

CHEMICAL ENGINEERING

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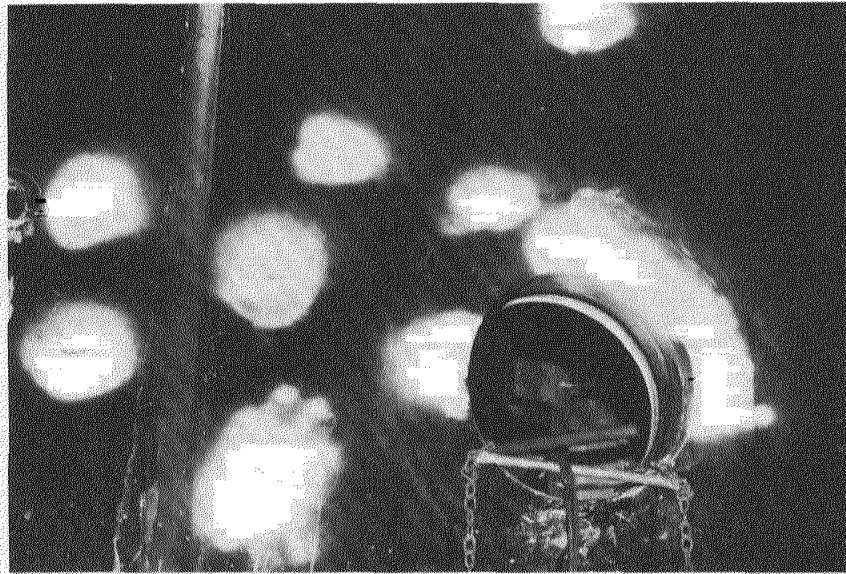
How to prevent stress cracking
in stainless steels I-II
—DALE MCINTYRE

Controlled shotpeening prevents
stress—corrosion cracking
—JAMES DALY

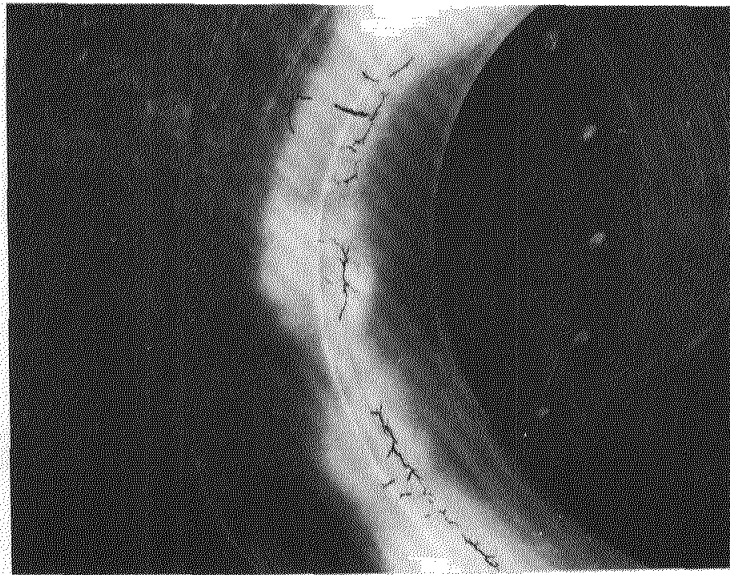
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Compliments of: Metal Improvement Company, Inc.



Interior view of stress corrosion cracking on a type 316L stainless steel ammonia processing tank.



Close-up view of stress corrosion cracking at the heat affected zone of a welded nozzle.

The above photographs were taken in 1976 prior to controlled shotpeening. On site controlled shotpeening was subsequently performed and a recent inspection (Spring 1989) has shown no reoccurrence of stress corrosion cracking in the shotpeened areas.

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

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

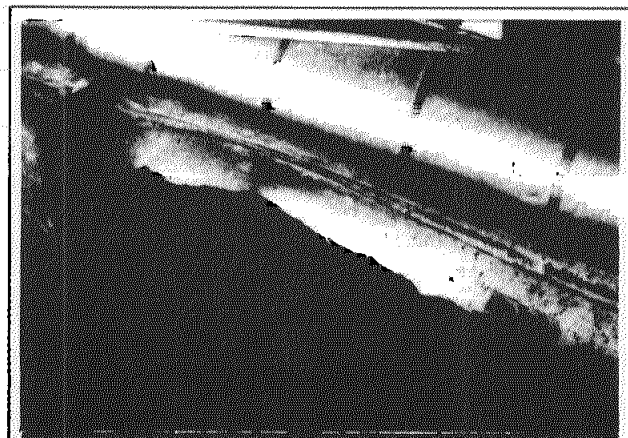
SCC of stainless steels results from a combination of three conditions:

- 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.

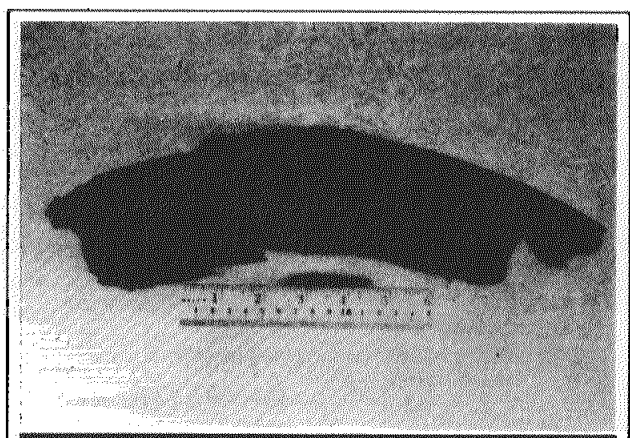
Environments that contain stress-cracking agents may be regarded as of three types:

- Process streams having high bulk concentrations of a



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

Fig. 1



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 ²⁻	S ²⁻ /Cl ⁻	S ₄ O ₆ ⁼	SO ₃ ⁼	SO ₄ ⁼	C ⁻ O 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	1	3	X
304L		5	5	5		1	4	1	2	5	3,4	3,4	4	1	1	1	1	3,4	X
309S		5	5	5		1	4	1	2		3	3	1	1	1	1	1	3	X
310S		5	5	5		1	4	1	2		3	3	1	1	1	1	1	3	X
316		5	5	5	4	1	4	1	2	5	3	3	1	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	1	3	X	
317L	5	5	5		1	4	1	2		3,4	3,4	1	1	1	1	1	3	X	
321	5	5	5		1	4	1	2	5	1	1	1	1	1	1	1	1	X	
347	5	5	5		1	4	1	2	5	1	1	4	1	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. 1.

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.

