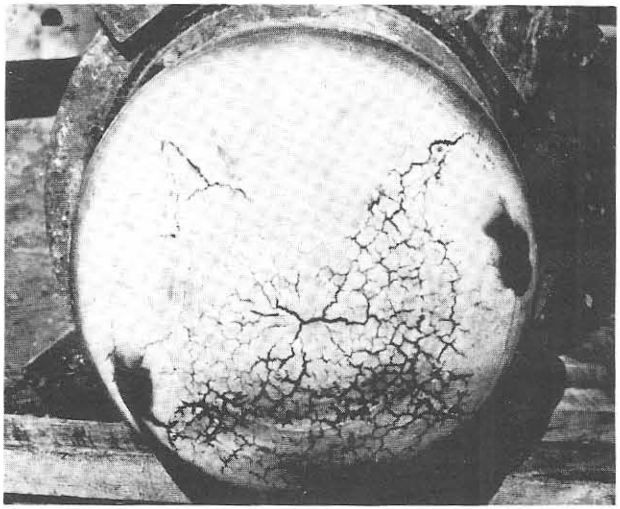


FIGURE 66 – Stress corrosion of Type 304 autoclave (Mallinckrodt Chemical Works).

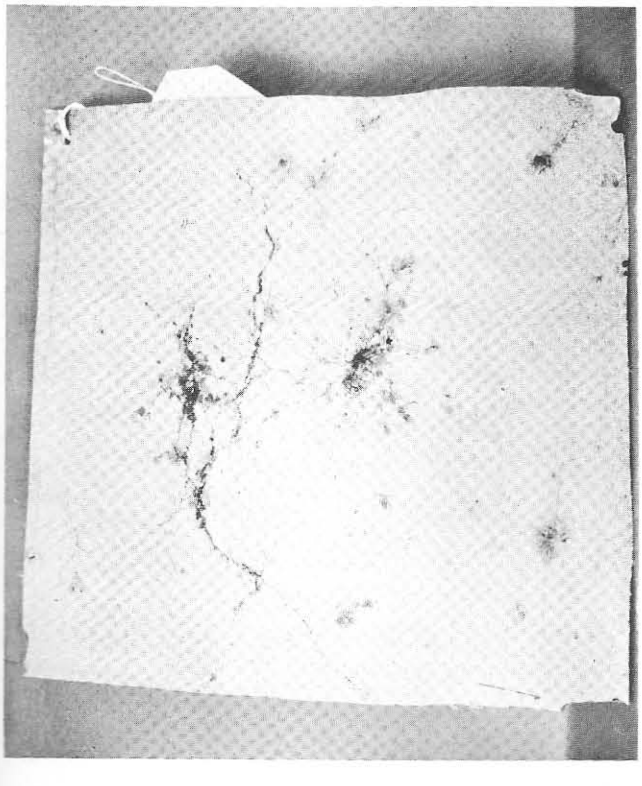


FIGURE 67 – External stress corrosion of Type 304 vessel.

containing a few parts per million of chloride. Rain penetrated the insulation and leached out the chlorides, and then the solution dried and concentrated. This plant experienced many such cracks on insulated vessels and lines. Similar experiences are frequent and have been called external SCC.

Figure 68 shows the location of cracks in a vertical stainless steel condenser. Splashing in the dead space caused alternate wetting and drying. This problem was solved by simply venting the dead space so the tubes were wet at all time!

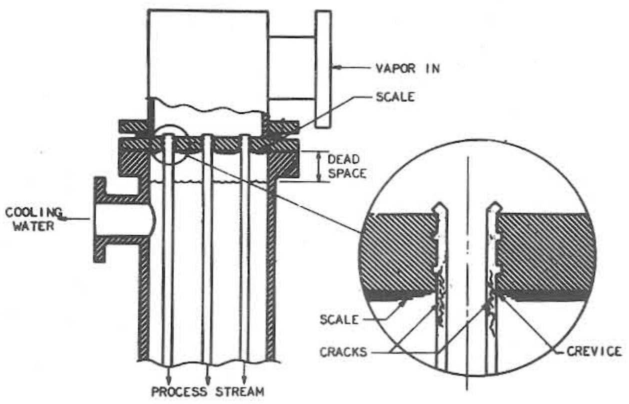


FIGURE 68 – Cracking of Type 316 tubes in dead space area (J. A. Collins).

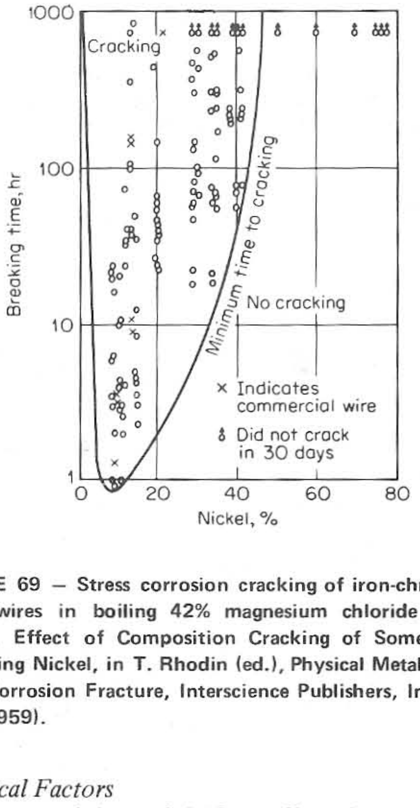


FIGURE 69 – Stress corrosion cracking of iron-chromium-nickel wires in boiling 42% magnesium chloride (H. R. Copson, Effect of Composition Cracking of Some Alloys Containing Nickel, in T. Rhodin (ed.), Physical Metallurgy of Stress Corrosion Fracture, Interscience Publishers, Inc., New York (1959).

