CHAPTER

THREE

EIGHT FORMS OF CORROSION

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*, or parting; (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, though not a form of corrosion, often occurs indirectly as a result of corrosive attack and is therefore included in this chapter.

UNIFORM ATTACK

Uniform attack is the most common form of corrosion. It is normally characterized by a chemical or electrochemical reaction that 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 3-1 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.

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. These expedients, which can be used singly or in combination, are described further in Chap. 6.

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.

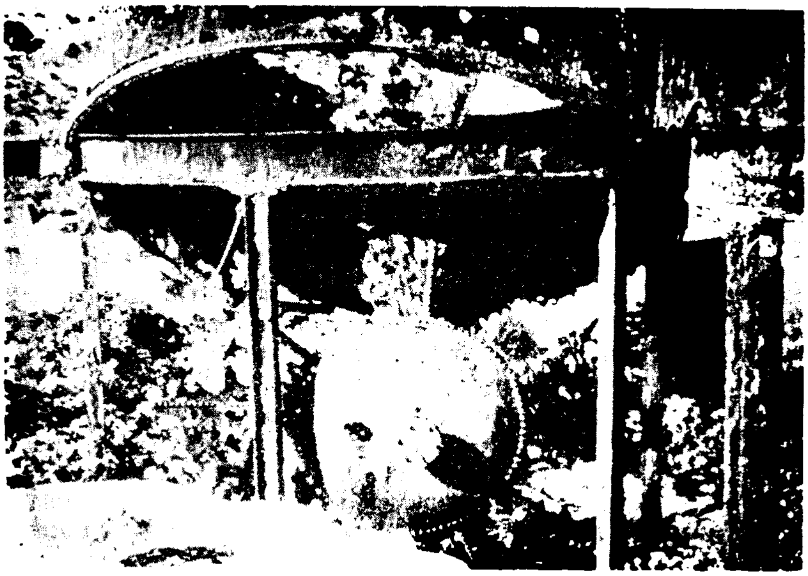

Figure 3-1 Rusting of abandoned steel tank.

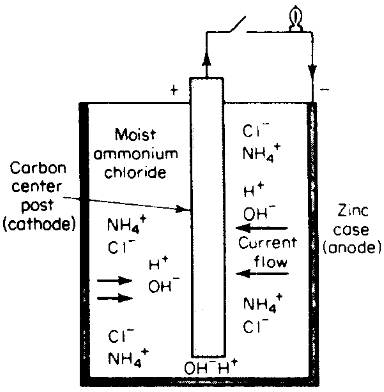

Figure 3-2 Section of dry-cell battery.

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 Fig. 3-2 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 that carries the current. Magnesium may also be used as the anodic material or outer case.

3-1 EMF and Galvanic Series

The potential differences between metals under reversible, or noncorroding, conditions form the basis for predicting corrosion tendencies as described in Chap. 9. Briefly, the potential between metals exposed to solutions containing approximately one gram atomic weight of their respective ions

Table 3-1 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
	$Pt\text{-}Pt^{+2}$	+1.2
Noble or	$Pd\text{-}Pd^{+2}$	+0.987
cathodic	$Ag\text{-}Ag^{+}$	+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	$Al\text{-}Al^{+3}$	−1.662
anodic	$Mg\text{-}Mg^{+2}$	−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. See also Table 9-1. These potentials are listed in accordance with the Stockholm Convention. See J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry*, Plenum Press, New York, 1970.

(unit activity) are precisely measured at a constant temperature. Table 3-1 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 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 3-1.

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

Table 3-2 Galvanic series of some commercial metals and alloys in seawater

↑	Platinum
	Gold
Noble or	Graphite
cathodic	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) (80 Ni, 13 Cr, 7 Fe)
	Nickel (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	Cadmium
anodic	Commercially pure aluminum (1100)
	Zinc
↓	Magnesium and magnesium alloys

galvanic series listed in Table 3-2 yields a more accurate prediction of galvanic relationships than the emf series. Table 3-2 is based on potential measurements and galvanic corrosion tests in unpolluted seawater conducted by The International Nickel 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 3-2 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 3-2. The alloys grouped in these brackets are somewhat similar in base composition—for example, copper and copper alloys. The bracket indicates that in most practical applications there is 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 3-2. A yacht with a Monel hull and steel rivets became unseaworthy because of rapid corrosion of the rivets. Severe attack occured 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, for 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 containing no metal.

These examples emphasize the fact that design engineers should be particularly aware of the possibilities of galvanic corrosion, since they specify 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, 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 seawater, 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 seawater.

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.

3-2 Environmental Effects

The nature and agressiveness 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 3-3 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 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.

Haney* shows that zinc becomes less active and potentials may reverse in the presence of inhibiting ions such as nitrates, bicarbonates and/or carbonates in water.

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

Table 3-3 Change in weight of coupled and uncoupled steel and zinc, g

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

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*E. G. Haney, The Zinc-Steel Potential Reversal in Cathodic Protection, *Materials Performance*, **21**:44–50 (Apr. 1982).

the tantalum-platinum couple, current does not begin to flow until 110°C is reached and 100 mA/ft^2 flows at 265°C. Tantalum is cathodic to *clean* high-silicon iron in strong sulfuric acid, but the current drops rapidly to zero. Above 145°C 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 atmopshere. 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.

3-3 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.

3-4 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 greatest than if the anodic and cathodic areas were equal in size. Figure 3-3 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.

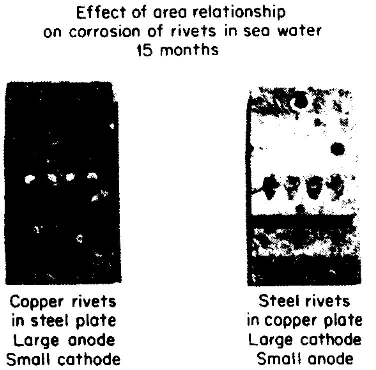

Figure 3-3 Area effect on steel-copper couple. (*International Nickel Company.*)

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 Fig. 3-4. The steel was coated with the same phenolic paint, with the coating covering only a small portion of the stainless steel below the weld.

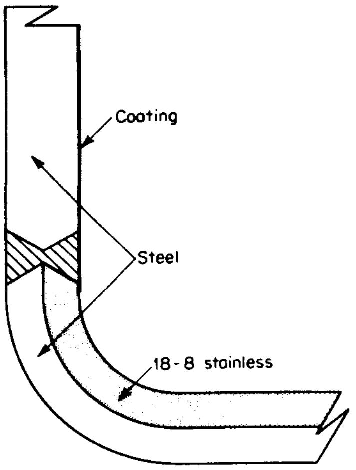

Figure 3-4 Detail of welded steel and stainless clad tank construction.

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-in. band above the weld shown in Fig. 3-4. 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 conducting 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 for 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 the uninitiated, but the above information should clarify this point.

3-5 Prevention

A number of procedures or practices can be used for combating or minimizing galvanic corrosion. Sometimes one is sufficient, but a com-

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*The more popular expression "gilding the lily" is a misquotation from Shakespeare's *King John*, which states "to gild refined gold, to paint the lily—to throw perfume on violet, to smooth the ice, or add another hue unto the rainbow—is wasteful and ridiculous excess."

bination 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 *completly* 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 3-5 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 one described in connection with Fig. 3-4. 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 Fig. 3-5, 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 brazing alloy more noble than at least one of the metals to be joined. Welded joints using welds of the same alloy are even better.

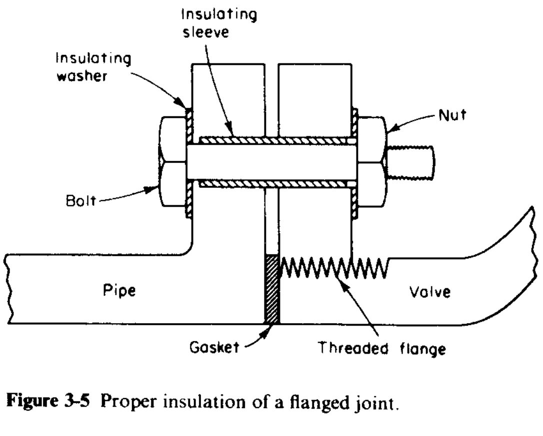

Figure 3-5 Proper insulation of a flanged joint.

7. Design for the use of readily replaceable anodic parts or make them thicker for longer life.
8. Install a third metal that is anodic to *both* metals in the galvanic contact.

3-6 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:

Cathodic protection The concept of cathodic protection is introduced at this point because it often utilizes the principles of galvanic corrosion. This subject is discussed in more detail in Chap. 6. Cathodic protection is simply the protection of a metal structure by making it the cathode of a galvanic cell. Galvanized (zinc-coated) steel is the classic example of cathodic protection of steel. The 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 3-3 and Fig. 3-6. 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 (see Chap. 6).

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*

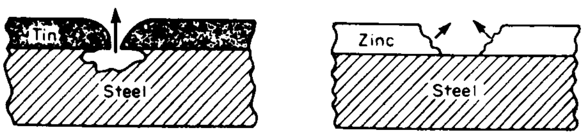

Figure 3-6 Galvanic corrosion at perforation in tin- and zinc-coated steel. Arrows indicate corrosive attack.

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 individual 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" that 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

Intensive 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 heads. As a result, this form of corrosion is called *crevice corrosion* or, sometimes, *deposit* or *gasket corrosion.*

3-7 Environmental Factors

Examples of deposits that may produce crevice corrosion (or deposit attack) are sand, dirt, corrosion products, and other solids. The deposit acts as a shield and creates a stagnant condition thereunder. The deposit could also be a permeable corrosion product. Figure 3-7 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,

Figure 3-7 Crevice corrosion of a silver heating coil.

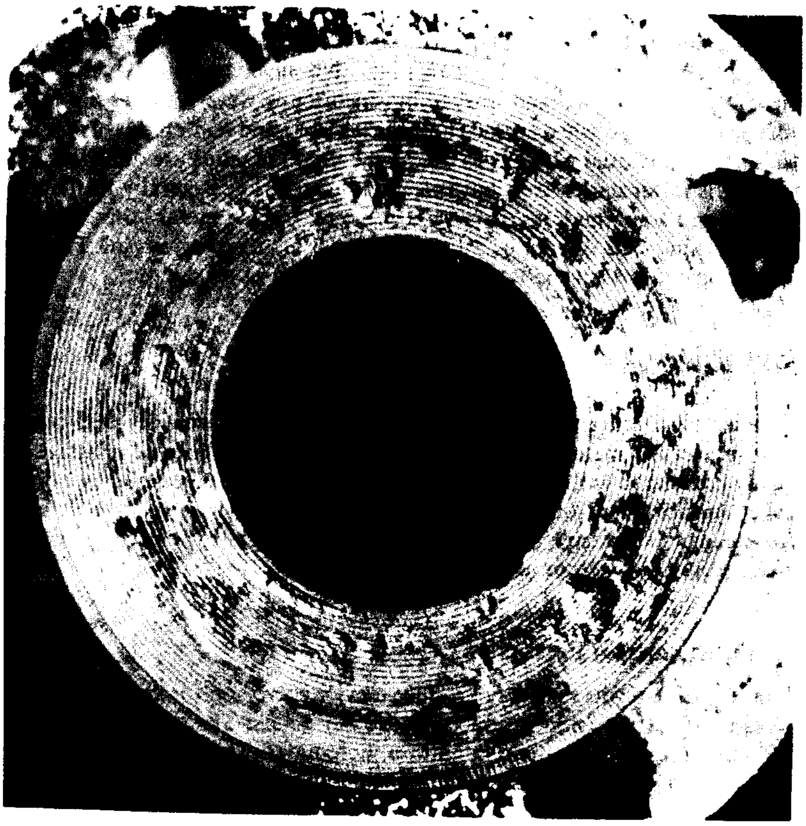

Figure 3-8 Gasket (crevice) corrosion on a large stainless steel pipe flange (*E. V. Kunkel.*)

asbestos, wax, and fabrics are examples of materials that can cause this type of corrosion. Figure 3-8 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., $\frac{1}{8}$-in.) grooves or slots. Fibrous gaskets, which have a wick action, form a completely stagnant solution in contact with the flange face; this condition forms an almost ideal crevice corrosion site.

3-8 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* have shown that although metal-ion and oxygen concentration differences do exist during crevice corrosion, these are not its 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 seawater (pH 7) as shown in Fig. 3-9. The overall reaction involves the dissolution of metal M and the reduction of oxygen to hydroxide ions as discussed in Chap. 2. Thus:

$$\text{Oxidation} \qquad M \rightarrow M^+ + e \tag{3.1}$$

$$\text{Reduction} \qquad O_2 + 2H_2O + 4e \rightarrow 4OH^- \tag{3.2}$$

Initially, these reactions occur uniformly over the entire surface, including the interior of the crevice. Charge 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 Fig. 3-10. This tends to produce an excess of positive charge in the solution (M^+), which is necessarily balanced by the migration of chloride ions into the crevice.† 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:

$$M^+Cl^- + H_2O = MOH\downarrow + H^+Cl^- \tag{3.3}$$

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*G. J. Schafer and P. K. Foster, *J. Electrochem. Soc.*, **106**:468 (1959); G. J. Schafer, J. R. Gabriel, and P. K. Foster, *ibid.*, **107**:1002 (1960); L. Rosenfeld and I. K. Marshakov, *Corrosion*, **20**:115*t* (1964).

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

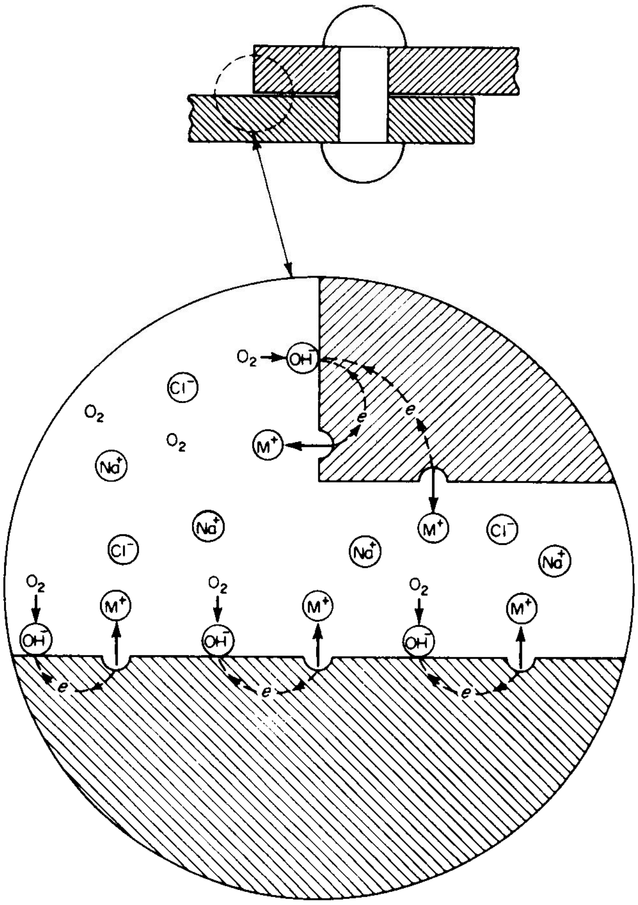

Figure 3-9 Crevice corrosion—initial stage.

Equation (3.3) shows that an aqueous solution of a typical metal chloride dissociates into an insoluble hydroxide and a free acid. For reasons that are not yet understood, both chloride and hydrogen ions accelerate the dissolution rates [Eq. (3.1)] of most metals and alloys. These are both present in the crevice as a result of migration and hydrolysis, and consequently the dissolution rate of M is increased, as indicated in Fig. 3-10. This increase in dissolution increases migration, and the result is a rapidly accelerating, or autocatalytic, process. The fluid within crevices exposed to neutral dilute sodium chloride solutions has been observed to contain 3 to 10 times as much chloride as the bulk solution and to possess a pH of 2 to 3.

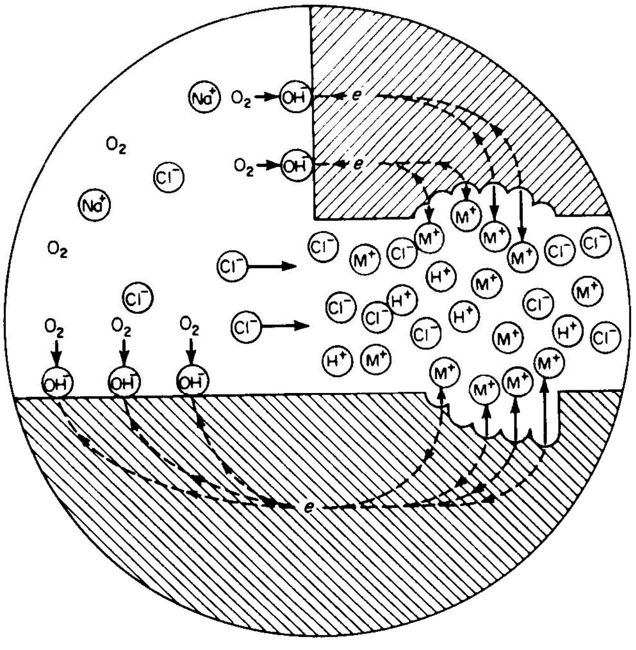

Figure 3-10 Crevice corrosion—later stage.

Table 3-4 Effect of geometric and electrochemical parameters on crevice corrosion resistance*

Parameter†	Increasing parameter causes crevice corrosion resistance to:
Critical anodic current density, i_c	Decrease
Crevice width, w	Increase
Passive potential range, E_p	Increase
Active potential range, E_a	Decrease
Solution specific resistance, ρ	Decrease

*B. J. Fitzgerald, Thesis, University of Connecticut, 1976. See also: C. Edeleanu and J. G. Gibson, *Chem. & Ind.*, 301 (1961); M. N. Folkin and V. A. Timonin, *Dokl. Akad. Nauk. SSSR*, **164**:150 (1965); W. D. France and N. D. Greene, *Corrosion*, **24**:247 (1968).

†Electrochemical parameters must be determined under actual or simulated crevice conditions.