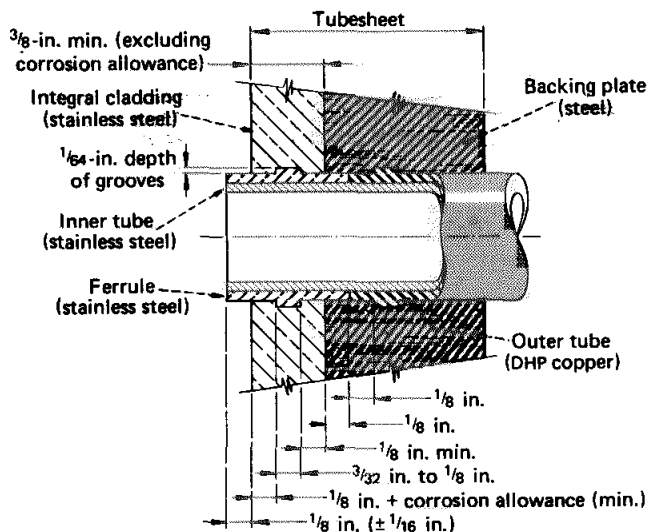
Several of the new low-interstitial ferritic and austenitic-ferritic alloys are serviceable in areas where the regular 300 and 400 stainlesses are not. In heat-exchanger tubing especially, 18-2, 26-1 and 3RE60 stainless steels have proven their worth in many hot chloride-bearing waters and process streams 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% NaNO₃ will prevent stress-corrosion cracking of 304 stainless steel in boiling 42% MgCl₂, and that 0.005M Na₂CrO₄ 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].

(To be concluded in *Chem. Eng.*, May 5, 1980.)

Kenneth J. McNaughton, Editor

References

- Dillon, C. P., Guidelines for Control of Stress-Corrosion Cracking in Nickel-Bearing Stainless Steels and Nickel-Base Alloys, MTI Manual No. 1, June 1979, Materials Technology Institute of the Chemical Process Industries.
- Speidel, M. O., Stress-Corrosion Crack Growth in Austenitic Stainless Steel, *Corrosion* (Houston), Vol. 33, No. 6, June 1977.
- Direct Calculation of Economic Appraisals of Corrosion Control Measures, Standard RP-02-72, Natl. Assn. of Corrosion Engineers, Katy, Texas.
- Ashbaugh, W. G., and Doughty, S. E., Bimetallic Heat Exchanger Tubes Solve Dual Corrosion Problem, *Met. Prog.*, Dec. 1960, pp. 115-132.
- Davison, R. L., Elder, G. B., and Montero, A. J., internal memo, Union Carbide Corp., Nov. 8, 1979.
- Ashbaugh, W. G., External Stress-Corrosion Cracking of Stainless Steel Under Thermal Insulation", *Mater. Prot.*, May 1965, pp. 18-23.
- Protection of Austenitic Stainless Steels in Refineries Against Stress-Corrosion Cracking by Use of Neutralizing Solutions During Shutdown, Standard RP-01-70, Natl. Assn. of Corrosion Engineers, Katy, Texas, 1970.
- Park, Y. S., Agrawal, A. K., and Staehle, R. W., Inhibitive Effect of Oxyanions on the Stress-Corrosion Cracking of Type 304 Stainless Steel in Boiling 20N NaOH solution, *Corrosion* (Houston), Aug. 1979, pp. 333-339.
- Dillon, C. P., Stress-Corrosion Cracking of Austenitic Stainless Steels, internal memo, Union Carbide Corp., Apr. 17, 1961, File No. MF: 760:17.
- Sprowls, D. O., Shumaker, M. B., Walsh, J. D., and Coursen, J. W., Evaluation of Stress-Corrosion Cracking Susceptibility Using Fracture Mechanics Techniques, Alcoa Laboratories, Report on NASA Contract NAS8-21487.

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

Stress-corrosion cracking in stainless steels can be eliminated by removing tensile stresses, providing cathodic protection, lowering the temperature, and using intelligent design techniques.

Dale R. McIntyre, Battelle Memorial Institute*

□ In Part I of this two-part series [1], we looked at conditions that cause stress-corrosion cracking (SCC) and at various ways of changing the alloy-environment combination to prevent it. Here are some other ways of stopping this phenomenon, which is a major factor in limiting the use of stainless steel in the chemical process industries.

Eliminating tensile stresses

This is a very effective method for preventing stress-corrosion cracking. In process vessels and piping, stresses due to internal pressure are usually quite low, typically only 25% of the ultimate tensile strength. Most SCC failures are due to residual stresses from welding and fabrication [2].

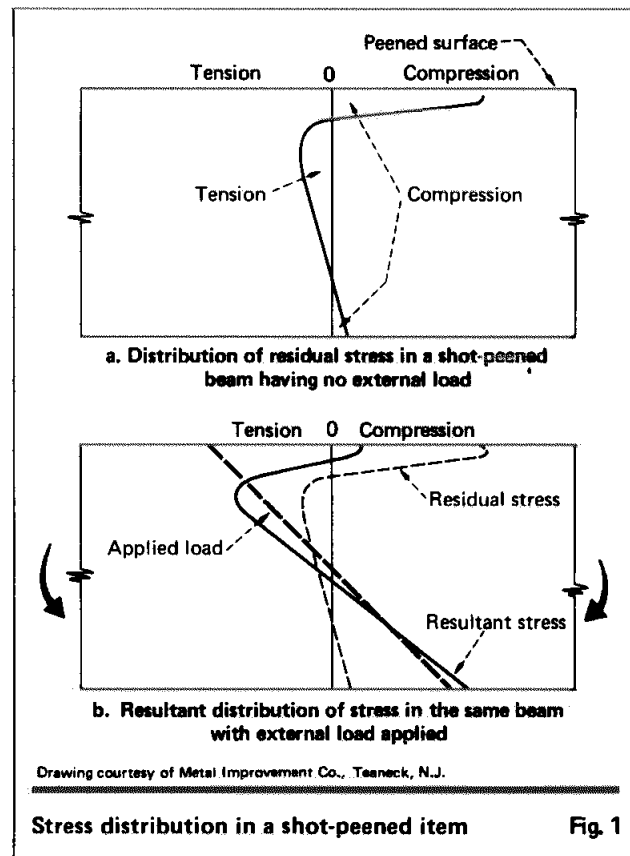
The three most common methods for SCC prevention by eliminating tensile stresses are thermal stress relief, shot peening, and heat treatment.

Thermal stress relief for the 300 series stainless steels should be done above 1,600°F; lower temperatures will not completely eliminate fabrication stresses [3]. Thermal stress relief eliminates only fabrication stresses; obviously, service stresses from fit-up and internal pressure are still present. Still, the lowered stress levels may make the austenitic stainless steels economical by extending the initiation time.

