

*Edited by Richard W. Greene and the Staff of
Chemical Engineering Magazine*

THE CHEMICAL ENGINEERING GUIDE TO
CORROSION CONTROL
IN THE
PROCESS INDUSTRIES



The Chemical Engineering Guide to Corrosion

Edited by
Richard W. Greene
and
the Staff of Chemical Engineering



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The
Chemical Engineering
Guide to Corrosion

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INTRODUCTION

Yearly costs of corrosion to industry are in the billions of dollars. What should the chemical engineer do in such situations? Pipes rust, tanks develop pinholes, vessel walls stress crack. Corrosion problems range from discoloration of structures to catastrophic failure of machinery and equipment. Also, plants must be built to handle new processes and existing facilities must be changed to accommodate process modifications.

Here are guidelines to help cope with a variety of corrosion and materials-selection problems. THE CHEMICAL ENGINEERING GUIDE TO CORROSION contains articles that appeared in *Chemical Engineering* during the past five years. It covers theory and applications in a variety of areas that will help you to make the proper materials selection and to solve many problems you may face. The book is divided into seven sections:

Section I—Basics on corrosion prevention, monitoring and water-treating. Includes topics on stopping stress corrosion-cracking, preventing hydrogen embrittlement, performing acoustic-emission testing, and controlling biofouling in cooling water.

Section II—Materials selection and identification. Tells how to identify the various metals and alloys found in the typical chemical-process-industries (CPI) plant, and offers tips on picking the best ones for a specific use.

Section III—Paints and coatings. Details the various formulations available for the CPI, when to use them, how to inspect them, and more.

Section IV—Materials to resist chlorides and chlorine. Includes high-performance stainless steels, alloys for desalting, and alloys to resist chlorine.

Section V—Metals and alloys. Covers wear and corrosion, high-temperature effects, steels, and refractory metals and alloys.

Section VI—Fiberglass-reinforced plastics and other polymers. Includes FRP, plastic pumps and piping, and, in general, how to select plastics.

Section VII—Refractories, insulation and ceramics. Details selection, installation and failure analysis.

These seven sections contain a wealth of practical information that design, project, process and research engineers can use to eliminate materials failures. Numerous charts, graphs and guidelines are presented to simplify the often-complex task of materials selection. This book offers expert advice and practical solutions—information that will remain current for years to come.

The
Chemical Engineering
Guide to Corrosion

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Stop stress-corrosion cracking

A network of branched cracks in equipment or piping indicates the presence of this type of corrosion. Preventing it requires selection of the proper metal or alloy.

James L. Gossett, Fisher Controls International, Inc.

□ The wrong combination of environment, material, and minimum tensile strength will produce stress-corrosion cracking (SCC) in any metal or alloy: steel, stainless steel, nickel-based alloys, aluminum, titanium—even gold.

Many of these failures occur only under the most severe laboratory conditions and in the past were usually not encountered in the field. However, such conditions now are found commercially with greater frequency as chemical-processing, oil-refining and power plants are using higher pressures and temperatures to increase efficiencies. The table lists common environments known to cause SCC.

Knowing how stress-corrosion cracking occurs and how to avoid it will help you to select equipment and piping that will not crack in process and utility applications.

Identifying SCC

SCC is a progressive type of failure that produces cracking at stress levels that are well below those of a material's tensile strength. The break or fracture appears brittle, with no localized yielding, plastic deformation or

elongation. SCC has a characteristic appearance, which in many cases makes it easy to identify (see Fig. 1). Rather than a single crack, a whole network of fine, feathery, branched cracks will form (see Fig. 2).

Severe general corrosion will not be found where SCC develops. The rate of general attack will always be quite low. If the rate were high, metal would be removed faster than a crack could penetrate the material. Thus, a crack would have no chance to begin and grow.

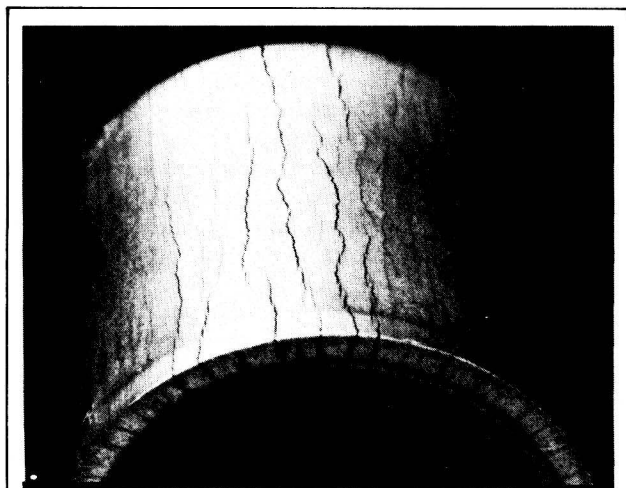
Pitting is frequently seen, and will often serve as a stress concentrator to initiate cracking. One or more cracks will grow from the pit, eventually leading to failure.

