

Stress-Corrosion Prevention

An engineering approach to stress-corrosion cracking of austenitic stainless steel—how it can occur and steps to prevent its occurrence.

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The question, "How do I prevent stress-corrosion cracking?" should be asked, and answered, by: the design engineer, the engineer in construction and maintenance, and the engineer who operates the plant. Each one should be aware of the possibility of cracking and the steps necessary to prevent stress-corrosion cracking.

It can occur in steel, copper alloys, aluminum, and nearly every alloy system. This discussion will be limited to austenitic stainless steels. These are the iron-chromium-nickel alloys, Types 304, 304L, 316, 321, 347, CF-8, HK-40, and alloy 800.

Figures 1 and 2 show a typical stress-corrosion cracking failure of austenitic stainless steel. This failure was noted 15 days after the start of operation. Notice that one crack was located on the bend of the tube, but that the other was not.

Figure 3 shows other cracks in Type 304L tubing. This tubing had been bent into U-tubes; the residual stress,

either by itself or added to the applied stress, caused the cracking in the presence of chloride solution.

Figure 4 shows the transgranular, branching path of the crack, typical of stress-corrosion cracking. Note that the crack is not connected with the adjacent pit.

Figure 5 shows the path of the crack through the 2.1-mm. wall thickness.

To understand how to prevent stress-corrosion cracking, it would be helpful to understand how it happens. Unlike many failure phenomena which are unexplainable, this one is blessed with a surplus of theoretical explanations. None of them is generally accepted as explaining all the known facts. Indeed, in a summary of the proceedings of the 1967 Conference on Fundamental Aspects of Stress Corrosion Cracking, the chairman stated, "The aim of the conference was to develop a basis for quantitative prediction of the incidence of stress-corrosion cracking. This objective was

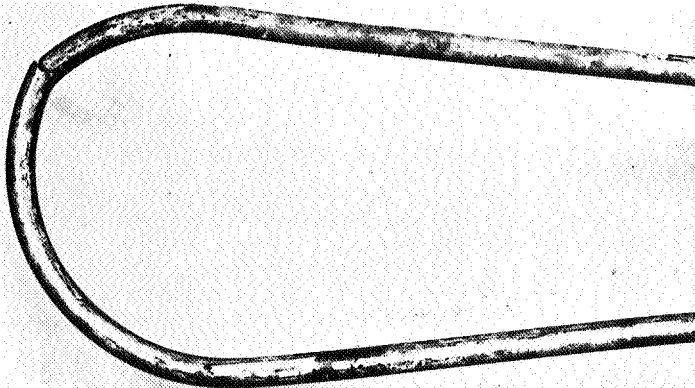


Figure 1. Failure in bend in Type 304L tubing. X/3.

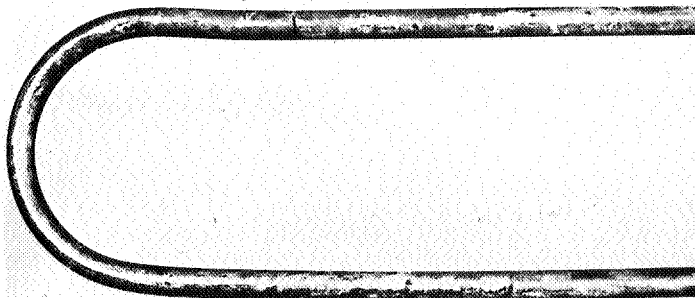


Figure 2. Failure in straight section of Type 304L tubing. X/3.

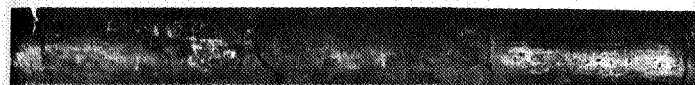


Figure 3. Failures in Type 304L tubing that had been bent into U-tubes. 1X.