Example—A flash tank handled a 120°C stream of water and organic chlorides. Rolled-in 316L stainless-steel tubes in the reboiler were failing by stress-corrosion cracking every six months. A seal-welded 316L stainless-steel tube bundle was stress-relieved at 1,650°F and installed in the reboiler. This bundle lasted four years before replacement became necessary.

Thermal stress relief will sensitize regular carbon grades of stainless steel, regardless of structure. In some environments, sensitization leads to accelerated intergran-

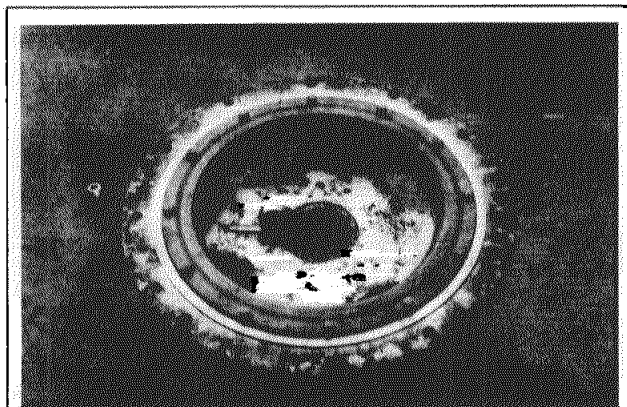
*To meet the author, see *Chem. Eng.*, Apr. 7, p. 112.



ular attack (IGA), so this must be considered whenever stress-relieved equipment is used. However, a moderately high, predictable rate of IGA often is preferable to rapid, unpredictable SCC.

Shot peening is one of the most promising methods for prevention of SCC. During shot peening, the wetted surfaces of the item are cold-worked with steel shot under carefully controlled conditions to produce a thin layer of metal with a net residual compressive stress [4]. Stress-corrosion cracks cannot propagate through compressive stresses; therefore, the SCC problem is eliminated.

Ordinary shot blasting, as used to clean steel surfaces before painting, is *not* equivalent to controlled shot peening and is *not* a reliable SCC prevention method. In controlled shot peening, shot size, shape and velocity and the intensity of cold-work are carefully and continuously monitored. No such controls are used in shot blasting.



Extensive SCC in the head of a 316 stainless-steel centrifuge handling a hot salt slurry

Fig. 2

Done properly, shot peening produces a layer of material about 0.02 in. thick that has residual compressive stresses of yield-point magnitude. Not only are welding stresses cancelled out, but subsequent application of service stresses should still leave the surface with net compressive stresses. This is an important advantage over stress relieving, which may delay but not necessarily eliminate SCC. Theoretically, shot peening should eliminate SCC entirely.

For maximum effectiveness, shot peening should be the last manufacturing operation before the item is placed in service. No welding or torch heating should be performed on an item that has been shot-peened unless the heat-affected area is re-peened after heating. On process vessels, shot peening should be performed after the final hydrostatic test. The deliberately severe hydrotest stresses would reduce the magnitude of compressive stresses on a previously shot-peened surface.

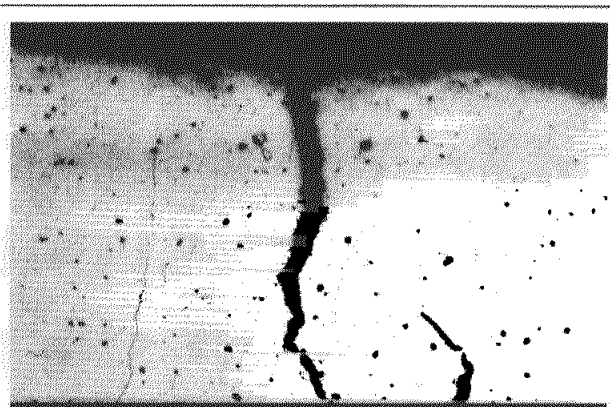
Shot peening an item that is already stress-cracked will *not* retard further cracking and may, in fact, accelerate it. The residual compressive stresses induced on the surface by peening are balanced by subsurface residual tensile stresses of equal magnitude (Fig. 1). Peening an item already cracked may accelerate the crack growth, due to the presence of these added tensile stresses.

To be effective, peening must be done to at least 100% coverage (100% coverage is the time taken to completely cover the entire surface with shot; any additional time is referred to as being in excess of 100% coverage). Some applicators spread fluorescent dye over the surface before peening. After peening, black-light inspection quickly highlights any areas missed.

It must be remembered that the protective layer of compressive stresses is relatively thin (0.02 in. maximum). If pitting or general corrosion proceeds to the point where this layer is penetrated, SCC can then take place.

If the above-mentioned cautions are observed, dramatic savings can be obtained by the judicious use of shot-peened stainless instead of high-alloy equipment.

Example—A Type 316 stainless-steel centrifuge separated solids from a 60°C organic chloride stream. After one year in operation, extensive stress-corrosion cracking had taken place on all the wetted parts (Fig. 2). A replacement centrifuge made out of Hastelloy C, which



Cross-section of 304 stainless-steel check valve cracked by SCC after 3 wk in a 7% NaOH line

Fig. 3

would have been fully resistant to SCC, was estimated at \$450,000. Instead, a new 316 stainless-steel centrifuge was purchased for \$150,000. Shot peening added only \$2,000 to the cost. The shot-peened 316 stainless-steel centrifuge was installed and, when last inspected after 18 mo in service, showed no evidence of SCC.

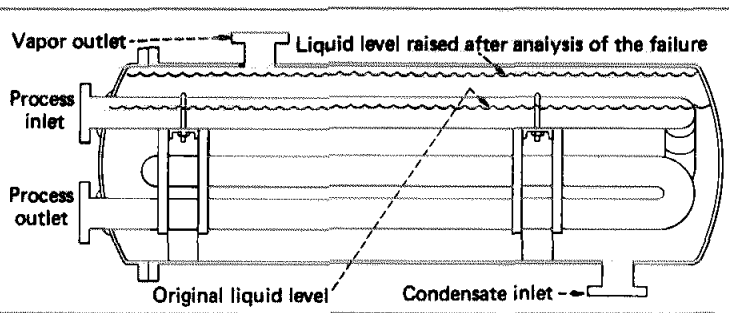
Shot peening has been used successfully on pump shafts, piping and process vessels. Shot-peening service centers have recently been able to shot-peen small-diameter heat-exchanger tubing; the cost makes 304 and 316 competitive with more-expensive specialty stainless steels for brackish-cooling-water service.