Metallurgical Factors

The susceptibility of SCC is affected by the average chemical composition, preferential orientation of grains, composition, and distribution of precipitates, dislocation interactions, and progress of the phase transformation (or degree of metastability). These factors further interact with the environmental composition and stress to affect time to cracking, but these are secondary considerations.

Figures 69 (Ni added to 18 Cr-Fe base) and 70 show the effects of alloy composition in austenitic stainless steels and mild steels. In both cases there is a minimum in time to cracking as a function of composition. In fact, this observation of a minimum in time to cracking versus composition is a common (although not universal) observation in other alloy systems (e.g., Cu-Au).

In the past it has been a common generalization that pure metals do not crack. This has been challenged by

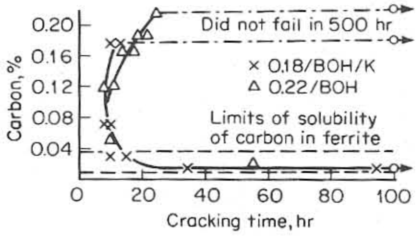


FIGURE 70 – Effect of carbon content on the cracking time of mild steel exposed to boiling calcium ammonium nitrate (R. N. Parkins).

observations of cracking in 99.999% pure copper exposed in ammoniacal solutions containing $Cu(NH_3)_5^{2+}$ complex ions.[10] While generally the use of pure metals is often an available avenue for preventing cracking, it should be pursued only with caution.

High-strength aluminum alloys exhibit a much greater susceptibility to SCC in directions transverse to the rolling direction than in those parallel to the longitudinal direction. This effect is due to the distribution of precipitates which results from rolling.

Figure 71 shows the increase in resistance to stress corrosion as the amount of ferrite is increased in cast stainless steels. Pools of ferrite in the austenitic matrix tend to block the progress of cracks.

Mechanism

Although stress corrosion represents one of the most important corrosion problems, the mechanism involved is not well understood. This is one of the big unsolved questions in corrosion research. The main reason for this situation is the complex interplay of metal, interface, and environment properties. Further, it is unlikely that a specific mechanism will be found which applies to all metal-environment systems. The most reliable and useful information has been obtained from empirical experiments. Some of the possible *operating steps* or processes involved are discussed immediately below.

Corrosion plays an important part in the initiation of cracks. A pit, trench, or other discontinuity on the surface of the metal acts as a stress raiser. Stress concentration at the tip of the *notch* increases tremendously as the radius of notch decreases. Stress corrosion cracks are often observed to start at the base of a pit.

Once a crack has started, the tip of the advancing crack has a small radius and the attendant stress concentration is great. Using audio-amplification methods, Pardue[11] showed that a mechanical step or jump can occur during crack propagation. In fact, *pings* were heard.

The conjoint action of stress and corrosion required for crack propagation was demonstrated by Priest.[12] An advancing crack was stopped when cathodic protection was applied (corrosion stopped, stress condition not changed). When cathodic protection was removed, the crack started moving again. This cycle was repeated several times. In this research, the progress of the crack was photographed and projected at the actual speed of propagation.

Plastic deformation of an alloy can occur in the region immediately preceding the crack tip because of high stresses. If the alloy is metastable, a phase transformation could occur (e.g., austenite to martensite in the nickel stainless steels). The newly formed phase could have different strength, susceptibility to hydrogen, or reactivity.

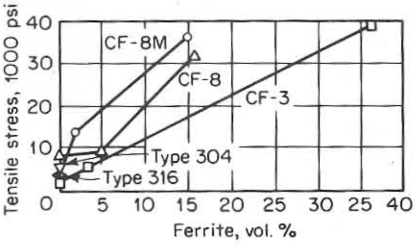


FIGURE 71 – Effect of ferrite on stress required to induce stress corrosion cracking in several cast stainless alloys. Type 304 and 316 with zero ferrite also plotted. Specimens exposed 8 hours in condensate from 875 ppm chloride water at 400 F. (M. G. Fontana, F. H. Beck, J. W. Flowers, Metal Progr., Vol. 86, p. 99 (1961) December.

If the alloy is not metastable, the coldworked (plastically deformed) region might be less corrosion resistant than the matrix because of the continuous emergence of of slip steps. This is a dynamic process and could explain why severely deformed metals (before exposure to a corrosive) do not exhibit sufficiently high corrosion rates to account for rapid penetration of cracks.

The role of tensile stress has been shown to be important in rupturing protective films during both initiation and propagation of cracks. These films could be tarnish films (as in the case of brasses), thin oxide films, layers richer in the more noble component (as in the case of copper-gold alloys and some of the stainless steels and alloys), or other passive films. Breaks in the passive film or enriched layer on stainless steel allows more rapid corrosion at various points on the surface and thereby initiates cracks. Breaking of films ahead of the advancing crack would not permit healing, and propagation would continue. Rapid local dissolution without stifling is required for rapid propagation.

In the case of intergranular cracking, the grain-boundary regions could be more anodic, or less corrosion resistant, because of precipitated phases, depletion, enrichment, or adsorption, thus providing a susceptible path for the crack. Another example of local dissolution concerns mild steels which crack in nitrate solutions. In this case, iron carbide is cathodic to ferrite.

These examples indicate the complex interplay between metal and environment and account for the specificity of environmental cracking of metals and alloys.

Methods of Prevention

As mentioned above, the mechanism of SCC is imperfectly understood. As a consequence, methods of preventing this type of attack are either general or empirical in nature. SCC may be reduced or prevented by application of one or more of the following methods:

1. Lowering the stress below the threshold value if one exists. This may be done by annealing in the case of residual stresses, thickening the section, or reducing the load. Plain carbon steels may be stress-relief annealed at 593 to 649 C (1100 to 1200 F), and the austenitic stainless steels are frequently stress relieved at temperatures ranging from 816 to 927 C (1500 to 1700 F).