Table 3-5 Ranking of alloys in U.S. Navy tests for resistance to crevice corrosion in filtered seawater at 30° C

30 day tests on 3 panels with 120 gritfinish and torque of 75 in.-lb

Rank	Alloy	Composition (wt%) Cr	Ni	Mo	Mn	Cu	Other	Number of sides (*S*) attacked	Maximum depth (*D*) of attack (mm)	*CCI* (*S* × *D*)
	Hastelloy C-276	15.5	54.7	15.5	0.5	0.1	3.8 W	0	0.00	0.00
	Inconel 625	22.3	61.0	8.5	0.1	—	3.6 Nb	0	0.00	0.00
1	29-4 (A.L.)	29.6	0.1	4.0	—	—	—	0	0.00	0.00
	29-4-2 (A.L.)	29.5	2.2	4.0	—	—	—	0	0.00	0.00
	29-4C* (A.L.)	28.8	0.8	3.8	0.2	—	0.6 Ti	0	0.00	0.00
	Monit (Uddeholm)	25.3	4.1	3.8	0.4	0.4	—	0	0.00	0.00
2	Crucible SC-1	25.6	2.1	2.9	0.2	—	0.5 Ti	1	0.05	0.05
3	Ferralium 255 (Cabot)	26.2	5.6	3.2	0.8	1.8	0.19 N	2	0.08	0.16
4	Hastelloy G-3 (Cabot)	22.8	43.7	7.0	0.8	1.8	3.5 Co	1	0.21	0.21
5	Haynes 20 Mod (Cabot)	21.6	25.5	5.0	0.9	—	0.5 Co	2	0.46	0.92
6	26-1S	25.0	0.2	1.0	0.2	—	1.1 Ti	4	0.30	1.2
7	20Mo-6	23.9	33.4	5.6	0.4	3.3	—	3	0.53	1.6
8	EB 26-1 (A.L.)	25.9	0.1	1.0	—	—	0.1 Nb	4	0.46	1.8
9	A.L. 4X	20.2	24.4	4.4	1.4	1.5	0.019 P	4	0.50	2.0
10	A.L. 6X	20.4	24.6	6.4	1.4	—	—	4	0.62	2.5
11	254 SMO (Avesta)	20.0	17.9	6.1	0.5	0.8	0.2 N	5	0.51	2.6
12	Hastelloy G (Cabot)	22.2	46.8	5.8	1.5	1.8	3.5 Co	4	0.87	3.5
13	904L (Uddeholm)	20.5	24.7	4.7	1.5	1.6	—	5	0.74	3.7
14	AISI 216	20.0	6.0	2.5	8.0	—	0.35 N	6	0.64	3.8

15	254SFER (Avesta)	29.4	22.2	2.1	1.7	0.1	0.15 N	5	0.90	4.5
16	254 SLX (Avesta)	19.9	25.0	4.7	1.6	1.7	0.04 N	6	0.92	5.5
17	Rex 734	21.3	9.4	2.7	3.8	—	0.42 N	6	1.00	6.0
18	Type 317 LM	19.5	14.5	4.1	1.3	0.2	0.056 N	6	1.07	6.4
19	Nitronic 50	21.1	13.7	2.3	4.8	—	0.26 N	6	1.10	6.6
20	Jessop 700	20.7	25.2	4.4	1.6	0.2	0.28 Nb	5	2.00	10
21	Type 316	17.5	10.7	2.4	1.6	0.3	—	6	1.93	12
22	Carpenter 20 Cb-3	19.4	33.2	2.2	0.4	3.2	0.51 Nb	5	3.10	16
23	Jessop 777	20.8	25.6	4.5	1.4	2.2	0.24 Nb	6	2.90	17
24	44 LN	25.0	5.9	1.5	1.8	0.1	0.2 N	6	3.35	20
			Perforated							
	AISI 444	18.9	0.1	2.0	0.4	—	0.4 Nb	6	1.21	7.2
	AISI 329	27.0	4.2	1.4	0.3	0.1	—	6	1.29	7.7
	34 LN	16.8	13.8	4.2	1.6	—	0.14 N	6	1.04	6.2
			Attack outside crevice areas							
	AISI 439	17.7	0.3	—	0.3	—	0.4 Ti	6	0.72	4.3
	AISI 317L	18.9	12.2	3.6	1.7	—	0.056 N	6	1.92	12
	AISI 317L+	18.3	15.8	4.2	1.5	0.2	0.16 Co	6	1.09	6.5
	Incoloy 825	22.0	44.0	2.7	0.4	1.7	0.7 Ti	6	2.42	15

*Three additional panels were tested for 82 days with the same results.

As the corrosion within the crevice increases, the rate of oxygen reduction on adjacent surfaces also increases, as shown in Fig. 3-10. 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 that 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 (see Chap. 9), 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.

Section 4-17 describes tests for crevice corrosion (also called occluded cell corrosion), and Fig. 4-19 illustrates a multiple crevice corrosion test technique that is very popular. This form of corrosion is difficult to study since the area of corrosion is hidden and test results are often scattered because of variations in the incubation period preceding the start of the attack. Theoretical and experimental studies offer promise in evaluating this type of attack. The effects of various geometric and electrochemical parameters on crevice corrosion resistance are now more clearly understood and are summarized in Table 3-4. The critical anodic current density and the active and passive potential ranges have been described in Chap. 9. Examination of this table shows that optimum crevice corrosion resistance will be achieved with an active-passive metal possessing:

1. A narrow active-passive transition
2. A small critical current density
3. An extended passive region

Titanium is an example of such a material, as are the high-nickel alloys (e.g., Hastelloy C). Type 430 stainless steel with a large critical current density, a wide active-passive transition, and a limited passive region is extremely susceptible to crevice corrosion. The crevice width is also an important variable. All materials are susceptible to crevice corrosion provided the crevice width is sufficiently narrow (e.g., 1 micrometer or less). This information provides a basis for estimating the probable crevice corrosion resistance of a given alloy.

Streicher* developed a Crevice Corrosion Index (CCI) to assist in the selection of materials of construction. This is based on the product of the number of sides attacked, S, and the maximum depth of attack, D; that is, $CCI = S \times D$. Table 3-5 ranks stainless alloys with the best in the top group. This excellent paper includes discussion of initiation, growth, effects of alloying elements, materials selection, and also a good bibliography.

Materials Technology Institute published MTI Technical Report No. 8, *A Sensor for Monitoring Crevice Corrosion—An Analysis and Evaluation—Phase 2*, (March 1983). A device is described that could be used for exposure to plant and other solutions for determining whether or not susceptibility to crevice corrosion exists.

3-9 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 or plant flow sheet, if possible.
6. Remove wet packing materials during long shutdowns.
7. Provide uniform environments, 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.

3-10 Filiform Corrosion

Although not immediately apparent, *filiform corrosion* (filamentary corrosion occuring on metal surfaces) is a special type of crevice corrosion. In most instances it occurs under protective films, and for this reason it 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 that have been exposed to the atmosphere. The red-brown corrosion filaments are readily visible.

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*M. A. Streicher, Analysis of Crevice Corrosion Data From Two Sea Water Exposure Tests on Stainless Alloys, *Materials Performance*, **22**:37–50 (May 1983).

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, corrosion occuring 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 Fig. 3-11. The filaments are $\frac{1}{10}$ in. or less wide, and corrosion occurs only in the filament head. The blue-green color of the active head 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 (see Fig. 3-12). Corrosion filaments are initiated at edges 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° 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 3-6

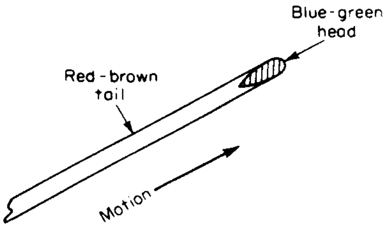
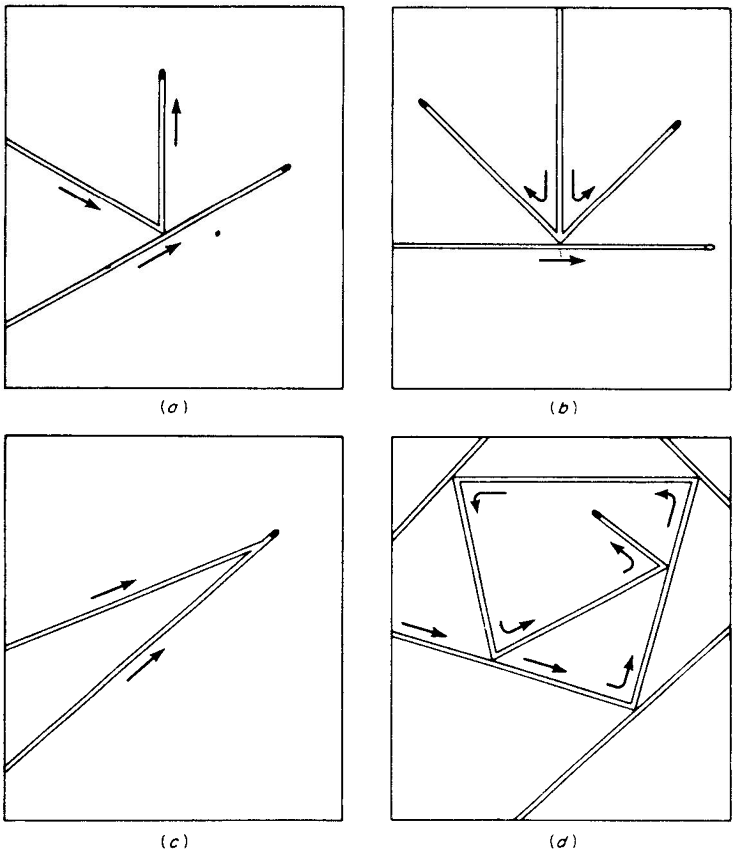


Figure 3-11 Schematic diagram of a corrosion filament growing on an iron surface (magnified).



(a) (b) (c) (d)

Figure 3-12 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; (*d*) "death trap."

Table 3-6 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

Source: M. Van Loo, D. D. Laiderman, and R. R. Bruhn, *Corrosion*, **9**:2 (1953).

shows that filiform corrosion occurs primarily between 65 and 90% 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.

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* 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 Fig. 3-13. 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 Fig. 3-13, atmospheric water continuously diffuses into the active head and out of the

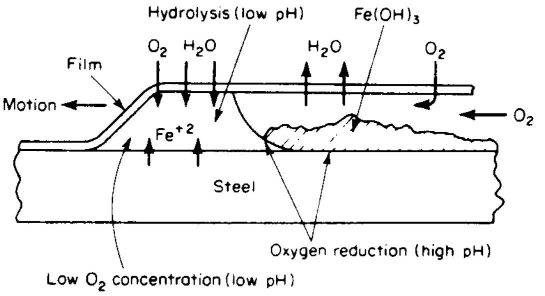


Figure 3-13 Cross section of a corrosion filament on a steel surface.

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*For further details see W. H. Slabaugh and M. Grotheer, Mechanism of Filiform Corrosion, *Ind. Eng. Chem.*, **46**:1014 (1954).

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 head, where hydrolysis of the corrosion products produces an acidic environment. Thus, filiform corrosion can be viewed as a self-propagating crevice. Although Fig. 3-13 adequately 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 store 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 that 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 they 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 numbers 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.

3-11 Pit Shape and Growth

Figure 3-14 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 3-15 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

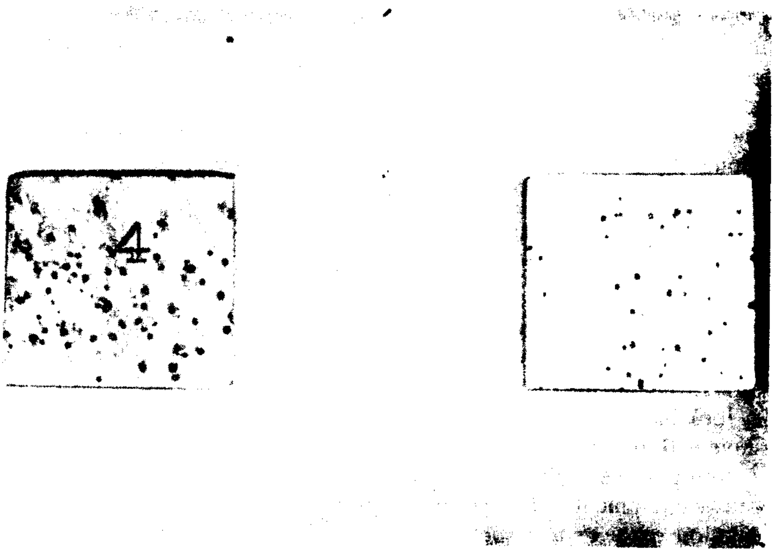

Figure 3-14 Pitting of 18-8 stainless steel by acid-chloride solution.

Figure 3-15 Pitting of a copper pipe used for drinking water.

metal at an ever-increasing rate. In addition, pits tend to undermine or undercut the surface as they grow. This aspect, illustrated in Fig. 3-16, 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.

Pitting may be considered as the intermediate stage between general overall corrosion and complete corrosion resistance. This is shown diagrammatically in Fig. 3-17. Specimen *A* shows no attack whatsoever. Specimen *C* has 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 Fig. 3-17. 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* observed a striking example of this during a study of the effects

Figure 3-16 Pitting of stainless steel condenser tube.

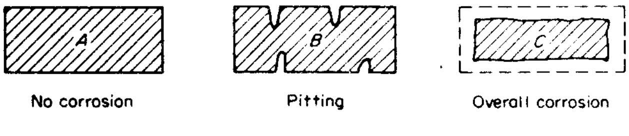

Figure 3-17 Diagrammatic representation of pitting corrosion as an intermediate stage.

*O. L. Riggs, J. D. Sudbury, and M. Hutchinson, *Corrosion*, **16**:94–98 (June 1960).

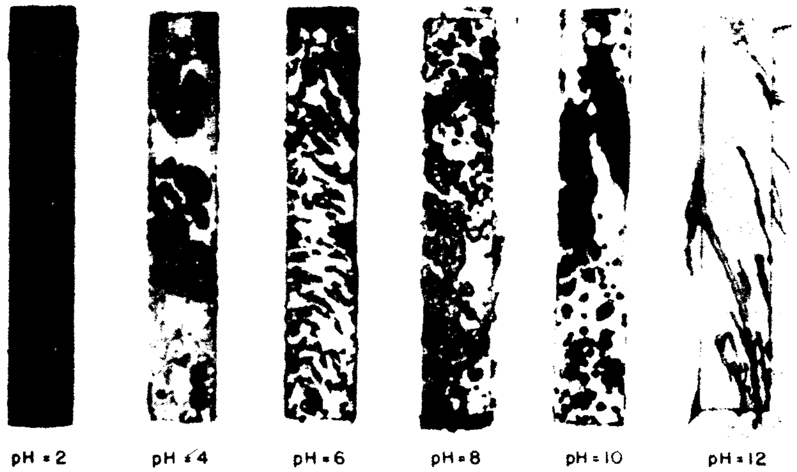

Figure 3-18 Corrosion of steel after 24 hours in 5% NaCl and 500-lb/in.^{2} oxygen pressure. (*Continental Oil Co.*)

of high oxygen pressure and pH on the corrosion of steel by a 5% NaCl brine. Figure 3-18 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.

3-12 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 stimulating and necessary for the continuing activity of the pit. This is illustrated schematically in Fig. 3-19. 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 electroneutrality. Thus, in the pit there is a high concentration of MCl and, as a result of hydrolysis [see Eq. (3.3)], 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.

Although Fig. 3-19 indicates how a pit grows through self-stimulation, it does not immediately suggest how this process is initiated. Evans* 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 that

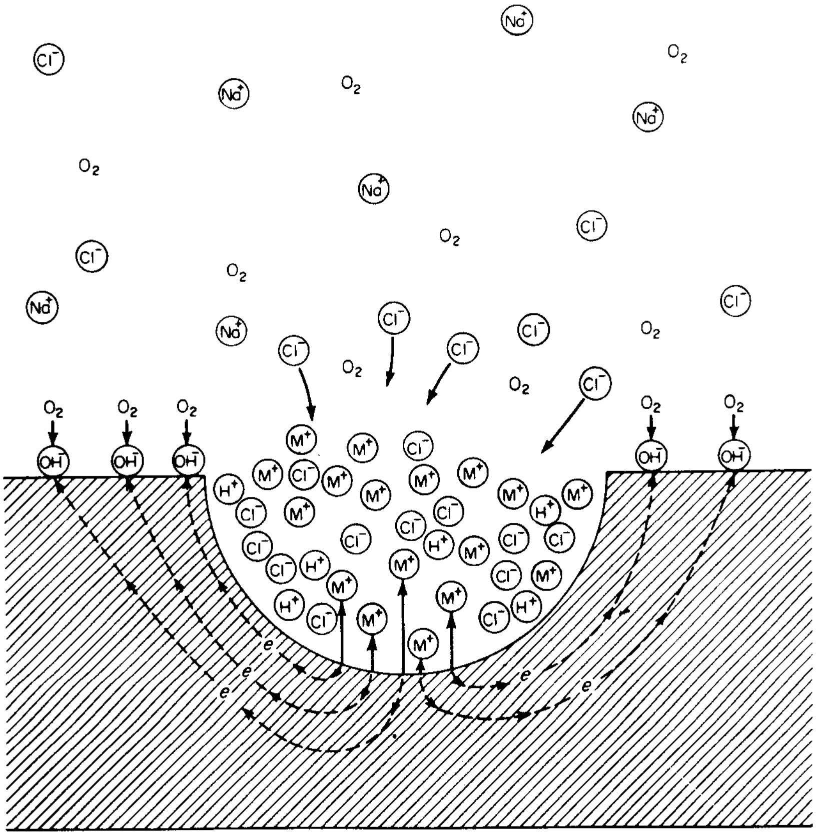

Figure 3-19 Autocatalytic processes occurring in a corrosion pit.

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*U. R. Evans, *Corrosion*, 7:238 (1951).

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 author has observed that new pits are indeed unstable—many become inactive 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

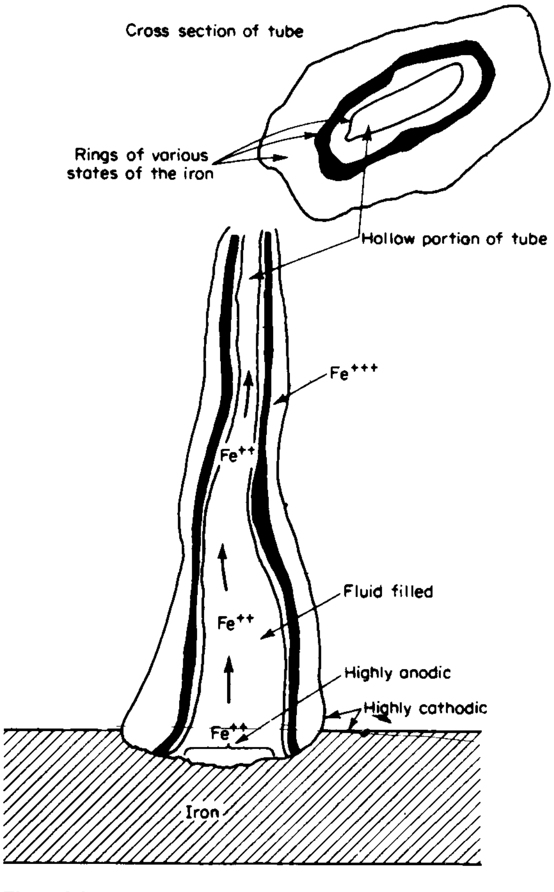

Figure 3-20 Corrosion tube growth mechanism. (*Continental Oil Co.*)

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 tubular corrosion products shown in Fig. 3-18 grow by a mechanism similar to that described above. Figure 3-20 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 Fig. 3-20. The oxides forming the tube were identified by x-ray diffraction.

Comparison of Figs. 3-20, 3-19, and 3-10 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 that show pitting attack are particularly susceptible to crevice corrosion (e.g., stainless steels in seawater or ferric chloride). However, the reverse is not always correct—many systems that show crevice attack do not suffer pitting on freely exposed surfaces. It appears that pitting, though 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.

3-13 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 seawater 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:

$$Cu^{2+} + 2e \rightarrow Cu \qquad (3.4)$$

$$Fe^{3+} + e \rightarrow Fe^{2+} \qquad (3.5)$$

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.

