Chapter 16

Stress-Corrosion Cracking

Locations

In principle, stress-corrosion cracking could occur wherever a specific corrodent and sufficient tensile stresses coexist. Because of improved water-treatment programs and improved boiler design, the occurrence of caustic stress-corrosion cracking* is much less frequent now than it was years ago. However, stress-corrosion cracking continues to appear occasionally in water tubes, superheater tubes, and reheater tubes. Stress-corrosion cracking may also occur in stressed components in the steam drum, such as bolts (Fig. 16.1).

General Description

The term *stress-corrosion cracking* refers to metal failure resulting from a synergistic interaction of a tensile stress and a specific corrodent to which the metal is sensitive. The tensile stresses may be either applied, such as those caused by internal pressure, or residual, such as those induced by

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**Caustic embrittlement* is presently considered an obsolete, historical term for this phenomenon.

Figure 16.1 Steam drum bolt that failed by caustic stress-corrosion cracking. Note the typical brittle character of the fracture. *(Courtesy of National Association of Corrosion Engineers.)*

welding. In boiler systems, carbon steel is specifically sensitive to concentrated sodium hydroxide, while stainless steel is specifically sensitive both to concentrated sodium hydroxide and to chlorides.

Gross attack of the metal is not necessary for this phenomenon and, in fact, does not characteristically accompany it. The combination of concentrated sodium hydroxide, some soluble silica, and tensile stresses will cause continuous intergranular cracks to form in carbon steel (Fig. 16.2). As the cracks progress, the strength of the remaining intact metal is exceeded, and a brittle, thick-walled fracture will occur.

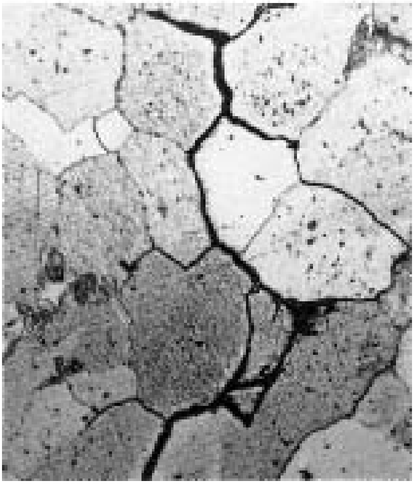

Figure 16.2 Caustic stress-corrosion cracking: continuous intergranular cracks running through a tube wall. (Magnification: 500X.)

Critical Factors

There are two principal factors that govern stress-corrosion cracking in the boiler environment. First, the metal in the affected region must be stressed in tension to a sufficiently high level. The stresses may be applied and/or residual. Second, concentration of a specific corrodent at the stressed metal site must occur. The specific corrodent for carbon steels in boiler systems is sodium hydroxide; for stainless steels the corrodent can be sodium hydroxide or chlorides. (Concentration of corrodents may occur by any of the modes outlined in Chap. 4, "Caustic Corrosion.") Small leaks may also result in concentration of corrodents.

Instances of caustic stress-corrosion cracking in boiler metal operating below 300°F (149°C) are rare. Concentrations of sodium hydroxide as low as 5% have caused cracking, but concentrations in the range of 20 to 40% greatly increase susceptibility.

Identification

Failures caused by stress-corrosion cracking always produce thick-walled fracture faces regardless of the degree of metal ductility. Branching is frequently associated with these cracks. Unless failure has occurred, stress-corrosion cracking may be difficult to see with the unaided eye, since the cracks tend to be very fine and tight. Occasionally, evidence of the presence of concentrated sodium hydroxide, such as whitish, highly alkaline deposits or the presence of crystalline magnetite, may be observed at the crack site.

Elimination

To eliminate problems with stress-corrosion cracking it is necessary to gain control of either tensile stresses or concentration of corrodents.

Tensile stresses can be either applied or residual. *Applied stresses* are service-generated stresses including hoop stresses caused by internal pressure and bending stresses from constrained thermal expansion and contraction. Generally, hoop stresses are subject to minimal control, since the essential function of the boiler tubes and other pressurized components demands containment of pressurized substances. Bending stresses, however, may be reduced or eliminated by altering operational parameters or by redesign of the affected components.