2. Eliminating the critical environmental species by, for example, degasification, demineralization, or distillation.

3. Changing the alloy is one possible recourse if neither

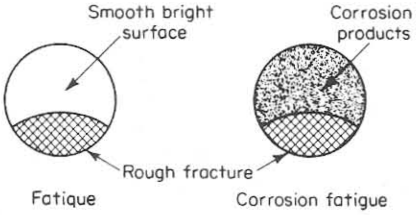


FIGURE 72 – Schematic illustration of fatigue and corrosion-fatigue failures.

the environment nor stress can be changed. For example, it is common practice to use Inconel (raising the nickel content) when Type 304 stainless steel is not satisfactory. Although carbon steel is less resistant to general corrosion, it is more resistant to SCC than are the stainless steels. Thus, under conditions which tend to produce SCC, carbon steels are often found to be more satisfactory than the stainless steels. For example, heat exchangers used in contact with sea water or brackish waters are often constructed of ordinary mild steel.

4. Applying cathodic protection to the structure with an external power supply or consumable anodes. Cathodic protection should only be used to protect installations where it is positively known that SCC is the cause of fracture, since hydrogen embrittlement effects are accelerated by impressed cathodic currents.

5. Adding inhibitors to the system if feasible. Phosphates and other inorganic and organic corrosion inhibitors have been used successfully to reduce SCC effects in mildly corrosive mediums. As in all inhibitor applications, sufficient inhibitor should be added to prevent the possibility of localized corrosion and pitting.

Corrosion Fatigue

Fatigue is defined as the tendency of a metal to fracture under repeated cyclic stressing. Usually, fatigue failures occur at stress levels below the yield point and after many cyclic applications of this stress. A schematic illustration of a typical fatigue fracture in a cylindrical bar is shown in Figure 72. Characteristically, fatigue failures show a large smooth area and a smaller area which has a roughened and somewhat crystalline appearance. Studies have shown that during the propagation of a fatigue crack through a metal, the frequent cyclic stressing tends to hammer or pound the fractured surfact smooth. A crack propagates until the cross-sectional area of the metal is reduced to the point where the ultimate strength is exceeded and rapid brittle fracture occurs. The surface of a brittle fracture usually has a roughened appearance. The unusual appearance of fatigue fractures has led to the common misstatement which attributes such failures to metal *crystallization*. This is obviously incorrect, since all metals are crystalline, and the roughened surface which appears on the roughened fracture is the result of brittle fracture and not crystallization.

Fatigue tests are conducted by subjecting a metal to cyclic stresses of various magnitudes and measuring the time to fracture. Results of such tests are shown in Figure 73. The fatigue life of steel and other ferrous materials usually becomes independent of stress at low stress levels. As shown in Figure 73, this is called the fatigue limit. In general, it is assumed that if a metal is stressed below its fatigue limit, it will endure an infinite number of cycles without fracture. If the specimen used in the fatigue test is notched prior to testing, the fatigue resistance is reduced, as shown in Figure 73. The fatigue resistance is directly related to the radius or the sharpness of the notch. As the notch radius is reduced, the fatigue resistance is likewise reduced. Nonferrous metals such as aluminum and magnesium do not possess a fatigue limit. Their fatigue resistance increases as the applies stress is reduced but does not become independent of stress level.

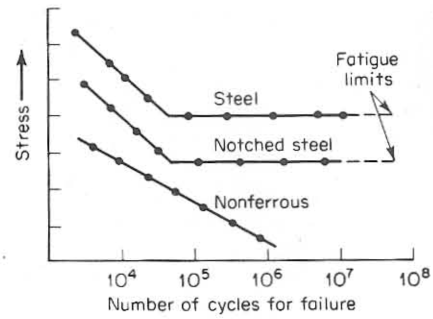


FIGURE 73 – Schematic illustration of the fatigue behavior of ferrous and monoferrous alloys.

Corrosion fatigue is defined as the reduction of fatigue resistance due to the presence of a corrosive medium. Thus, corrosion fatigue is not defined in terms of the appearance of the failure, but in terms of mechanical properties. Figure 72 illustrates a typical corrosion fatigue failure. There is usually a large area covered with corrosion products and a smaller roughened area resulting from the final brittle fracture. It is important to note that the presence of corrosion products at a fatigue-fracture point does not necessarily indicate corrosion fatigue. Superficial rusting can occur during ordinary fatigue fracture, and the presence of rust or other corrosion products does not necessarily mean that fatigue life has been affected. This can only be determined by a corrosion fatigue test.

Corrosion fatigue is probably a special case of SCC. However, the mode of fracture and the preventive measures differ and it is justifiable to consider it separately.

Environmental Factors. Environmental factors strongly influence corrosion fatigue behavior. In ordinary fatigue the stress-cycle frequency has only a negligible influence on fatigue resistance. This factor is of great convenience in fatigue testing since tests can be conducted rapidly at high rates of cyclic stressing. However, corrosion-fatigue resistance is markedly affected by the stress-cycle frequency. Corrosion fatigue is most pronounced at low stress frequencies. This dependence is readily understood since low-frequency cycles result in greater contact time between metal and corrosive. Thus, in evaluating corrosion fatigue resistance, it is important to conduct the test under conditions identical to those encountered in practice.

Corrosion fatigue is also influenced by the corrosive to which the metal is exposed. Oxygen content, temperature, pH, and solution composition influence corrosion fatigue. For example, iron, steel, stainless steels, and aluminum bronzes possess good corrosion fatigue resistance in water. In sea water, aluminum bronzes and austenitic stainless steels retain only about 70 to 80% of their normal fatigue resistance. High-chromium alloys retain only about 30 to 40% of their normal fatigue resistance in contact with sea water. It is apparent that corrosion fatigue must be defined in terms of the metal and its environment.