The oldest known form of SCC is "season cracking" of brass sleigh bells and cartridge cases. Shortly after the use of brass cartridges became common in the mid-1800s, cracking was often noted. The shells always cracked on the crimped end, where residual stresses were highest, and usually during the rainy season when shells were stored in barns. Thus, the name season cracking.

The three required elements of SCC are all found here. The brass used for the cartridge is a susceptible material. Crimping deforms the brass, and creates a stress above the minimum level for SCC. Finally, the barnyard provides the environment. Decaying manure and other organic material produce ammonia, which is known to stress-crack brass. Moisture is required to absorb the ammonia.

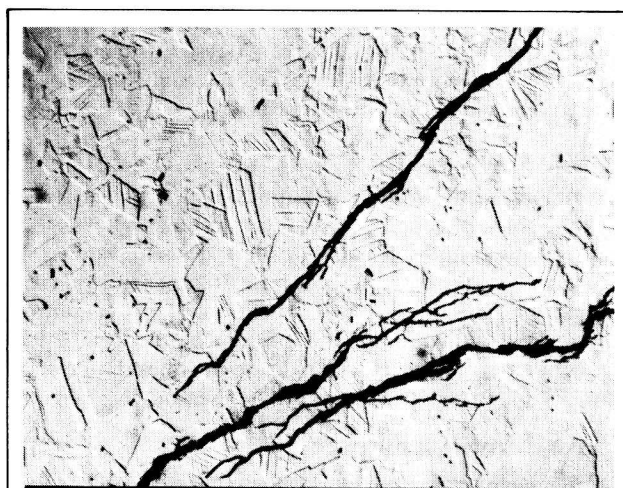
Environment and materials

A typical stress-cracking environment is an aqueous solution containing certain ions. A minimum ion concen-



A typical network of branched cracks on a U-bend sample of Type 316 stainless steel

Fig. 1



Photomicrograph of Type 316 shows multiple lacy, branched cracks (magnified 440 ×)

Fig. 2

tration is required to produce SCC. As the concentration increases, the environment becomes more severe, reducing the time to failure. Although the minimum ionic concentration may not be present throughout the solution, SCC may still develop, however. The reason for this is that ions can collect in crevices and pits, concentrating to very high levels. Concentrations of 10, 100, or even 1,000 times the overall average can easily develop.

Ion concentration is a particular problem with Type 316 stainless steel in dilute chloride solutions. Solutions with just 10-100-ppm chlorides can pit Type 316. The concentration in the pits will rise to the 1,000-10,000-ppm range required for chloride SCC. Thus, one must be conservative in selecting materials for such environments.

Temperature also is a factor. In general, the likelihood of SCC increases with increasing temperature. A minimum threshold temperature exists for most systems, below which SCC is rare. This holds for most types of SCC, except for hydrogen embrittlement, which is most severe at ambient temperatures.

Almost all common metals and alloys are susceptible to SCC. A material's susceptibility is dependent upon various metallurgical conditions, including cold-work, residual stresses, machining stresses, heat-treating, hardness and strength level. At higher hardness levels, failure occurs extremely fast. As the level drops, the time to failure becomes longer and longer, until a level of immunity is reached. This immune level is about Rockwell 22 for carbon steel, alloy steel, and the 400 series stainless steels, in several environments, including sour gas or H₂S.

Stress level

Surface tensile stresses are the final requirement for SCC. These stresses can be caused by cyclic loads, applied tensile loads, or residual stresses from the original forming operations (i.e., heat treatment, casting or welding). A threshold stress level exists below which SCC will not occur. For different materials, this threshold may vary anywhere from 10 to 100% of a material's yield strength. SCC of Type 316 has occurred where the stress was from bending a 1/4-in.-thick plate to a 4-ft radius.

Although it is seldom practical, design stresses can be made to follow these threshold levels in special cases. This is risky, however, as some stresses, such as residual ones, may exceed expected levels. Undetected internal defects—inclusions, porous areas or shrinkage—act as stress risers and produces unexpectedly high stress levels. Let us look at the basic forms of SCC.