Heat treatment: Hardenable stainless steels are usually quenched from high temperatures. Quenching induces internal stresses from thermal contraction and structural changes that are great enough to propagate SCC. These stresses are reduced by tempering. Normally, the higher the temperature, the lower the internal stresses. Therefore, martensitic stainless steels often show marked variations in SCC susceptibility, due to differences in heat treatment. In general, the lower-strength heat treatments show better SCC resistance. For instance, 410 stainless steel shows its best cracking resistance when quenched and tempered to less than Rockwell "C" hardness 22 [5] and the martensitic precipitation-hardened stainlesses show markedly improved SCC resistance in the over-aged conditions [6]. This is unfortunate since a principal reason for using hardenable stainless is the need for high strength.

A solution-annealing heat treatment will prevent intergranular SCC of regular-carbon austenitic stainless steels that have been sensitized by welding. The high solution-annealing temperature (1,850-2,050°F) and the need for a water quench make this method impractical for many field applications. Solution-annealing is not effective in preventing the transgranular SCC normally observed in high-chloride environments.

Cathodic protection

Stress-corrosion cracking normally takes place in a fairly narrow range of potential. As a result, adjusting the potential with cathodic protection (CP) can prevent SCC. The following incident gives an example of cathodic protection on stainless steel that was totally inadvertent but, oddly enough, effective.



316L stainless-steel reactor in which the tubes cracked at the liquid-vapor interface Fig. 4

Example—A feed/tails intercooler cooled a 120°C tubewise organic stream with 50°C scrubber water on the shell. The scrubber water had about 700 ppm chlorides and 40-50 ppm organic acid, and was oxygen-saturated. The intercooler was originally installed with 316 stainless tubes, a 316 tubesheet and a Monel* shell. After four yr in service, an inspection revealed serious corrosion of the shell but, surprisingly, no damage to the 316 stainless tubes. A new shell of 316 stainless was ordered. Within a year, one-third of the tubes were leaking in the U-bends. Examination revealed classical transgranular stress-corrosion. Apparently the Monel shell and the copper ions in solution provided a form of cathodic protection to the tubes. When the Monel was removed, rapid SCC of the stainless resulted.

In general, galvanic coupling of heat-exchanger tubes with a less-noble shell material is not a reliable method for preventing SCC. The complex geometry of a heat-exchanger bundle normally results in some areas being "shadowed," or cut off from current distribution. However, the above example confirms laboratory studies indicating that cathodic protection is a valid option for SCC prevention.

A potential shift of at least 100 mV cathodic is required [7]. This can be accomplished either by impressed currents from a rectifier, or by galvanic coupling to sacrificial anodes of less-noble metals. Zinc, aluminum, lead and magnesium have all been used successfully for cathodic protection of Series 300 stainlesses. Iron is less successful, since the potential shift is not as large.

Cathodic protection should not be used on martensitic or precipitation-hardened stainless steels. Cathodic polarization or coupling to less-noble metals produces hydrogen at the surface of the stainless, which will greatly *accelerate* cracking in stainless having martensitic structure.

Cathodic protection works best for austenitic stainless immersed in neutral or near-neutral chloride solutions. As the pH of the solution becomes more acidic, larger and larger currents are required to produce the needed potential shift. The current demand for strongly acid solutions may make this method impractical [8].

Many SCC failures are due to concentration of low levels of chlorides under deposits, behind flanges or in vapor spaces above a liquid level. In such cases, impressed-current CP or sacrificial anodes would not be effective, since they require electrical continuity to function. In some cases, sacrificial coatings such as zinc or solder have

*Monel is a trademark of International Nickel Co.

been applied. However, the life of many such coatings in chloride-bearing waters is short, and once the coating is consumed, the stainless is left unprotected.

Another concern with sacrificial coatings using lead, aluminum, zinc or cadmium is the relatively low melting points of these active metals. During welding or fire exposure, contact with such liquid metals may cause catastrophic fluxing attack on the stainless (in the case of lead and aluminum) or intergranular cracking (with zinc and cadmium) [9].

Temperature reduction

As stated earlier, stress-corrosion cracking usually takes place above some threshold temperature. Exposure to the same environment below that threshold temperature will not cause cracking.

For austenitic stainless steels in chloride solutions, the threshold temperature is approximately 50°C. In caustic solutions, the threshold temperature is about 150°C. Where process constraints permit, lowering the temperature below threshold can render a stress-cracking environment innocuous.

Lines carrying products with high viscosity or high freezing points must be heat-traced to keep the products fluid. All too often, such lines are steam-traced at temperatures far in excess of those required to keep the products moving. Rapid SCC can result.

Example—A run of 304 stainless steel tubing was installed to carry a 7% NaOH solution to a cooling-water treatment pump. This line was heat-traced to keep the NaOH liquid during the winter. The handiest source of heat was a nearby superheated 200-psi steam header that normally operated at 290°C (550°F). After three weeks in service, the line cracked at several valves, fittings and bends in the tubing (Fig. 3). All the cracks were found to be due to stress-corrosion. 70-psi steam (132°C, or 270°F, which is below the threshold temperatures for cracking) was substituted for the high-temperature steam; after a year, no further failures have been reported.

Whenever possible, electric tracing is preferred to steam tracing, mainly because of the lower temperatures normally employed.

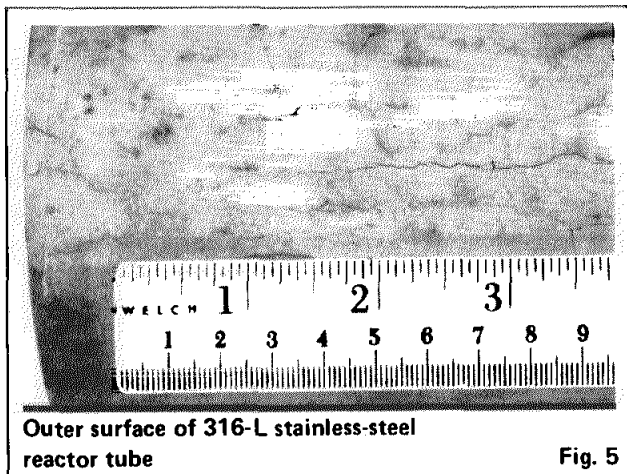
Design practices

A high percentage of SCC failures take place in aqueous streams that have harmlessly low chloride levels in the bulk composition. Stress-corrosion cracking results from local concentration to high levels due to crevices, evaporation, intermittent immersion, and so forth.

Thus, the most fruitful area for improved design is in the avoidance of places where chlorides can concentrate.