Mechanism. The mechanism of corrosion fatigue has not been studied in detail, but the cause of this

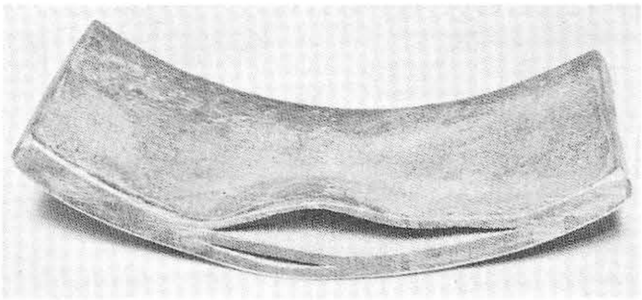


FIGURE 74 – Cross section of a carbon steel plate removed from a petroleum process stream showing a large hydrogen blister. Exposure time: 2 years (Imperial Oil Limited, Ontario, Canada).

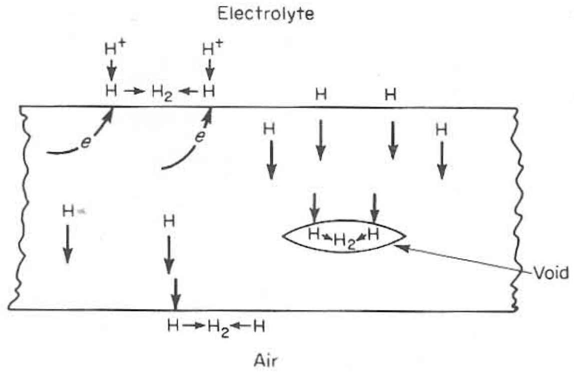


FIGURE 75 – Schematic illustration showing the mechanism of hydrogen blistering.

type of attack is qualitatively understood. Corrosion-fatigue tests of iron and ferrous-base materials show that their fatigue life curves resemble those of nonferrous metals. Also, corrosion fatigue seems to be most prevalent in mediums which produce pitting attack. These two facts indicate that fatigue resistance is reduced in the presence of a corrosive because corrosion pits act as stress raisers and initiate cracks. It is most likely that the corrosion is most intense at the crack tip, and as a consequence, there is no stable pit radius. Since the pit or radius continuously decreases due to simultaneous mechanical and electrochemical effects, the fatigue curve of a ferrous metal exposed to a corrosive resembles that of a nonferrous metal. A corrosion-fatigue failure is usually transgranular and does not show the branching which is characteristic of many stress corrosion cracks. The final stages of corrosion fatigue are identical to those occurring during ordinary fatigue: final fracture is purely mechanical and does not require the presence of a corrosive.

Prevention. Corrosion fatigue can be prevented by a number of methods. Increasing the tensile strength of a metal or alloy improves ordinary fatigue but is detrimental to corrosion fatigue. In the case of ordinary fatigue resistance, alloys with high tensile strength resist the formation of nucleating cracks. It should be noted, however, that once a crack starts in a high-tensile-strength material it usually progresses more rapidly than in a material with lower strength. During corrosion fatigue, a crack is readily initiated by corrosive action; hence, the resistance of high-tensile material is quite low. Corrosion fatigue may be eliminated or reduced by reducing the stress on the component. This can be accomplished by altering the design, by stress-relieving heat treatments, or by shot-peening the surface to induce compressive stresses. Corrosion inhibitors are also effective in reducing or eliminating the effects of corrosion fatigue. Corrosion-fatigue resistance also can be improved by using coatings such as electrodeposited zinc, chromium, nickel, copper, and nitride coatings. When electrodeposited coatings are applied it is important to use plating techniques that do not produce tensile stresses in the coating or change hydrogen into the metal.

Hydrogen Damage

Characteristics

Hydrogen damage is a general term which refers to mechanical damage of a metal caused by the presence of, or interaction with, hydrogen. Hydrogen damage may be classified into four distinct types: (1) hydrogen blistering, (2) hydrogen embrittlement, (3) decarburization, and (4) hydrogen attack.

Hydrogen blistering results from the penetration of hydrogen into a metal. An example of blistering is shown in Figure 74. The result is local deformation and, in extreme cases, complete destructionof the vessel wall. Hydrogen embrittlement also is caused by penetration of hydrogen into a metal, which results in a loss of ductility and tensile strength. Decarburization, or the removal of carbon from steel, is often produced by moist hydrogen at high temperatures. Decarburization lowers the tensile strength of steel. Hydrogen attack refers to the interaction between hydrogen and the component of an alloy at high temperatures. A typical example of hydrogen attack is the disintegration of oxygen-containing copper in the presence of hydrogen. Decarburization and hydrogen attack are high-temperature processes.

Hydrogen blistering and hydrogen embrittlement may occur during exposure to petroleum, in chemical process streams, during pickling and welding operations, or as a result of corrosion. Since both of these effects produce mechanical damage, catastrophic failure may result if they are not prevented.

Environmental Factors

Atomic hydrogen (H) is the only species capable of diffusing through steel and other metals. The molecular form of hydrogen (H_2) does not diffuse through metals. Thus, hydrogen damage is produced only by the atomic form of hydrogen. There are various sources of nascent or atomic hydrogen–high temperature moist atmospheres, corrosion processes, and electrolysis. The reduction of hydrogen ions involves the production of hydrogen atoms and the subsequent formation of hydrogen molecules. Hence, both corrosion and the application of cathodic protection, electroplating, and other processes are major sources of hydrogen in metals. Certain substances such as sulfide ions, phosphorous, and arsenic compounds reduce the rate of hydrogen-ion reduction. Apparently most of these function by decreasing the rate at which hydrogen combines to form molecules. In the presence of such substances there is a greater concentration of atomic hydrogen on the metal surface.

