

ALKALIES

Sodium Hydroxide

Sodium hydroxide solutions at comparatively low temperatures and concentrations are quite noncorrosive to both the chromium and chromium-nickel alloys. Higher and inconsistent corrosion rates occur in more concentrated solutions and are somewhat accelerated under applied pressure¹².

Typical corrosion rates for several stainless steels are shown in Table 15.32. Potassium hydroxide solutions would be expected to show similar action on stainless steels.

The isocorrosion graph in Figure 15.9 summarizes the performance of the austenitic chromium-nickel stainless steels in sodium hydroxide. The indicated rates hold true primarily for Types 304 and 316. A stress-corrosion cracking zone based on failures reported in the literature is also shown in the graph. The boundary of the cracking zone is shown as a broken line, because the zone still may not be completely defined. Most of the cracking failures have occurred at temperatures near the boiling point. Where failures have been reported below the boiling point, there is a possibility that sodium chloride may have been present in the solutions and contributed to the failures. Aeration and corrosion rates may also be factors influencing the cracking.

TABLE 15.32. CORROSION OF STAINLESS STEELS BY SODIUM HYDROXIDE SOLUTIONS^{a,b}

Type	Concentration, %	Temperature, °F	Test duration, days	Corrosion rate, mpy
410	20	122 to 140	134	0.1
430	20	122 to 140	134	0.1
309	20	122 to 140	134	<0.1
310	20	122 to 140	134	<0.1
302	20	122 to 140	134	<0.1
304	22	122 to 140	133	<0.1
410	72	245 to 255	119	6 ^a
430	72	245 to 255	119	32 ^a
304	72	245 to 255	110	3.7 ^a
316	72	245 to 255	110	3.1 ^a
329	72	245 to 255	110	0.3 ^a
21Cr-34Ni-0.5Cu	72	245 to 255	119	0.1 ^a
302	73	212 to 248	88	38 ^b
304	73	212 to 248	88	45 ^b

^a Solution was moderately aerated.

^b No aeration of solution.

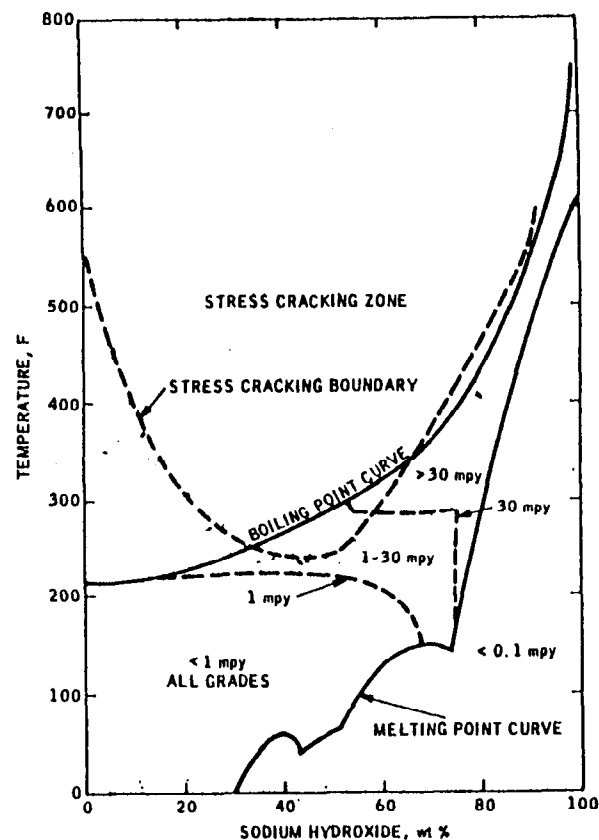


FIGURE 15.9. Isocorrosion chart for austenitic Cr-Ni stainless steels in sodium hydroxide^{14A}.

Ammonium Hydroxide

Stainless steels show good resistance to all concentrations of ammonia and ammonium hydroxide solutions up to the boiling point. Above the atmospheric boiling point, the corrosion rate may increase rapidly, particularly in anhydrous ammonia. In liquid ammonia containing ammonium acetate at 483° F and 1200 psig, Type 304 had a rate of 1060 mpy; under the same conditions, Type 316 had a rate of 14 mpy.