Season cracking

Ammonia and amine compounds will produce season cracking of all copper, brass and bronze alloys. The required stress and ion-concentration levels are low.

Season cracking can occur at temperatures from ambient on up. The use of copper in systems containing any concentration of ammonia is not recommended. Alloying copper with nickel, such as cupro-nickel alloys or Monel* alloys produces immunity to season cracking.

Caustic embrittlement

Caustic embrittlement is generally encountered in boilers or steam systems where sodium or calcium scales form

*Monel (and Inconel) are registered trademarks of Huntington Alloys, Inc.

These environments are known to cause stress-corrosion cracking in certain alloys and metals

Alloy/metal	Environment
Aluminum-base	Chlorides Humid industrial atmospheres
Copper-base	Ammonium ions Amines
Gold	Potassium permanganate
High-strength stainless and alloy steels	Hydrogen sulfide Chlorides Humid industrial atmospheres
Low-alloy steels	Boiling, concentrated hydroxides Boiling, concentrated nitrates
Nickel-base	Hot, concentrated hydroxides Hydrofluoric acid vapors
Stainless—300 series	Hot chlorides Boiling, concentrated hydroxides
Stainless—400 series	Hydrogen sulfide Chlorides Reactor cooling-water
Titanium-base	Chlorides Methyl alcohol Solid chlorides above 550°F

on heated surfaces. The susceptibility of a welded steel structure to SCC is a well-defined function of sodium hydroxide concentration and temperature. As-welded steel is acceptable at all NaOH concentrations below 120°F, and at low concentrations to 180°F. Stress-relieving carbon steel will extend the service range another 30-70°F. The 300 series stainless steels resist caustic embrittlement to high temperatures at low NaOH concentrations. Nickel 200 and Inconel 600 alloys are the best for caustics.

Chloride SCC

Chloride stress-corrosion cracking is the most widely encountered and most extensively studied form of SCC. Much is still unknown, however, about its mechanism. One theory says that hydrogen, generated by the corrosion process, diffuses into the base metal in the atomic form and embrittles the lattice structure.

A second, more widely accepted theory proposes an electrochemical mechanism. Stainless steels are covered with a protective oxide film. The chloride ions rupture the film at weak spots, resulting in anodic (bare) and cathodic (film-covered) sites. The galvanic cell produces accelerated attack at the anodic sites, which when combined with tensile stresses produces cracking.

The minimum stress level required for chloride SCC for 300 series stainless is extremely low. Most of the commonly used fabrication techniques (welding, cold-drawing, rolling, bending or crimping) will produce residual stress exceeding the minimum value. Annealing to relieve the residual stresses is seldom effective. Heating to 1,000-1,200°F is required to stress-relieve, within a reasonable time period. Heating in this temperature range, however, severely reduces corrosion resistance.

This is because chromium carbides precipitate in the grain boundaries, producing a "sensitized" structure, which is very undesirable in most corrosive environments. Heating to 1,700-1,900°F prevents sensitization, but may cause other problems. The likelihood of warpage is

greatly increased, and new residual stresses may result if the part is cooled too fast.

Alloys to use

A minimum solution temperature of 140°F is usually required for chloride SCC of the 300 series. As the temperature increases above 140°F, the time to failure will decrease. An extreme example of this is a boiling solution on a heated surface. Very severe extensive cracking can develop in hours. A surface concentration of only 1,000 ppm of chloride ions is all that is required for SCC of the 300 series. Most natural waters contain chlorides of at least such levels.

For all practical purposes, all the 300 series stainless steels have the same susceptibility to SCC. The corrosion resistance does improve, however, starting from 302 and 304 and going to 316 to 317. However, the improvement is so small that a stress-cracked 304 part should never be replaced with a 316 one.

Carpenter 20 CB-3* and Incoloy† 825 specialty stainless steels have a higher alloy content than does 316, and both resist chloride SCC. These two are highly economical SCC-resistant alloys. Although both can stress-crack in extremely severe laboratory tests, experience has found them to be immune in field applications.

The Inconel and Monel alloys and titanium are immune to chloride SCC. They are typically used where additional general corrosion resistance is required.

E-Brite‡ 26-1 and 29-4 alloys are relatively new, improved versions of the 400 series stainless steels, such as 410. All hardened E-Brite alloys readily resist cracking. The E-Brites are only slightly more expensive than Type 316.