Hydrogen Blistering

A schematic illustration of the mechanism of hydrogen blistering is shown in Figure 75. Here, the cross-sectional

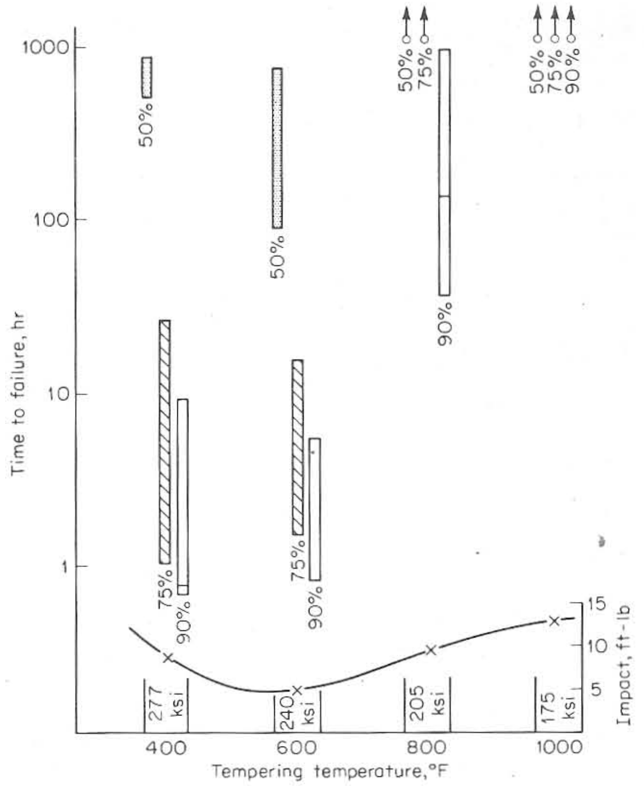


FIGURE 76 – Time to failure vs tempering temperature for 4340 steel at stress levels of 50, 75, and 90% yield stress. Specimens exposed to wetting and drying 3.5% NaCl solution at room temperature.

view of the wall of a tank is shown. The interior contains an acid electrolyte, and the exterior is exposed to the atmosphere. Hydrogen evolution occurs on the inner surface as a result of a corrosion reaction or cathodic protection. At any time, there is a fixed concentration of hydrogen atoms on the metal surface, and some of these diffuse into the metal rather than combining into molecules, as shown. Much of the hydrogen diffuses through the steel and combines to form hydrogen molecules on the exterior surface. If hydrogen atoms diffuse into a void, a common defect in rimmed steels, they combine into molecular hydrogen. Since molecular hydrogen cannot diffuse, the concentration and pressure of hydrogen gas within the void increases. The equilibrium pressure of molecular hydrogen in contact with atomic hydrogen is several hundred thousand atmospheres, which is sufficient to rupture any known engineering material.

Hydrogen Embrittlement

The exact mechanism of hydrogen embrittlement is not as well known as that of hydrogen blistering. The initial cause is the same, penetration of atomic hydrogen into the metal structure. For titanium and other strong hydride-forming metals, dissolved hydrogen reacts to form brittle hydride.

There are indications that a large fraction of all the environmentally activated cracking of ferritic and martensitic iron-base alloys and the titanium-base alloys is due in some way to the interaction of the advancing crack with hydrogen. The general characteristics of such cracking susceptibility are illustrated in Figure 76 for the cracking of Type 4340 steel (C-0.40, Mn-0.70, P-0.04, S-0.04, Si-0.30, Ni-1.8, Cr-0.8, Mo-0.25). This figure[13] shows that higher strength levels are more susceptible to cracking and that higher stresses cause cracking to occur more rapidly. These trends are in fact general for most alloys subject to hydrogen embrittlement; i.e., the alloys are most susceptible to cracking in their highest strength level. The tendency for embrittlement is also increased with hydrogen concentration in the metal as shown in Figure 77. This figure[14] shows that after a given length of time, cracking occurs at successively higher stresses as the cathodically charged hydrogen is removed by baking treatments and the tremendous differences in stresses involved.

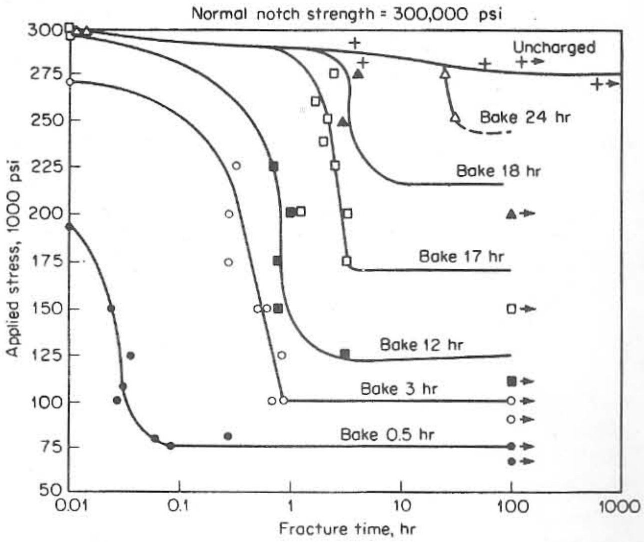


FIGURE 77 – Static fatigue curves for various hydrogen concentrations obtained by baking 4340 steel different times at 300 F.

Most of the mechanisms which have been proposed for hydrogen embrittlement are based on slip interference by dissolved hydrogen. This slip interference may be due to the accumulation of hydrogen near dislocation sites or microvoids, but the precise mechanism is still in doubt.