Pages 409, 410

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"Corrosion Resistance of Metals and Alloys"

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Forgotten Phenomena

Corrosion of stainless steel by hot caustic

Research using solutions of chemically pure caustic (sodium hydroxide [NaOH]) led to the development of a diagram that attempts to delineate the parameters of concentration and temperature governing stress corrosion cracking (SCC) of type 300 series austenitic stainless steels (SS), such as types 304 (UNS S30400), 316 (S31600), and their low-carbon forms, types 304L (S30403) and 316L (S31603). This diagram (Figure 1) is analogous to a similar diagram for caustic embrittlement of carbon steel under stress from welding or cold-forming. The term caustic embrittlement is a misnomer because the phenomenon is simply SCC of steel in the alkaline solution.

The 1 mpy (0.0254 mm/y) isocorrosion line in Figure 1 is nearly constant at 100°C (212°F) from ~20% to 50% caustic. The dashed line delineating SCC (labeled Apparent SCC boundary) is U-shaped, with the minimum at ~40% caustic and ~240°F (115°C).

In actuality, there is a real possibility that type 300 series SS may lose passivity and undergo rapid general corrosion in hot 40% to 50% caustic. Probable safe limits are well below those indicated by the diagram, perhaps 70°C (158°F) for 50% caustic and 80°C (177°F) for 40% solution. However, oxidizing contaminants can maintain passivity. Extra-low interstitial ferritic SS grades, such as alloy 26-1 (S44627), have been used instead of Ni (UNS N02200) in caustic evaporators provided the chlorate content is sufficiently high.

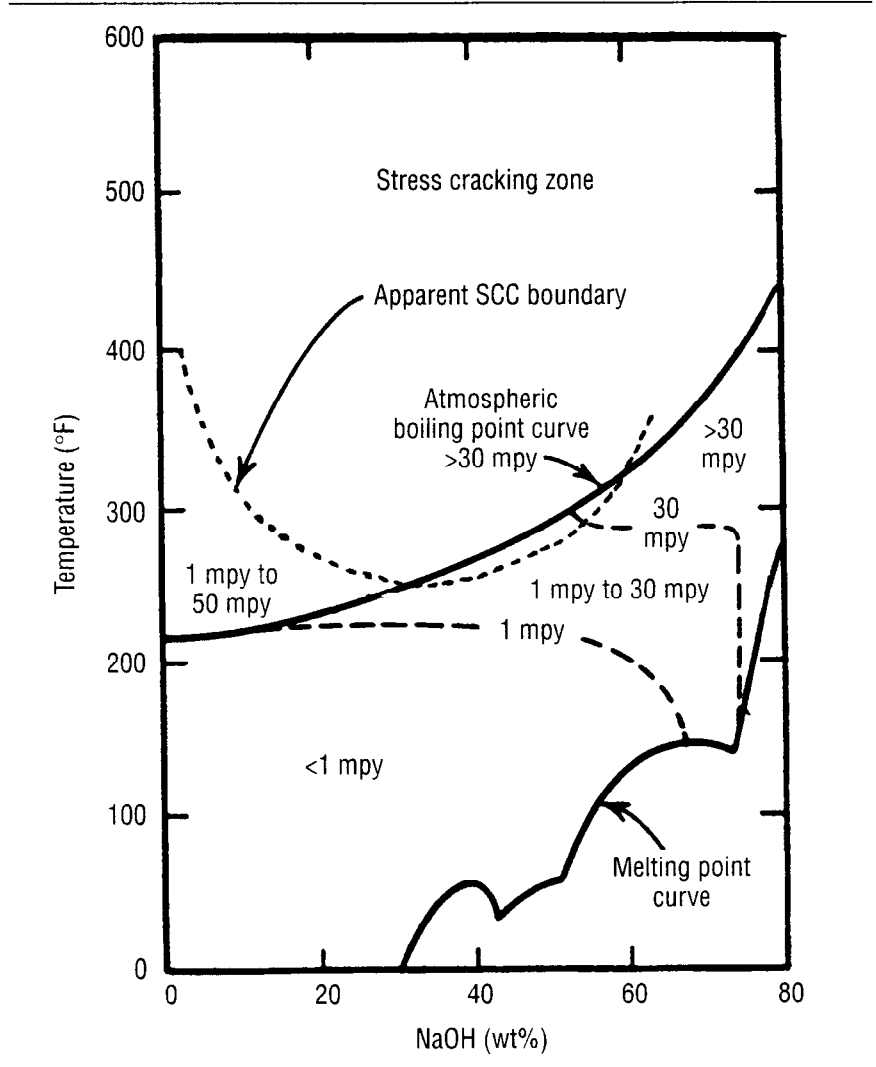


FIGURE 1
Isocorrosion diagram for type 300 series austenitic SS in NaOH (caustic).¹

Above 300°C (570°F), the danger of caustic SCC is very great. Bellows-type piping expansion joints made of type 321 (S32100, Fe-18% Cr-10% Ni-Ti stabilized) in 300-lb to 400-lb steam (~215°C to 230°C [420°F to 445°F]) are prone to rapid SCC if there is entrainment of caustic from boiler treatment. When high-temperature caustic SCC of SS

is encountered, there is a characteristic gunmetal blueing of the surface.

