3.52 Polythionic Acid Stress Corrosion Cracking

3.52.1 Description of Damage

a) Intergranular SCC that can occur in sensitized austenitic stainless steels and some Ni alloys (Alloy 800 and Alloy 600) when sulfide scale formed on the surface during operation is exposed to air and moisture. The combination of sulfide scale, air (i.e. oxygen), and moisture creates sulfur acids on the surface that then cause polythionic acid stress corrosion cracking (PTA SCC). It normally occurs during shutdowns or start-ups.

b) Usually occurs adjacent to welds or in high-stress areas.

c) Cracking may propagate rapidly through the wall thickness of piping and components in a matter of minutes or hours.

3.52.2 Affected Materials

Austenitic stainless steels (300 series SS) and austenitic alloys (Alloy 600/600H and Alloy 800/800H/800HT). Alloys 625 and 825 are also susceptible but require extended periods at much higher temperatures [>1200 °F (650 °C)] to sensitize.

3.52.3 Critical Factors

a) A combination of environment, susceptible material, and tensile stress are required.

1. Environment—Susceptible metals form a surface sulfide scale when exposed to sulfur compounds in a high-temperature reducing process environment. The scale may then react with air (oxygen) and moisture to form sulfur acids (polythionic acids, $H_2S_xO_6$).

2. Material—The material must be susceptible to sensitization and in a sensitized condition.

3. Tensile Stress—The stress can be residual or applied.

b) Affected alloys become sensitized during exposure to elevated temperatures during manufacture, welding, or high-temperature service. Sensitization refers to the composition/time/temperature-dependent formation of chromium carbides in the grain boundaries of the metal. Sensitization occurs in the 700 °F to 1500 °F (370 °C to 815 °C) temperature range. However, chemically stabilized grades of stainless steel, e.g. Types 321 and 347, can withstand service temperatures greater than 700 °F without suffering detrimental sensitization. Some refiners permit the use of these alloys at temperatures substantially greater than 700 °F without requiring thermal stabilization.

c) The carbon content and the thermal history of the alloy have a significant effect on sensitization susceptibility. Regular and high carbon grades of stainless steels such as Types 304/304H and 316/316H are particularly susceptible to sensitizing in the weld HAZ. Low carbon "L" grades (<0.03 % C) are less susceptible and usually can be welded without sensitizing. The L grades will not sensitize provided long-term operating temperatures do not exceed about 750 °F (400 °C).

d) Residual tensile stresses in most components, especially in non-stress-relieved welds, are usually sufficient to promote cracking and are the most common source of the tensile stress needed to cause cracking.

3.52.4 Affected Units or Equipment

a) All units where sensitized alloys are used in high-temperature sulfur-containing environments. Commonly damaged equipment includes heat exchanger tubes and components, furnace tubes, and piping.

b) Fired heaters burning oil, gas, coke, and most other sources of fuel may be affected depending on sulfur levels in the fuel and combustion conditions in the firebox. (Fuel-rich conditions will favor formation of sulfide scales instead of oxide scales.) In places where there are environmental restrictions on the burning of high sulfur fuels, the occurrences of fire-side PASCC have diminished.

c) FCC Units—Air rings, plenums, slide valves, cyclone components, expansion joint bellows, and piping.

d) Hydroprocessing Units—Heater tubes, hot feed/effluent exchanger tubes, pressure vessels (including heat exchangers and reactors), piping, and bellows.

e) Crude and Coker Units—Heater tubes and piping.

f) Boilers and other high-temperature equipment exposed to sulfur-containing combustion products can also be susceptible if sensitized alloys are involved.

3.52.5 Appearance or Morphology of Damage

a) Typically occurs next to welds (Figure 3-52-1 and Figure 3-52-4) but can also occur in the base metal. It is usually quite localized and may not be evident until a leak appears during start-up or, in some cases, operation.

b) Cracking propagates intergranularly. (Figure 3-52-2 and Figure 3-52-5)

c) Corrosion or loss in thickness is usually negligible.

3.52.6 Prevention/Mitigation

a) If potentially susceptible equipment will be opened or exposed to air, preventive measures should be taken to minimize or eliminate PTA SCC. These include (i) flushing the equipment during or immediately after shutdown with alkaline or soda ash solution to neutralize the acids formed after shutdown and exposure to air and moisture or (ii) purging with dry nitrogen or nitrogen/ammonia during the shutdown to prevent air exposure and the formation of polythionic acids. Refer to guidelines in NACE SP0170.

b) Furnace tubes that have coke on the tube ID should undergo some form of decoking process prior to or concurrent with the alkaline washing if the tube IDs will be exposed to air. Alkaline washing with coke present has low effectiveness. Refer to NACE SP0170 for guidance.

c) Keeping the firebox heated above the dew point to prevent acids from forming on the heater tube internal surfaces, if practical, will also prevent PTA SCC. This can also be accomplished by using dehumidification equipment to reduce the water dew point inside the tubes below ambient.

d) Low carbon grades of stainless steel such as 304L, 316L, and 317L provide some measure of improvement over higher carbon grades. The L grades will sensitize if exposed more than several hours above about 1000 °F (540 °C) or long-term above 750 °F (400 °C).