Hydrogen embrittlement is distinguished from SCC generally by the interactions with applied currents. Cases where the applied current makes the specimen more anodic and accelerates cracking are considered to be SCC, with the anodic-dissolution process contributing to the progress of cracking. On the other hand, cases where cracking is accentuated by current in the opposite direction which accelerates the hydrogen-evolution, reactions are considered to be hydrogen embrittlement. These two phenomena are compared with regard to cracking mode and applied current in Figure 78.

Prevention

Hydrogen blistering may be prevented by application of one or more of the following preventative measures:

1. **Using Clean Steel.** Rimmed steels tend to have numerous voids, and the substitution of killed steel greatly increases the resistance to hydrogen blistering because of the absence of voids in this material.

2. **Using Coatings.** Metallic, inorganic, and organic coatings and liners are often used to prevent the hydrogen blistering of steel containers. To be successful, the coating or liner must be impervious to hydrogen penetration and be resistant to the mediums contained within the tank. Steel

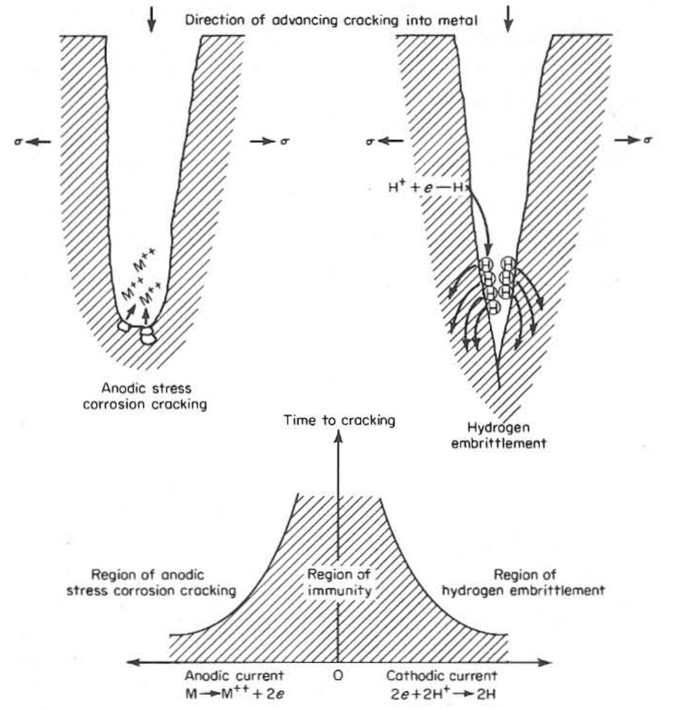


FIGURE 78 – Schematic differentiation of anodic stress corrosion cracking and cathodically sensitive hydrogen embrittlement (R. W. Staehle).

clad with austenitic stainless steel or nickel is often used for this purpose. also, rubber and plastic coatings and brick linings are frequently employed.

3. **Using Inhibitors.** Inhibitors can prevent blistering since they reduce corrosion rate and the rate of hydrogen-ion reduction. Inhibitors, however, are primarily used in closed systems and have limited use in once-through systems.

4. **Removing Poisons.** Blistering usually occurs in corrosive mediums containing hydrogen-evolution poisons such as sulfides, arsenic compounds, cyanides, and phosphorous-containing ions and rarely occurs in pure acid corrosives. Many of these poisons are encountered in petroleum process streams, which explains why blistering is a major problem in the petroleum industry.

5. **Substituting Alloys.** Nickel-containing steels and nickel-base alloys have very low hydrogen diffusion rates and are often used to prevent hydrogen blistering.

Although hydrogen embrittlement, like hydrogen blistering, results from the penetration of hydrogen into a metal or alloy, methods for preventing this form of damage are somewhat different. For example, the use of clean steels has relatively little influence on hydrogen embrittlement since the presence of voids is not involved. Hydrogen embrittlement may be prevented by application of one or more of the following preventative measures:

1. **Reducing Corrosion RARate.** Hydrogen embrittlement occurs frequently during pickling operations where corrosion of the base metal produces vigorous hydrogen evolution. By careful inhibitor additions, base-metal corrosion can largely be eliminated during pickling with a subsequent decrease in hydrogen pickup.

2. **Altering Plating Conditions.** Hydrogen pickup during plating can be controlled by the proper choice of plating baths and careful control of plating current. If electroplating is performed under conditions of hydrogen evolution, poor deposits and hydrogen embrittlement are the result.

3. **Baking.** Hydrogen embrittlement is an almost reversible process, especially in steels. That is, if the hydrogen is removed, the mechanical properties of the treated material are only slightly different from those of hydrogen-free steel. A common way of removing hydrogen in steels is by backing at relatively low temperatures [93 to 149 C (200 to 300 F)]. See Figure 77.

4. **Substituting Alloys.** The materials most susceptible to hydrogen embrittlement are the very-high-strength steels. Alloying with nickel or molybdenum reduces susceptibility.

5. **Practicing Proper Welding.** Low-hydrogen welding rods should be specified for welding if hydrogen embrittlement is a problem. Also, it is important to maintain dry conditions during welding since water and water vapor are major sources of hydrogen.