The role of chlorides in caustic cracking is often misunderstood. Chlorides, if present, are not a factor. There have been failures of alloys 800 (N08800, Fe-30% Ni-20%

Continued on page 65

Phorgotten Phenomena

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Cr) and 825 (N08825, Fe-40% Ni-20% Cr-3% Mo-2% Cu), high-Ni alloys that are very resistant to chloride SCC, used as replacements for type 300 series SS. Russian investigators reported that chlorides, a common contaminant in concentrated caustic, do not aggravate SCC and may even play an inhibitive role.

Alloy 600 (N06600, Ni-15% Cr-8% Fe) is satisfactory in hot caustic service. For bellows, alloy 625 (N06625, Ni-20% Cr-8% Mo-Cb stabilized) is currently used almost exclusively.

C.P. Dillon, FNACE
C.P. Dillon & Associates
940 Park Street
St. Albans, WV 25177

Reference

I. J.K. Nelson, "Materials of Construction for Alkalies and Hypochlorites," in *Process Industries Corrosion—The Theory and Practice*, eds. B.J. Moriz, W.L. Pollock (Houston, TX: NACE, 1986), p. 300.

**Corrosion Scientists,
Engineers, Practitioners...**

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C.P. Dillon is the 1998 NACE International T.J. Hull Award recipient for his outstanding contributions in the field of publications. He is the author of *Corrosion Control in the Chemical Process Industries*, 2nd Edition (St. Louis, MO: MTL, 1997), now in its second printing. This book is available from NACE.

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STRESS CORROSION CRACKING

Stress corrosion cracking is something which the design engineer should always keep in mind in specifying materials, particularly in the case of pressure vessels. The presence of internal stress should always be taken into account when deciding the magnitude of externally applied stresses to which the equipment can be safely subjected. Unfortunately there are no guiding rules which can be followed. About all that can be said is that stress corrosion cracking is specific both for the metal and for the environment. In certain special environments the presence of tensile stresses may lead to the cracking of certain metals. With other environments or with other metals or alloys no difficulty is encountered. Reliance must be placed on practical experience or on laboratory or field tests.

The term stress corrosion cracking is used to indicate the combined action of static tensile stress and corrosion which leads to cracking. The principal factors are the magnitude of the stress, the nature of the environment, the length of time involved and the internal structure of the alloy. These factors are not independent, but interact, one accelerating the action of another. Their relative importance varies with conditions.

If stress corrosion cracking is to occur there must be tensile stresses at the surface. The stresses may be internal or applied, the two types being additive. Examples of internal stresses are those produced by deformation during cold work, by unequal cooling from high temperature and by internal structural rearrangements involving volume changes. Stresses induced when a piece is deformed, those induced by press and shrink fits and those near welds, rivets and bolts may be classed as internal stresses.

In many cases these concealed stresses are of greater importance than actual operating stresses. This is true also of pressure vessels, except perhaps for those operating at loads which are high in relation to the strength of the material. When the factor of safety required in design is considered, operating stresses are generally low enough to be of comparatively little importance, except as they add to the internal stresses.

The actual stresses may vary greatly from point to point within the metal, and in some locations are much higher than the average value. A nonuniform stress distribution is expected, nevertheless a high localized stress is considered more damaging than a uniform load. Generally tensile stresses in the neighborhood of the yield strength are present in stress corrosion cracking failures, but failures are known which have occurred at much lower stresses. In any case the stress levels are low enough so that normally a great deal of general corrosion could be tolerated. The interaction of the stress and corrosion produces cracking where it would not otherwise be expected.

Stress corrosion cracking has been observed in almost all metal systems. Yet for each metal specific environments are required to produce it. No stress corrosion

cracking has occurred in a vacuum. The environment that induces cracking frequently attacks the metal only superficially if stresses are absent. Many of the environments that cause cracking tend to produce a pitting type of corrosion.

One of the curious aspects of stress corrosion cracking is the wide difference in time required for failure, which varies from a matter of minutes to many years. Associated with this is the probability of cracking. Specimens which are apparently similar may not behave alike, with perhaps 40% cracking in a short time, and the rest remaining uncracked for a much longer time. Laboratory tests require severe conditions to produce cracking in reasonable time, whereas in service much milder conditions may cause cracking in the longer time available.