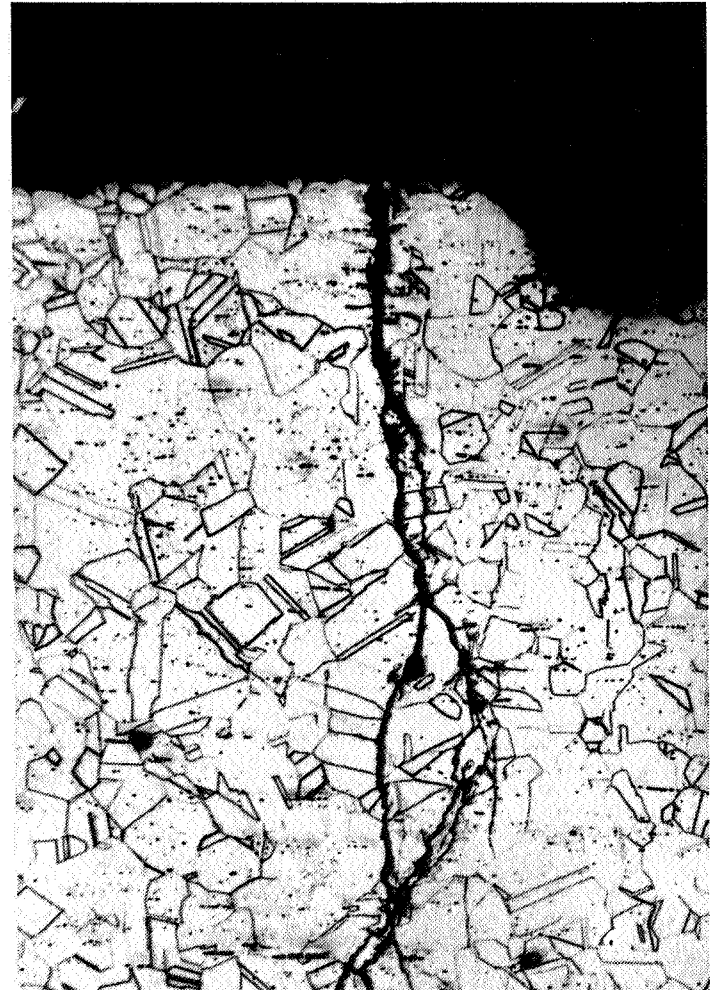


Figure 4. Transgranular, branching path of a typical stress-corrosion crack. 100X.