References

1. G. J. Schafer and P. K. Foster. J. Electrochem. Soc., Vol. 106, p. 468 (1959); G. J. Schafer, J. R. Gabriel, and P. K. Foster. J. Electrochem. Soc., Vol. 107, p. 1002 (1960); L. Rosenfeld and I. K. Marshakov, Corrosion, Vol. 20, p. 115t (1964).
2. W. H. Slabaugh and M. Grotheer. Mechanism of Filiform Corrosion, Ind. Eng. Chem., Vol. 46, p. 1014 (1954).
3. O. L. Riggs, J. D. Sudbury, and M. Hutchinson. Corrosion, Vol. 16, p. 94 (1960) June.
4. U. R. Evans. Corrosion, Vol. 7, p. 238 (1951).
5. N. D. Greene and M. G. Fontana. A Critical Analysis of Pitting Corrosion, Corrosion, Vol. 15, p. 41 (1959) January; Also, An Electrochemical Study of Pitting Corrosion in Stainless Steels, Part 1, Pit Growth, Part 2, Polarization Measurements, p. 48-60 in this same volume by the same authors.
6. L. R. Honnaker. Chem. Eng. Progr., Vol. 54, p. 79 (1958).
7. M. L. Holzworth, F. H. Beck, and M. G. Fontana. Corrosion, Vol. 7, p. 441 (1951).
8. R. V. Trax and J. C. Holzwarth. Corrosion, Vol. 16, p. 105 (1960).
9. R. W. Staehle, F. H. Beck, and M. G. Fontana. Mechanism of Stress Corrosion of Austenitic Stainless Steels, Corrosion, Vol. 15, p. 51 (1959).
10. E. N. Pugh, W. G. Montague, A. R. C. Westwood. Corrosion Sci., Vol. 6, p. 345 (1966).
11. W. M. Pardue, F. H. Beck, and M. G. Fontana. Am. Soc. Metals Trans. Quart., Vol. 54, p. 539 (1961).
12. D. K. Priest, F. H. Beck, and M. G. Fontana. Trans. Am. Soc. Metals, Vol. 47, p. 473 (1955).
13. R. A. Davis, G. H. Dreyer, and W. C. Gallaugher. Corrosion, Vol. 21, p. 93t (1934).
14. H. H. Johnson, E. J. Schneider, and A. R. Troiano. Trans. AIME, Vol. 212, p. 526 (1958).

DISCUSSION

Question:

Do you have parting corrosion with Inconel?

Answer:

Selective leaching? No, I have never seen it in Inconel. I have seen it in silicon containing stainless type alloys. Maybe someone else has.

Comment:

We have, in a pump made of Monel. The nickel dissolved, leaving the copper.

Comment:

For instance, one of the strong bits of evidence that copper is not dissolved and redeposited, somebody found twins in the deposited copper, (due to cold working). It is of academic importance because the end result is the same.

Question:

Do you see much problem with corrosion with liquid-vapor phase?

Answer:

The water line or liquid line corrosion? Yes, I have seen it in steels, copper alloys, brass and that sort of thing, but it is not too common. Well, it is almost a concentration cell effect. It would fall more in that category because for instance, in a strong acid tank or an acid tank where you are exposed to air and dissolved oxygen as in the surface layers, you can get that effect.

Comment:

My favorite topic was that you get inadequate atmosphere over the concentrated sulfuric. Concentrated sulfuric does not attack steel worth mentioning. But, if you vent that tank, you can get blistering in the steel, and so on. I went along for years happily telling people to put a vent on their tank, until somebody finally asked me where do you find one of these tanks. There are vents that can be put on tanks to control the humidity. On cast iron, we did the same thing. We ran full scale tests, took the pipe, and demonstrated that the gray cast iron was several times superior to carbon steel. The immediate question that comes up today is does ductile iron perform the same way. Our data says that it does. You do not have the same mechanical locking that you do with plain graphite, but ductile iron pipe is also better than carbon steel. However, when you get down to the nitty gritty of it, and when you want to buy some piping, you frequently find that on cost and availability, you might as well put the pipe in Type 304 and be done with it.

Comment:

This brings up a point. I am on one of these government committees, Office of Pipeline Safety Standards. We receive accident reports. In many cases it is cast iron, it is a gas line, or it is an oil line or something, usually natural gas, and you have graphitization. You see, you dissolve Fe and you have still the same dimension, but it does not have any strength. Due to vibration, trucks passing, or a construction operater hitting it with a bulldozer, the pipe cracks, and the gas leaks, and then there is an explosion in an apartment building or something. Fortunately, they have gone to ductile irob, which is not brittle, but I am sure there are a million miles of pipeline still in the ground made up of old cast iron that is badly graphitized and very brittle.

Question:

You mention in your write-up that pitting is autocatalytic. I have seen several cases where the pits for some reason or other are stifled. After a while, they stop growing. I have noticed in the literature what 2 or 3 people mentioned, and what comes to mind immediately in Inco mentions that for Monel, for some reason, the pit growth is stifled over 20 or 30 mils. Can you comment on this?

Answer:

Well, I cannot explain it. In fact, that is what makes it so difficult to study. Dr. Greene and I have a paper that is 15 or more years old, on a study of the pitting of stainless steel. This is what happened. Sometimes, pits would form and grow, and other times they would stop. Why it does that, I do not know. I think in most cases, the danger is there because the pit tends to grow faster. Why it stops in some cases, I do not know.

Question:

Do you think that this phenomena would be more prevalent in steel where oxygen pitting or something causes a more shallow pock mark rather than a deep pit?

Answer:

I tend to regard pitting as something where the depth is greater than the diameter. Of course, they do have these big craters that are called pits. One of the nicest pieces of work that has been done in this regard was done by Floyd Brown. I had the idea years ago, but I could not talk any of my students into doing the experiment. It was to find out what is the composition of the environment at the bottom of the pit or the crack, or the crevice. This is to let the pit form, then freeze the specimen. You machine off the ice, and now you have trapped that liquid in the pit. By micro-chemical methods you can analyze it. You cannot stick a pipette or something down into a pit or a crack. The pH can go way down in chloride environments, as low as 4. In other words, it is very acidic at the bottom of the pit as opposed to 6 or 7 on the outside. In spite of the fact that sometimes a pit stops, if you see any evidence of pitting in corrosion testing, you run like hell because it is so unpredictable.

Question:

We, from time to time, will say that pitting rate is one third power. Is that a good rule of thumb? In other words, the depth of attack can be plotted as one third power.