Example—A 316-L stainless-steel serpentine reactor used condensate on the shell side to control the reaction temperature at 190°C. By chance, the liquid level was normally maintained in the middle of the top bank of tubes (Fig. 4). Condenser leaks occasionally resulted in organic chlorides being introduced into the unit condensate header in small amounts (the average chloride-ion concentration in the condensate was 13 ppm).

After nine months in service, the reactor began leaking; examination indicated extensive stress-corrosion in the top



row of tubes (Fig. 5 and 6). No tubes below the liquid level were cracked.

Alternate wetting and drying on the partly exposed surface of the top row of tubes resulted in concentration of the low level of chlorides in the condensate to levels high enough to cause SCC. The number of condenser leaks was reduced, thus reducing chloride levels in the condensate. However, it was considered uneconomical to render the condensate completely free of chlorides.

In this case, the problem was solved by simply raising the liquid level in the shell about a foot. This completely covered the top row of tubes and eliminated the vapor space where chlorides could concentrate. To date, two and a half years later, no further SCC failures have occurred.

As stated earlier, the initiation time for SCC is often controlled by the pitting tendency, since cracks usually start at pits. Pitting is aggravated by stagnant conditions and low flow rates. Consequently, designing for high flowrates on stainless equipment (> 3 ft/s in brackish river water) minimizes pitting under deposits and hence minimizes the possibility of SCC.

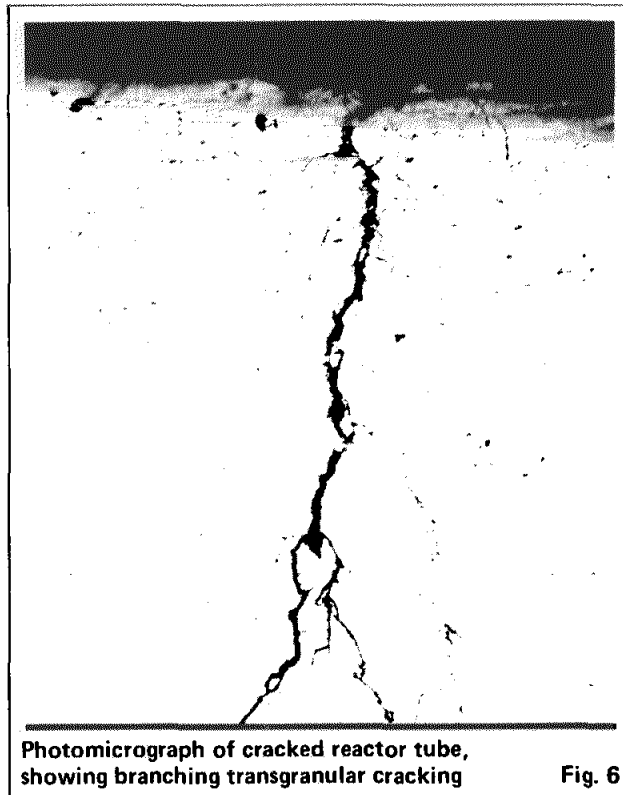
When designing heat exchangers, putting the cooling water on the tube side will often give velocities high enough to prevent pitting and thus minimize stress-corrosion cracking. For instance, 316 stainless steel is not recommended for seawater, yet some successes have been reported using 316-tubed condensers with seawater on the tube side [10]. However, the tubes in these cases were carefully cleaned of all deposits on a weekly or monthly schedule.

Repair-welding stress-cracked vessels

Attempts to weld up the cracks in a stress-corrosion-cracked stainless steel vessel often meet with failure, especially if welding heat is applied directly to the cracks. Thermal stresses and corrodents trapped in the cracks combine to cause the cracks to propagate ahead of the welding arc. Arc-gouging out the cracks, or grinding them out, will also cause the cracks to run ahead of the heated zone, and should therefore be avoided.

A procedure that has been used with some success:

- Clean the vessel wall down to bare metal.
- Define the crack as precisely as possible, using dye penetrant testing.



- Mark out a rectangle enclosing the crack with at least 6 in. of apparently sound metal on all sides.
 - Apply torch heat around the boundary of the rectangle. Any tight, previously unnoticed stress-corrosion cracks will open up under the heat.
 - Dye-check the heated area.
 - If no cracks are observed, proceed by torch-cutting out the marked area and welding in a patch.
 - If new cracks show up in the heated area, however, move back another 6 in. all around and try again.
- If still more cracks appear on the second attempt, SCC is widespread, and weld repair is impractical.

Kenneth J. McNaughton, Editor

References

1. McIntyre, D. R., How to Prevent Stress-Corrosion Cracking in Stainless Steels—I, *Chem. Eng.*, Apr. 7, 1980, pp. 107-112.
2. Izumiya, M., Problems Concerning Stress-Corrosion Cracking of Austenitic Stainless Steel Used in Chemical Plants, *Corrosion* (Houston), Jan. 1979, pp. i, ii.
3. Sangdahl, G. S., "Stress-Relieving of Austenitic Stainless Steel," *Metals Handbook*, 8th ed., Vol. 2, pp. 253-254.
4. Friske, W. H., Shot-Peening to Prevent the Corrosion of Austenitic Stainless Steels, Report No. AI-75-52, Rockwell Intl. Corp., Atomics Intl. Div., Sept. 15, 1975.
5. Burns, D. S., Laboratory Test for Evaluating Alloys for H₂S Service, *Mater. Perform.*, Jan. 1976, pp. 21-28.
6. Armco 17-4PH Precipitation-Hardening Stainless Steel, Armco Steel Corp. Product Bull. S-6C.
7. Mears, R. P., Brown, R. H., and Dix, E. H., A Generalized Theory of Stress-Corrosion of Alloys, Proc., Symp. on Stress-Corrosion Cracking of Metals, ASTM/AIME, 1944, p. 323.
8. Laliberté, L. H., Mueller, W. A., and Sharp, W. B. A., Cathodic Protection of Stainless Steels in Bleach Plant Filtrates: A Laboratory Investigation, presented at *Corrosion/78*, sponsored by the Natl. Assn. of Corrosion Engineers, Mar. 6-10, 1978, Houston, Tex.
9. Sadigh, S., The Effect of Molten Zinc on Some Commercial Alloys, presented at *Corrosion/79*, sponsored by the Natl. Assn. of Corrosion Engineers, Mar. 12-16, 1979, Atlanta, Ga.
10. Deverell, H. E., and Maurer, J. R., Stainless Steels in Sea Water, *Mater. Perform.*, Mar. 1978, pp. 15-19.

Controlled shotpeening prevents stress-corrosion cracking

Peening of a metal surface with fine shot can turn tensile stresses in the metal surface into compressive stresses.