Considerable time may be required before corrosion proceeds to the extent that it begins to be accelerated by the tensile stresses present. The more severe the corrosive conditions and the higher the stress level the sooner this will happen. With some alloys there is an incubation period, during which precipitation or other structural changes may be occurring. For example, aluminum-magnesium alloys (over 6% magnesium), immediately after heat treatment, may not show any susceptibility to cracking in accelerated laboratory tests, but after aging at room temperature for 6 months, stress corrosion cracks may form rapidly in the same test.

As just indicated the internal structure of the metal or alloy can be of considerable importance. The internal structure is dependent upon composition, upon the method of fabrication and whether the metal is as-cast, hot worked or cold worked. It is also dependent on thermal treatments and the extent of natural aging.

There have been numerous reviews and books on stress corrosion cracking.^{9, 20-24} There is also a voluminous literature. This should be consulted for detailed information. The more important instances of stress corrosion cracking are discussed below.

Caustic Embrittlement

A well-known example of stress corrosion cracking is the caustic embrittlement of steel in steam boilers.²⁵ The cracking is associated with the presence of sodium hydroxide in the boiler and hence the name caustic embrittlement. The metal away from the cracks, however, is ductile and not brittle. When a boiler lets go because of caustic embrittlement, results can be disastrous as illustrated in Fig. 1.²⁶ Other examples of severe explosions have been cited by Zapffe.²⁷

The cracking is said usually to be predominantly intercrystalline, and Fig. 2 is an illustration of this. This photomicrograph was prepared from the steel of an autoclave exposed to 50% caustic soda at 250° F and 400 psi. This is perhaps a more concentrated solution than normally encountered in steam boilers, but it is an excellent example of caustic embrittlement just the same. Oxides are present in the cracks, which



Fig. 1 Power plant after explosion due to caustic embrittlement of steam boiler²⁶

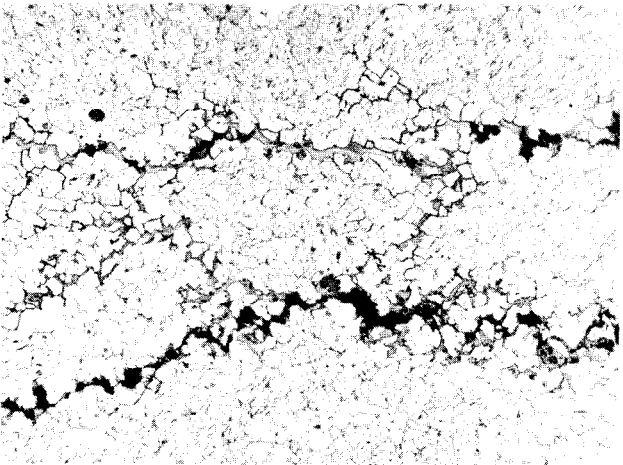


Fig. 2 Caustic embrittlement of steel exposed to 50% caustic soda at 250° F. 250 X

is typical. In other cases the cracks may be partly transcrystalline, or even, as illustrated in Fig. 5, predominantly transcrystalline. It used to be thought that stress corrosion cracks were characteristically intergranular, but many cases are now known when the cracking follows a path across the grains.

In steam boilers the caustic present concentrates at small leaks or capillary spaces. The caustic concentration builds up to high values at such places. High tensile stresses must be present, of course, and usually the cracking takes place along rows of rivets where there may be slight leaks. Salt deposits have been observed in some cracked rivet seams.

In laboratory tests a U-bend specimen with a bolt through the legs is convenient for studying caustic embrittlement. Specimens of this nature are shown in Fig. 3. The U-bend specimen has tensile stresses in the outer fibers in the neighborhood of the yield point, and high stress gradients such as frequently occur in practice. Any cracking is located on the outside of the bend as shown in the figure. The white material in the cracks is residual caustic. These steel specimens were exposed to boiling 33% sodium hydroxide containing 0.1% lead oxide for 14 days.

U-bend specimens of this type were used by Berk and Waldeck²⁸ to outline dangerous concentrations and temperatures of caustic. They obtained no cracking in 30 days or longer at concentrations below 15% or above 43% or at temperatures below 180° F. However, under long-time service conditions, cracking has been observed well outside these limits.²⁹ Also it is known that constituents present in small amounts may act as accelerators or as inhibitors of the cracking.