Sulfide stress-cracking

Hydrocarbon streams are termed "sour" when they contain hydrogen sulfide. Careful material selection is required to prevent sulfide stress-cracking. NACE Standard MR-01-73, Sulfide Stress Cracking Resistance Material for Oil Field Equipment, is a widely accepted guide for sour service, and has even been adopted as law in some states. The characteristics of sulfide SCC and the methods used to prevent it are similar to those for hydrogen embrittlement. The ideas discussed here can be applied to both situations, and hydrogen embrittlement will not be discussed separately.

As little as 750 ppm H₂S in 65-psia methane can cause sulfide stress-cracking. It is most severe in the 20-120°F range, and is almost never seen below 20°F. Above 120°F, stress cracking may still occur, although it will probably be chloride SCC, not sulfide stress-cracking. Most deep sour wells contain chlorides in addition to H₂S. Therefore, materials must be carefully selected.

Resistant alloys

Carbon and alloy steels will resist sulfide SCC provided their hardness is less than Rockwell 22. Post-weld heat treatment (PWHT) is generally recommended. These same requirements apply to cast steels such as types WCB and LCB. Although the base metal may be softer than Rockwell 22, "hard spots" are nearly always present in the

* Carpenter 20 CB-3 is a registered trademark of Carpenter Technology Corp.

† Incoloy is a registered trademark of Huntington Alloys, Inc.

‡ E-Brite is a registered tradename of Allegheny Ludlum Steel Corp.

weld heat-affected zone. PWHT will eliminate such spots.

The restrictions for Type 410 are similar to restrictions on the wrought and cast carbon steels, except that the maximum hardness allowed is Rockwell 25. The composition of Type 416 is the same as that of 410, except for the addition of sulfur to produce free-machining characteristics. This alloy is not, however, acceptable for sour service. As a matter of fact, no free-machining alloys are acceptable.

Annealed 304, 316 and 317 are three acceptable austenitic stainless steels. Components made from these materials must be free of cold-work and be softer than Rockwell 22. Standard, cold-worked 316 parts should not be used unless they have been annealed.

Some parts, particularly noise- and cavitation-reducing trim in valves, are made of 17-4PH (precipitation-hardening) stainless steel. When heat-treated in H900 condition, 17-4PH is quite brittle and extremely susceptible to stress-corrosion cracking. For H₂S service, the NACE specification requires that one use a double H1150 heat treatment to achieve maximum hardness of Rockwell 32. The double H1150 should also be considered for other corrosive services to prevent some other form of SCC where H₂S is not present. If the double treatment cannot be used, H1075, H1100, or H1150 (single) should be considered. These treatments reduce hardness, strength, wear, galling, cavitation and erosion resistance. If a reduction in these properties is unacceptable, use other materials.

Two other high-strength stainless steels acceptable for sour service are A-286 and S20190 (this is the standard designation for Nitronic§ 50 and Carpenter 22Cr-13Ni-5Mn alloys). A-286 is a precipitation-hardening alloy with excellent resistance to SCC and general corrosion.

S20190 in the high-strength condition has recently been approved by NACE for sour service. The maximum allowable hardness is Rockwell 35. Where the choice exists, S20190 should be selected over 17-4 PH for even mildly corrosive or sour applications.

The various nickel-based alloys are highly resistant to most forms of stress-corrosion cracking. This makes them very attractive engineering alloys, but they are more expensive than the stainless steels. Monel, Monel K-500, Inconel 600, 625, 718, and X-750 and Hastelloy|| C and B alloys are used most commonly. Standard MR-01-75 limits all these alloys to Rockwell 35 maximum.

§ Nitronic is a registered trademark of Armco Steel Corp.

|| Hastelloy is a registered trademark of Stellite Div., Cabot Corp.

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How to prevent stress-corrosion cracking in stainless steels—I

Stress-corrosion cracking, or fear of it, is a major factor limiting the use of stainless steels in refineries and chemical plants today. However, it is not inevitable; it can be delayed, even eliminated, in many cases.

Dale R. McIntyre, Battelle Memorial Institute

□ Stainless steels as a class offer the chemical engineer many attractive features: good corrosion resistance, weldability, fabricability and reasonable cost. However, any engineer hoping to take advantage of these benefits must consider the possibility of stress-corrosion cracking.

Stress-corrosion cracking (SCC) is an interaction between tensile stress and corrosion, which results in localized cracking. The cracking can take place at very low stresses and in environments where general corrosion, as measured by reduction in wall thickness, is negligible.