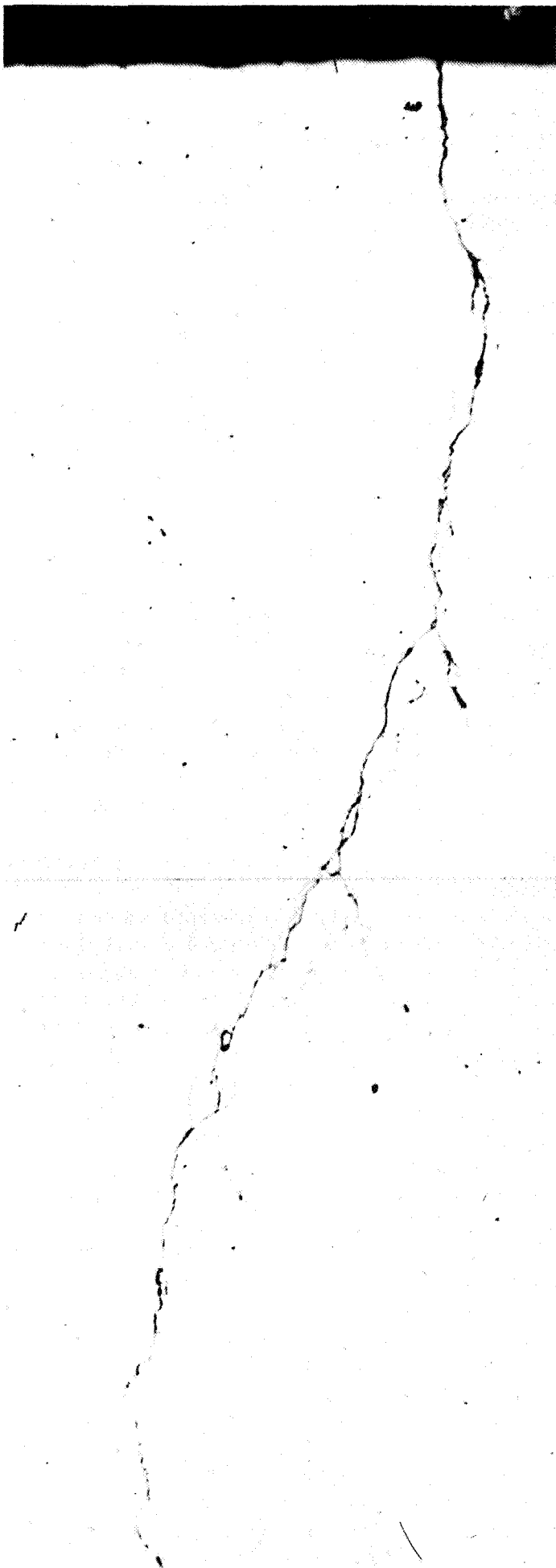


Figure 5. Path of the crack through the 2.1-mm. wall of the Type 304L tubing. 100X.

far too ambitious and unrealistic in terms of available knowledge. It must be said honestly, and can be said without contradiction, that there presently is no reliable fundamental theory of stress-corrosion cracking in any alloy-environment system which can be used to predict the performance of equipment in environments where conditions are readily defined." (1)

Many theories on the mechanism

Among the theories to explain the mechanism of stress-corrosion cracking of austenitic stainless steels are the following: (2)

1. *Electrochemical.* A cell forms on the surface between areas which differ slightly in potential, the more active stressed area becoming the anode. Corrosion commences and continues at the anode, starting the crack. The point of the crack, being under the highest stress, remains the anode, while walls of the crack and the outer surface are large cathode areas.

2. *A modification for intergranular cracking.* At grain boundaries a continuous anodic constituent exists; therefore the crack follows it.

3. *Another electrochemical modification.* Stress causes protective oxide films on the metal surface to break down, exposing unprotected metal underneath. This exposed metal is anodic and continues to corrode rapidly. The film-covered sides of the crack act as cathodes.

4. *A combination of electrochemical and mechanical effects.* Solid corrosion products of an electrochemical reaction form in an existing crack, are large in volume, and wedge the metal walls apart, allowing the point of the crack to proceed.

5. *Stress-sorption.* Stress weakens the bonds between atoms of metal in a surface, forming dislocations. At these dislocations, chloride or other damaging ions are adsorbed if the potential of the surface is above a critical value. The bonds break, forming a crack in which adsorption continues. This theory accounts for the fact that the damaging ions are so specific—chloride but not iodide, for example—and for the interference of other specific ions such as benzoate and acetate. (3)

6. *Hydrogen embrittlement.* Hydrogen is deposited at a cathode which exists for any of several reasons (cathodic protection, galvanic cell, corrosion as in the acidic solution within a pit). Some hydrogen atoms enter the metallic atom lattice, especially in the presence of a catalyst such as sulfide. Presence of these atoms embrittles the metal and increases internal stresses in the metal, forming cracks. (4)

Each of the theories is supported by laboratory tests under certain specific sets of conditions. None of the theories can explain all the stress-corrosion cracking of austenitic steels which has occurred. Fortunately, it is possible to minimize the possibility of cracking without choosing among these theories.

One large chemical company, knowledgeable in the field of stress-corrosion cracking, has reported the 1971 cost for materials and maintenance due to stress-corrosion cracking at \$4.1-million. This compares to a cost to the company of \$4.7-million for fatigue failures. (5) Recognizing that this

cost is for just one company, it can be seen that the problem is significant.

How is stress-corrosion cracking recognized? The pattern of cracking in austenitic stainless steels is generally predominantly transgranular, as seen in Figure 4. There is usually no noticeable pitting or metal loss by corrosion. Cracking is sudden and in many cases, failure occurs without warning. Laboratory examination is necessary to determine whether cracking is transgranular or intergranular.

Residual stresses from cold bending were factor

In one recent experience, tubes in a U-tube heat exchanger were wetted with brackish water during a hydrostatic test of the shell. When the unit was started, stress-corrosion cracking of the U-bends occurred. In this case there were residual stresses from the cold bending of the U-tubes. The chlorides in the brackish water residue concentrated as the tubes were heated. When the chlorides reached a critical concentration, corrosion of the surface initiated stress-corrosion cracking.