In laboratory tests it is difficult to obtain consistent behavior in pure caustic. Cracking is readily produced by adding certain oxidizing agents or accelerators. Thus cracking in boiling 33% sodium hydroxide can

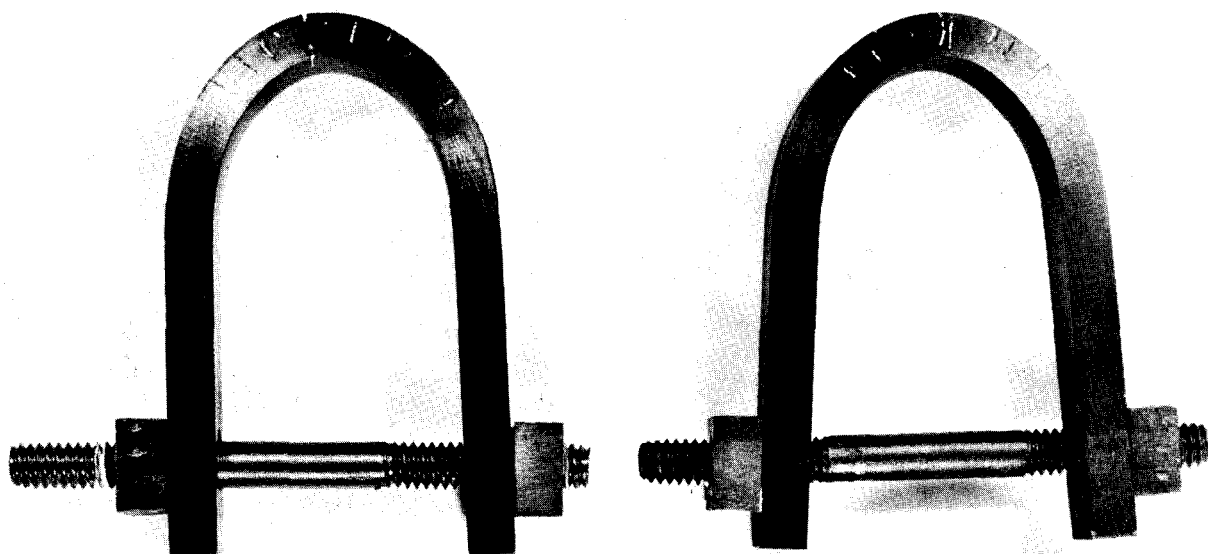


Fig. 3 Steel U-bend specimens after exposure for 14 days to boiling 33% sodium hydroxide containing 0.1% lead oxide. Natural size



Fig. 4 Intercrystalline cracking of steel U-bend specimens after 15 days in boiling 33% sodium hydroxide containing 0.1% lead oxide. 500 X

be consistently obtained by the addition of 0.1% lead oxide. Figure 4 illustrates the intergranular nature of the cracking in steel U-bend specimens exposed to this media. Cracking can also be consistently obtained under similar conditions by the addition of 0.3% sodium silicate. Figure 5 shows that under these slightly altered conditions the cracking was transcrystalline. Figures 4 and 5 are for the same steel and practically identical conditions except for the change in minor constituents in the caustic. Other stress corrosion cracking systems are known where slight changes in conditions have changed the path of the cracking. This fact is not explained by some of the theories of stress corrosion cracking.

Under service conditions caustic embrittlement is sometimes avoided by adding inhibitors of the cracking to the water. Thus tannins, lignins, quebracho extract, waste sulfite liquor, sodium nitrate, sodium phosphate and other additives have been beneficial in some cases.

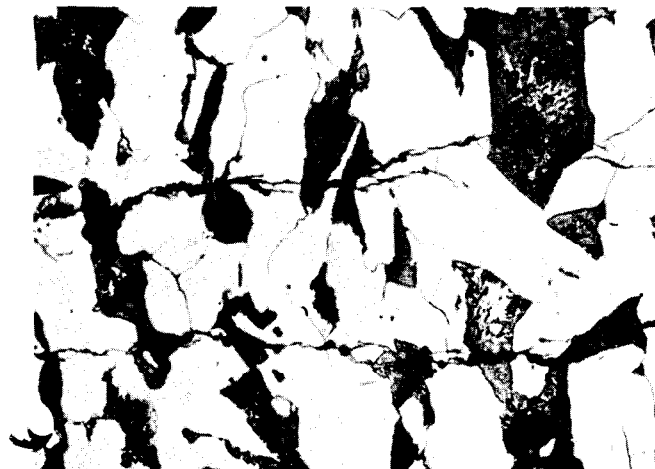


Fig. 5 Transcrystalline cracking of steel U-bend specimens after 12 days in 33% sodium hydroxide containing 0.3% sodium silicate at 300° F. Same steel as Fig. 4. 500 X

An embrittlement detector has been devised which can be attached directly to a pressure vessel to determine whether or not the water is capable of producing caustic embrittlement.³⁰ The detector has a base which consists of a rectangular block with a hole through which the water circulates. The test specimen is clamped to this base. It is bent and maintained under stress by means of an adjusting screw which passes through the specimen and presses against this base block. A small hole conducts the water from the base block to the contact surface between the base and the specimen. By correct setting of the clamping nuts and adjusting screw a very slow leak of steam is established. Thus a concentrated solution forms under the bent area of the specimen. If the water is embrittling and sufficient time is allowed, such as 30 days or more, the specimen will crack. If the water is not embrittling no cracking will occur.