Answer:

For a rate of penetration of pitting? I would say no; that means it slows up, doesn't it? I would be afraid of that. If it were the third power, I would go along with it.

Comment:

No, I mean one third power.

Comment:

Well, I think it might depend on the type of metal. You get these galvanic couples.

Comment:

You are right, it depends on the metal, like on the stainless steel. I would think that it could be pretty destructive.

Question:

What is knife-line attack?

Answer:

Well, this is one reason why the so-called extra low carbon stainless steels took over. We first ran into this in 1950. This was back in the jet-assist program, the pre-rocket era. They used fuming nitric as a fuel. They bought some 347 (columbium stabilized stainless steel) tanks to store it, and it only attacked the parent metal right next to the weld. The mechanism is that, if you heat this steel up to a very high temperature, and then cool it rapidly, such as would happen if you were welding very thin material. You cannot spend much time welding, so it cools rapidly. Everything stays in a solution: solumbium, carbon, everything else. As you heat back up [you see the chormium carbide forms at lower temperature say 1200 F (649 C)], but the columbium carbide does not tie up the carbon until you get up to 1900 F (1038 C). So to sum it up, if you take a piece of Type 347, heat it to above 2250 F (1232 C) and quench it, columbium and carbon are in solution, and now you heat it back up to 1200 F (649 C), but chromium carbide forms, so it is just like the columbium going along for the ride. Of course, the way to solve it would be to heat it up to 1900 F (1038 C), then the chromium carbide dissolves, and columbium carbide forms, and that is what you want. In other words, the columbium is added, not to improve corrosion resistance (general corrosion), but to tie up the carbon so you do not get chromium carbide formation that gives you intergranular sensitivity.

Question:

We have using your Type 347 rod to weld Type 304 L. If you weld it, you should have have any problems, but if you develop a leak and re-weld it, won't you have knife-line attack on the Type 347 weld?

Answer:

Let's take the first part, they use Type 347 rod to weld Type 304. Well, this was one of the first misconceptions of the use of columbium, to avoid the conventional weld decay. In fact, I ask my students this question every year on the exam. This doesn't do you one bit of good, because the weld decay is way out in the parent plate in the Type 304, so now if they repair welds, again you have to follow the thermal history. If it is heated to a high temperature, cooled rapidly, and then sensitized, you will get the knife-line attack. But, you can determine whether or not it is going to happen by looking at the thermal history of the metal itself, because when you are welding, you are doing some sort of heat treatment. In a cross weld, it would help as far as the previous weld is concerned, but it sure does not help the parent plate.

Question:

What is the influence of the higher nickel—this phenomenon with the columbium in the higher nickel alloys?

Answer:

Maybe an Inco or Carpenter man could answer that.

Comment:

In the 20CB3, we use columbium. I would say there are two differences between it and Type 347 (at least one difference and one similarity). We find that with the higher nickel, we have a little bit more of a problem with carbon, so we have to put in more columbium than you do in Type 347, so we put in much more than we have in the ratio in Type 347. You can get the knife-line type problem that we have just been talking about. You have to go back to the 1200 F (649 C) temperature for some considerable time though. Just welding on top of a weld, you won't normally se it, unless it is a really big weld with a lot of heat input. So, you can't sort of put one weld on top of another and not get into trouble on sheet and tubing and that type of thing. But, on a very heavy section you might get into trouble.

Question:

Isn't there a difference in the temperature in solubility for higher nickel alloys?

Answer:

I am not sure if there is. If there is, it is not really relevant. If you are taling of welding, I would say that the columbium or the titanium would pretty well be a solution by 1850 or 1900 F (1010 or 1038 C), and columbium may be a little higher (we start to go in about 1800 F (982 C). But, if you are welding, you go way above that anyway, so I don't know that it really matters too much. You go high enough to put them in solution. I don't think nickel plays a role in that way.

Comment:

Well, I think as a general statement you can say that the more complex alloys behave differently than 18-8 types. In fact, this probably would make the basis for a real good study.

Comment:

Well, I mentioned this specifically because I think we are going to see more about the problem of conservation of materials, the proper utilization of materials. I think we are going to see more clad construction. When you get into this, we are going to get into stress relieving, and somebody is going to get bitten.

Comment:

I am glad you brought that point up. This is going to be one of the big problems in the coal conversion business.

Question:

Getting back to this gentleman's question of welding of the Type 304L with the Type 347 rod, why weld with Type 347, why not use a Type 308L rod?

Comment:

I hate to tell you this, but that plant welds everything with a Type 347. The Type 347 makes a good rod, it is 2 to 5% ferrite, it handles well, it welds well, and they like it.

Question:

We presently have an Incoloy 825 reactor containing a fluidized bed operating at around 900 F (482 C). We have signs of excessive erosion-corrosion in the reactor, toward the bottom area of it. I was wondering if you would comment on effective means of combating this with a particular metallized coating, such as chromium or tungsten carbide. The reactor composition of the reactor gases contain about 10% HCl, 6% water, carbon dioxide and oxygen, nitrogen, and maybe up to 50 ppm free chloride.

Answer:

I think if you can get the tungsten carbide on there, it might do a good job. Let me tell you why I am saying that. We had a coal conversion meeting at Ohio State University in April, 1974. Somebody asked the question about the Type 347 line in this pilot plant. Somebody asked what was the line made of. He said Type 347. How long does it last? Well, not very long. Well, how long? Three to four hours. See, this was an elbow, and the fluid contains fly ash. This is an ingenious solution to the problem. It does not apply directly to yours. They had a sweeping elbow so they would not get as much as erosion corrosion. So they used a straight right angle, this pipe this way and this one this way, then they had a plug screwed in, facing the fluid coming at it and then they made the plugs out of tungsten carbide, and it is working fine.