The term *residual stress* refers to stresses that are inherent in the metal itself. They are the result of manufacturing or construction processes such as welding or tube bending. Residual hoop stresses may also remain from the manufacturing process. These stresses can be relieved by proper annealing techniques.

Avoiding concentrated corrodents is generally the most successful means of reducing or eliminating stress-corrosion cracking. Avoiding departure from nucleate boiling (DNB), keeping internal surfaces sufficiently free of deposits, and avoiding formation of steamlines and waterlines in components receiving high heat flux, are first steps. Other steps may include preventing in-leakage of alkaline-producing salts through condensers, heat exchangers, process streams, and caustically regenerated demineralizer systems; preventing contamination of desuperheating or attemperator water by alkaline materials or chlorides; and preventing boiler-water carryover.

The use of inhibitors, such as sodium nitrate or a combination of sodium nitrate and one of many selected organics, has been successful in reducing caustic stress-corrosion cracking. A coordinated phosphate program, which is designed to eliminate the formation of free sodium hydroxide, may also be valuable.

Cautions

Stress-corrosion cracks are commonly difficult to identify through visual inspection. The use of dye penetrants, magnetic-particle inspections, and ultrasonic testing in suspect regions may disclose the presence of stress-corrosion cracks. Dwell time for dye penetrants must be increased to accommodate the typical tightness of these cracks.

It is conceivable that stress-corrosion cracking could be confused with other cracking modes that produce thick-walled fractures, such as hydrogen damage, corrosion fatigue, creep rupture, and some forms of severe overheating. Confirmation of a diagnosis of stress-corrosion cracking requires metallographic examination.

Related Problems

See also the section titled Creep Rupture in Chap. 2, “Long-Term Overheating”; Chap. 3, “Short-Term Overheating”; Chap. 14, “Hydrogen Damage”; and Chap. 15, “Corrosion-Fatigue Cracking.”

CASE HISTORY 16.1

Industry:	Pulp and paper
Specimen Location:	Steam supply line to a soot blower, recovery boiler
Specimen Orientation:	Vertical
Years in Service:	15
Water-Treatment Program:	Oxygen scavenger
Drum Pressure:	400 psi (2.8 MPa)
Tube Specifications:	2⅜ in. (6.0 cm) outer diameter, 304 stainless steel

Figure 16.3 shows one of several stainless steel soot-blower lines that had cracked. Failures of this type can be quite dangerous, since steam can be released into occupied areas.

The line contained several thick-walled cracks that ran as long as 25 in. (63.5 cm) down the tube. Note that the cracks are not tight but have spread apart, an unusual feature for stress-corrosion cracking.

Close visual and microstructural examinations revealed that the cracks originated on the external surface. Microstructural examinations also revealed severe cold working of the metal.

An uncontaminated segment of the crack face was examined under a scanning electron microscope equipped for energy-dispersive spectroscopy.

Figure 16.3 Extensive longitudinal crack in a stainless steel soot-blower line. Note that the crack edges have spread apart.

Elemental analysis of substances covering the crack face revealed the presence of chlorine.

The line failed by stress-corrosion cracking resulting from exposure of the external surface to chlorides of unknown origin. The longitudinal direction of the cracking reveals that circumferential (hoop) stresses were responsible. It is apparent from the spreading apart of the cracks and the evidence of cold-worked metal in the microstructure that the tube contained high residual hoop stresses resulting from tube-forming processes. The level of residual stresses was calculated to be 29,000 psi (200 MPa). The residual stresses, added to service stresses generated by internal pressure, acted synergistically with the chlorides to produce the cracks illustrated.

CASE HISTORY 16.2

Industry:	Pulp and paper
Specimen Location:	Economizer
Specimen Orientation:	Bend
Years in Service:	15
Water-Treatment Program:	Phosphate
Drum Pressure:	800 psi (5.5 MPa)
Tube Specifications:	2 in. (5.1 cm) outer diameter

A section of an economizer tube having a 90° bend at its midpoint contains a pair of thick-walled cracks on opposite sides of the tube (Fig. 16.4). The tube had an oval rather than a circular cross section through the bend, and the cracks were located at opposite ends of the long axis of the oval.