All steels are not equally susceptible to caustic embrittlement. Deoxidation practice and the residual elements present have some effect. However, the improvements have been minor and no steel has been devised which is completely resistant. Low-alloy steels crack as readily as plain mild steel.^{27, 29}

A welded construction is sometimes recommended as being superior to a riveted construction, the argument being that this should prevent the concentration of caustic at leaks and capillary spaces. Welds are apt to introduce high internal stresses, however, and welded pressure vessels have failed by caustic embrittlement.³¹ As-welded steel tanks are recommended for caustic service up to 140° F, but for higher temperatures welded tanks must be stress relieved.²⁹ A low-temperature stress relief of welds has been proposed.³² This consists of heating a narrow band each side of the weld to 350–400° F and quenching. This produces localized stretching with a resultant decrease in stress. Of course, where practical, a full stress relief anneal of the entire vessel is far safer.

Nickel cladding has been used successfully to prevent caustic embrittlement. Where the clad areas are joined by welding care must be taken to insure sound welds. The cracking illustrated in Fig. 2 was in an autoclave lined with nickel. The welds were defective and allowed the caustic to contact the steel with the result that cracking of the steel occurred.

Lowering the tensile stresses present when possible is a standard means of preventing caustic embrittlement. This and other means of preventing stress corrosion cracking are considered further below.

Stress Corrosion Cracking of Iron

In addition to caustic embrittlement, iron and steel alloys are subject to rapid stress corrosion cracking in some nitrate solutions.³³ Cracking has occurred in concentrated calcium nitrate and concentrated ammonium nitrate. Highly stressed bridge cable wire cracked in dilute ammonium nitrate and in dilute so-

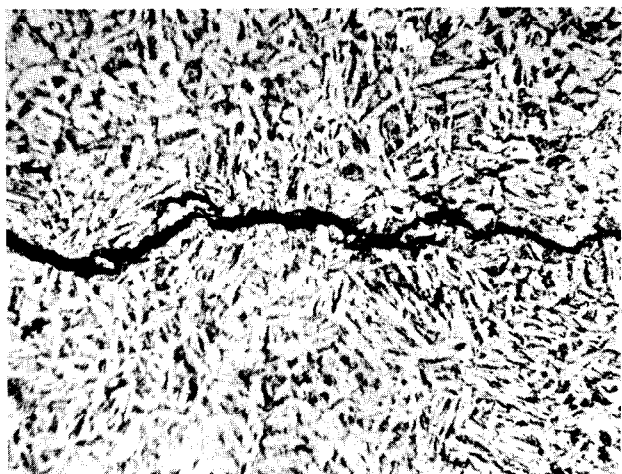


Fig. 6 Transcrystalline cracking of steel U-bend specimens exposed for 6 days to water saturated with a 50:50 mixture of hydrogen sulfide and carbon dioxide at 100° F.³⁸ 500 ×

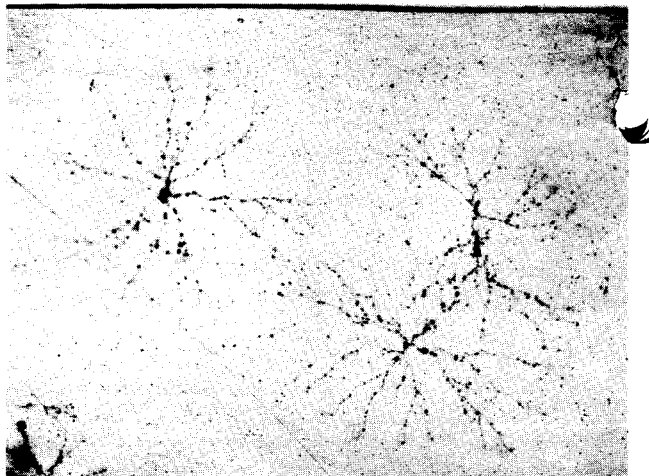


Fig. 8 Stress corrosion cracking of stainless steel kettle handling a baked bean sauce high in chlorides. Natural size