e) Improved resistance to PTA SCC cracking can be achieved with chemically stabilized versions of these alloys containing small amounts of titanium (Ti) or niobium (Nb) and tantalum (Ta). [Note that niobium was also called columbium (Cb), but niobium is now the generally accepted name.] Types 321 and 347 SS are the chemically stabilized grades of austenitic stainless steel most commonly used. Alloy 20Cb-3 as well as Alloys 825 and 625 are also chemically stabilized.

f) Supplemental requirements in ASTM specifications provide for mill products to be delivered in a thermally stabilized condition rather than simply solution annealed. This heat treatment will minimize potential sensitization problems at higher temperatures, e.g. as found in a heater.

g) A thermal stabilization heat treatment at 1650 °F (900 °C) may be applied to chemically stabilized austenitic stainless steel welds after all welding is complete to reduce sensitization and PTA SCC susceptibility at the welds. This heat treatment is also applied after welding material that was thermally stabilized in the mill in order to restore the thermal stabilization destroyed by the heat of welding.

h) The degree of sensitization and resultant susceptibility to PTA SCC can be determined by laboratory corrosion testing according to ASTM A262 Practice C. This test is also used as a quality control check at the mill on chemically stabilized grades, with a sensitizing heat treatment applied prior to testing in order to assess resistance to sensitization.

3.52.7 Inspection and Monitoring

a) PTA SCC is most effectively managed by prevention rather than through inspection. PTA SCC can be an inspection challenge because the cracking may not occur until well into a turnaround.

b) Monitoring for PTA SCC cracking during operation is not effective. Conditions causing the cracking are not usually present while the unit is online.

c) PT examination is the most common method used to detect PTA SCC. (Figure 3-52-1 and Figure 3-52-3) However, because the cracks are filled with a tight deposit, flapper wheel sanding or grinding may be needed to improve the PT sensitivity.

d) ECT can detect surface cracks on the crack initiation side.

e) AET has had some success in detecting and locating PTA SCC. However, results sometimes can be inconclusive, and quality AET data may be difficult to obtain.

f) Angle beam UT (SWUT and PAUT) crack detection techniques may be useful depending on thickness, metallurgy, and accessibility considerations and limitations.

g) FMR can be used to determine the degree and extent of sensitization.

3.52.8 Related Mechanisms

Intergranular corrosion and intergranular attack.

3.52.9 References

1. *ASM Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH, p. 327.

2. NACE SP0170, *Protection of Austenitic Stainless Steels and Other Austenitic Alloys from Polythionic Acid Stress Corrosion Cracking During a Shutdown of Refinery Equipment*, NACE International, Houston, TX.

3. D.V. Beggs, and R.W. Howe, “Effects of Welding and Thermal Stabilization on the Sensitization and Polythionic Acid Stress Corrosion Cracking of Heat and Corrosion-resistant Alloys,” Paper No. 541, *Corrosion/93*, NACE International, Houston, TX.

4. L. Scharfstein, “The Effect of Heat Treatments in the Prevention of Intergranular Corrosion Failures of AISI 321 Stainless Steel,” *Materials Performance*, September 1983, pp. 22–24.

5. E. Lendvai-Linter, “Stainless Steel Weld Overlay Resistance to Polythionic Acid Attack,” *Materials Performance*, Vol. 18, No. 3, 1979, p. 9.

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7. R.L. Piehl, “Stress Corrosion Cracking by Sulfur Acids,” *Proceedings of the API Division of Refining*, Vol. 44, No. 3, 1964, pp. 189–197.

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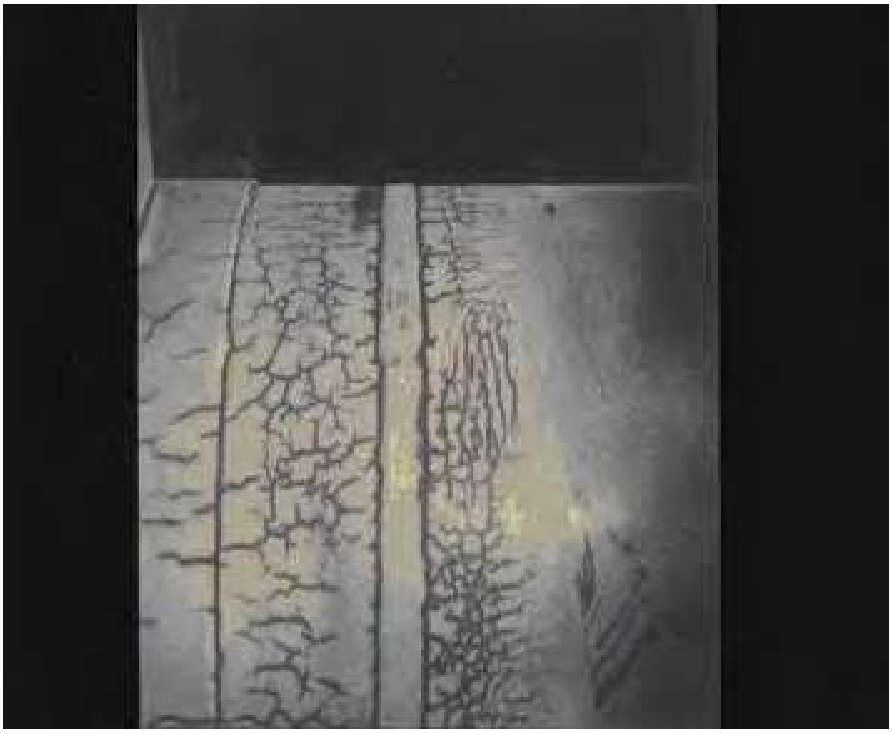