3-14 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 3-21 demonstrates this point. The material is type 316 stainless steel and the environment an acid-ferric chloride mixture at elevated temperature. This

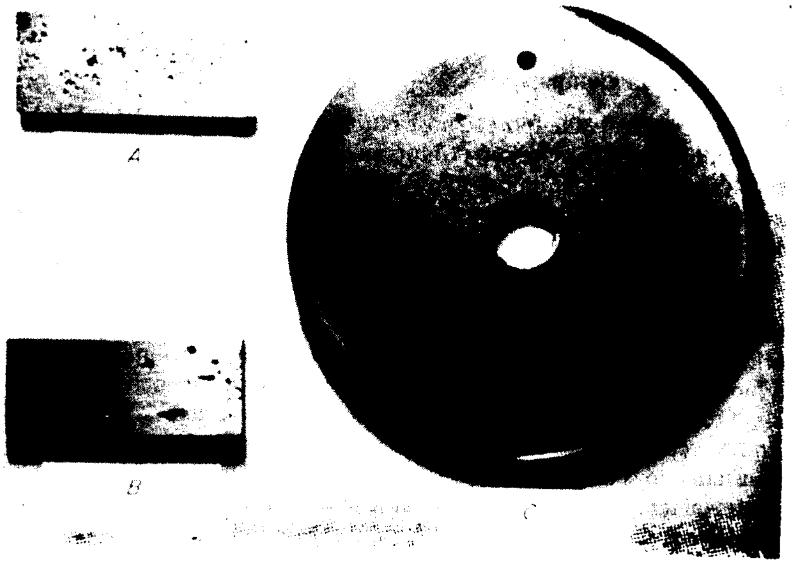

Figure 3-21 Effect of velocity on pitting of stainless steel.

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."

3-15 Metallurgical Variables

As a class, the stainless steel alloys are more susceptible to damage by pitting corrosion than are any other group of 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 3-7.

Holding types 304 and 316 stainless steel in the sensitizing temperature range (950 to 1450°F) decreases their pitting resistance. Austenitic stainless steels exhibit the greatest pitting resistance when solution-quenched above 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 seawater often can be alleviated by the substitution of steel tubes.

Table 3-7 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

Source: N. D. Greene and M. G. Fontana, *Corrosion* **15**:25*t* (1959).

Although the general corrosion of steel is much greater than that of stainless steel, rapid perforation due to pitting does not occur.

3-16 Evaluation of Pitting Damage

Since pitting is a localized form of corrosion, conventional weight loss tests 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 Fig. 3-22. Note that the average pit depth is a poor way to estimate pit damage, since it is the deepest pit that causes failure.

Examination of Fig. 3-22 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 Fig. 3-23, 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* occuring 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

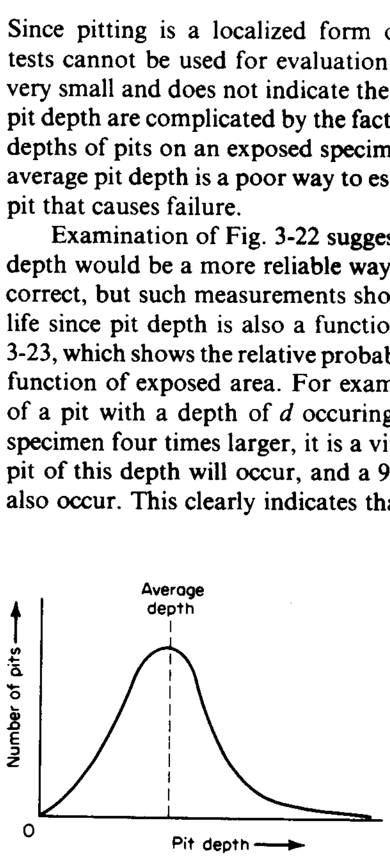

Figure 3-22 Relationship between pit depth and the number of pits appearing on a corroded surface.

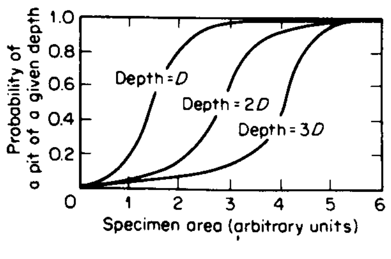

Figure 3-23 Pit depth as a function of exposed area.

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.

3-17 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 18-8SMo (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 seawater 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.

|	Type 304 stainless steel
Increasing	Type 316 stainless steel
pitting	Hastelloy F, Nionel, or Durimet 20
resistance	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.*

INTERGRANULAR CORROSION

The more reactive nature of grain boundaries was discussed in Chap. 2. 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,

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*For additional reading on pitting, refer to N. D. Greene and M. G. Fontana, A Critical Analysis of Pitting Corrosion, *Corrosion*, **15**:41–47 (Jan. 1959). Also, An Electrochemical Study of Pitting Corrosion in Stainless Steels—Part 1, Pit Growth; Part 2, Polarization Measurements, pp. 48–60 in this same volume by the same authors.

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.

3-18 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 950 to 1450°F, they become *sensitized* or susceptible to intergranular corrosion. For example, a procedure to sensitize intentionally is to heat at 1200°F for 1 hr.

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 Fig. 3-24. 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.

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.

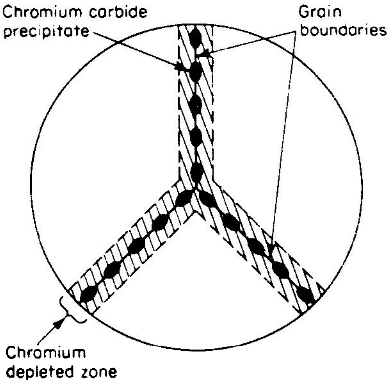

Figure 3-24 Diagrammatic representation of a grain boundary in sensitized type 304 stainless steel.

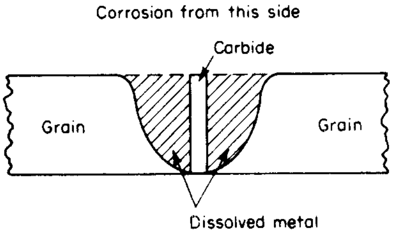

Figure 3-25 Cross section of area shown in Fig. 3-24.

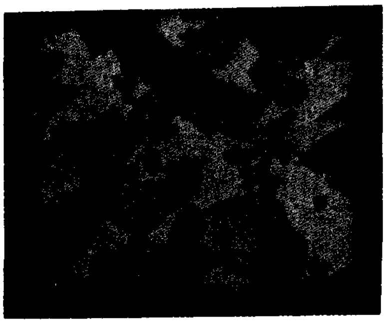

Figure 3-26 Electron photomicrograph of carbides isolated from sensitized type 304 stainless steel (13,000 ×).

If the alloy were cut into a thin sheet and a cross section of the grain-boundary area made, it would look something like Fig. 3-25. 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 Du Pont, using the electron microscope, have shown that the carbide forms as a film or envelope around the grains in a leaflike structure. Figure 3-26, 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 Fig. 3-25, 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.

3-19 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 Fig. 3-27 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 is explained in Sec. 3-20.

The metal in the weld decay zone must have been heated in the sensitizing range. Figure 3-28* is a "tablecloth analogy" of heat flow and temperatures associated with welding. Visualize a mountainlike 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 centerline in Fig. 3-28 is the center of the weld, which is the hottest (above the melting point).

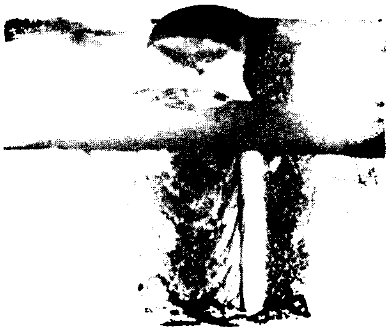

Figure 3-27 Intergranular corrosion in weld decay zone—right, type 304; left, stabilized with titanium.

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*L. R. Honnaker, *Chem. Eng. Progr.*, **54**:79–82 (1958).

The lines with the crosses represent temperatures in the sensitizing zone. These lines correspond to the weld decay zone in Fig. 3-28.

Figure 3-29* 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 $\frac{1}{32}$ in. 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.

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.

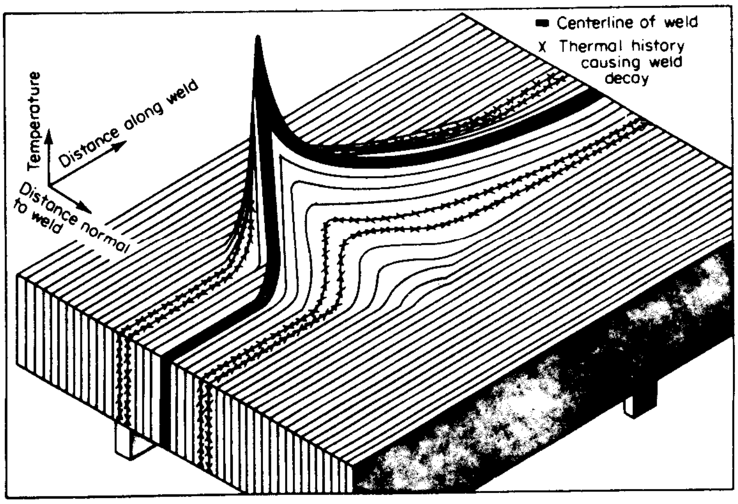

Figure 3-28 Tablecloth analogy of heat flow and temperatures during welding. Visualize a mountainlike block being moved beneath an elastic striped tablecloth. The rise and fall of each stripe represents the rise and fall of temperature in a welded plate. (*Du Pont Company*)

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*L. R. Honnaker, *Chem. Eng. Progr.*, **54**:79–82 (1958).

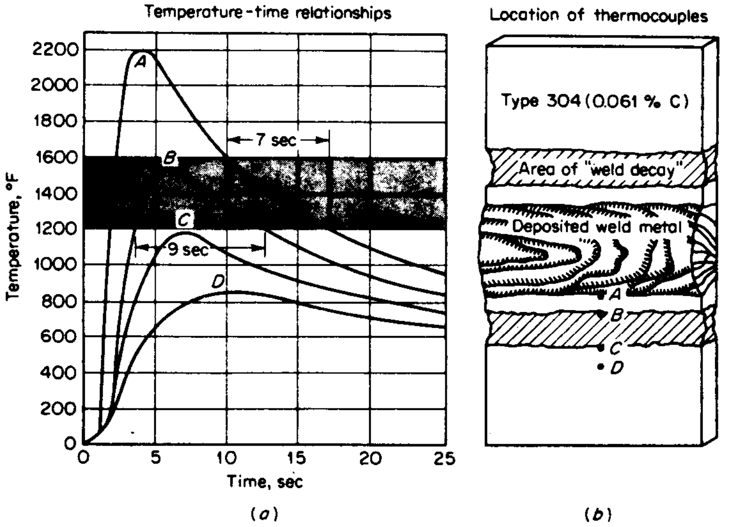


Figure 3-29 Temperatures during electric-arc welding of type 304 stainless steel. (*Du Pont Company*)

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, 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.

3-20 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 to 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 will 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 Fig. 3-27 does not show weld decay, because it is type 321. The same picture would obtain 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 3-30 shows a situation similar to Fig. 3-27, 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 around 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.

These stainless steels 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

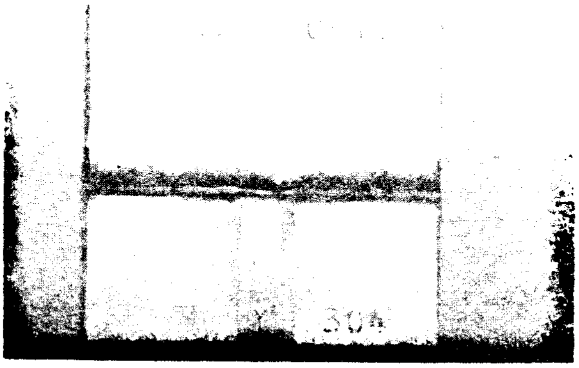


Figure 3-30 Elimination of weld decay by type 304L.

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.

Carbon pickup (surface carburization) during production of austenitic stainless steels has caused premature failures. It occurs when these steels are cast into molds containing carbonaceous materials such as organic binders and washes or baked oil sand. The hot metal absorbs carbon from the carbon-containing environment.

Increased carbon content of the stainless steel can degrade corrosion

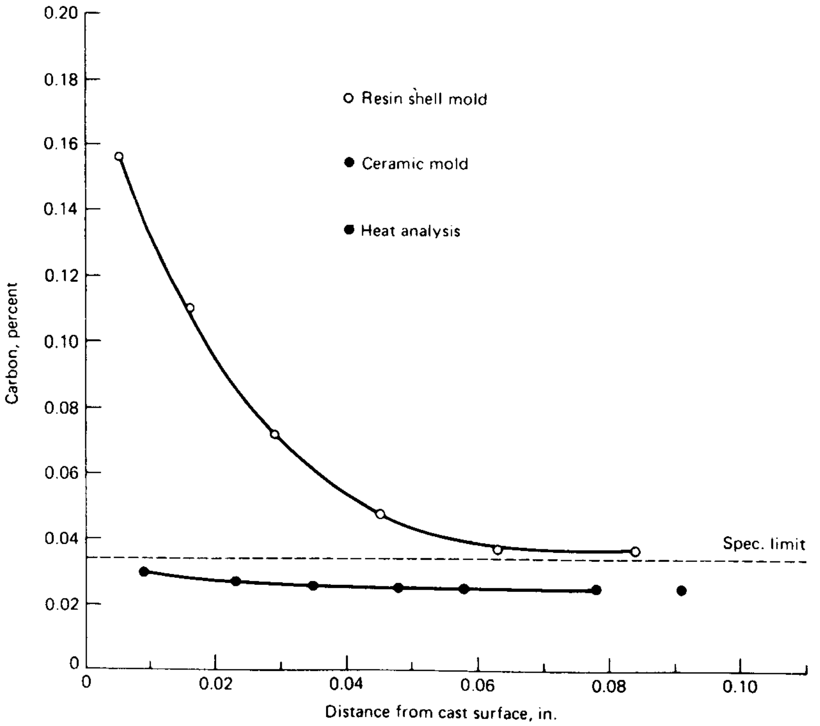


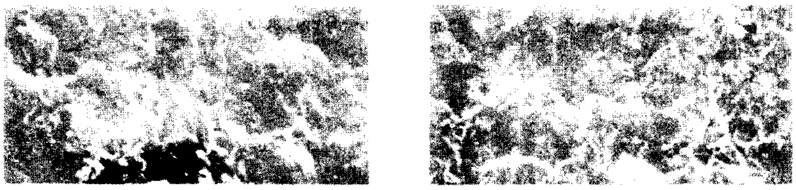
Figure 3-31 Carbon profiles of CF-3 castings.

resistance particularly to environments that are aggressive from the standpoint of intergranular attack. Resistance to pitting is also decreased.

Figure 3-31 shows carbon profiles for CF-3 (18-8, 0.03% C max) cast in a resin shell mold.* The carbon content near the surface is 0.16% as compared to 0.03% in the metal as poured. Higher carbon is in excess of the specification limit. Metal cast in a ceramic mold shows practically no carbon pickup. Similar situations occur in other austenitic stainless steels.

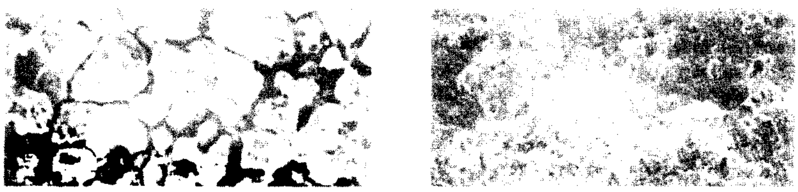
Figure 3-32 shows scanning electron microscope photographs of the surfaces after the Huey test (Sec. 4-19). Intergranular attack is evident on the resin shell casting but not on the ceramic mold casting.

Corrosion could continue into the metal beyond the carburized metal because intergranular corrosion, pitting, and stress corrosion could be initiated and propagated by crevice and/or notch effects. A number of case histories substantiate failure or reduced service life. Carbon pickup can be recognized if (1) castings are attacked more than wrought components, (2) intergranular attack occurs on a low-carbon (0.03%) material, (3) two castings of the same alloy show a substantial difference in attack, (4) machined surfaces show less attack than adjacent as-cast surfaces, and (5) carbon content near the surface is higher than in the main body of the casting.



Resin shell casting Ceramic mold casting

(a) Before corrosion test



Resin shell casting Ceramic mold casting

(b) After Huey test: annealed condition

|— 0.01 in. —|

Figure 3-32 Scanning electron microscope (SEM) photographs of CF-3 casting surfaces.

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*W. A. Luce, M. G. Fontana, and J. W. Cangi, *Corrosion*, **28**:115 (1972); also W. H. Herrnstein, J. W. Cangi, and M. G. Fontana, *Materials Performance*, **14**:21–27 (1975).

Table 3-8 Corrosives causing problems due to carbon pickup

Corrosives	Plants
Acetic acid	Adipodinitrile
Acetic + formic acid	Electroplating
Chromic acid	Metal refining
Fluoboric acid	Nitric acid
Metal plating solutions	Phosphoric acid
Nitric acid	Plutonium recovery
Nitric + adipic acid	Sulfuric acid
Nitric + hydrofluoric acid	Synthetic fiber
Phosphoric acid	Wet-process phosphoric acid
Phosphoric + sulfuric acid	Xylene
Sulfuric acid	
Sulfuric acid + copper sulfate	

Table 3-9 Corrosives that induce intergranular corrosion in austenitic stainless steel

Acetic acid
Acetic acid + salicylic acid
Ammonium nitrate
Ammonium sulfate
Ammonium sulfate + H_2SO_4
Beet juice
Calcium nitrate
Chromic acid
Chromium chloride
Copper sulfate
Crude oil
Fatty acids
Ferric chloride
Ferric sulfate
Formic acid
Hydrocyanic acid
Hydrocyanic acid + sulfur dioxide
Hydrofluoric acid + ferric sulfate
Lactic acid
Lactic acid + nitric acid
Maleic acid
Nitric acid
Nitric acid + hydrochloric acid
Nitric acid + hydrofluoric acid
Oxalic acid
Phenol + naphthenic acid
Phosphoric acid
Phthalic acid
Salt spray
Seawater
Silver nitrate + acetic acid
Sodium bisulfate
Sodium hydroxide + sodium sulfide
Sodium hypochlorite
Sulfamic acid
Sulfite cooking liquor
Sulfite digester acid
  (calcium bisulfite + sulfur dioxide)
Sulfite solution
Sulfur dioxide (wet)
Sulfuric acid
Sulfuric acid + acetic acid
Sulfuric acid + copper sulfate
Sulfuric acid + ferrous sulfate
Sulfuric acid + methanol
Sulfuric acid + nitric acid
Sulfurous acid
Water + starch + sulfur dioxide
Water + aluminum sulfate

Table 3-8 lists corrosive areas wherein corrosion due to carbon pickup was observed. Table 3-9 lists corrosives that can induce intergranular attack.*

If a certain specified carbon content is desired for a given corrosive environment, then the metal surface should meet the specification.

Carbon pickup is particularly critical for the very low carbon stainless steels (0.03% C max) and, of course, for the newer high-purity ferritic stainless steels. Sometimes the entire casting is "out of specification."

Future demands on stainless steel castings Consumers and users of high-alloy castings, such as the chemical process industries, will demand better quality castings in the future. There are indications that castings for "commercial" use may have to meet "nuclear" industry standards in many cases. Higher pressures and temperatures and increasing costs of maintenance and downtime call for better corrosion resistance and integrity of castings. Consumerism and product liability considerations call for predictable and reliable performance of equipment. Castings must be characterized by good quality, accurate dimensions, and easy reproducibility and will require documentation and certification. Inspection will be more critical. Premature failure because of defects or incorrect alloy composition must be avoided. Specifications must be carefully followed. Good liaison between the designer and producer is a must. Quality control and quality assurance are key words. These remarks also apply to wrought products.

3-21 Knife-Line Attack

The stabilized austenitic stainless steels are attacked intergranularly, under certain conditions, because of chromium carbide precipitation. Columbium or titanium fails to combine with the carbon. Figure 3-33 shows a section of a type 347 (18-8 + Cb) drum that contained fuming nitric acid. Severe intergranular attack occurred in a narrow band, 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.† 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 appre-

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*G. A. Nelson, "Corrosive Data Survey," NACE, 1967.