The internal surface had sustained shallow, general metal loss. Sparkling crystals of black magnetite were associated with this corrosion.

Microstructural examinations revealed that the cracks originated at the bottom of shallow pits. The cracks exhibited branching as they propagated through the tube wall. Crack paths were principally across the metal grains (transgranular).

Stress-corrosion cracking in carbon steels requires the joint action of concentrated sodium hydroxide and tensile stresses. The sodium hydroxide apparently concentrated beneath porous iron oxide deposits that were present on the internal surface. The presence of crystalline magnetite indicates exposure to concentrated sodium hydroxide. The shallow pits acted as stress concentrators, elevating the normal stress level. In addition, stresses from internal pressure would be highest along the narrow ends of the oval cross section, where the cracks formed. The longitudinal orientation of the cracks reveals that internal pressure provided the stresses necessary for stress-corrosion cracking.

Figure 16.4 Longitudinal crack along the side of a 90° bend in an economizer tube. A similar crack is located along the opposite side.

CASE HISTORY 16.3

Industry:	Pulp and paper
Specimen Location:	Superheater, recovery boiler
Specimen Orientation:	Vertical
Years in Service:	11
Water-Treatment Program:	Coordinated phosphate
Drum Pressure:	1200 psi (8.3 MPa)
Tube Specifications:	2 in. (5.1 cm) outer diameter, 304 stainless steel
Fuel:	Black liquor

Recurrent failures of the type illustrated in Figs. 16.5 and 16.6 plagued the superheater section of this boiler. Note the fine cracks adjacent and parallel to the weld. Surface branching of the crack is apparent in Fig. 16.6.

Microstructural examinations revealed branched cracks running across the grains (transgranular) and originating on the internal surface. The cracks are located in the heat-affected zone immediately adjacent to the weld.

This failure is caustic stress-corrosion cracking. The source of sodium hydroxide is probably carryover from the steam drum. Stresses are residual welding stresses, as indicated by the circumferential crack propagation and the proximity of the cracks to the weld. Cracks resulting simply from stresses imposed by internal pressure would be longitudinally oriented.

Figure 16.5 Appearance of stress-corrosion crack on the external surface. Crack is located within the red circle.

Figure 16.6 Appearance of crack on the internal surface. Note the branching and proximity to the weld bead.

CASE HISTORY 16.4

Industry: Petrochemical
Specimen Location: Superheater, first stage
Specimen Orientation: Vertical
Years in Service: 3 weeks
Water-Treatment Program: Phosphate
Drum Pressure: 600 psi (4.1 MPa)
Tube Specifications: 1½ in. (3.8 cm) outer diameter, 304 stainless steel
Fuel: Waste gas

The tube illustrated in Fig. 16.7 is one of numerous tubes that failed in this boiler. The tubes had been moderately cold-bent during installation, and were not stress-relief-annealed. The steam drum lacked adequate devices for separation of steam and water, and load swings were frequent, possibly causing carryover of boiler water.

Microstructural analysis revealed plastically deformed grains from the cold bending. The cracks were highly branched and ran between the grains (intergranular) as they passed through the tube wall. They originated on the internal surface.

The source of stress in this case was residual stresses from the bending operation. This is apparent from the circumferential orientation of the cracks, the fact that the cracks have spread apart, and the proximity of the cracks to the bent zones of the tubes. The corrodent was sodium hydroxide from boiler-water carryover.

This case is an excellent example of the value of understanding failure mechanisms and performance of materials. Stainless steel superheater tubes in a boiler of this pressure are unusual. The original tubes were carbon steel that cracked after 9 months of service. Two steps were taken to improve service life. First, stainless steel tubes were specified to replace the carbon steel. Second, moderate bends were put in the tubes, apparently to relieve the thermal expansion and contraction stresses that had caused cracking in the carbon steel tubes. Unfortunately, despite the greater general corrosion resistance of stainless steels, they are also susceptible to caustic stress-corrosion cracking. In addition, the bends placed in the tubes to relieve thermal stresses provided high residual stresses instead. The stainless steel tubes failed after 3 weeks.

Figure 16.7 Transverse crack resulting from caustic stress corrosion in a bent stainless steel superheater tube. Note small “window” that has been blown out of the wall.