Several users have reported cracking of austenitic tubes and tube-sheets. Low chloride concentrations in water on the shell side became concentrated in the crevice between the tube and tube sheet. Once the temperature and chloride concentration were high enough, cracking occurred. (6)

Several intergranular failures in austenitic steels in nuclear power plants have occurred in chloride-free water. These failures were in sensitized stainless steels in high-temperature, oxygenated water (550°F, <0.2 ppm. dissolved oxygen). (7)

In another recent experience there was stress-corrosion cracking of HK-40 tubes at welds before start-up of the plant. The corrodent was SO₂ from a neighboring chemical plant and moisture from the air. The stresses present were residual welding stresses. (8)

Sensitized Types 304 and 304L stainless steel have undergone intergranular stress-corrosion cracking in petroleum refinery equipment handling sulfur-containing streams. (9) High-temperature sulfidation produces sulfide scales which, during downtimes, react with water and oxygen to produce polythionic acids, H_xS_yO_z. These are the corrosive agents.

These examples have several points in common: 1) the materials were austenitic steel; 2) there was a tensile stress, either residual or applied; and 3) there was a corrodent on the surface. Regardless of the theory which may operate, these three variables must exist simultaneously for stress-corrosion cracking to take place.

All the commercial grades of austenitic stainless steel, and alloy 800 as well, have been reported to have cracked in laboratory tests and in service. In 1960, F. L. LaQue (10) stated "... while there may be moderate differences in susceptibility among the common austenitic grades, it is evident that under crucial conditions of use the occurrence of stress-corrosion cracking cannot be avoided by choosing one grade in preference to another." Laboratory tests and service experience since 1960 have agreed with that statement. Similarly, solution-annealed material will crack as readily as carbide-precipitated stainless steel.

Chlorides do not affect all stainless steels

There are stainless steels which will not be subject to chloride stress-corrosion cracking. These include some ferritic and martensitic steels. There are exceptions; a ferritic 18% chromium steel will crack in laboratory tests if nickel content reached 1% or copper 0.5%. (11) The resistant steels include the various 400 types—410, 430, the new molybdenum-containing proprietary chromium steels 18 Cr-2 Mo, 26 Cr-1 Mo with titanium, electron-beam-refined 26 Cr-1 Mo, 29 Cr-4 Mo and proprietary mixed-structure ferritic-austenitic steels. Unfortunately they do not have the combination of weldability, high-temperature strength and low-temperature ductility which make the austenitic steels so useful in process plants.

The tensile stress necessary for stress-corrosion cracking can be residual stress such as that remaining after steel mill, forming, welding, handling, or erection procedures. If not residual stress, applied stresses in service from pressure, weight, or other applied loads would be sufficient to cause stress-corrosion cracking. Laboratory tests have shown that higher stresses decrease the time, chloride content, or temperature necessary before cracking occurs. For each combination of concentration of chlorides, temperature, time, and metal condition there is probably a minimum stress required for cracking to occur.

At low temperatures, where solutions freeze, there is no possibility of stress-corrosion cracking. Above this limit, the risk of cracking increases with increasing temperature. At still higher temperatures, if water is a vapor and there can be no solution of chlorides, there is no danger of cracking. Laboratory tests have produced cracking at temperatures between 23°F and 626°F.

Chlorides are the principal corrodent involved in stress-corrosion cracking of austenitic stainless steel. They are present in most water, in the air, and on all surfaces. A solution of chlorides is required for corrosion to begin. Further, the chlorides must be present in some unknown critical concentration before corrosion and cracking occur. Cracks have occurred at concentrations as low as 2 to 5 ppm. chloride. It does make some difference whether the salt is sodium, calcium or magnesium chloride. Generally, the higher the chloride concentration, the faster the cracking will take place. High pH will be less likely to cause cracking than low pH. Note that water is necessary; a dry salt will not cause stress-corrosion cracking, because there is no ionized solution to conduct the galvanic current necessary for corrosion.

Laboratory tests have not clearly established the conditions at which cracking will or will not occur. The tests have generally shown trends or directions, but the results do not yet fit into a formula useful for prediction of success or failure.