James J. Daly, Metal Improvement Co.

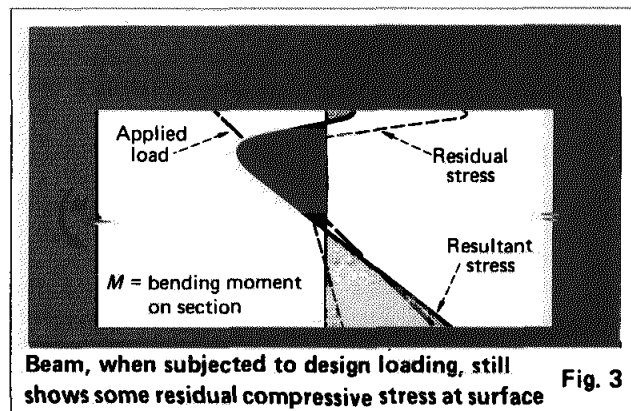
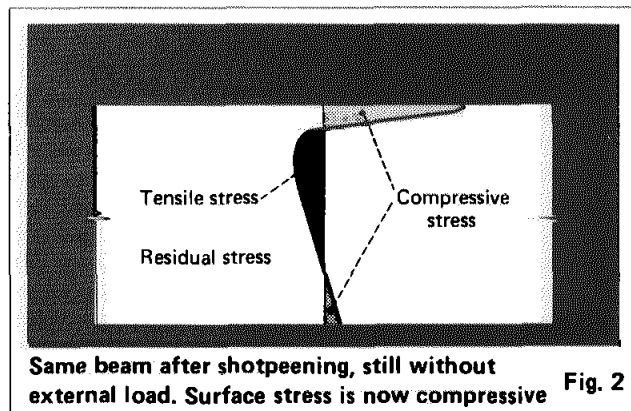
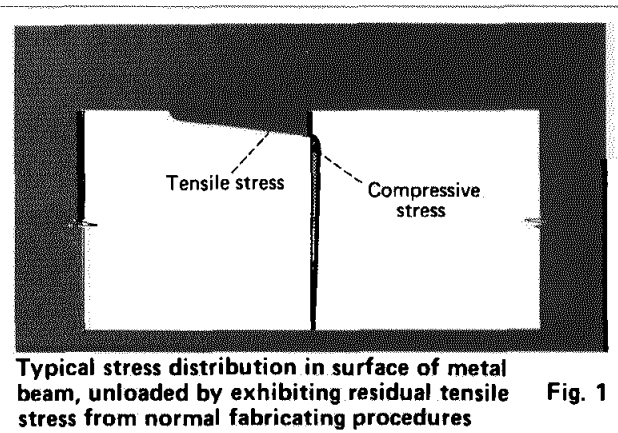
Many corrosion failures of equipment and components can be traced to residual surface *tensile* stresses that cannot, in any practical manner, be quantitatively allowed for in original design.

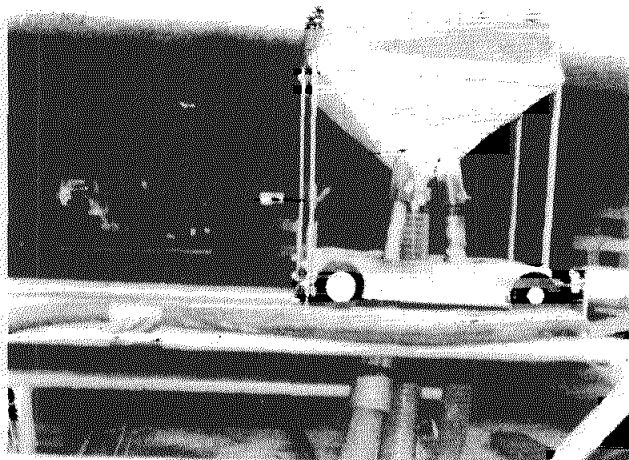
These are stresses induced during manufacture of the equipment, regardless of the metal or alloy, although some materials are less susceptible than others. Welding, drilling, threading, grinding, shrinkfitting, bending, and wrapping without preforming are examples of manufacturing operations that create residual surface tensile stresses. These stresses, in effect, reduce the surface intergranular cohesiveness.

Where corrosion starts

Since corrosion begins at places where the corrosive agent can most readily penetrate the surface (exemplified in pit-type corrosion), the phenomenon of stress-corrosion cracking originates at the grain boundaries of the tensile-stressed surface layer. The cracks propagate inward until failure of the equipment results. The process occurs more readily and rapidly in corrosive atmospheres but is quite evident in typical industrial environments.

Original equipment (or components or replacement parts) in which the inherent, residual, surface tensile stresses have not been eliminated can be subject to corrosion cracking literally from the moment it is manufactured (even before being placed in actual service). Reserve items kept in inventory, for example, will exhibit surface cracking if the heretofore mentioned conditions are present. It is not uncommon that, by the time a new facility's valves, piping, pumps, vessels and towers are hooked up and the process is on stream, stress-corrosion cracking is well underway. Subsequent dynamic stressing of the equipment—subjecting it to weight or pressure and to cyclic loading—increases the total surface stress, and speeds corrosion and premature failure.





Controlled shotpeening of bottom of copper-silicon-alloy sulfuric acid tank Fig. 4

Table II Effect of heat on stress-corrosion resistance of shotpeened type 304 stainless

Specimen*	Heated to, °F	Time held at temp., h	Time to stress-corrosion cracking in 42% aqueous Mg Cl ₂
Unopened	1,000	16	3
Peened	1,000	16	103 NF†
Unpeened	1,050	144	10
Peened	1,050	144	202 NF†

*Standard U-bent specimens
 †NF—No failure—test terminated

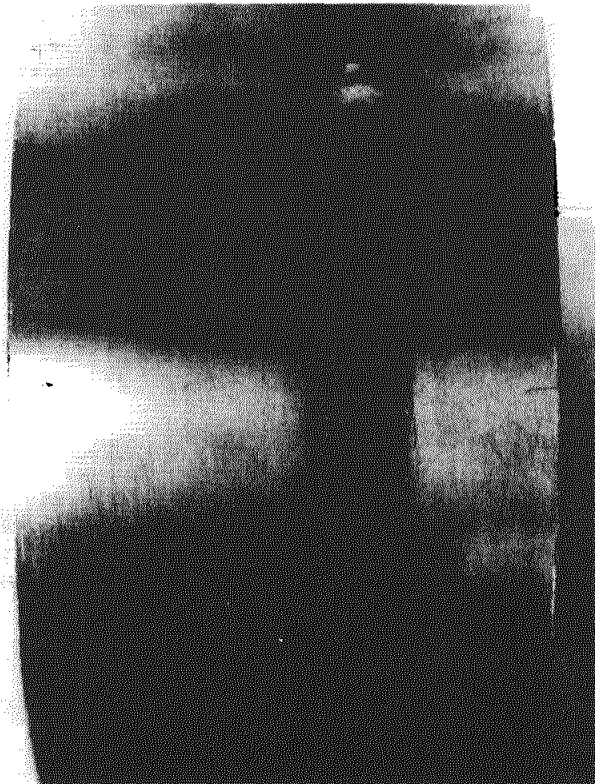
Approaches to the stress-corrosion problem