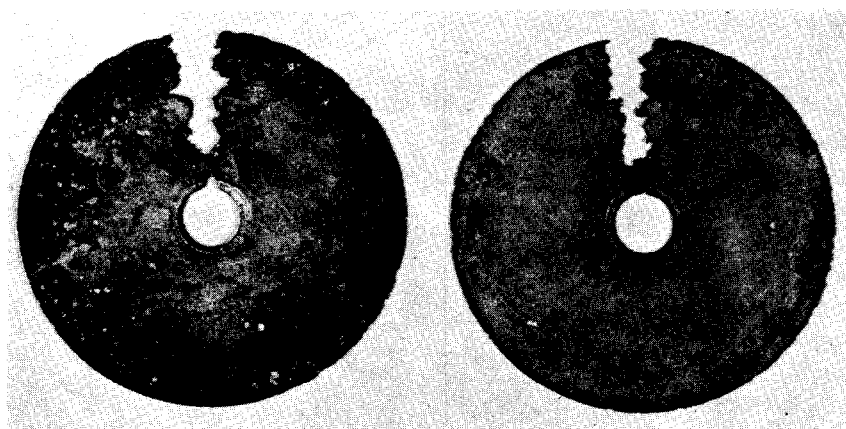


Fig. 7 Stress corrosion cracking of stainless steel around stenciled identification marks and at machined edges. The specimens were exposed in 12% hydrofluoric acid containing 0.2% fluosilicic acid. Natural size

Stainless Steel

Figure 7 shows an instance of stress corrosion cracking of Type 302 stainless steel. Disk-shaped specimens were immersed for 7 days in a solution containing 12% hydrofluoric acid and 0.2% fluosilicic acid at 182° F. Cracks formed around stenciled identification marks causing these sections of the specimens to fall away completely. Cracks can also be seen at the machined edges.

Figure 8 shows another instance of stress-corrosion cracking, this time of a Type 304 stainless steel kettle handling a baked bean sauce which was high in chlorides. The cracks had a radiating pattern and tended

to line up with small sharp pits.

Stress corrosion cracks in stainless steel are usually transcrystalline. A typical example is shown in Fig. 9. These cracks occurred in a specimen exposed to a boiling calcium-magnesium chloride brine. Intergranular cracking has been observed, but only when the heat

dium nitrate, but not in distilled water, dilute ammonium sulfate, ammonium nitrite or sodium hydroxide.³⁴ Cracking has occurred in concentrated nitric acid and also in dilute nitric acid containing manganese dichloride as an accelerator.³⁵ All these failures were largely intergranular.

Transcrystalline cracking has been observed in tanks holding certain gases under pressure. This has been attributed to moisture and traces of hydrogen cyanide,³⁶ and to moisture and traces of hydrogen sulfide.³⁷ Figure 6 shows the transcrystalline cracking of steel U-bend specimens exposed for 6 days to water at 100° F saturated with a 50:50 mixture of hydrogen sulfide and carbon dioxide.³⁸ Embrittlement by hydrogen may be involved in this cracking. Cracking of similar nature has occurred in high-pressure gas condensate wells containing hydrogen sulfide and carbon dioxide.³⁹ Ammonium thiocyanate seemed important in the stress corrosion cracking of steel gas mains.⁴⁰ Undoubtedly additional corrosives which cause stress corrosion cracking of steel will come to light. This should be considered in exposures involving new chemicals.

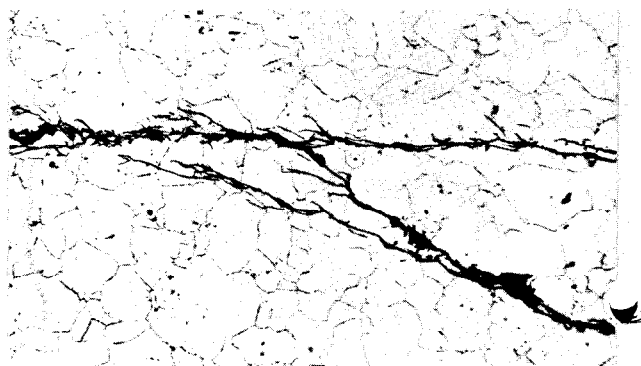


Fig. 9 Transcrystalline nature of the stress corrosion cracking of stainless steel. 100 ×

treatment has been such as to make the stainless steel susceptible to general intergranular corrosion.