In austenitic-stainless-steel piping and vessels, SCC usually results in leakage, not catastrophic failure. However, severe strength loss and catastrophic failure are possible in extreme cases. Fig. 1 presents a photograph of a 6-in., Schedule 5, Type 304 stainless-steel transfer line that was inadvertently left half-full of brackish hydrotest water with the steam-tracing on. After one year, a 150-psi hydrotest caused a jagged 2-ft rupture due to the extensive



The strength of this Type 304 stainless-steel pipe was reduced 93% by SCC

Fig. 1

stress-corrosion cracking in this line. Normal burst pressure of 6-in., Schedule 5, Type 304 stainless-steel pipe is 2,130 psi, so its strength was reduced 93% by SCC.

Stress-cracking agents in process streams are not the only cause of SCC; many failures take place due to traces of SCC agents in the air. Fig. 2 shows a Type 304 stainless-steel heat-exchanger flange so badly weakened by *external* SCC, from the breakdown of polyvinyl chloride (PVC) dust in the air, that pieces could be broken off by hand.

Conditions that cause SCC

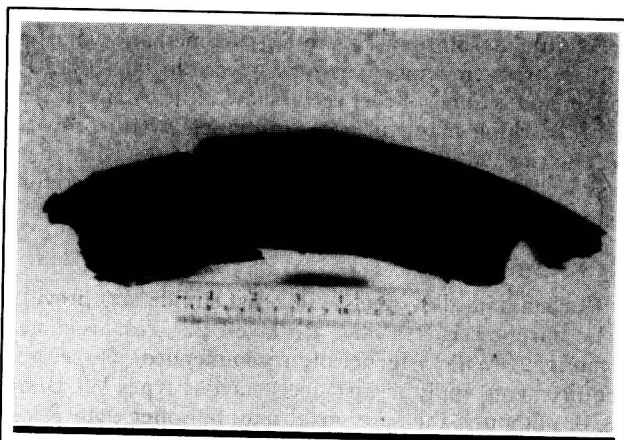
SCC of stainless steels results from a combination of three conditions:

- A susceptible alloy-environment combination.
- Tensile stress.
- Elevated temperatures.

"Stainless steel" is a rather loose term denoting all iron-base, low-carbon alloys having a chromium content in excess of 11%. Since stainless steels vary widely in strength, structure and composition, it is not surprising that they also vary widely in resistance to SCC. Table I lists a number of environments in which the stainless steels are known to crack. However, Table 1 is meant as a guide only; stress-corrosion cracking is not inevitable, even in solutions in which a given stainless is listed as being nonresistant.

Environments that contain stress-cracking agents may be regarded as of three types:

- Process streams having high bulk concentrations of a



Type 304 stainless-steel heat-exchanger flange weakened by SCC due to PVC dust

Fig. 2

Aqueous environments that can cause SCC in stainless steels

Table I

Material	Class	Environment																Ultra-pure H ₂ O + O ₂	Seawater
		Cl ⁻ , acid	Cl ⁻ , neutral	Cl ⁻ , oxidizing	Br ⁻	I ⁻	OH ⁻	F ⁻	S ⁼	S ⁼ /Cl ⁻	S ₄ O ₆ ⁼	SO ₃ ⁼	SO ₄ ⁼	CrO ₄ ⁼	NO ₃ ⁻	NH ₃			
405	Ferritic	1					1		4					1	5	1	1	X	
18-2		4	1	4			3		1	1						1		X	
26-1		4	1	4			4		2				5	1	1	1		X	
26-1S		4	1	4			4		2				5	1	1	1		X	
29-4		1	1	1			4		2					1	1	1		4	
430			1						1	1				1	1	1		X	
434			1							3									
431	Martensitic, quenched and tempered or precipitation-hardened	5	5	5			4	2	5				2	1	1	1		X	
410		5	2		5	5	2	5	5	5				1	2	1	2	X	
CA-6NM			5						5	2								X	
440 A, B, C		5	5	5					5									X	
PH15-7Mo		5	4				1	5					5	1	1	1		X	
17-4PH		5	4				1	5	5				5	1	1	1		X	
PH13-8Mo		5	4					5										X	
17-7PH		5	5				1	5										X	
Custom 450		4	1	4			4	2	2	2			2	1	1	1		X	
Custom 455		4	1	4			4	2	2				2	1	1	1		X	
202	Austenitic	5	5	5		1	4	1	2		3	3	1	1	1	1		X	
216		5	5	5		1	4	1	2		3	3	1	1	1	1		X	
216L		5	5	5		1	4	1	2		3, 4	3, 4	1	1	1	1		X	
Nitronic 50		5	4	5		1	4	1	2		3	3	4	1	1	1	1	4	
Nitronic 60		5	5	5		1	4	1	2		3	3	1	1	1	1		X	
304		5	5	5		1	4		2	5	3	3	4	1	1	1	3	X	
304L		5	5	5		1	4	1	2	5	3, 4	3, 4	4	1	1	1	3, 4	X	
309S		5	5	5		1	4	1	2		3	3	1	1	1	1	3	X	
310S		5	5	5		1	4	1	2		3	3	1	1	1	1	3	X	
316		5	5	5	4	1	4	1	2	5	3	3	1	1	1	1	3	X	
316L		5	5	5		4		2		3, 4	3, 4	1	1	1	1	1	3, 4	X	
317		5	5	5		1	4	1	2		3	3	1	1	1	1	3	X	
317L		5	5	5		1	4	1	2		3, 4	3, 4	1	1	1	1	3	X	
321		5	5	5		1	4	1	2	5	1	1	1	1	1	1	1	X	
347		5	5	5		1	4	1	2	5	1	1	4	1	1	1	1	X	
329	Duplex	4	5	5		2	4	2				1	1	1	1		X		
3RE60		4	1	5			3		4	4		1	1	1	1	3	4		
18-18-2		4	4	5		1	4	1				1	1	1	1		X		