†M. L. Holzworth, F. H. Beck, and M. G. Fontana, *Corrosion*, 7:441–449 (1951).

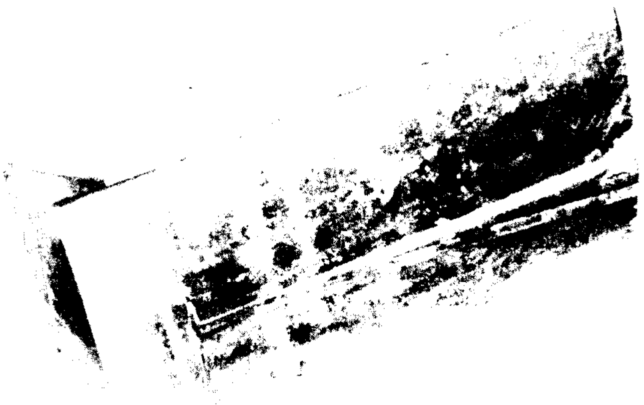

Figure 3-33 Knife-line attack on type 347 stainless steel.

ciable 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. Columbium 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, 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 2600 to 2700°F. A sharp thermal gradient exists in the metal because of the relatively poor thermal conductivity of 18-8 and because the welding operation on this thin ($\frac{1}{16}$-in.) 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 Fig. 3-34. 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 1950°F. Focus attention now on the narrow band of metal adjacent to the weld. This was heated to around

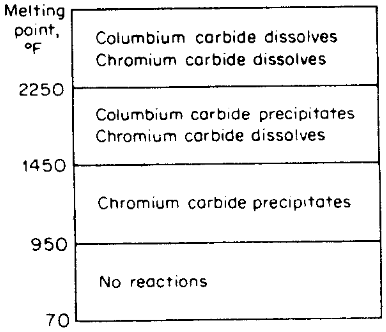

Figure 3-34 Schematic chart showing solution and precipitation reactions in types 304 and 347.

2600°F and cooled rapidly. According to the chart this band of metal has everything in solution (no precipitation of either carbide). If this metal is now heated in the sensitizing range of about 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 2300°F, and quench in water. Now heat it for $\frac{1}{2}$ hr at 1200°F and cool. The *entire sample* sensitizes essentially the same as 18-8 (no Cb).

The obvious remedy for avoiding knife-line attack is to heat the completed structure (after welding) to around 1950°F. According to the chart, chromium carbide dissolves and columbium carbide forms, which is the desired situation. The rate of cooling after the 1950°F 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 given superior performance in cases where the stabilized steels exhibited knife-line attack.

3-22 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.

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 alloys (*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 that describes 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.

3-23 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 that contrasts 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 3-35 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 occured after several years in potable-water service.

Figure 3-36 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

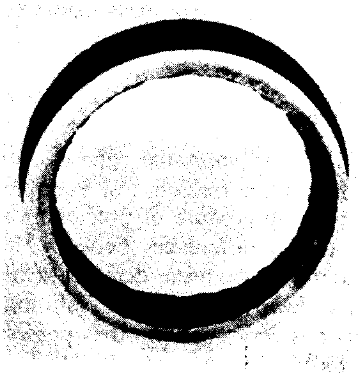

Figure 3-35 Uniform dezincification of brass pipe.

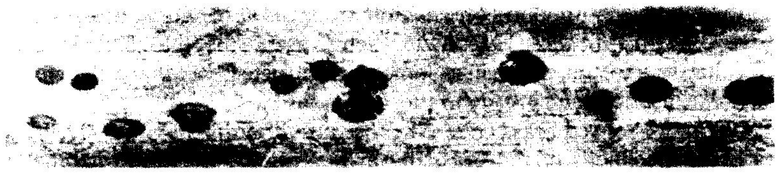

Figure 3-36 Plug-type dezincification.

exchanger with boiler water on one side and fuel combustion gases on the outside. Figure 3-37 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 Fig. 3-37. 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 Fig. 3-36).

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).

Figure 3-37 Section of one of the plugs shown in Fig. 3-36.

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

Failures of red brass (15% zinc) because of dezincification rarely occur. Tensile specimens of red brass, naval brass (35% zinc), and Muntz metal (40% zinc) exposed for several months to a chloride solution at 80°C showed losses in tensile strength of 5%, 30%, and 100%, respectively. Again, this shows the very low strength of dezincified alloy.

3-24 Dezincification: Mechanism

Two theories have been proposed for 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, whereas 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 easy contact between the solution and the brass.

3-25 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.

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 redoposited 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 (70–90% Cu, 30–10% Ni) are utilized.

3-26 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*.

Figure 5-1 shows the microstructure of gray cast iron. What actually 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 cast iron is in an environment that 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 (see Chap. 5) 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.

Graphitization of gray cast iron has reached the public eye because of failures of underground pipelines, particularly those handling hazardous materials. Graphitized pipe has cracked because of soil settlement or impact by excavating or earth-moving equipment. In several cases explosions, fires, and fatalities have occurred. This was emphasized to me during a three-year term as a member of the Technical Pipeline Safety Standards Committee of the U.S. Department of Transportation. Underground pipelines made of gray cast iron should be selected only after consideration of graphitization.

Bloom and Tuovinen* conducted dispersive analysis and metallurgical studies of graphitic residues from gray cast iron pipe that had been in service for about 40 years in Columbus, Ohio. Years ago I recommended use here of ductile (nodular) cast iron instead of gray cast iron (brittle). Ductile iron pipe with a cement mortar lining has been giving excellent performance.

3-27 Other Alloy Systems

Selective leaching by aqueous environments occurs in other alloy systems under appropriate conditions, especially in acids. Selective removal of

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*P. R. Bloom and O. H. Tuovinen, Characterization of Graphitic Corrosion Residue of Cast Iron in a Water Distribution System, *Materials Performance*, 21–23 (Feb. 1984).

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 rare 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 results in better passivity and resistance to pitting.

With reference to other alloy systems another constructive application of dealloying involves the preparation of Raney nickel catalyst by selectively removing aluminum from an aluminum-nickel alloy by action of caustic.

The term *dealloying* is frequently used and is preferred by some corrosionists. Dealloying is defined* as a corrosion process whereby one constituent of an alloy is preferentially removed from the alloy leaving an altered residual structure (like dezincification). Pryor† shows that dealloying occurs much slower in an aluminum bronze than in yellow brass.

3-28 High Temperatures

M. G. Fontana's early work on high-temperature oxidation of stainless steels showed selective oxidation of chromium when exposed to low-oxygen atmospheres at high temperatures (1800°F). When there is competition 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.‡ Pitting of type 430 (17% Cr) trim on automobiles was attributed to depletion of chromium during bright-annealing operations. Chromium contents as low as 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 1475°F. The alloy was destroyed by conversion to a spongy mass.

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*R. H. Heidersbach and E. D. Verink, *Corrosion*, **28**:397–418 (Nov. 1972).

†M. J. Pryor, The Dealloying of a Cu-8.9% Al Solid Solution, *J. Electrochem. Soc.*, **130**: 1625–1627 (July 1983).

‡R. V. Trax and J. C. Holzwarth, *Corrosion*, **16**:105–108 (1960).

¶R. Bakish and F. Kern, *Corrosion*, **16**:89–90 (1960).

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 that 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 3-38 shows a typical wavy appearance of an erosion-corrosion failure. This pump impeller was taken out of service after three weeks of operation. Figure 3-39 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.

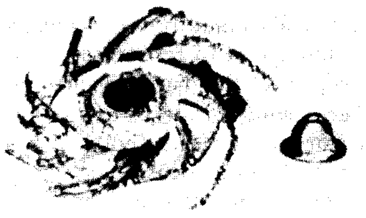

Figure 3-38 Erosion corrosion of stainless alloy pump impeller.

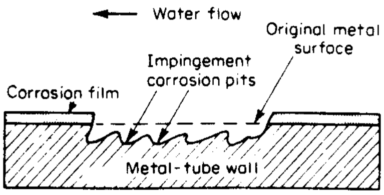

Figure 3-39 Erosion corrosion of condenser tube wall.

Most metals and alloys are susceptible to erosion-corrosion 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.

3-29 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 re-forming 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 that fluid.

Stainless steels depend on passivity for resistance to corrosion. Consequently these materials are vulnerable to erosion corrosion. Figure 3-40 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. This material showed no weight loss and was completely passive under stagnant conditions as shown by the x on the abscissa at 60°C. The impeller shown in Fig. 3-38 gave approximately two years of life,

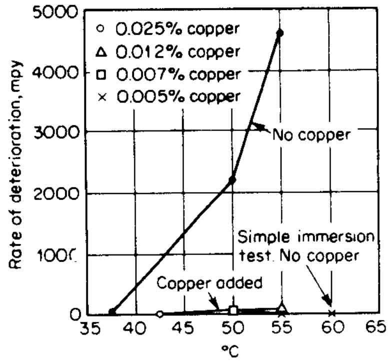

Figure 3-40 Effect of temperature and copper-ion addition on erosion corrosion of type 316 by sulfuric acid slurry (velocity, 39 ft/sec).

which was reduced to three 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 one week and lead bends were rapidly attacked in a plant handling a 3% sulfuric acid solution at 90°C. As a result of these failures erosion-corrosion tests were made, and the results are plotted in Fig. 3-41. 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

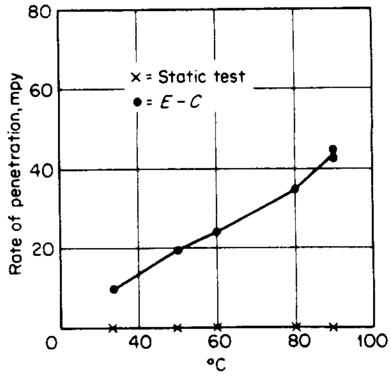

Figure 3-41 Erosion corrosion of hard lead by 10% sulfuric acid (velocity, 39 ft/sec).

surface scales formed. Figure 3-42 shows the effect of pH of distilled water at 50°C on erosion corrosion of carbon steel. Little attack is shown for pH values of 6 and 10 and high rates at a pH of 8 and below pH 6. The scale on the 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 probably because they hinder transfer of oxygen and ions. Erosion-corrosion tests in boiler feedwater at 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 seawater and chloride solutions and also to fuming nitric acid.

The behavior of steel and low-alloy-steel tubes handling oils at high

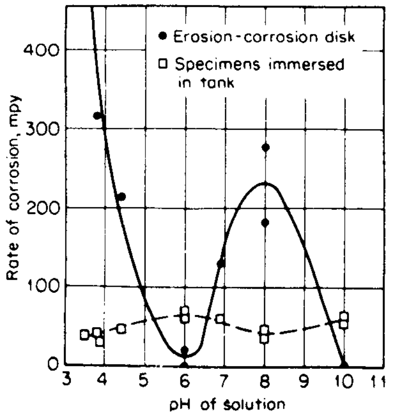

Figure 3-42 Effect of pH of distilled water on erosion corrosion of carbon steel at 50°C (velocity, 39 ft/sec)

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.

3-30 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 and particularly when the solution contains solids in suspension. Figure 3-40 and 3-41 show large increases in attack because of velocity. Figure 3-42 indicates that misleading results could be obtained when only static tests, or tests at very low velocities, are made. The specimens in the tank were subjected to only a mild swirling motion. Table 3-10 shows the effect of velocity on a variety of metals and

Table 3-10 Corrosion of metals by seawater moving at different velocities

	Typical corrosion rates, mdd*		
Material	1 ft/sec†	4 ft/sec‡	27 ft/sec¶
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

*Milligrams per square decimeter per day.
†Immersed in tidal current.
‡Immersed in seawater flume.
¶Attached to immersed rotating disk.
Source: International Nickel Co.

alloys exposed to seawater. These data show that the effect of velocity may be nil or extremely great.

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 3-10 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.

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 Fig. 3-40, which involved rapid erosion corrosion of type 316 centrifugals handling a sulfuric acid slurry.

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 3-43 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 3-44 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.

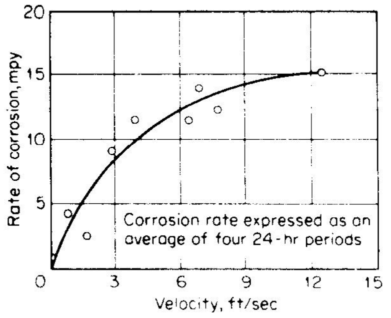

Figure 3-43 Erosion corrosion of 3003 aluminum by white fuming nitric acid at 108 F.

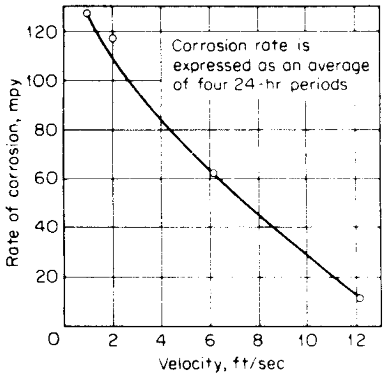

Figure 3-44 Erosion corrosion of type 347 stainless steel by white fuming nitric acid at 108 F.

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

3-31 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 laminar (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). Laminar flow develops after the liquid has progressed down the tube a relatively short distance.

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, and other obstructions that disturb the laminar flow pattern may result in erosion corrosion. Impellers and propellers are typical components operating under turbulent conditions.

3-32 Impingement

Many failures are directly attributed to impingement. Figure 3-45 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 sometimes bubbles of gas in the liquid increase the impingement effect. Air bubbles are an important factor in accelerating impingement attack.

Figure 3-46 shows severe erosion corrosion, caused by impingement in less than one year of service, of a slide valve in contact with a fluidized catalyst and oil at 900°F in a refinery. This was originally solid steel about 3 in. in diameter. Figure 3-47 shows two types of erosion corrosion in a thermal cracking furnace for oil. The tube on the left contained superheated steam.

Figure 3-45 Impingement failure of elbow in steam condensate line.

Figure 3-46 Erosion corrosion of slide valve at 900°F in petroleum refinery.

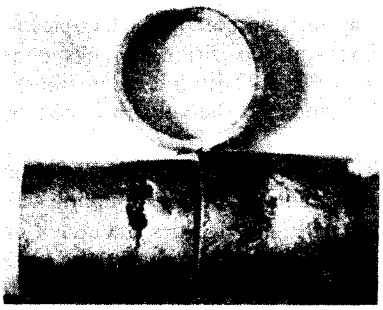

Figure 3-47 Impingement by escaping steam from cracked tube (left).

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° can cause impingement attack.

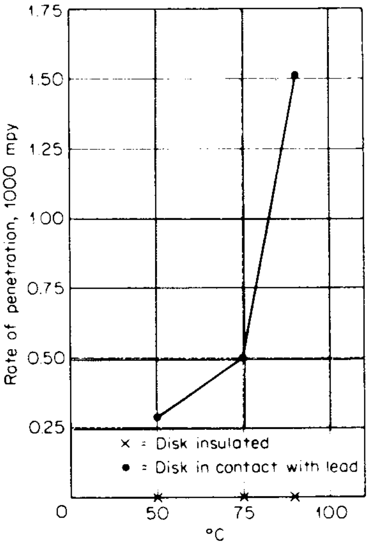

Figure 3-48 Effect of contact with lead on erosion corrosion of type 316 by 10% sulfuric acid (velocity, 39 ft/sec).

3-33 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 3-48 shows that attack on type 316 by itself was nil in high-velocity sulfuric acid but increased to very high values when this 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 Fig. 3-42 doubtless contributed to increased attack because the scale is cathodic to the substrate steel by about 500 millivolts (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.

3-34 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 seawater as shown in Table 3-10. 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 seawater 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, seawater, 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.

Hardening by heat treatment results in changes in microstructure and heterogeneity and generally decreases resistance to corrosion, as noted in Chap. 2. For example, the precipitation-hardened stainless steels would not be expected to give as good performance as type 304 stainless steel under erosion-corrosion conditions.

A good example of poor performance by a high-hardness material concerned the centrifugals and conditions discussed in connection with Fig. 3-40. 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.

3-35 Combating Erosion Corrosion

Five methods for the 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) coatings, and (5) cathodic protection.

Better materials The reasons for using better materials that give improved 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 laminar flow. Increasing the diameter and streamlining bends reduces impingement effects. 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 toward 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 that 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 our 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 seawater. 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.

3-36 Cavitation Damage

A special form of erosion corrosion, *cavitation damage*, 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 that 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 and thus increase corrosion. This mechanism is shown schematically in Fig. 3-49. 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. (6) The exposed area corrodes and the film reforms. The repetition of this process results in deep holes.

Examination of Fig. 3-49 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 Fig. 3-49. In actual practice, it appears that cavitation damage is the result of both mechanical and chemical action.

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. Smooth finishes on pump impellers and propellers reduce damage since smooth surfaces do not provide sites

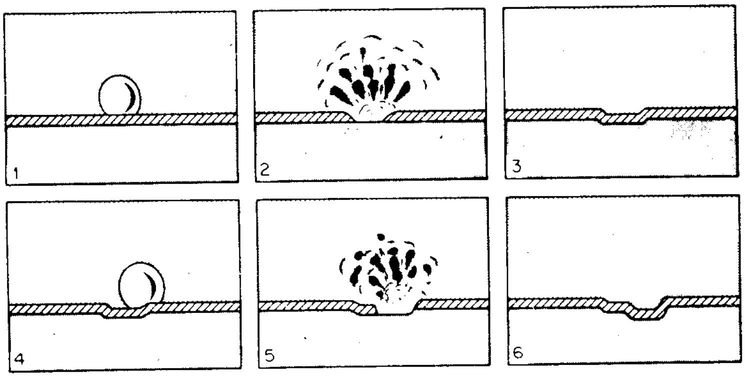

Figure 3-49 Schematic representation of steps in cavitation. (*R. W. Henke*)

for bubble nucleation. Coating metallic parts with resilient coatings such as rubber and plastic have also proved 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, apparently because of the formation of hydrogen bubbles on the metal surface, which cushions the shock wave produced during cavitation.

3-37 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 named because the resulting pits are similar to the indentations 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 that 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 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 race on a shaft as shown in Fig. 3-50. 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.
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 Fig. 3-50, but rather on interfaces, which are subject to repeated small relative displacements. This point is best illustrated by considering fretting corrosion occuring 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 that occurs during shipment. Normal operation of 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 Figs. 3-51 and 3-52, 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,

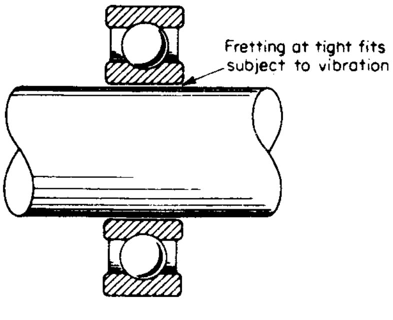

Figure 3-50 Example of typical fretting corrosion location.

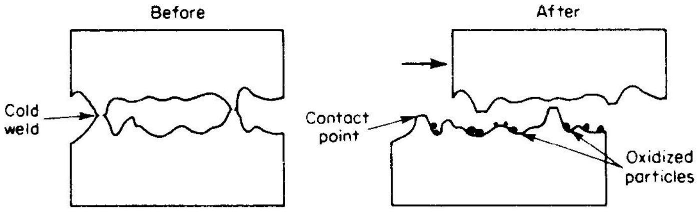

Figure 3-51 Schematic illustration of the wear-oxidation theory of fretting corrosion.