Figure 3-52-1—Dye penetrant (PT) inspection showing extensive OD PTA SCC around welds.

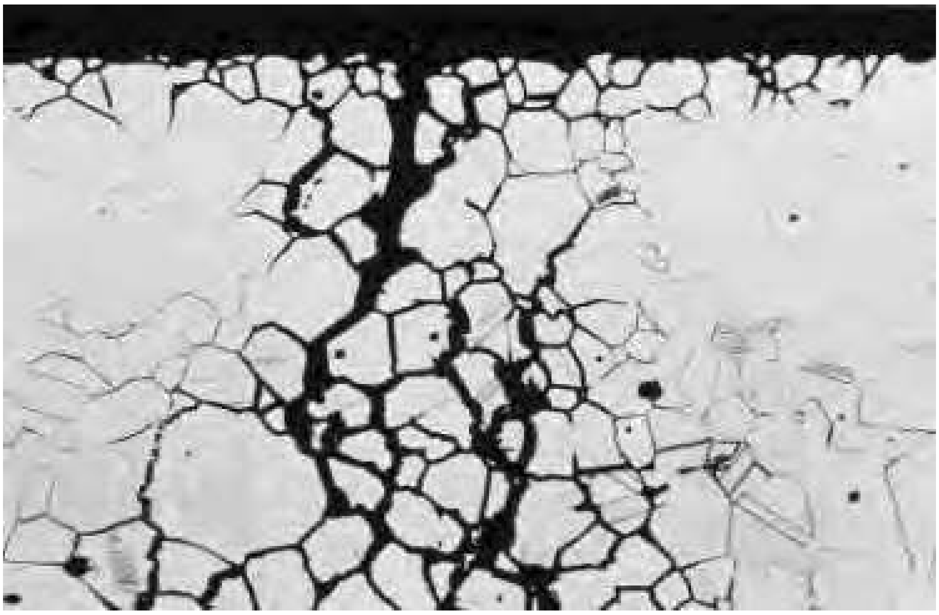

Figure 3-52-2—High-magnification photomicrograph of metallographic sample showing intergranular cracking and grain dropping.

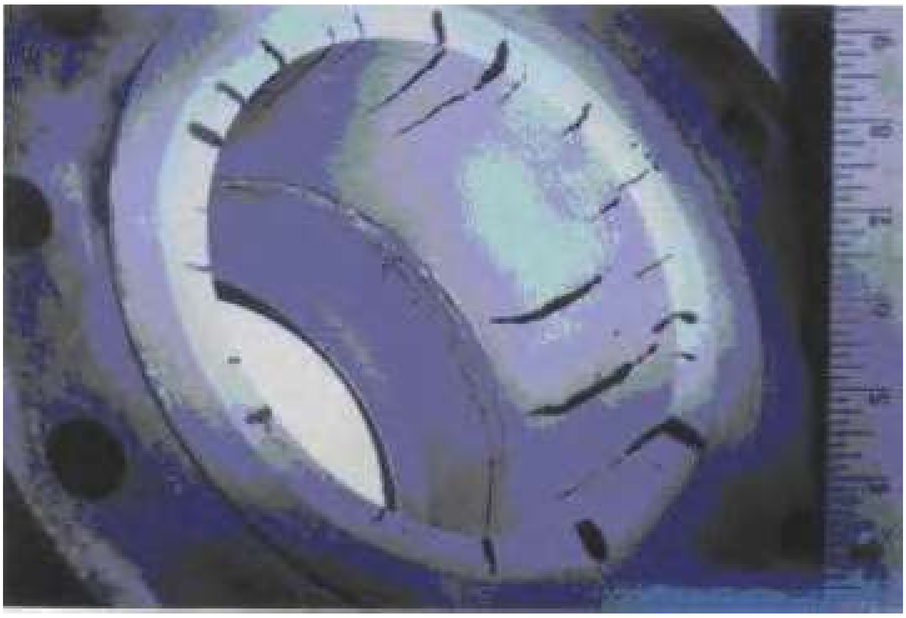

Figure 3-52-3—PT inspection of a Type 304 stainless steel catalyst withdrawal line piping and weld neck flange.

Figure 3-52-4—Cross section of the catalyst withdrawal line attached to the flange in Figure 3-50-3 showing cracking in the weld HAZ. Magnification 3X.

Figure 3-52-5—Higher-magnification view showing intergranular cracking. Magnification 200X.