The stresses required to cause cracking in the stainless steels sometimes seem comparatively low, a stress of less than 20,000 psi being reported sufficient by Scheil in one instance.²³ Some Type 347 tubing was found to be susceptible to cracking in boiling calcium magnesium chloride brine after stress-relief annealing from 1350° F, but resistant to cracking after a slow cool from 1600° F. Slow cooling is essential as quenching stresses may be sufficient to cause cracking.

Ferritic stainless steels are less susceptible to stress corrosion cracking than the austenitic alloys. Generally, cracking cannot be avoided by shifting from one austenitic grade to another, although there may be real differences in behavior, with increased corrosion resistance and increased austenitic stability being helpful.⁴¹

A thorough review of environments causing stress corrosion cracking of stainless steels was prepared recently by Nathorst.⁴² The number of environments seems large, but in spite of this the austenitic chromium nickel stainless steels perform satisfactorily under many service conditions.

Most cases of cracking involve the presence of chloride ions, particularly if the solution is acid. Hot concentrated solutions of chlorides of magnesium, calcium, barium, cobalt, zinc, lithium, ammonium and sodium all cause rapid cracking.⁴³ Cooler or more dilute solutions may be satisfactory. Organic chlorides, such as ethyl chloride, which decompose in the presence of moisture to form hydrochloric acid may cause cracking.⁴⁴

In many cases where some other environment was thought to cause cracking, closer investigation has shown that chlorides were actually present, even if only as an impurity. Thus cracking has been reported in sulfite waste liquors of the cellulose industry, but in almost every case brackish waters were used. Likewise cracking has been reported in steam and hot water, but in such cases it appears that the design is such as to allow local concentrations of chlorides.

Stainless steels are susceptible to stress corrosion cracking in hot concentrated caustic solutions. The presence of sodium sulfide and reducing substances is said to increase the danger of cracking in caustic. Rees has reported cracking in moist hydrogen sulfide.²⁴ Cracking has also been reported in some other environments.⁴²

Copper Alloys

Perhaps the best known example of stress corrosion cracking in copper alloys is the season cracking of brass,⁴⁵⁻⁴⁷ so-called because the cracks resemble those in seasoned wood. Exposure to moist ammoniacal atmospheres is believed to be necessary to produce the

cracking, but oxygen and carbon dioxide have a contributing effect. Cracking is fast in contaminated atmospheres, but has occurred under apparently normal outdoor and indoor conditions. Evans has speculated on the role of ammonia in promoting the cracking.²⁴

Susceptibility to cracking increases with tensile stress. Stresses of 12,000 to 20,000 psi readily cause cracking, but cracking is rare with stresses below 12,000 psi. Susceptibility to cracking increases greatly with zinc content. Alloys with 85 to 90% copper are practically immune, and with 90% copper they are fairly free from cracking. Two-phase brass compositions, such as 60 copper, 40 zinc, are more susceptible than alloys with less zinc. Special brasses which contain other elements behave similarly to the straight zinc brasses. The cracking is usually intergranular, but transcrystalline cracking has been reported, particularly in the beta phase of high zinc brasses.

As compared with the brasses, other commercial copper alloys, as aluminum bronze, tin bronze, silicon bronze and cupronickel show comparatively little tendency to season crack, although failures are known, and sometimes the failures may occur in other than ammoniacal atmospheres. For example, the ASME Boiler Code cautions on the use of silicon bronze in steam above 212° F. Cook²⁴ reported pure copper to be immune to cracking for all practical purposes. Thompson and Tracy⁴⁸ found most additions to copper to cause a rapid increase in susceptibility to cracking, but larger additions of the same elements caused the susceptibility to decrease again.

An acid mercury salt solution is sometimes used as an inspection test to determine the susceptibility of copper alloys to stress corrosion cracking.^{29, 49-52} Metallic mercury is liberated on the surface and penetrates stressed metal intergranularly. This is a different type of attack than stress corrosion cracking, but results are roughly comparable. However, cracking in service has been known to occur in material which has passed the mercury test.

A better but more difficult test involves exposure to a gas phase containing ammonia, air, water vapor and carbon dioxide.^{48, 49} This relates directly to service conditions. For reproducible results the temperature must be controlled and also the composition of the gas phase. With this test there seems to be no threshold stress below which cracking will not occur in time. This probably relates to the fact that some intergranular attack occurred in the absence of stress. This test is particularly suited for experimental studies.

Aluminum Alloys

Pure aluminum is quite resistant to stress corrosion cracking. On the other hand aluminum alloys containing more than 12% zinc or more than 6% magnesium have cracked in such mild environments as the atmosphere and tap water.^{23, 53}