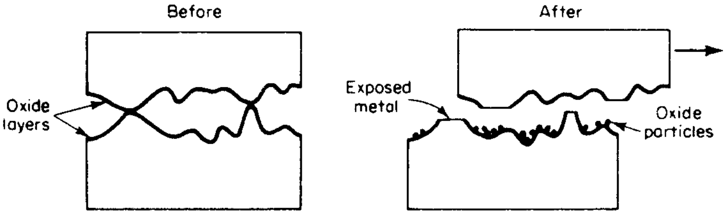

Figure 3-52. Schematic illustration of the oxidation-wear theory of fretting corrosion.

the wear-oxidation hypothesis is based on the concept that frictional wear causes the damage and subsequent oxidation is a secondary effect.

The oxidation-wear concept, illustrated in Fig. 3-52, 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 Fig. 3-52. 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 Figs. 3-51 and 3-52 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 Figs. 3-51 and 3-52.

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.
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 3-11 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 that 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 worn 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.

Table 3-11 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.

A comprehensive text on this subject, covering mechanisms, testing techniques, and case histories is recommended to readers desiring further information.* Two points are worth noting. First, Waterhouse suggests that fretting rather than fretting corrosion should be used to describe the phenomenon since corrosion products are not always present. Second, there appears to be a misconception concerning the cause of corrosion at screw-plate interfaces and other shielded sites on surgical implants. Cohen† was the first to suggest that the observed attack is due to fretting, and this idea has been amplified by Waterhouse (pp. 56–59) and others. This appears to be incorrect since the attack is characteristic of crevice corrosion rather than fretting. Relative motion between orthopedic plates and screws may initiate crevice attack, but it is not the primary cause of the observed corrosion since similar attack is observed at shielded sites on nonstressed components.

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 stress-corrosion cracking, 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 stress-corrosion cracking, whereas it rapidly accelerates hydrogen-embrittlement effects. Hence, the importance of considering stress-corrosion cracking and hydrogen embrittlement as separate phenomena is obvious. For this reason, the two cracking phenomena are discussed separately in this chapter.

During stress-corrosion cracking, the metal or alloy is virtually unattacked over most of its surface, while fine cracks progress through it. This is illustrated in Fig. 3-53. This cracking phenomenon has serious consequences since it can occur at stresses within the range of typical design stress. The stresses required for stress-corrosion cracking are compared with the total range of strength capabilities for type 304 stainless steel in Fig. 3-54. Exposure to boiling $MgCl_2$ at 310°F (154°C) is shown to reduce the strength capability to approximately that available at 1200°F.

The two classic cases of stress-corrosion cracking are "season cracking" of brass, and the "caustic embrittlement" of steel. Both of these obsolete terms describe the environmental conditions present that led to stress-corrosion cracking. Season cracking refers to the stress-corrosion cracking

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*R. B. Waterhouse, *Fretting Corrosion*, Pergamon Press, New York, 1972.

†J. Cohen, *J. Bone Joint Surg.* **44A**:307 (1962).

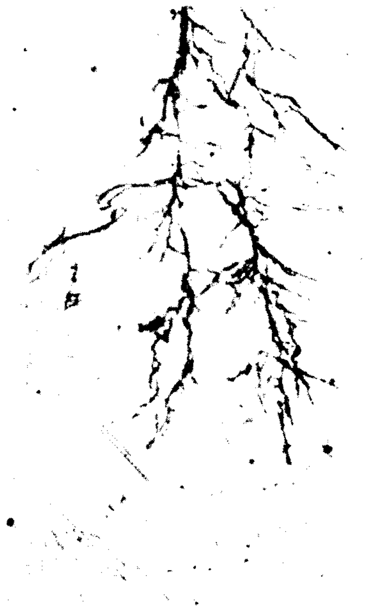

Figure 3-53 Cross section of stress-corrosion crack in stainless steel (500 ×).

failure of brass catridge cases. During periods of heavy rainfall, especially 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 Fig. 3-55.

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 3.56 shows a plate that 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 result shown above.

Not all metal-environment combinations are susceptible to cracking. A good example is the comparison between brasses and austenitic stainless

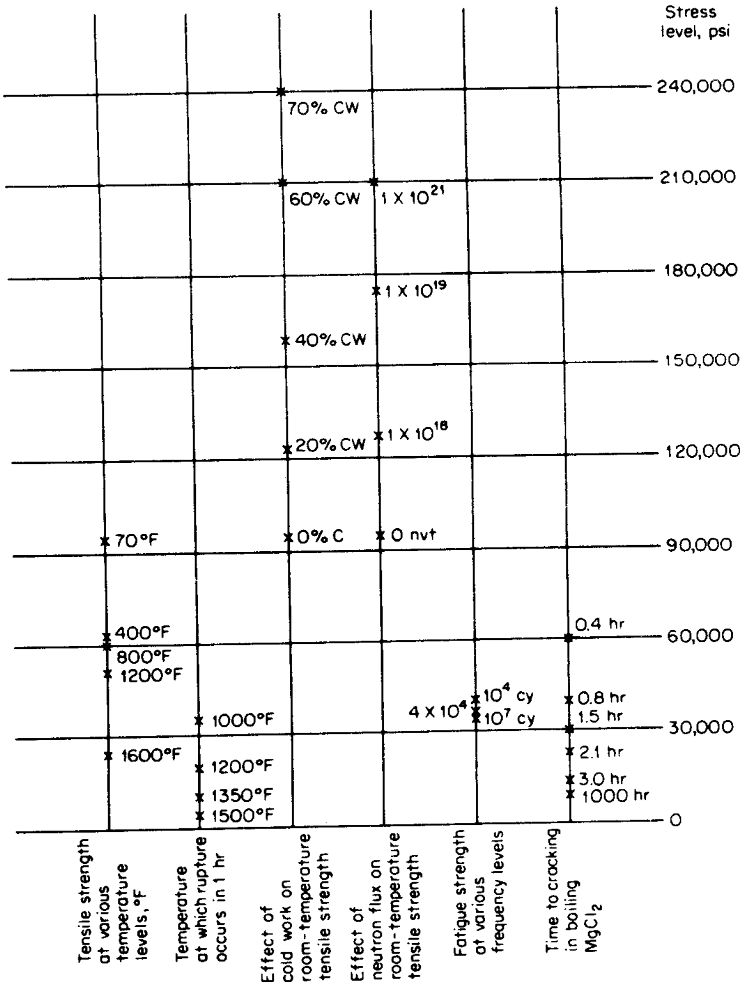

Figure 3-54 Comparison of fracture stresses by various techniques compared with stress-corrosion cracking. Material: type 304 stainless. (*Courtesy Dr. R. W. Staehle, Ohio State University*)

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.

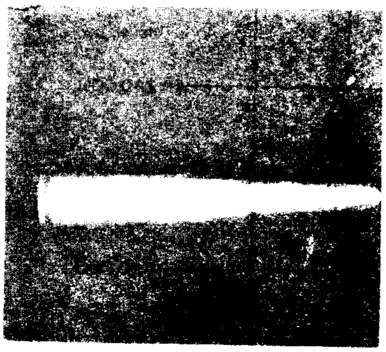

Figure 3-55 Season cracking of German ammunition.

Figure 3-56 Carbon steel plate from a caustic storage tank failed by caustic embrittlement. (*Imperial Oil, Limited, Ontario, Canada*)

The important variables affecting stress-corrosion cracking are temperature, solution composition, metal composition, stress, and metal structure. In subsequent sections these factors will be discussed together with comments on crack morphology, mechanisms, and methods of prevention.

3-38 Crack Morphology

Stress-corrosion cracks give the appearance of a brittle mechanical fracture, when, in fact, they are the result of local corrosion processes. However, even though stress-corrosion cracking is not strictly a mechanical process, it is still convenient to label the process and general features of Fig. 3-53 as a crack.

Both intergranular and transgranular stress-corrosion cracking are observed. Intergranular cracking proceeds along grain boundaries, while

Figure 3-57 Intergranular stress corrosion cracking of brass. (*E. N. Pugh*)

Figure 3-58 Stress corrosion cracking of the head of a 6Al-4V-Ti alloy tank exposed to anhydrous N_2O_4.

transgranular cracking advances without apparent preference for boundaries. Figure 3-53 is an example of transgranular cracking, and Fig. 3-57 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 Figs. 3-53 and 3-57 is of this type. An interesting case is shown in Fig. 3-58, 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 (Fig. 3-56), and in other cases they exhibit multibranched "river delta" patterns (Fig. 3-53). Depending on the metal structure and composition and upon the environment composition, crack morphology can vary from a single crack to extreme branching.

3-39 Stress Effects

Increasing the stress decreases the time before cracking occurs, as shown in Fig. 3-59. 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-environ-

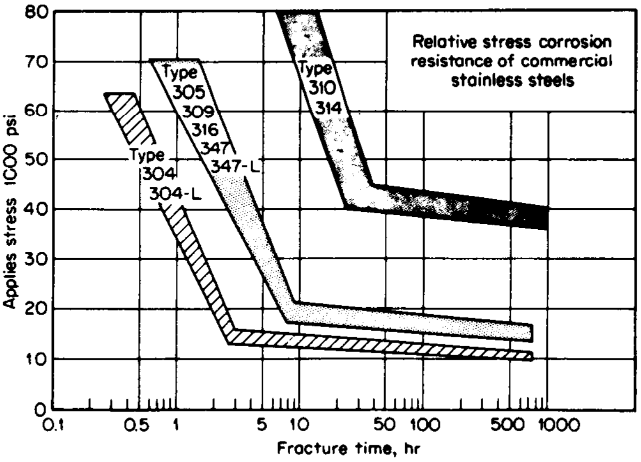

Figure 3-59 Composite curves illustrating the relative stress-corrosion-cracking resistance for commercial stainless steels in boiling 42% magnesium chloride.

ment 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 stress-corrosion cracking 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 that has been propagated by corrosion-product stresses is shown in Fig. 3-60. In this figure, the corrosion products appear to exert a wedging action.

This *wedging action* of 10,000 lb/in.^{2} (10 ksi) results in very high stresses at the crack tip because the tip is a sharp notch which is a great stress concentrator. Hudak and Page* show that highly localized stresses of about

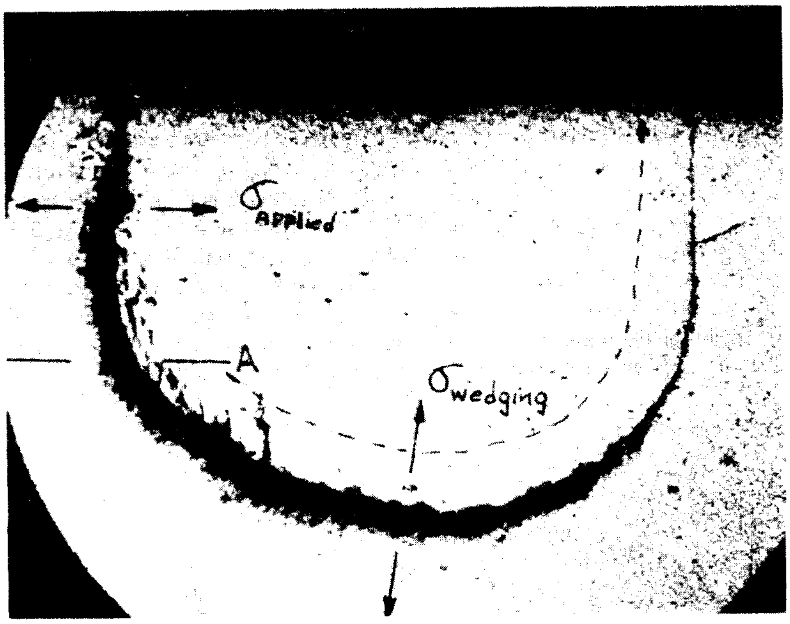

Figure 3-60 The wedging action of corrosion products. This crack in stainless steel has proceeded in its circular path under the influence of stresses produced only by corrosion products. [*H. W. Pickering, M. G. Fontana, and F. H. Beck, Corrosion, 18: 230t (June, 1962)*]

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*S. J. Hudak and R. A. Page, Analysis of Oxide Wedging During Environment Assisted Crack Growth, *Corrosion*, 285–290 (July 1983).

2000 MPa (megapascals), or approximately 289 ksi, may be achieved. These authors approached the problem using fracture mechanics. High stresses result in *denting* of heat exchanger tubes as described in the next paragraph.

A phenomenon termed *denting* has been observed in nuclear steam generators. Inconel tubes are crushed (dented inward) where they pass through carbon steel tube supports and also at contact with steel tube sheets. These annular spaces become filled with steel corrosion products whose volume is greater than the metal consumed and the consequent pressure moves the Inconel tube wall inward. Obviously, stresses greater than the yield point of the alloy are produced. This situation is similar to the wedging action of corrosion products in the stress-corrosion crack shown in Fig. 3-60.

A similar situation involves high-silicon iron and ordinary gray cast iron exposed to oleum (fuming sulfuric acid). The acid penetrates along the graphitic flakes (see Fig. 5-1), corrodes the "steel" matrix, builds up pressure in these confined spaces, and cracks the iron, sometimes catastrophically (see Sec. 7-2). An experience of this type in the 1930s provided my first acquaintance with wedging action.

3-40 Time to Cracking

The parameter of time in stress-corrosion cracking phenomena is important since the major physical damage during stress-corrosion cracking 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 mechanical action. This is illustrated in Figs. 3-61 and 3-62. Figure 3-61 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.

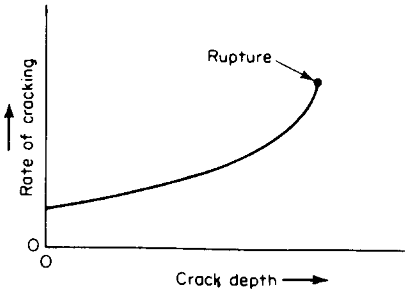

Figure 3-61 Rate of stress-corrosion crack propagation as a function of crack depth during tensile loading.

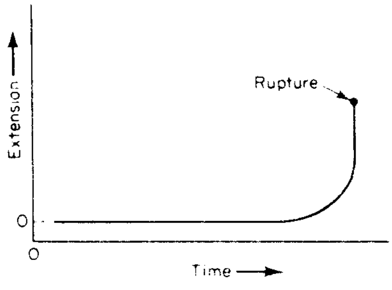

Figure 3-62 Specimen extension as a function of time during constant-load stress-corrosion cracking test.

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 3-62 illustrates the relationship between the time of exposure and the extension of a specimen during stress-corrosion cracking. 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.

A common and important question frequently asked concerning stress corrosion cracking is: How long should a stress-corrosion cracking test be conducted? Figures 3-61 and 3-62 indicate that the test should be conducted until failure occurs. Short-term stress-corrosion cracking tests should be avoided since very little physical and mechanical evidence of cracking is apparent until after it has occurred.

3-41 Environmental Factors

At present there appears to be no general pattern to the environments that cause stress-corrosion cracking of various alloys. Stress-corrosion cracking is well known in various aqueous mediums, but it also occurs in certain liquid metals, fused salts, and nonaqueous inorganic liquids (see Figs. 3-58 and 8-7).

The presence of oxidizers often has a pronounced influence on cracking tendencies. Figure 3-63 shows the combined effects of chloride and dissolved oxygen on the stress-corrosion cracking 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 3-12 lists a number of environment-alloy systems in which cracking occurs. New environments that cause stress-corrosion cracking 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

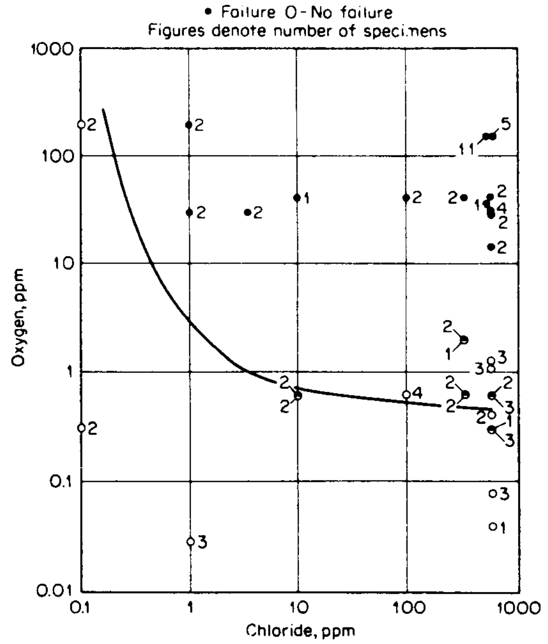

Figure 3-63 Proposed relationship between chloride and oxygen content of alkaline-phosphate-treated boiler water, and susceptibility to stress-corrosion cracking of austenitic stainless steel exposed to the steam phase with intermittent wetting. [*W. Lee Williams, Corrosion, 13:539t, (Aug. 1957)*]

changed. It is usually characteristic of crack-producing environments that the alloy is negligibly attacked in the nonstressed condition. Although stress-corrosion cracking of steel is frequently reported in hydrogen sulfide solutions and cyanide-containing solutions, as shown in Table 3-12, these failures are undoubtedly due to hydrogen embrittlement rather than stress-corrosion cracking. (See Secs. 3-47 to 3-50.)

As is the case with most chemical reactions, stress-corrosion cracking 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 cracking at least as low as 100°C. The effect of temperature on the cracking of austenitic stainless steels is shown in Fig. 3-64. Similar data for the caustic embrittlement of as-welded steel are presented in Fig. 3-65.

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.

Table 3-12 Environments that may cause stress corrosion of metals and alloys

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

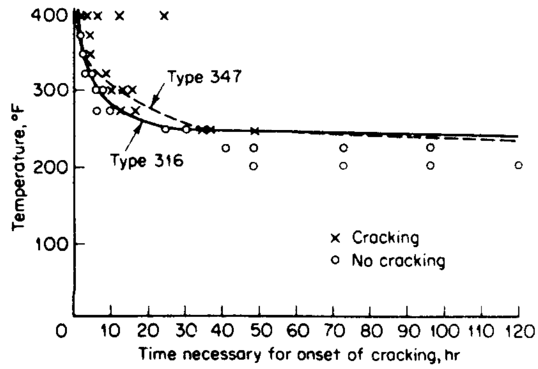

Figure 3-64 Effect of temperature on time for crack initiation in types 316 and 347 stainless steels in water containing 875 ppm NaCl. [*W. W. Kirk, F. H. Beck, M. G. Fontana, Stress Corrosion Cracking of Austenitic Stainless Steels in High Temperature Chloride Waters, in T. Rhodin (ed.), Physical Metallurgy of Stress Corrosion Fracture, Interscience Publishers, Inc., New York,* 1959.]