Since stress-corrosion cracking originates in the tensile-stressed surface layer in contact with a corrosive atmosphere, preventing it involves removal of its prerequisites, and may be accomplished through one or more of the following: (1) redesigning and/or choosing a new material of construction that, by virtue of its constituency and grain structure, is less susceptible to crack propagation; (2) preventing contact between metal and atmosphere through use of an inert, impenetrable coating; (3) converting the residual surface tensile stress to surface compressive stress through controlled shotpeening. Number 3 is usually the least costly by far, and in most cases it can alleviate the problem by itself. Numbers 1 and 2 do not remove the major cause of stress-corrosion cracking, namely residual surface tensile stress. Combinations of 1 and 3, or 2 and 3, offer some interesting possibilities.

What is controlled shotpeening?

Controlled shotpeening describes those exacting procedures that involve the uniform impacting of a metal surface—with either fine steel shot or glass beads—to induce surface compressive stress to the required depth. It may be likened to the effect produced by hundreds of thousands of tiny peening hammers striking with blows of equal intensity.

The resulting layer, several thousandths of an inch in



Cracks show in unpeened stainless steel pipe weld after 23-h exposure to boiling 42% aqueous MgCl₂ solution Fig. 5

depth, is compressively stressed—and stress cracks, the precursor of the type of corrosion discussed here, will not occur, even in a corrosive environment. The maximum residual compressive stress that can be produced in a surface layer through controlled shotpeening and the stress that effectively retards corrosion cracking is equal, at least, to half the yield strength of the metal.

Individual equipment components and replacement parts, as well as complete assemblies, can be shotpeened to prevent corrosion—if not as a final step before shipment, then upon their arrival in the field, or even after installation as part of an onstream system.

The depth of surface compression induced by controlled shotpeening is governed by a number of variables including shot size and quality, peening intensity, and thoroughness of coverage, as well as the hardness and strength of the metal. To be effective, 100% visual coverage is required.

Special machines and procedures are used

Equipment and procedures for controlled peening of components and assemblies to prevent stress corrosion and fatigue failure have been developed. The machines and setups are unlike those of conventional blasting and peening operations. They require skillful engineering planning, much of which is based on past experience.

Attaining uniform depths of compressive stress depends upon uniform and precise control of each of the peening parameters. Usually, many test runs are conducted before the actual peening procedures are final-

TABLE 1. Peened and unpeened specimens used in corrosion tests

Stainless Description	steel type	Dimensions, in	How produced	Peened or unpeened
Boss-to-pipe weldment	321	3 $\frac{3}{8}$ -O.D.x $\frac{1}{2}$ -wall boss; 7 $\frac{1}{2}$ -O.D.x $\frac{1}{8}$ -wall pipe	Fusion weld	Unpeened
Boss-to-pipe weldment	321	3 $\frac{3}{8}$ -O.D.x $\frac{1}{2}$ -wall boss 7 $\frac{1}{2}$ -O.D.x $\frac{1}{8}$ pipe	Fusion weld	Peened
Circumferential weldment	347	5 $\frac{1}{2}$ O.D.x $\frac{1}{4}$ wall	Uniform 100% weld penetration	Unpeened
Circumferential weldment	347	5 $\frac{1}{2}$ O.D.x $\frac{1}{4}$ wall	Greater than 100% weld penetration	Peened
Circumferential weldment	347	5 $\frac{1}{2}$ O.D. x $\frac{1}{4}$ wall	Uniform 100% weld penetration	$\frac{1}{2}$ Unpeened $\frac{1}{2}$ peened
Hexagonal tube	316	2 $\frac{1}{2}$ side	Explosion formed; 20% cold worked	$\frac{1}{2}$ Unpeened $\frac{1}{2}$ peened

ized for each job. Test strips must be preserved and all procedures documented to assure exact repeatability. Repeatability is extremely important to ensure integrity of the shotpeening process. Therefore, test strips must be processed before, during and after each peening operation.

Where shotpeening is used

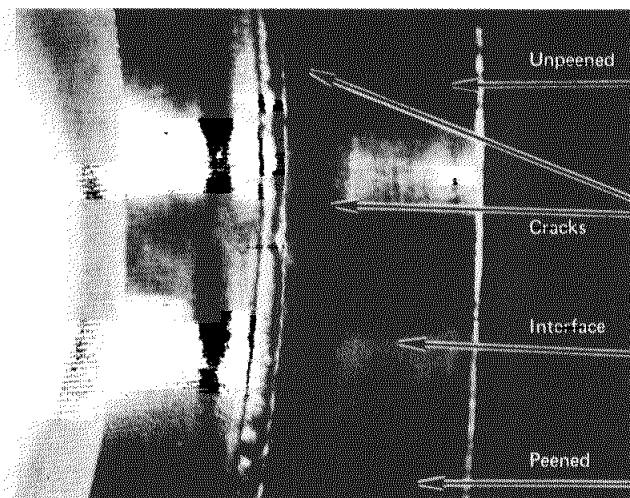
Success in preventing stress corrosion and fatigue failure through controlled shotpeening has been achieved with such metals of construction used in the chemical process industries as high-carbon steel, Types 304, 316, 321 and 347 stainless steels, the Inconels, aluminum alloys and copper-silicon alloys. Large tank sections, pump bodies, evaporators, compressors, converters, tower components, assemblies, heat-exchanger tubing and other heat-exchanger surfaces, tubesheets, and simple, as well as complex, steel and nonferrous castings can be treated. Mechanical components such as coil springs, gears, pump shafts, diaphragm couplings, and pressure-switch diaphragms are additional applications where controlled shotpeening has a substantial record of corrosion problem solving.

Fatigue applications are also numerous and include pipeline expansion joints (bellows), and compressor, turbine and pump components such as connecting rods, valves, shafts, impellers, blades, rotors and disks, etc. In a recent development, the problem of intergranular cracking has been attacked successfully in austenitic stainless steels. In sensitized Ni-Cr-Fe alloys, chromium carbides precipitate, with a subsequent depletion of chromium adjacent to the grain boundaries. Reduction of the chromium content leaves the material susceptible to intergranular corrosion.