Code: 1 Resistant
 2 Resistant unless cold-worked or hardened
 3 Resistant unless sensitized
 4 Resistant except at high temperatures and concentrations
 5 Nonresistant
 X Not recommended for this environment

Portions of this table have been taken from Ref. 7.

stress-cracking agent (such as a chloride or sulfide).

■ Process streams having low levels of SCC agents that concentrate at leaks, under deposits, and so on.

■ External atmospheric conditions that contain low levels of an SCC agent.

Without doubt, the most common stress-cracking agent is the aqueous chloride ion. (SCC is an electrochemical process, and water is necessary to allow electron flow; completely dry chloride compounds are not normally cracking agents.) Common in brackish river water, seawater and coastal atmospheres, the chloride ion can cause SCC of austenitic stainless steels even at extremely low concentrations. Failures have been reported in steam condensate having as little as 0.5 ppm chlorides. Such low levels are not normally dangerous to stainless. However, in spots where evaporation and concentration raise the local level of chloride—such as crevices, deposits and liquid-vapor interfaces—cracking can still take place. Under these conditions, the only safe level of chlorides is zero.

Caustic environments may also crack stainless steels, and are perhaps the second most common cause of unexpected SCC failures. The austenitic stainless steels find many uses in such environments at temperatures below 150°C. Above that temperature, however, cracking can take place. Many high-pressure steam systems have low levels of caustic present that may concentrate at flange leaks, stainless valve stems, etc. and cause cracking.

The hardenable stainless steels, whether quenched and tempered or precipitation-hardened, encounter their worst problems in environments that involve exposure to ionic hydrogen. Stress-corrosion cracking takes place in these alloys via a hydrogen-embrittlement mechanism. As a result, their serviceability in corrosive environments depends on the generation and absorption of ionic hydrogen. Hardenable stainless steels crack most readily in environments containing ions, such as sulfides and arsenic, that "poison" the hydrogen recombination reaction. Coupling a hardenable stainless steel to a less-noble material, such that the stainless becomes the cathode in an electrolytic cell, frequently results in rapid stress-corrosion cracking of the stainless.

Tensile stresses are necessary for the propagation of stress-corrosion cracks. However, these stresses need not be applied ones; residual tensile stresses from forming, welding and heat-treating have the same effect. This is important to remember in pressure vessels and piping. Applied stresses are usually quite low, but welding and fabrication stresses are often at or beyond the yield point.

Stress-corrosion cracks usually require a certain amount of initiation time before they appear, even if all conditions required for cracking are present. In austenitic stainless steels, initiation time is often controlled by the pitting tendency, since cracks usually propagate from pits. Consequently, molybdenum-bearing alloys such as 316 and 317 will show longer initiation times than alloys such as 304.