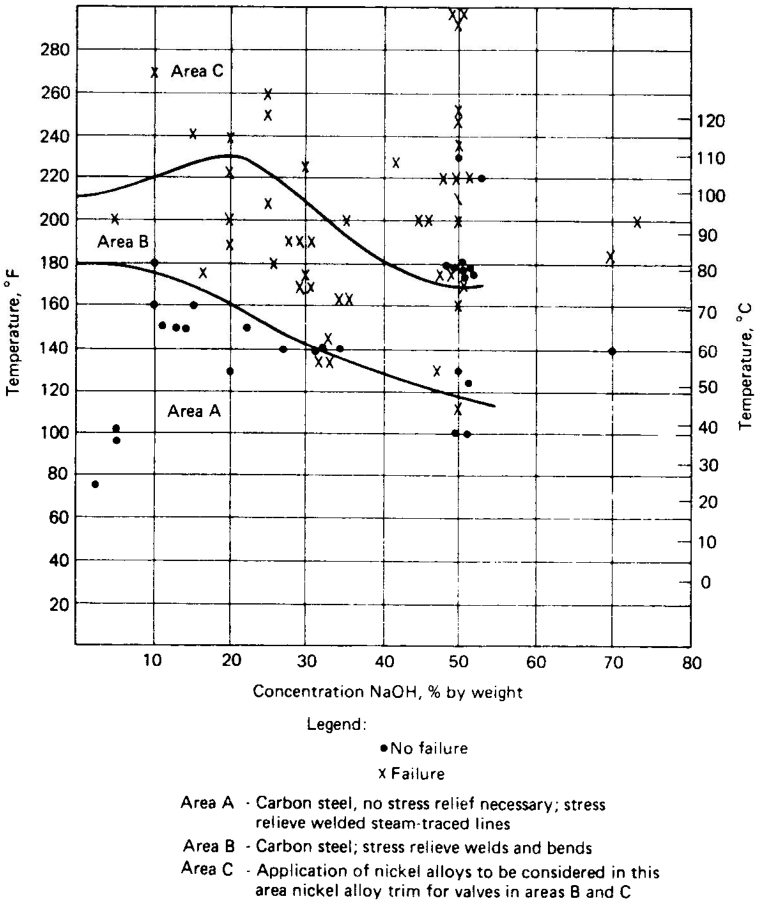

Figure 3-65 NACE caustic soda chart superimposed over the data on which it is based (MTI Publication No. 15, 1985). [*Data from H. W. Schmidt, et al, Corrosion, 7, 295–302, (1951).*]

The autoclave* shown in Fig. 4-10 is used for stress-corrosion tests under vapor condensation conditions involving chloride-containing water at 400°F. Liquid condensing on the top of the autoclave drips on the specimen and flash-dries, thus concentrating the chloride. At these temperatures sodium chloride is present in the vapor phase. Cracking of 18-8 stainless steels in two 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.

*R. W. Staehle, F. H. Beck, and M. G. Fontana, Mechanism of Stress Corrosion of Austenitic Stainless Steels, *Corrosion*, **15**:51 (1959).

Good correlation is obtained between these tests and actual service failures. Figure 3-66 is an excellent example. This high-pressure autoclave was forged from 18-8 stainless steel with a 2-in. 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 3-67 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 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 stress-corrosion cracking.

Figure 3-68 shows the location of cracks in a vertical stainless steel condenser. Splashing in the dead space caused alternate wetting and drying.

Figure 3-66 Stress corrosion of type 304 autoclave. (*Mallinckrodt Chemical Works*)

Figure 3-67 External stress corrosion of type 304 vessel.

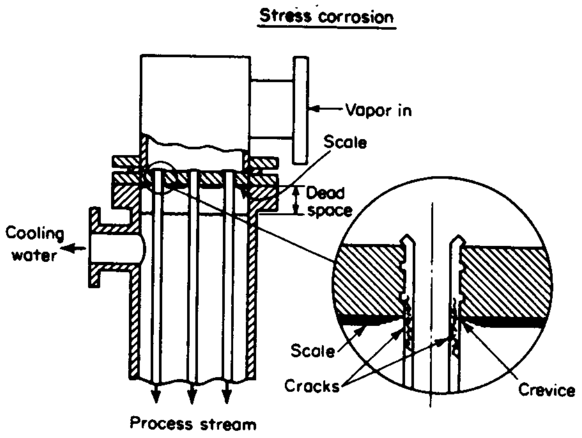

Figure 3-68 Cracking of type 316 tubes in dead-space area. (*J. A. Collins*)

This problem was solved simply by venting the dead space so that the tubes would be wet at all times! S. Haruyama is the author of an excellent paper titled "Stress Corrosion Cracking by Cooling Water of Stainless Steel Shell and Tube Heat Exchangers" (*Materials Performance*, pp. 14–19, Mar. 1982). It covers a study of 715 *heat exchangers* in commercial plant service for several years. Some of his conclusions follow. The mode of cracking (SCC) was transgranular in 47% of the cases followed by transgranular plus intergranular at 16% and intergranular at 8%. Causes for cracking were led by a wide margin by existence of *vapor space* in 34% of the cases. Replacement by another material at 31% was by far the favoured method for preventing SCC. Types 304, 316, and 321 showed similar performance but more failures occurred with the low carbon grades (see Chapter 5) for 304 and 316. No failures of ferritic or duplex alloys were reported. Horizontal exchangers and those with water *inside* the tubes were less susceptible. Cooling by seawater was not included in this study.

A survey by D. R. McIntyre (*Chem. Eng.*, p. 132, Apr. 5, 1982) of several

Gulf Coast chemical plants "revealed that each lost an average of one vertical condenser *per year* to improper venting practice." Two other pertinent papers are "Coping with an Improperly Vented Condenser" by K. J. Bell (*Chem. Eng. Progr.*, pp. 54–55, July 1983) and "Troubleshooting Shell and Tube Heat Exchangers" by S. Yokell (*Chem. Engin.*, pp. 57–80, July 25, 1983).

In connection with heat exchanger tubing, Smallwood* presents an excellent summary of tubing reliability. He describes corrosion-type defects as: (1) substitution of an inadequate alloy through error, (2) selective weld metal attack, (3) improper pickling, (4) corrosion during testing or handling, (5) residual stresses, (6) improper heat treatment, (7) imbedded tramp metal, (8) preferred-grain orientation, (9) surface roughness, (10) dents, and (11) high-temperature contamination. An example of the latter is carbon pickup because of local or general carburization of the metal. (Carbon pickup of castings is discussed in Sec. 3-20). Examples of all of these defects are discussed. Mechanical defects are also covered, and methods for defect detection, such as ultrasonic, are presented. A quality-assurance program is outlined.

3-42 Metallurgical Factors

The susceptibility to stress-corrosion cracking 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 3-69 (Ni added to 18 Cr-Fe base) and 3-70 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 observations of cracking in 99.999% pure copper exposed in ammoniacal solutions containing $Cu(NH_3)_5^{2+}$ complex ions.† 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 stress-corrosion cracking 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 3-71 shows the increase in resistance to stress corrosion as the

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*R. E. Smallwood, Heat Exchanger Tubing Reliability, *Materials Performance*, **16**:27–34 (Feb. 1977).

†E. N. Pugh, W. G. Montague, A. R. C. Westwood, *Corrosion Sci.*, **6**:345 (1966).

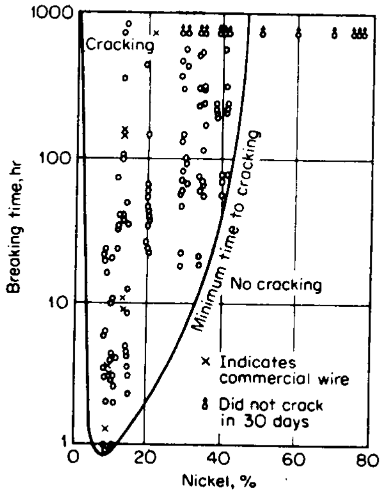

Figure 3-69 Stress-corrosion cracking of iron-chromium nickel wires in boiling 42% magnesium chloride. [*H. R. Copson, Effect of Composition on Stress Corrosion Cracking of Some Alloys Containing Nickel, in T. Rhodin (ed.), Physical Metallurgy of Stress Corrosion Fracture, Interscience Publishers, Inc., New York, 1959*]

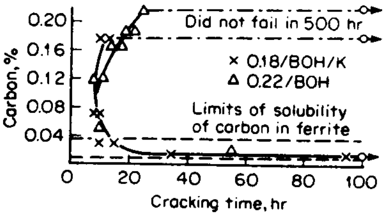

Figure 3-70 Effect of carbon content on the cracking time of mild steel exposed to boiling calcium ammonium nitrate. *(R. N. Parkins)*

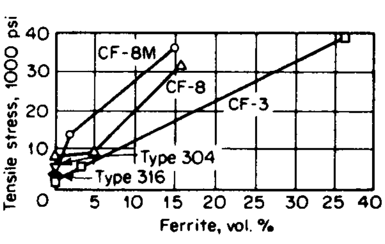

Figure 3-71 Effect of ferrite on stress required to induce stress-corrosion cracking in several cast stainless alloys. Type 304 and 316 with zero ferrite also plotted. Specimens exposed 8 hr in condensate from 875-ppm chloride water at 400°F. [*M. G. Fontana, F. H. Beck, J. W. Flowers, Metal Progr., 86:99 (Dec. 1961)*]

amount of ferrite is increased in cast stainless steels. Pools of ferrite in the austenitic matrix tend to block the progress of cracks.

3-43 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 that 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* showed that a mechanical step or jump can occur during crack propagation. In fact, "pings" were heard with the naked ear.

The *conjoint* action of stress and corrosion required for crack propagation was demonstrated by Priest.† 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. If the alloy is not metastable, the cold-worked (plastically deformed) region might be less corrosion resistant than the matrix because of the continuous emergence 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 propa-

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*W. M. Pardue, F. H. Beck, and M. G. Fontana, *Am. Soc. Metals Trans. Quart.*, **54**: 539–548 (1961).

†D. K. Priest, F. H. Beck, and M. G. Fontana, *Trans. Am. Soc. Metals*, **47**:473–492 (1955).

gation 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 that 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.

A very large amount of research and development work has been done during the past decade or so on stress-corrosion cracking. The importance of this subject is emphasized by the fact that more effort and funds have been expended on stress corrosion than on all other forms of corrosion combined. Extensive study is continuing, particularly in the fields of nuclear energy and coal-conversion systems. The collapse of the Silver Bridge into the Ohio River with a loss of about two-score lives has focused public attention on this problem. Costly failures in industrial plants have prompted extensive investigation.

Many detailed steps and mechanisms for stress-corrosion cracking of specific metal-environment combinations have been postulated. Two basic "models" for a general mechanism are (1) the *dissolution* model wherein anodic dissolution (Fig. 3-79) occurs at the crack tip because strain ruptures the passive film at the tip, and (2) the *mechanical* model, wherein specific species adsorb and interact with strained metal bonds and reduce bond strength. The first seems more universal than the second. Many ramifications of these models have been postulated. Hydrogen embrittlement may be an operative factor particularly for high-strength alloys. For most engineering work past experience is the best guide, with reliable and valid testing second. In all cases chemistry, metallurgy, and mechanics (stress field) must be considered.

At this writing, a handbook on stress-corrosion cracking and corrosion fatigue is under preparation by Roger W. Staehle. This project is sponsored by the Advanced Research Projects Agency (ARPA). The primary objective of the handbook is to serve the engineering design community. Publication is scheduled for 1986. This book should provide the best and most useful engineering information on stress-corrosion cracking and its corollary, corrosion fatigue.

3-44 Multienvironment Charts

In addition to information presented elsewhere in this book, here are several charts (tables) showing cracking tendencies for metal and alloy systems in a *variety* of environments including *liquid* metals. These tables are from

Materials Technology Institute of the Chemical Process Industries, Inc. (MTI) Manual No. 15, titled *Guidelines for Preventing Stress Corrosion Cracking in the Chemical Process Industries*. It should be emphasized that these are only guidelines, but they do present a good picture.

Table 3-13 shows the situation for carbon steels. The A-designation means ASTM, Gr is grade, and HSLA is high-strength low alloy steel. Chapter 5 describes materials including metals and nonmetallics. *Low-alloy* or medium-strength steels exhibit yield strengths below 180,000 lb/in.^{2}. Low-alloy steels with *very high strengths* (i.e., AISI 4340) are much more susceptible to stress corrosion than weaker steels. In general, susceptibility to cracking increases with strength level. Values of K_{ISCC} are usually a smaller fraction of the tensile strength. K_{ICSS} is the critical plane strain intensity factor, which covers stress corrosion. Fracture mechanics is discussed later in this chapter.

Figure 3-72 shows potential ranges over which the SCC of carbon steels can occur in five solutions (from MTI manual). This means that changes in solution composition or temperature could shift the potential of

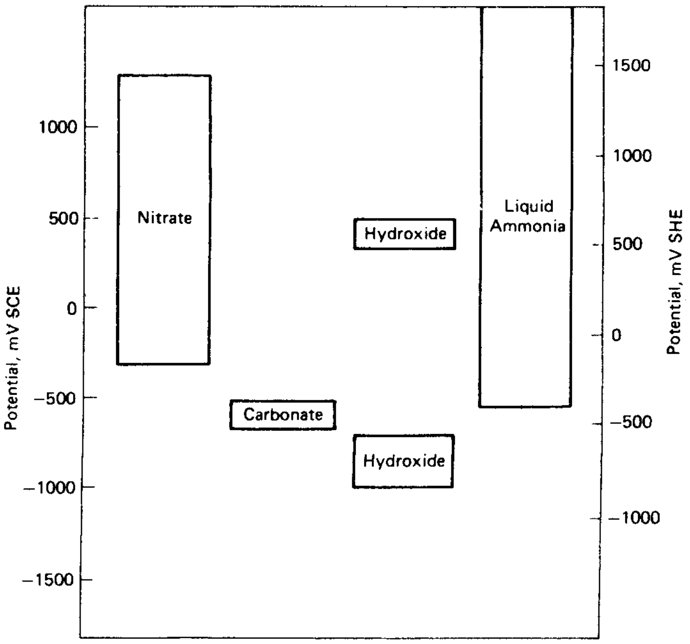

Figure 3-72 Schematic diagram showing potential ranges over which SCC of carbon steels occurs in various solutions.

Table 3-13 Environments vs. low-alloy steels

	Cl^-, Acid	Cl^-, Neutr.	Cl^-, Oxid.	Sea-water	High-Purity H_2O	OH^-	HCN	S^{2-}	S^{2-}/Cl^-	Carbon-ates
A516 Gr. 70 C-M	X	1	1	1	A	5	2	2	2	4
A106B C-Mn	X	1	1	1	A	5	2	2	2	4
A285 Gr. C C-Mn	X	1	1	1	A	5	2	2	2	4
A242 HSLA	X	1	1	1		5	2	2	2	4
A517 Gr. F HSLA	X	1	1	1		5	5	5	5	4
A387(22)2 1/4 Cr-1Mo	X	1	1	1		5	2	2	2	4
AISI 4140	X	3	3	3	3	5	5	5	5	4
AISI 4340	X	3	3	3	3	5	5	5	5	4

	SO_3^{2-}	SO_4^{2-}	CrO_4	NO_3^-	NH_3	$CO-CO_2$ $-H_2O$	Amines	Hf	Cd	Al	Bi
A516 Gr. 70 C-M	1	A	1	5	4	4	4	1	5	X	1
A106B C-Mn	1	A	1	5	4	4	4	1	5	X	1
A285 Gr. C C-Mn	1	A	1	5	4	4	4	1	5	X	1
A242 HSLA	1	A	1		4	4	4	1	5	X	1
A517 Gr. F HSLA	1	A	1	5	4	4	4	1	5	X	1
A387(22)2 1/4 Cr-1Mo	4	A	1		4	4	4	5	5	X	1
AISI 4140	4	A	1	5	4	4	4	5	5	X	1
AISI 4340	4	A	1	5	4	4	4	5	5	X	1

	Hg	Li	Pb	Sn	Zn	PO_4^{3-}
A516 Gr. 70 C-M	1	5	1	1	5	4
A106B C-Mn	1	5	1	1	5	4
A285 Gr. C C-Mn	1	5	1	1	5	4
A242 HSLA	1	5	1	1	5	4
A517 Gr. F HSLA	1	5	1	1	5	
A387(22)2 1/4 Cr-1Mo	1	5	1	1	5	
AISI 4140	1	5	1	1	5	
AISI 4340	1	5	1	1	5	

Notes: 1 Resistant.
2 Resistant unless cold-worked or hardened above R_c22.
3 Resistant unless hardened above R_c33.
4 Resistant except at certain temperature-concentration ranges—see text.
5 Nonresistant.
X Not recommended for this environment—rapid general attack or pitting.
A Resistant unless anodically polarized.

Table 3-14 Environments vs. various wrought stainless steels

	Cl Acid	Cl Neutr.	Cl Oxid.	F SiF_6^{-2}	OH	$S^=$	S^{-2}/Cl	SO_4^{-2}	CrO_4^{-2}	NO_3	NH_3	O_2SCC	Sea-water	Cd	Al	Hg	Li	Pb	Zn
Ferritic																			
405	X	1	1		1	1	1		1	1	1	3	X	5	X	1	5	1	5
409	X	1	1		1	1	1		1	1	1	3	X	5	X	1	5	1	5
429	X	1	1		1	1	1		1	1	1	3	X	5	X	1	5	1	5
430	X	1	1		1	1	1		1	1	1	3	X	5	X	1	5	1	5
434	X	1	1		1	1	1		1	1	1	3	X	5	X	1	5	1	5
436	X	1	1		1	1	1		1	1	1	3	X	5	X	1	5	1	5
442	X	1	1		1	1	1		1	1	1	3	X	5	X	1	5	1	5
446	X	1	1		1	1	1		1	1	1	3	X	5	X	1	5	1	5
Martensitic																			
403	X	2	3	3	4	2	2	4	1	4			X	5	X	1	5	1	5
410	X	3	3	3	4	2	2	4	1	4			X	5	X	1	5	1	5
414	X	3	3	3	4	5	5	4	1	4			X	5	X	1	5	1	5
416	X	3	3	3	4	5	5	4	1	4			X	5	X	1	5	1	5
420	X	3	3	3	4	2	2	4	1	4			X	5	X	1	5	1	5
422	X	3	3	3	4	5	2	4	1	4			X	5	X	1	5	1	5
431	X	3	3	3	4	5	5	4	1	4			X	5	X	1	5	1	5
440A	X	3	3	3	4	5	5	4	1	4			X	5	X	1	5	1	5
440C	X	3	3	3	4	5	5	4	1	4			X	5	X	1	5	1	5
Duplex																			
SAF2205	4	4	4			2	2		1	1			X		X	1		1	5
Uranus 50	X	4	4		4	2	2		1	1			X		X	1		1	5
3RE60	X	4	4				5		1	1			X		X	1		1	5
Ferralium 255	4	4	4		4	2	2		1	1			X		X	1		1	5
AISI 329	X	4	4		4		5		1	1			X		X	1		1	[illegible]

Notes: 1 Resistant.
2 Resistant unless cold-worked or hardened above R_c22.
3 Resistant unless hardened above R_c33.
4 Resistant except at certain temperature-concentration ranges see text.
5 Nonresistant.
X Not recommended for this environment rapid general attack or pitting.