A cold-working process such as shotpeening will break up surface grains and form slip planes and/or dislocations that provide nucleation sites for carbide precipitation. Chromium-depleted grain boundaries are not formed at the surface, and the material is not susceptible to intergranular corrosion.

Shotpeening a sulfuric acid storage tank

Fig. 4 shows the bottom of a 47-ft-dia. copper-silicon-alloy, sulfuric acid storage tank being shotpeened, under controlled conditions. Shotpeening in this case



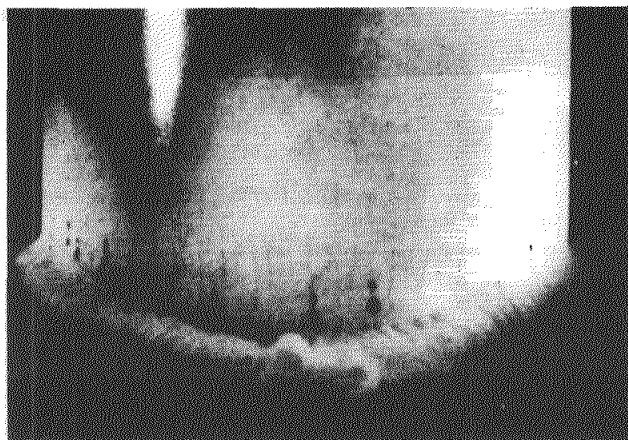
Inside surface of stainless steel pipe weld after 25-h exposure. Cracks in unpeened portion end abruptly at peened portion

Fig. 6

proved to be the answer to an unexpected corrosion problem in which stress cracking was evident after only four months' service. Tanks with shotpeened bottoms have been in service so far for over one year without sign of corrosion cracking. Tank configuration and dimensions are those of the original, and the fabrication procedures are unchanged except for the addition of controlled shotpeening.

Piping system

For a proposed sodium piping system to be fabricated of austenitic stainless steel, accelerated tests were conducted at the manufacturer's plant to evaluate shotpeening. The items tested were similar in dimensions, configuration and methods of manufacture to the probable components of the system. Welding of the boss to the pipe induced the required tensile stress adjacent to the weld area. Stress-corrosion behavior was determined by immersion in boiling (300°F) 42% aqueous magnesium chloride, and then examining for signs of cracking. (This is a standard test for evaluating stress-corrosion resistance of austenitic stainless steels.) Examination was made by unaided eye and with a micro-



Stainless steel boss-to-pipe weldment shows serious cracks after 22-h $MgCl_2$ test (liquid penetrant examination) Fig. 7

scope. Test items are described in Table I, and the outcome of the tests is given below.

Results

Boss-to-pipe weldments—The unpeened specimens were severely cracked after only 24 h in the boiling magnesium chloride solution. The photograph shows the condition after 165½ h. At this time, sizable longitudinal cracks had appeared around the circumference of the boss and adjacent to the weld. While none of these appeared to be through-cracks, fine cracks were visible on the inside surface. Through-cracks were present on the 7½-in. O.D. pipe section. As for the peened specimen after 264 h of immersion, at which time the test was terminated, only two small cracks were detected in the boss section, and one in the pipe.

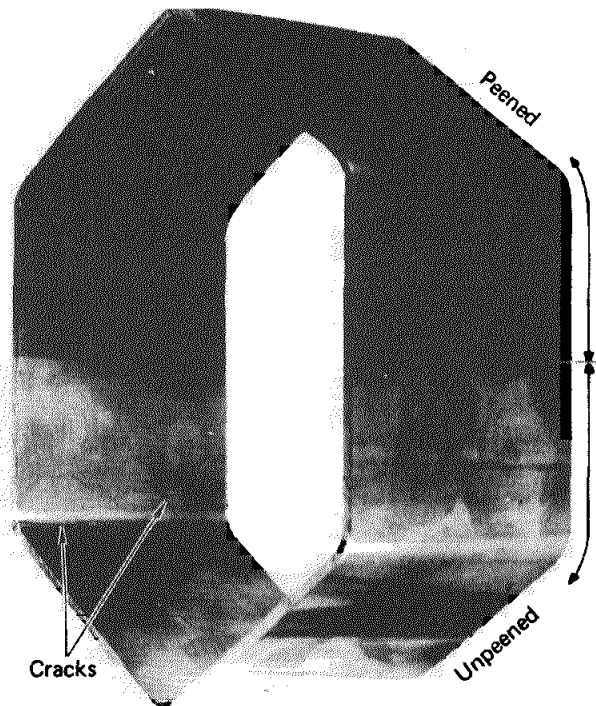
Circumferential pipe weldments—The first unpeened specimen, after 47 h of exposure, had developed ½-in.-long longitudinal cracks, spaced ½ to 1 in apart on the outside surface adjacent to the weld, as well as cracks on the inside surfaces. The second specimen, which had been peened, developed no cracks after 120 h. On the ½ peened/½ unpeened, welded and machine-finished specimen, after only 22-h exposure, cracks appearing in the unpeened area stopped where the peened surface began.

Hexagonal tube: After 24 h, cracking was evident in corners and flat surfaces of the unpeened half, while no cracks appeared in the peened portion.

From the results, we concluded that shotpeening would greatly increase resistance to stress-corrosion cracking but, to achieve the desired degree of success, it must be properly controlled. Monitoring would involve the means and methods to assure complete cold working of the surface by peening to a uniform depth. It is believed, for example, that the two cracks in the boss section resulted from lack of peening coverage in those areas.

Shotpeening saves redesign

Faced with a stress-corrosion situation and knowing the reasons for it, one might logically suggest a redesign that minimizes required welding, machining and fin-



Unpeened surface of hexagonal stainless steel tube shows cracks after 23 h of $MgCl_2$ exposure. No cracks are detectable in the peened portion Fig. 8

ishing operations. However, engineering, new material, and time factors can make the cost prohibitive.

Instead, with controlled shotpeening, the original design and basic manufacturing techniques can be retained. The tensile-stressed surface areas need merely be carefully shotpeened to induce a residual compressive stress.

Controlled shotpeening of equipment and component surfaces has, for a number of years, been regarded by the power industry—both nuclear and fossil-fueled—and the builders of its equipment as a practical and relatively inexpensive means of preventing stress corrosion and fatigue failure. Since both the production of power and much of the large spectrum of chemical processing employ many of the same classes of equipment and alloys of construction and often experience similar environmental problems, the chemical process industries might look more seriously at controlled shotpeening for preventing corrosion.

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