Stress level plays an important role in the initiation time for SCC; the higher the stress, the shorter the initiation time. Hardenable stainless steels often exhibit a minimum critical-stress intensity, K_{ISCC} , below which cracks will not propagate (see Table II). Parts designed with stresses and geometries such that K_{ISCC} is not exceeded should not fail

Critical stress intensities for some hardenable stainless steels

Table II

Material	Heat-treat condition	Critical stress intensity, ksi $\sqrt{\text{in.}}$		
		Air	Seacoast	3.5 NaCl %
15-5PH	H900	71.8	35.9	32.3
	H1150	75.7	>72.0	>72.0
AM355	SCT850	36.6	>18.3	5.5
	SCT1000	70.0	>35.0	28.0
431	TS = 125 ksi	75.7	>37.8	43.0
	TS = 200 ksi	79.2	<39.6	11.9
PH13-8Mo	H950	62.6	>31.3	>45.9
	H1050	87.8	>43.9	>65.8
PH15-7Mo	RH950	30.6	15.3	10.1
	RH1050	40.7	20.1	12.1
17-7PH	RH1050	47.0	11.7	9.4

H900 - Solution annealed and precipitation-hardened at 900 °F; RH - Solution annealed, refrigerated and precipitation-hardened; SCT - Sub-zero cooling transformation; TS - Hardened to this tensile strength. Data from Ref [10]. ksi = 1,000 psi.

Effectiveness of SCC prevention methods

Table III

Prevention method	Ferritic	Austenitic	Martensitic	Duplex
Materials selection	1,2,3	1,2,3	1,2,3	1,2,3
Barrier coatings	3	3	4	3
Eliminating the stress-cracking agent	1,2	1,2	1,2	1,2
Adding inhibitors	NA	2	NA	NA
Thermal stress relief	4	4	NE	4
Heat treatment	*	*	1,3	NE
Shot peening	1,2	1,2	4	1,2
Cathodic protection	X	1, not 2	X	1, not 2
Lowering the temperature	2,3	2,3	NE	2,3
Design techniques	2	2	2	2

Code:

- 1 Eliminates SCC in process streams having high SCC-agent concentration.
 - 2 Eliminates SCC in process streams having concentration effects (wetting and drying).
 - 3 Eliminates external cracking from atmospheric SCC agents.
 - 4 Will delay the onset of SCC.
- NE Not effective for these alloys.
X Not effective, may accelerate cracking.
NA No industrial application reported.
* Effective only for intergranular SCC of sensitized material.

in service. Austenitic stainless steels also exhibit the K_{ISCC} behavior, but K_{ISCC} is so low in many chloride solutions (~6 ksi $\sqrt{\text{in.}}$) that it is impractical to design equipment made out of these steels for such conditions [2].

Temperature is the third element normally required to produce stress-corrosion cracking. Each alloy/environment system usually has a temperature range in which cracking occurs. Austenitic stainless steels, for example, seldom crack in chlorides below about 50°C, and cracking in caustic solutions is rare below 150°C.

Prevention of SCC

Knowledge of the necessary conditions for SCC suggests techniques for prevention. These are:

- Changing the alloy/environment combination.
- Eliminating tensile stresses.
- Cathodic protection.
- Lowering the temperature.
- Design techniques.

These options will be outlined more fully in the sections below. Table III presents a summary of the different methods for SCC prevention, and their observed effectiveness on different environments and alloy classes.

Changing the alloy/environment

Changing the alloy/environment combination can take the following forms: materials selection; barrier coatings; eliminating the stress-cracking agent; adding inhibitors.

Materials selection, which simply means the use of materials resistant to the environment in question, is without doubt the most effective method for controlling SCC. However, it is not always the most economical. Materials-selection options include: resistant alloys or nonmetals; and composite construction with bimetallic tubing or plate.

As Table I shows, several of the "lean alloy" ferritics such as 405, 409 and 430 are not susceptible to chloride SCC. However, these alloys should be used with caution since they pit readily in chloride-bearing streams. A leak from a pit is just as troublesome as a leak from a crack.

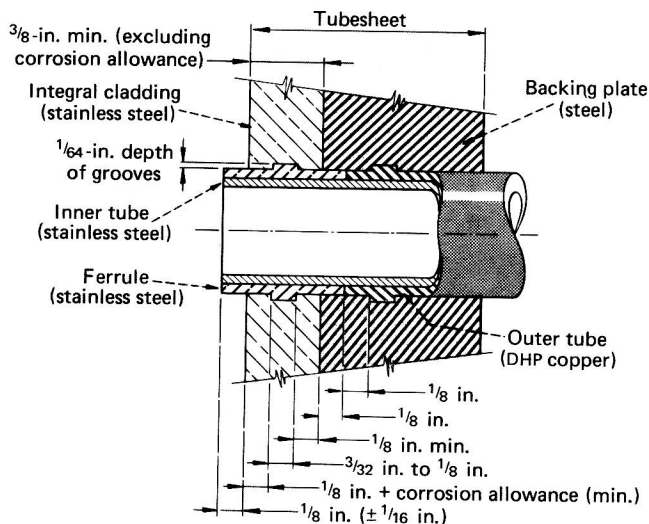
Several of the new low-interstitial ferritic and austenitic-ferritic alloys are serviceable in areas where the regular 300 and 400 stainlesses are not. In heat-exchanger tubing especially, 18-2, 26-1 and 3RE60 stainless steels have proven their worth in many hot chloride-bearing waters and process streams that quickly crack 304 and 316. For severe applications, titanium or the high-nickel alloys such as Hastelloy* C or G often are used.