Table 3-15 Environments vs. copper alloys

CDA Number	Cl^-,	CrO_4^{-2}	HPO_4^{-2}	HCO_4^{-2}	OH^-	S^{-2}	S^{-2}/Cl^-	SO_2	SO_3^{-2}	SO_4^{-2}	NO_2^-	NO_3^-	NH_3	Steam	Sea-water	Bi	Hg	Li	Pb	Sn	Zn	Amines $+O_2$
110 ETP Copper	1				1	1							2		1	5	5	5	1	1		2
122 DHP Copper	1				1	1	X						2		1	5	5	5	1	1	1	2
220 Bronze	1				1	1							5		1	5	5	5		1	1	5
230 Red Brass	1				4	1		1		4	5	5	5		1	5	5	5	5	5	1	5
260 Cartridge Brass			4	4	4	1		5		4	5	5	5		1	5	5	5	5	5	1	5
270 Yellow Brass	4		4	4	4	1				4	5	5	5		2	5	5	5	5	5	1	5
280 Muntz Metal	4		4	4	4	1				4	5	5	5		2	5	5	5	5	5	1	5
443 Admiralty Brass	1	1	1	1	4	1		5		4	5	5	5		1	5	5	5	5	5	1	5
687 Inh. Al Brass	1				4	1		5		4	5	5	5		1	5	5	5	5	5	1	5
464 Naval Brass	1				4	1				4	5	5	5		1	5	5	5	5	5	1	5
510 Phosphor Bronze	1				1	1		1					5		1	5	5	5			1	5
613 Al Bronze	1				1	1							5		1	5	5	5			1	1
614 Al Bronze D	1				1	1							5	5	1	5	5	5			1	5
630 Ni-Al Bronze	1				1	1							5		1	5	5	5			1	5
655 High-si Bronze	1				1	1							2	5	1	5	5	5			1	2
675 Mn Bronze	3*				1	1							5		3*	5	5	5			1	5
70690-10 Cu-Ni	1				1	1	X	1		1	1	1	4		1	5	5	5			1	2
715 70-30 Cu-Ni					1	1	X	1		1	1	1	4		1	5	5	5			1	2
836 Ounce Metal	1				1	1							5		1	5	5	5			1	5
865 Mn Bronze	1				1	1							5		3*	5	5	5			1	5
905 G Bronze	1				1	1							5		1	5	5	5			1	5
922 M Bronze	1				1	1							5		1	5	5	5			1	5
957 Ni-Al-Mn Bronze	1				1	1							5		1	5	5	5			1	5
958 Ni-Al Bronze	1				1	1							5		1	5	5	5			1	5
964 Copper Nickel	1				1	1	X						4		1	5	5	5			1	2
770 Nickel Silver						1	1	5				5	5		5	5	5	5			1	5

Table 3-15

CDA Number	N_2H_4 $+O_2$	Pb-Sn Solder	Cl^-, Oxid.	Citrates	Tartrates
110 ETP Copper		1			
122 DHP Copper		1			
220 Bronze					
230 Red Brass	5	5	1		
260 Cartridge Brass	5	5	4	4	4
270 Yellow Brass	5	5	4	4	4
280 Muntz Metal	5	5	4		
443 Admiralty Brass	5	5	4	4	4
687 Inh. Al Brass	5	5	1		
464 Naval Brass	5	5			
510 Phosphor Bronze		1			

Notes: * Chlorinated solvents.
1 Resistant.
2 Resistant unless hardened or cold-worked.
3 Resistant unless sensitized.
4 Resistant except for special temperatures or concentrations—see text for discussion.
5 Nonresistant.
X Not recommended for this environment.

Table 3-16 Environments vs. aluminum alloys

	Cl^-, Neutr.	OH^-	NH_3	NO_3^-	S^{-2}	S^{-2}/Cl^-	*	Cl^-, Acid	Sea-water	SO_4^{-2}	Cd	Al	Bi	Hg	Li	Pb	Ga	Sn	**
1100	1	X	1	1	1	1	1	X	1		1	—	1	5	1	1	5	5	5
2024	5	X	1	1	1	1	5	X	5		1	—	1	5	1	1	5	5	5
3003	1	X	1	1	1	1	1	X	1		1	—	1	5	1	1	5	5	5
5052	1	X	1	1	1	1	1	X	1		1	—	1	5	1	1	5	5	5
5083	3	X	1	1	1	1	3	X	3		1	—	1	5	1	1	5	5	5
5154	1	X	1	1	1	1	1	X	1		1	—	1	5	1	1	5	5	5
6061	1	X	1	1	1	1	1	X	1		1	—	1	5	1	1	5	5	5
6063	1	X	1	1	1	1	1	X	1		1	—	1	5	1	1	5	5	5
7075	5	X	1		1	1	5	X	5		1	—	1	5	1	1	5	5	5
242	1	X	1	1	1	1	1	X	1		1	—	1	5	1	1	5	5	5
295	1	X	1	1	1	1	1	X	1		1	—	1	5	1	1	5	5	5
A332	1	X	1	1	1	1	1	X	1		1	—	1	5	1	1	5	5	5
A356	1	X	1	1	1	1	1	X	1		1	—	1	5	1	1	5	5	5
B443	1	X	1	1	1	1	1	X	1		1	—	1	5	1	1	5	5	5
514	1	X	1	1	1	1	1	X	1		1	—	1	5	1	1	5	5	5
920	1	X	1	1	1	1	1	X	1		1	—	1	5	1	1	5	5	5

Notes: * High purity H_2O.
** Alkali metals.
1 Resistant.
3 Resistant in some cases.
5 Nonresistant.
X Not recommended for this environment-rapid general attack or pitting.

Table 3-17 Environments vs. titanium and zirconium alloys

Type	UNS	Cl^-, Acid	Cl^-, Neutr.	Cl^-, Oxid.	OH^-	NH_3	NO_3^-	S^{-2}	S^{-2}/Cl^-
C.P. Gr. 1 Ti	R50250	1	1	1	X	1	4	1	1
C.P. Gr. 2 Ti	R50400	1	1	1	X	1	4	1	1
Ti-Pd Gr. 7	R52400	1	1	1	X	1	4	1	1
Ti-6Al-4V Gr. 5	R56400	2	2	2	X	1	4	1	1
Low Alloy Gr. 12		1	1	1	X	1	4	1	1
C.P. Zr	R70200	1	1	1	1	1	4	1	1
Zircaloy	R70400	A	A	A	1	1	4	1	1
Zircaloy	R70500	A	A	A	1	1	4	1	1

	O_2SCC	MeOH	Br_2	*	I	Hg	Ga	Cd	Sn	Ag	Ce
C.P. Gr. 1 Ti	1	5		1		5	5	5	1	1	
C.P. Gr. 2 Ti	1	5		1		5	5	5	1	1	
Ti-Pd Gr. 7	1	5		1		5	5	5	1	1	
Ti-6Al-4V Gr. 5	1	5		5		5	5	5	5	5	
Low Alloy Gr. 12	1	5		1		5	5	5	1	1	
C.P. Zr	1	5	5	5	5	5					5
Zircaloy	1	5	5	5	5	5					5
Zircaloy	1	5	5	5	5	5					5

Notes:
* Chlorinated solvents.
1 Resistant.
2 Resistant unless hardened or cold-worked.
3 Resistant unless sensitized.
4 Resistant except for special temperatures or concentrations—see text for discussion.
5 Nonresistant.
X Not recommended for this environment.
A Resistant unless anodically polarized—see text for discussion.

Table 3-18 Stress-corrosion cracking in additional environment—alloys systems

This table represents a consensus of CFI experience and should be used as a screening guide only.

UNS	Cl^-, Acid	Cl^-, Neutr.	Cl^-, Oxid.	F^- Br^-	SiF_6^{2-}	I	OH^-	S^{-2}	S^{-2}/Cl	$S_4O_6^{2-}$	SO_3^{2-}	SO_4^{2-}	CrO_4^{2-}
S15700	5	4			1	1		5				5	1
S17400	5	4			1			5				5	1
S17700	5	5			1			5				5	1
S20200	5	5	5		1	1	4	2		3	3	1	1
S20910	5	5	5		1	1	4	2		3	3	1	1
S21600	5	5	5		1	1	4	2		3	3	1	1
S21603	5	5	5		1	1	4	2		3,4	3,4	1	1
S21800	5	4	5		1	1	4	2		3	3	1	1
S30400	5	5	5		1	1^h	4	2	5	3	3	1	1
S30403	5	5	5		1	1^h	4	2	5	3,4	3,4	1	1
S30908	5	5	5		1	1	4	2		3	3	1	1
S31008	5	5	5		1	1	4	2		3	3	1	1
S31600	5	5	5	4	1	1^j	4	2	1^i	3	3	1	1
S31603	5	5	5		k	k	4	2	1^i	3,4	3,4	1	1
S31700	5	5	5		1	1	4	2	1^i	3	3	1	1
S31703	5	5	5		1	1	4	2	1^i	3,4	3,4	1	1
S32100	5	5	5		1	1	4	2		1	1	1	1
S32900	4	5	5		2	2	4					1	1
S34700	5	5	5		1	1	4	2		1	1	1	1
S38100	4	4	5		1	1	4					1	1
S43100	5	5	5		2		4					2	1
S44625	4	1	4				4	2					1
S44626	4	1	4				4	2					1
S44700	1	1	1				4	2					1
S45000	4	1	4		2		4	2				2	1
S45500	4	1	4		2		4	2				2	1
N02200	4	1	X	1	2	1	1	X				1	1
N02201	4	1	X	1	2	2,4	1	X				1	1
N04400	a	1	X	1	5	1	4					1	4
N05500	1	1	X		5	1	4					1	1
N06007	4	1	1	1	1	1	4				1	1	1
N06455	4	1		1	1	1		2	2^k	1			1
N06600	1	1		1	2	1	2	2,3		3	3	4^b	1
N06601	1	1		1	2	1	4	2					1
N06625	4^g	1		1	1	1		2	2^k	3	3		1
N06690	1	1		1		1							1
N07718	5^c	1											1
N07750		1		5^c					5^c				1
N08020	4	4	4	1	1	1	4		1	1		1	1
N08700	4	1	4	1	1	1						1	1
	4	1	4	1	1	1						1	1
N08366	4	1	4	1	1	1						1	1
	4	1	4	1	1	1						1	1
	4	1	4	1	1	1						1	1
N08904	4	1		1	1	1						1	1
N08800	4	1		1	1	1	4		1	3	3		1
N08825	4	1		1	1	1	4			1	1	1	1
N10001	4^f	1			4		4			1		4	1
N10002	4^g	1	3		4	1		1	2	1		4	1
N10276	2,3,4	1			1	1	4	1	2,3	1			1
N10655	1	1			4					1	1		1

Notes: 1 Resistant. 2 Resistant unless cold-worked or hardened. 3. Resistant unless sensitized. 4 Resistant except special temperature-concentration conditions—see text. 5 Nonresistant. X Not recommended for this environment.

NO_3^-	NH_3	Azo Dyes	O_2SCC	Sea-water	Cd	Al	Bi	Hg	Li	Pb	S	Sn	Zn	Alloy
1	1	1		X									5	PH15-7Mo
1	1			X									5	17-4PH
1	1	1		X									5	17-7PH
1	1	1		X	5	5							5	202
1	1	1		4	5	5							5	Nitronic 50
1	1	1		X	5	5							5	216
1	1	1		X	5	5							5	216L
1	1	1		X	5	5							5	Nitronic 60
1	1	1	3	X	5	5							5	304
1	1	1	3,4	X	5	5		4					5	304L
1	1	1	3	X	5	5		4					5	309S
1	1	1	3	X	5	5		4					5	310S
1	1	1	3	X	5	5		4					5	316
1	1	1	3,4	X	5	5		4					5	316L
1	1	1	3	X	5	5		4					5	317
1	1	1	3	X	5	5		4					5	317L
1	1	1	1	X	5	5		4					5	321
1	1	1		X	5	5							5	329
1	1	1	1	X	5	5		4					5	347
1	1	1		X	5	5							5	18-18-2
1	1	1		X									5	431
1	1	1		X									5	26-1 (XM-27)
1	1	1		X									5	26-1S (XM-33)
1	1	1		4									5	29-4
1	1	1		X									5	Custom 450
1	1	1		X									5	Custom 455
1	1		1				5	4	5	5	5	4		Ni 200
1	1		1				5	4	5	5	5	4		Ni 201
4	4		1	4			5	5	5	5	5	4		Monel 400
							5	5	5		5	5		K-500
1	1				5	5							1	Alloy G
1	1	1			5	5					4		1	Alloy C-4
1	1	1	5^e	4	5	5		1		4	4		4	Alloy 600
1	1	1	1		5	5					4			Alloy 601
1	1	1	5		5	5					4			Alloy 625
1	1	1	5		5	5					4			Alloy 690
1	1	1	5^c								5			Alloy 718
1	1	1	5^c	4							5	5		Alloy 750
1	1	1			5	5		4					5	Alloy 20 Cb-3
1	1	1			5	5		4					5	JS 700
1	1	1			5	5		4					5	2RN65
1	1	1			5	5		4					5	A-L 6X
1	1	1			5	5		4					5	JS-777
1	1	1			5	5		5						2RK65
1	1	1			5	5		4					5	904L
1	1	1	1		5	5		4					4	Alloy 800
1	1	1	5		5	5								Alloy 825
1	1	5	5		5	5			5		5		1	Alloy B
1	1	1	5	4	5	5					4		1	Alloy C
1	1	1	5		5	5					4		1	Alloy C-276
1	1				5	5					5		1	Alloy B-2

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[a] 10% $CuCl_2$ in HCl [b] pH 2.5, 289°C (552°F) [c] Aged 1 hour at 955°C (1750°F)/air cooled plus 8 hours at 718°C (1325°F)/furnace cooled to 621°C (1150°F)/air cooled [d] Aged 2 hours at 1149°C (2100°F)/air-cooled plus 24 hours at 843°C (1550°F)/air cooled plus 20 hours at 704°F (1300°F)/air cooled [e] Threshold stress yield point [f] Zinc chloride [g] Aluminum chloride in HCl at 450°C (842°F) [h] One suspected case [i] Under anaerobic conditions [j] Iodine in nuclear fuel elements [k] As cathode coupled to carbon steel in galvanic cell

the system into or out of the danger zone. Cathodic protection and/or inhibitor additions can inhibit cracking.

Table 3-14 is for some wrought stainless steels, Table 3-15 for copper alloys, Table 3-16 for aluminum alloys, Table 3-17 for titanium and zirconium alloys, and Table 3-18 for other stainless steels and high-nickel alloys. For additional information on titanium, the reader is referred to an excellent and lengthy review by Blackburn, Feeney, and Beck.*

In addition to the information in Table 3-17, *zirconium* and its alloys are resistant to stress corrosion in pure water, moist air, steam, and many solutions of sulfates and nitrates. It could crack in $FeCl_3$ and $CuCl_2$ solutions halogens in water, halogen vapors, and organic liquids such as carbon tetrachloride, and fused salts at high temperatures.

For an excellent review of *uranium* and its alloys, see N. J. Mangani, "Hydrogen Embrittlement and Stress Corrosion Cracking of Uranium and Uranium Alloys," in M. G. Fontana and R. W. Staehle, eds., *Advances in Corrosion Science and Technology*, vol. 6, pp. 89–161, Plenum Press, New York, 1976.

Columbium (niobium) and *tantalum* are not subject to usual stress corrosion. They can be embrittled by hydrogen. This embrittlement of tantalum in hot acids can be inhibited by contact with platinum.

Magnesium alloys are being used in many cases where light weight is an important factor, contrary to the general impression of the poor corrosion resistance of magnesium. Bare alloys have shown good resistances to water. Reliable protection systems such as coatings have been developed. Alloys containing manganese have good resistance, but those with high aluminum or zinc content are quite susceptible to stress corrosion.

3-45 Classification of Mechanisms

As described above, the complexity of the interactions between various environments, nature of the alloy, metallurgical structure, etc., indicates the impossibility of one unified mechanism for stress corrosion of all metal-environment systems.

M. A. Streicher (in a private communication to be published in 1985) classified some SCC mechanisms that may be operative in different systems as follows:

1. *Metallurgical Mechanisms*
    a. Dislocation coplanarity. Resistance to cracking corresponds to the dislocation pattern. The pattern in susceptible stainless steels tends

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*M. J. Blackburn, J. A. Feeney, and T. R. Beck, "Stress Corrosion Cracking of Titanium Alloys," in M. G. Fontana and R. W. Staehle, eds., *Advances in Corrosion Science and Technology*, vol. 3, pp. 67–292, Plenum Press, New York, 1973.

to form planar arrays, whereas in resistant alloys the dislocation patterns are cellular or tangled.

   b. *Stress-aging and microsegregation.* In stress aging of austenitic stainless steels, jerky plastic flow occurs. This phenomenon is associated with microsegregation of solute atoms to dynamic defects in the crystal structure. This type of segregation may account for transgranular stress-corrosion cracking behavior. The cracking rate is limited by the solute diffusion rate as well as electrochemical polarization.
   c. *Adsorption.* Surface active species adsorb and interact with strained bonds at the crack tip, causing reduction in bond strength and leading to cracking propagation.
2. *Dissolution Mechanisms*
   a. *Stress-accelerated dissolution.* Crack propagates by localized anodic dissolution. Principal role of plastic deformation is to accelerate the dissolution process.
   b. *Film Formation at Cracking Wall.* Based on the coplanarity mechanism, cracks initiate at the place of slip step emergence. Propagation is a result of the dissolution of yielding metal. As the crack progresses, the film on the crack walls is repaired and serves as a cathodic site.
   c. *Noble element enrichment.* The composition of the slip step has a lower nickel concentration than that of the enriched surface; and the slip step dissolves until the nickel is enriched to the same composition as the preexisting surface.
   d. *Film rupture.* Stress-corrosion cracking proceeds by successively breaking a passive film. At the point of rupture, dissolution proceeds until repassivation occurs.
   e. *Chloride ion migration.* The chloride ion migrates through the cracked film toward the region of highest stress. The chloride ion then acts to break down the film, thereby allowing metal dissolution.
3. *Hydrogen Mechanisms*
   a. *Hydride formation.* Hydrogen enters type 304 stainless steel to form martensite, which will diffuse into stringers normal to the direction of stress and then cause cracking.
   b. *Hydrogen embrittlement.* Hydrogen accumulates within the metal at the crack tip, leading to localized weakening, either by void formation or lowering the cohesive strength. Cracks propagate by mechanical fracture of the weakened region.
4. *Mechanical Mechanisms*
   a. *Tunnel Pitting and Tearing.* Crack propagates by formation of deep pits or tunnels via dissolution followed by linking of these pits or tunnels by ductile rupture.
   b. *Corrosion Product Wedging.* The corrosion products build up in existing cracks and then exert a wedging action.

3-46 Methods of Prevention

As metioned above, the mechanism of stress-corrosion cracking is imperfectly understood. As a consequence, methods of preventing this type of attack are either general or empirical in nature. Stress-corrosion cracking 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 1100 to 1200°F, and the austenitic stainless steels are frequently stress-relieved at temperatures ranging from 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 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 stress-corrosion cracking than are the stainless steels. Thus, under conditions which tend to produce stress-corrosion cracking, carbon steels are often found to be more satisfactory than the stainless steels. For example, heat exchangers used in contact with seawater 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 stress-corrosion cracking 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 stress-corrosion cracking effects in mildly corrosive mediums. As in all inhibitor applications, sufficient inhibitor should be added to prevent the possibility of localized corrosion and pitting.
6. *Coatings* are sometimes used, and they depend on keeping the environment away from the metal—for example, coating vessels and pipes that are covered with insulation. In general, however, this procedure may be risky for bare metal.
7. *Shot-peening* (also known as shot-blasting) produces residual compressive stresses in the surface of the metal. Woelful and Mulhall* show very substantial improvement in resistance to stress corrosion as a result of peening with glass beads. Type 410 stainless was exposed to 3% NaCl

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*M. Woelful and R. Mulhall, Glass Bead Impact Testing, *Metal Progr.* 57–59 (Sept. 1982).

at room temperature; type 304 to 42% $MgCl_2$ at 150°C; and aluminum alloy 7075-T6 to a water solution of $K_2Cr_2O_7$-CrO_3-NaCl at room temperature. A paper on this subject by Daley* is also of interest.

All of the exposed surface of the *completed* equipment must be shot peened for good results. The surface layer under compressive stress is quite thin—usually a few thousandths of an inch. An example of a successful application involves a type 316 centrifuge handling organic chlorides at 60°C that exhibited extensive SCC after one year. A shot-peened *replacement* 316 centrifuge showed no cracking after 42 months. Peening of cracked surfaces is *not* recommended.

3-47 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 Fig. 3-73. 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 surface 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

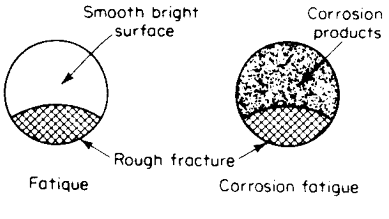

Figure 3-73 Schematic illustration of fatigue and corrosion-fatigue failures.