With regard to laboratory tests, the following comment on feedwater tubing tests is generally applicable. "Tests here are costly and sophisticated and even when done carefully, tell the investigator *only* about the behavior of *his alloy* in *his exact test environment*. If this test environment is not totally characterized, for example, omitting some trivial impurity that completely inhibits or enhances stress

corrosion, or if the test environment is in any way unrepresentative of the application, the tests can be completely misleading . . . naturally, not all tests can anticipate unknown, unforeseen, transient conditions of in-service applications." (12)

Laboratory test results and service experience show that there are only three ways to prevent stress-corrosion cracking:

1. Do not use austenitic stainless steels.
2. If austenitic stainless steels are used, do not apply tensile stress.
3. Prevent all contact of stainless steel by water or chlorides.

In practice, the last two alternatives are impossible.

There are materials which can be substituted for austenitic stainless steels when the design conditions allow. If design temperatures, stress, and corrodent allow, materials such as Type 430, alloy 600 or nickel-molybdenum-chromium alloy C are immune to chloride stress-corrosion cracking. Alloys 800, 825, alloy G, stainless steels 18 Cr-18Ni-2Si, and No. 20 are substantially more resistant than 18 Cr-8Ni alloys but are not immune. If 18-8 materials must be used, the possibility of stress-corrosion cracking can be minimized by doing those things which are known to be favorable and avoiding those which are unfavorable.

To minimize the possibility of stress-corrosion cracking one must minimize the stress, the temperature, the amount of chloride, and the time of contact with chloride solutions.

Proper design practice is helpful

All piping and equipment should be provided with drains so that condensate and test water can be removed. Use of these drains will minimize the time of contact of potentially corrosive solutions on austenitic stainless steel surfaces.

Austenitic stainless steel tubes should not be used in shell-and-tube heat exchangers with water on the shell side if the tube-side stream temperature is greater than 175°F. Small amounts of chloride in the cooling water can be concentrated in the crevice between the tube and tube sheet and can cause cracking. For the same reason, lap joints and other crevices should be avoided.

All attachments should be self-draining. There should be no flat surfaces or crevices where water can collect.

For metal temperatures between 125°F and 500°F, stainless steel which will be insulated should be painted. The insulation can form a crevice with the stainless steel which will hold water and concentrate chlorides.

During fabrication, testing, shipping, storage, and erection, stainless steel equipment should be protected against contamination by chlorides. This requires more than normal cleanliness and housekeeping. Marking materials, liquid penetrant materials, and test water should be of controlled chloride content.

Die-stamping should be minimized. Where permanent marking is required, low-stress stamps should be used. Cold-working should be minimized.

U-bent exchanger tubes should be of low-carbon or stabilized grades and heat-treated to remove residual stresses. High stresses can cause cracking during start-up or service conditions. Similar stresses exist in bent and formed

piping and vessels, but there is no practical way to remove stresses. In U-bent tubes, stresses can be and should be removed.

Contact of metal surfaces with chlorides even from such commonplace sources as perspiration, shop dirt, solvents, or paints should be minimized because the chlorides can be dissolved and concentrated during and after hydrostatic test.

In operation, chlorides should not be introduced into the system. If they are accidentally introduced, or if flooding leaves chlorides on stainless steel surfaces, they should be removed by flushing with condensate or demineralized water.

Any condition which could cause a combination of chloride concentration, stress, and temperature should be avoided. Cracking has been found to take place with chloride concentrations of less than 5 ppm. at zero applied stress, and at temperatures as low as 23°F, although not in combinations of these levels.

In refinery service below 800°F, Types 304, 316, 304L, and 316L should be specified in the solution-annealed condition. Above 800°F, Types 321, and 347 in the stabilized-annealed condition should be used. In the absence of certainty of these precautions against polythionic acid corrosion, protective measures are alkali washing of equipment before exposure to air, or nitrogen-ammonia blanketing, or dry inert gas purge. (9)

The current summary of precautions described to minimize the possibility of stress-corrosion cracking is based on experience developed over a period of time. Precautions such as those listed above must be continuously examined in the light of new experience. #

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DISCUSSION

Q. Is there any evidence that passivated surfaces of austenitic stainless steels are more resistant to stress corrosion cracking?

ZEIS: Yes, there is some laboratory experience which does

show that passivated surfaces have initial resistance to stress corrosion cracking. However, if there is any break in the passivated surface, corrosion resistance gets worse. It relates to the anode versus cathode area.