As with any corrosion-control technique, the use of specialty stainless steels or more-exotic alloys must be justified economically, since these materials impose penalties of higher cost, more-difficult fabrication and longer delivery times. Ref. 3 outlines methods for calculating annual costs based on anticipated life.

Bimetallic tubes can prevent water-side SCC in heat exchangers [4]. Such tubes require ferrules at the tube-sheet to effect a roll joint (Fig. 3). Bimetallic tubes with deoxidized high-residual-phosphorus (DHP) copper lightly drawn over 304 stainless steel currently have lower prices and better delivery times than many of the SCC-resistant specialty stainless steels [5].

For vessels, bimetallic plate, with a thin layer of

*Hastelloy is a trademark of Cabot Corp., Stellite Div.



Typical joint for duplex tube and tubesheet in heat exchanger

Fig. 3

stainless steel roll-bonded or explosion-clad to a carbon-steel backing plate, is sometimes used in environments that would stress-crack solid stainless. Even if the stainless cladding should crack, SCC will stop at the steel, and SCC cracks are usually too tight to allow significant amounts of corrodent to attack the steel. In thick sections, clad plate has the additional advantage of being about 25% cheaper than solid stainless. This approach should not be used in environments that stress-crack or severely corrode steel.

Materials selection for SCC resistance does not always mean more-expensive alloys. For instance austenitic-stainless-steel valve-bonnet bolts are particularly prone to SCC because bonnet leaks or atmospheric chlorides can concentrate under the bolt heads. Using B7 steel bolts coated with Xylan* resin over a zinc primer will eliminate this problem. Compared with stainless steel, the coated bolts are more resistant to SCC, as well as cheaper, stronger and less prone to galling.

Barrier coatings will prevent SCC in mild environments. Such coatings are often used to preclude external SCC under insulation, a widespread problem in coastal areas. Paint simply prevents chlorides from coming in contact with the stainless surface. For most coastal environments, a modified silicone paint is adequate [6]. In more-rigorous industrial environments, epoxy-phenolic coatings have been used. Insulated lines or vessels should be completely painted; uninsulated equipment need be painted only under slip-on flanges.

No paint system ever goes on without defects, so there is a possibility of SCC at pinholes and coating flaws. However, the incidence of external SCC can be greatly reduced with this method.

Eliminating the stress-cracking agent (which is often an unwanted impurity in a process stream) may not affect the process or the product, but will eliminate SCC.

Example—A 304L stainless-steel column stripped

*Xylan is a trademark of Whitford Corp.

organic chlorides from an 80°C solvent containing 0.2% water. After 18 mo in service, wet chloride-bearing process residues had accumulated in the column and the trays, causing extensive SCC.

A new 304L column was installed, and the process was revised to remove the water upstream of the column. Chloride-bearing process residues still accumulate, but examination of stressed samples exposed in the column indicates that no further SCC has taken place.

All too often, however, stress-cracking agents cannot be eliminated economically. Chlorides are so widespread that it is virtually impossible to ensure their absence.

In some cases, inhibitors are effective in counteracting stress-cracking agents. In particular, alkaline washes are used to prevent polythionic acid SCC during shutdowns in oil refineries [7]. Laboratory studies have shown that 3% NaNO_3 will prevent stress-corrosion cracking of 304 stainless steel in boiling 42% MgCl_2 , and that 0.005M Na_2CrO_4 will prevent SCC of 304 stainless steel in 20% NaOH [8]. No large-scale industrial application of these inhibitors has been reported.

Oxygen is apparently necessary for the SCC of austenitic stainless steels, and laboratory researchers have observed that mechanical or chemical deaeration will prevent SCC. In the field, however, failures have been reported in chloride-bearing water fully deaerated with an excess of sodium sulfite [9].

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