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*J. J. Daley, Controlled Shot Peening Prevents Stress Corrosion Cracking, *Chem. Eng.*, 113–116 (Feb. 16, 1976).

are shown in Fig. 3-74. The fatigue life of steel and other ferrous materials usually becomes independent of stress at low stress levels. As shown in Fig. 3-74, 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 Fig. 3-74. 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 applied stress is reduced but does not become independent of stress level.

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 3-73 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 stress-corrosion cracking. However, the mode of fracture and the preventive measures differ and it is justifiable to consider it separately.

Renewed attention has been given to corrosion fatigue because of potential catastrophic failures in aerospace, nuclear, and marine (offshore platforms, submarines) structures. Extensive testing and detailed theoretical studies have been conducted. Although the mechanism (or mechanisms) of this type of corrosion remains unclear, it is known that crack initiation and crack growth respond differently to environmental factors.

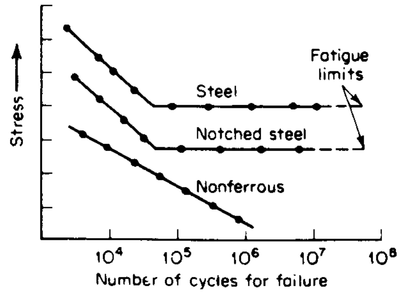

Figure 3-74 Schematic illustration of the fatigue behavior of ferrous and nonferrous alloys.

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 seawater, 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 seawater. It is apparent that corrosion fatigue must be defined in terms of the metal and its environment.

Bogar and Crooker* tested alloys of steel, aluminum, and chromium in natural seawater, ASTM seawater, and a 3% sodium chloride solution. They conclude "that solution composition seldom has a large or a consistent effect on marine corrosion fatigue test results." Davis, Vassilaros, and Gudas† tested metal matrix composites.

Mechanism The mechanism of corrosion fatigue has not been studied in detail, but the cause of this 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 that 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 that is characteristic of many stress-corrosion

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*F. D. Bogar and T. W. Crooker, Fatigue Testing in Natural and Marine Corrosion Environments Substitute Ocean Waters, *Materials Performance*, 37 (Aug. 1983).

†D. A. Davis, M. G. Vassilaros, and J. P. Gudas, Corrosion Fatigue and Stress Corrosion Characteristics of Metal Matrix Composites in Seawater, *Materials Performance*, 38–42 (Mar. 1982).

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.

Wei, Shim, and Tanaka* emphasize the complex interactions of loading, environmental and metallurgical variables. To make test information applicable to proper design, a model must quantify crack growth in terms of processes, including transport of deleterious species to the crack tip, localized chemical reactions at the crack tip, entry and diffusion of hydrogen, and embrittlement effects. R. P. Gangloff† discusses small cracks and also models the many factors and their interplay in corrosion fatigue and SCC.

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 charge hydrogen into the metal.

Many engineers associate fatigue and corrosion fatigue with rotating parts, but other types of equipment (usually considered static) could fail. For example, I have investigated several expensive failures of heat-exchanger tubing because of vibration. The design of equipment should ensure the avoidance of structural vibrations.

Suggested Reading

Devereaux, O., A. J. McEvily, and R. W. Staehle, eds., *Corrosion Fatigue: Chemistry Mechanics and Microstructure*, National Association of Corrosion Engineers, Houston, Tex., 1972.

Corrosion Fatigue: Mechanics, Metallurgy, Electrochemistry, and Engineering, ASTM STP 801, Information Center, Battelle Laboratories, Columbus, Ohio, 1981.

Corrosion Fatigue: Mechanics, Metallurgy, Electrochemistry, and Engineering, ASTM STP 801, American Society for Testing and Materials, Philadelphia, May 1983.

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*R. P. Wei, G. Shim, and K. Tanaka, "Corrosion Fatigue and Modeling," TMS-AIME Fall Meeting, 1983.

†R. P. Gandgloff, "Localized Chemistry Effects on the Growth Kinetics of Small Cracks," TMS-AIME Fall Meeting, 1983.

HYDROGEN DAMAGE

3-48 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
4. Hydrogen attack

Hydrogen blistering results from the penetration of hydrogen into a metal. An example of blistering is shown in Fig. 3-75. The result is local deformation and, in extreme cases, complete destruction of 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 a 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; they are discussed in detail in Chap. 11.

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

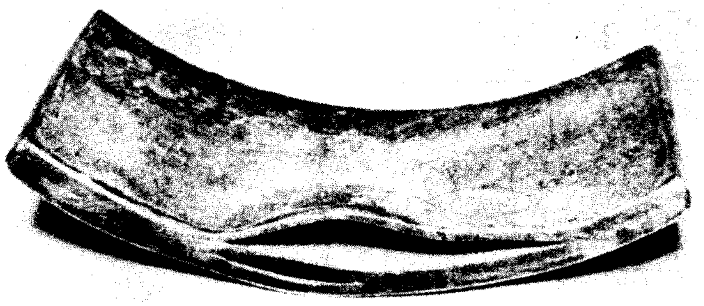

Figure 3-75 Cross section of a carbon steel plate removed from a petroleum process stream showing a large hydrogen blister. Exposure time: 2 years. (*Imperial Oil Limited, Ontario, Canada*)

produce mechanical damage, catastrophic failure may result if they are not prevented.

3-49 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.

3-50 Hydrogen Blistering

A schematic illustration of the mechanism of hydrogen blistering is shown in Fig. 3-76. Here, the cross-sectional 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 on cathodic protection. At any time there is a fixed concentration of hydrogen atoms on the metal surface, and some of these

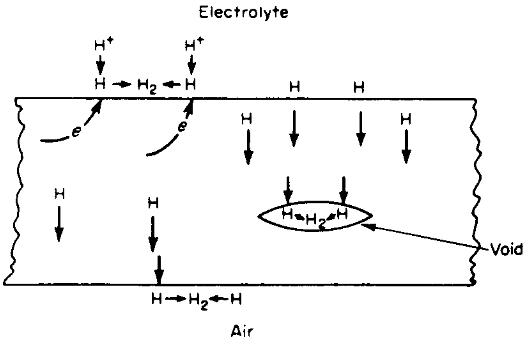

Figure 3-76 Schematic illustration showing the mechanism of hydrogen blistering.

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 blistering is most prevalent in the petroleum industry. It occurs in storage tanks and in refining processes. One method for control is to add an inhibitor, such as the polysulfide ion.

3-51 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 compounds. In other materials, such as iron and steel, the interaction between dissolved hydrogen atoms and the metal is not completely known.

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 Fig. 3-77 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* 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 Fig. 3-78. This figure† 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.

Most of the mechanisms that 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 stress-corrosion cracking

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*R. A. Davis, G. H. Dreyer, and W. C. Gallaugher, *Corrosion*, **20**:93*t* (1964).

†H. H. Johnson, E. J. Schneider, and A. R. Troiano, *Trans. AIME*, **212**:526–536 (1958).

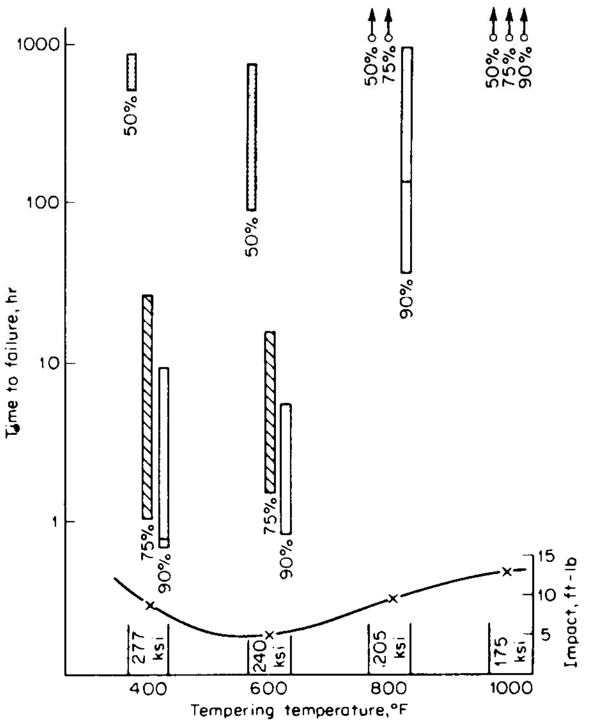

Figure 3-77 Time to failure vs. tempering temperature for 4340 steel at stress levels of 50, 75, and 90% of the yield stress. Specimens exposed to wetting and drying 3.5% NaCl solution at room temperature.

generally by the interactions with applied currents. Cases where the applied current makes the specimen more anodic and accelerates cracking are considered to be stress-corrosion cracking, 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 reaction, are considered to be hydrogen embrittlement. These two phenomena are compared with regard to cracking mode and applied current in Fig. 3-79.

Although hydrogen embrittlement is more or less the "universal" description, other terms are used. If absorption is due to contact with hydrogen gas, it is often described as hydrogen stress cracking. If hydrogen is absorbed because of the corrosion reaction it is called SCC or sometimes hydrogen stress cracking. If corrosion is due to the presence of hydrogen sulfide, a common term is sulfide stress cracking. A few ppm of absorbed hydrogen can cause cracking.

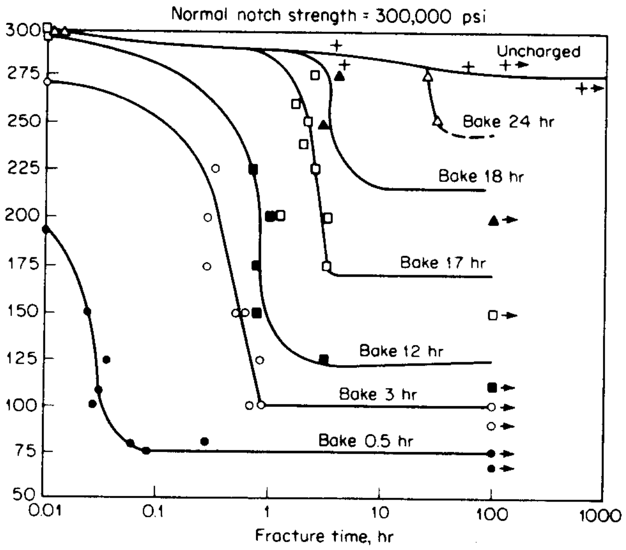

Figure 3-78 Static fatigue curves for various hydrogen concentrations obtained by baking 4340 steel different times at 300°F.

When hydrogen is initially present (before use) such as in electroplated articles, baking removes the hydrogen (Fig. 3-78). This procedure is also used during shutdowns of hydrogenation equipment involving high-strength steel components.*

Hydrogen cracking tendency decreases with increasing temperature, and significant change occurs above about 150°F (70°C). Except in corrosion reactions involving hydrofluoric acid or hydrogen sulfide, hydrogen stress cracking is usually not a problem with steels having yield strengths below 150 lb/in.^{2} (1,000 MPa). For these acids the limit drops to about 80 lb/in.^{2} (550 MPa).*

Stevens and Bernstein† state that crack growth results indicate that crack tip plasticity and branching plays a role in hydrogen-induced crack growth in HSLA steel. Pasco and associates‡ present an absorption model and also equations for calculating experimental results.

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*R. S. Treseder, Guarding Against Hydrogen Embrittlement, *Chem. Eng.*, 105–108 (June 29, 1981).

†M. F. Stevens and I. M. Bernstein, "Microstructural Effects on Hydrogen Embrittlement of a Ti-Containing HSLA Steel."

‡R. W. Pasco, K. Sieradzki, and P. J. Ficalora, "An Absorption Model for Stage II Crack Growth Rates."

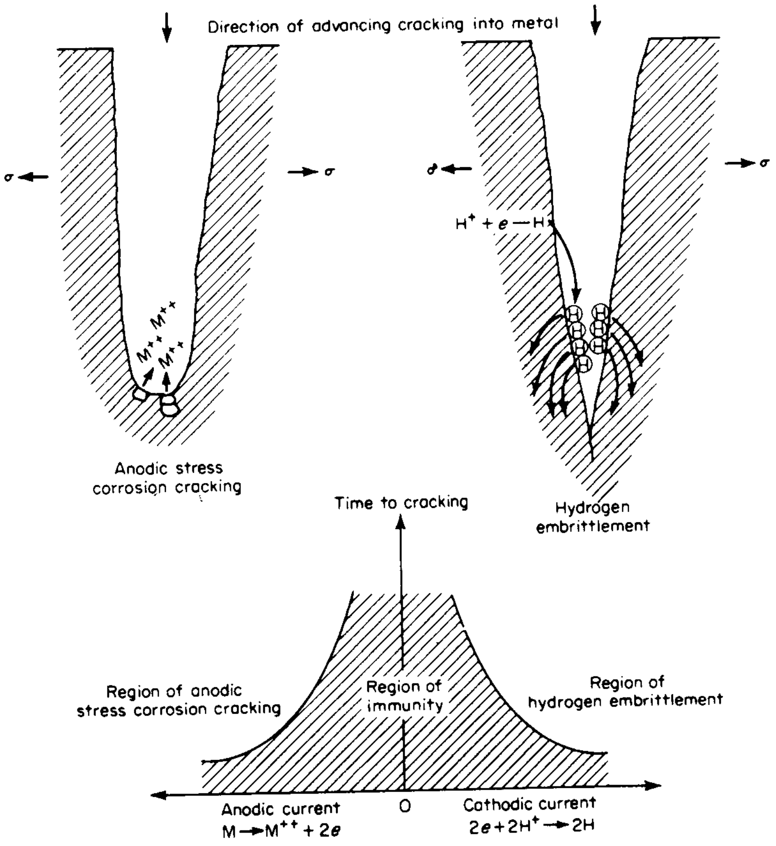

Figure 3-79 Schematic differentiation of anodic stress-corrosion cracking and cathodically sensitive hydrogen embrittlement. (*R. W. Staehle*)

Ahn and Soo* report on kinetic studies of embrittlement of Grade-12 titanium. Hanna† investigated hydrogen embrittlement of copper and shows the formation and effect of steam bubbles in copper at elevated temperatures.

For an in-depth study of metallurgical variables the reader is referred to "The Role of Metallurgical Variables in Hydrogen-Assisted Environmental Fracture," in M. G. Fontana and R. W. Staehle, eds., *Advances in Corrosion*

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*T. M. Ahn and P. Soo, "The Kinetics of Hydrogen Embrittlement in ASTM Grade-12 Titanium Alloy."

†M. D. Hanna, Hydrogen Embrittlement of Copper: Formation and Growth of Intergranular H_2O Bubbles."

Note: The last four of these references are papers presented during the TMS Fall Meeting 1983.

Science and Technology, vol. 7, pp. 53–175, Plenum Press, New York, 1980. Most engineering alloy systems and anodic cracking are included. Practically all conceivable variables are discussed, and an excellent bibliography is included.

In his paper Treseder also discusses *sulfide stress cracking*, which occurs in the presence of water and hydrogen sulfide. This problem is of great importance in the petroleum industry all the way from production through refining. Apparently the iron sulfide formed on the metal surface has a catalytic effect in increasing the amount of hydrogen that enters the metal as opposed to other corrosion reactions. Here again the critical strength level of the steel is 80 lb/in.^{2} (550 MPa). A hydrogen sulfide partial pressure above 0.05 lb/in.^{2} (absolute) can cause cracking.

Section 4-24 describes NACE test method TM-01-77 for "sour" environments to determine acceptable alloys, and some results are presented there. For most carbon and low-alloy steels a maximum hardness of Rockwell C 22 is recommended. Where higher strength is required, some alloys are acceptable up to RC-35. Selection of suitable materials is the *major* method for controlling sulfide stress cracking.

Turn, Wilde, and Troianos* discuss cracking of pipe steels and present additional information.

Treseder also describes *monitoring* as follows: "In-plant monitoring of process conditions that might lead to hydrogen embrittlement effects is being done by use of hydrogen probes. These are of two types: one consists of a thin-walled, closed-end steel tube inserted into the process stream, the other is in the form of a patch on the outside of the pipe or vessel. In each case the permeation rate of hydrogen through the steel is measured. These data can be correlated with plant conditions, and used to monitor mitigation measures such as inhibition."

3-52 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 clad with austenitic stainless steel or nickel is often used for this

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*J. C. Turn, B. E. Wilde, and C. A. Troianos, On the Sulfide Cracking of Line Pipe Steels, 0 (Sept. 1983).

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 preventive measures:

1. *Reducing corrosion rate.* 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 baking at relatively low temperatures (200 to 300°F). See Fig. 3-78.
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.

3-53 Fracture Mechanics

A thorough discussion of fracture mechanics is beyond the scope of this book, but a few remarks are appropriate. The reader is referred to MTI Manual No. 8, *Fracture Control for the Chemical Process Industries* (1983). This is a primer (simplified) manual intended for corrosion engineers and others who may not have a substantial background in engineering mechanics. Example of application are described. The manual states in a few words the basic premise of fracture mechanics: namely, fracture resistance of a material is expressed by the material's fracture toughness, termed K_{Ic}. Fracture occurs when the stress intensity K is equal to K_{Ic}.

In its simplest form, stress intensity K is expressed as $K = 1.77\sigma\sqrt{\alpha}$, where σ is the acting stress and α is the size of an existing crack. As stated above, fracture occurs when $K = 1.77\sigma\sqrt{\alpha} = K_{Ic}$. This applies for propagation of cracks due to mechanical stress. In the presence of a corrosive environment, the situation could be vastly different.

As described earlier in this chapter, SCC can greatly reduce the load-bearing capacity of a structural part. For SCC we replace K_{Ic} with K_{ISCC}, which is the threshold value for SCC and it is the highest-plane strain-stress intensity below which crack propagation does *not* occur. Figure 3-80 illustrates this point. For this case, stress-corrosion cracks should not propagate below a value of 15. In the area between the curve and the dotted line, crack growth may be slow, but eventually the rate would become fast and critical and catastrophic failure would result. In general, this applies to SCC and also corrosion fatigue.

The fracture mechanics approach is quite "clean" for high-strength low-alloy steels (i.e., 4340 in seawater), but the picture is somewhat confused

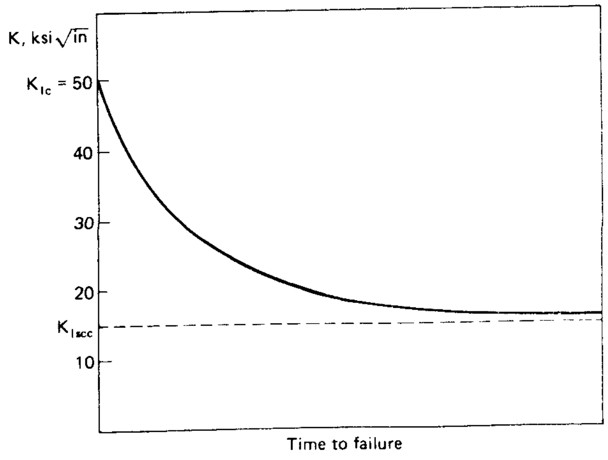

Figure 3-80 Stress corrosion test data.

for the austenitic stainless steels (i.e., 18-8) largely because of the branching nature of the cracks (Fig. 3-53). There are other limitations, for example, in thin-walled sheet and pipe. The best advice is not to fool with the fracture mechanics approach unless you have a good understanding of the subject.

I believe fracture mechanics entered the corrosion picture because times for crack initiation varied all over the place for many corrosion-resistant alloys. This variable is removed when you start with a precracked specimen and then follow its propagation.