3.67 Wet H_2S Damage (Blistering/HIC/SOHIC/SSC)

3.67.1 Description of Damage

This section describes four types of damage that result in blistering and/or cracking of carbon steel, one of which also affects low-alloy steels and some other high-strength or hardenable materials, in wet H_2S environments.

a) Hydrogen Blistering

Hydrogen blisters form bulges primarily on the ID surface of pressure vessels. Hydrogen blistering is rare in seamless pipe but can occur in seam-welded pipe. Blisters are caused by the hydrogen atoms that form on the surface of the steel as a result of corrosion reactions. Sulfur acts as a *recombination poison*, delaying the combining of hydrogen atoms into hydrogen gas molecules (H_2), allowing the hydrogen atoms to linger on the steel surface. The small hydrogen atoms can then readily diffuse into the steel. (This *hydrogen charging* effect applies to all types of wet H_2S damage.) The hydrogen atoms diffusing into the steel collect at discontinuities such as inclusions or laminations, where they then combine to form H_2 gas, because there is no recombination poison within the steel to inhibit the reaction. The hydrogen gas molecules thus become trapped at the site because they are too large to diffuse away through the steel. As corrosion proceeds, hydrogen atoms continue to form on the surface and then diffuse into the steel to become trapped as H_2 at the collection sites, building the H_2 gas pressure to the point where local deformation occurs, forming a blister. Blistering only results from hydrogen generated by corrosion, not from hydrogen gas in the process stream. (See Figure 3-67-1 and Figure 3-67-2 for blistering damage.)

HCN accentuates the problem by weakening protective films on the metal surface, thereby increasing the rate of corrosion. This in turn leads to increased hydrogen charging and associated wet H_2S damage. (This also applies to all types of wet H_2S damage.)

b) Hydrogen-induced Cracking (HIC)

HIC results from the same cause as blistering, i.e. from hydrogen atoms diffusing into the steel as a result of corrosion. However, in this case, when the hydrogen atoms diffuse into the steel, rather than forming blisters, internal separations parallel to the surface of the steel result. Again, it is the pressure buildup resulting from hydrogen atoms combining to form H_2 gas that cause the internal separations within the wall of the vessel. The separations are initially microscopic in size but can connect together to form macroscopic-sized cracks, by growing into one large separation on the same plane parallel to the surface or more commonly by linking up with HIC on different planes (at different depths into the wall), eventually forming a thru-wall leak path. Interconnecting cracks between HIC separations on different planes have a stair step appearance, and so HIC is sometimes referred to as “stepwise cracking.” (See Figure 3-67-3 to Figure 3-67-5 for HIC damage.)

c) Stress-oriented Hydrogen-induced Cracking (SOHIC)

SOHIC results from an array of HIC (separations or cracks) stacked on top of each other. When acted upon by a high stress level (residual or applied), the stacked HIC will connect and create a thru-thickness crack that is perpendicular to the surface. SOHIC most often occurs in the base metal adjacent to weld HAZs, the residual stress from welding being the most common driver of SOHIC. SOHIC can initiate from the stacked HIC alone, from sulfide stress cracks, or from other crack-like defects or stress concentrations. SOHIC is a potentially more damaging form of cracking than HIC because of its relatively higher rate of developing a thru-wall crack. In addition, an absence of visual blistering may leave a false sense of security that H_2S damage is not active, yet subsurface SOHIC may be present. (See Figure 3-67-6 to Figure 3-67-8 for SOHIC damage.)

d) Sulfide Stress Cracking (SCC)

SSC is the cracking of a susceptible metal under the combined action of tensile stress and corrosion in the presence of water and H_2S. SSC is a form of HE cracking (see 3.40) resulting from absorption of atomic hydrogen that is produced on the metal surface by the corrosion process. In addition to carbon steel and low-alloy steels, martensitic stainless steels such as Type 410 are also susceptible if hardness is not controlled to a low enough level.

SSC occurs in high-strength (high-hardness) steels but can also initiate in highly localized zones of high hardness in weld metal and HAZs. While SSC is uncommon in modern (post-1980) steels, zones of high hardness can sometimes be found in weld cover passes and attachment welds that are not tempered (softened) by subsequent passes. PWHT is beneficial in reducing the high hardness and residual stresses that render steel susceptible to SSC and is essential when welding hardenable low-alloy steels including Cr-Mo steels, as well as martensitic stainless steels. Some carbon steels contain REs that form hard areas in the HAZ that will not temper at normal stress-relieving temperatures. Using preheat helps minimize these hardness problems. While high-strength steels are susceptible to SSC, they are only used in limited applications such as valve internals and similar internal components in the refining industry.

Hard welds and hard spots within otherwise soft welds can arise with SAW when an active flux is used along with high welding voltage. This high hardness can lead to SSC. (See Reference 9.)

The time to failure by SSC decreases as the steel strength, level of tensile stress, and hydrogen charging potential of the environment increase. (See Figure 3-67-9 and Figure 3-67-10 for SSC damage.)

3.67.2 Affected Materials

Carbon steel, and in the case of SSC, low-alloy steels, and martensitic stainless steels.

3.67.3 Critical Factors

a) A liquid water phase containing H_2S, i.e. a *sour environment*, must be present and must contact the steel in order for wet H_2S damage to occur. (Equipment highly susceptible to SSC can fail even during short SW excursions such as might be encountered during equipment shutdowns.) Beyond this, the critical factors that affect and differentiate the various forms of wet H_2S damage are environmental conditions (H_2S level, pH, contaminants, and temperature), material properties [microstructure and hardness (which correlates to strength)], and tensile stress level (applied or residual).

b) All of these damage mechanisms are related to the absorption and permeation of hydrogen in steels.

c) H_2S level.

1. Hydrogen permeation increases with increasing H_2S partial pressure due to a concurrent increase in the H_2S concentration in the water phase.

2. A value of 50 ppmw H_2S in the water phase is often stated as the minimum concentration where wet H_2S damage can occur. However, there are cases where cracking has occurred at lower concentrations or during upset conditions where wet H_2S was not ordinarily anticipated. The presence of as little as 1 ppmw of H_2S in the water has been found to be sufficient to cause hydrogen charging of the steel.

3. Susceptibility to SSC increases with increasing H_2S partial pressure in the gas phase, as long as there is a water phase present concurrently. An H_2S partial pressure above about 0.05 psia (0.0003 Mpa) can cause SSC in steels with a tensile strength above about 90 ksi (620 MPa), in steels with localized zones of weld or weld HAZ hardness above 237 HB, or in non-PWHT'd or inadequately PWHT'd Cr-Mo steel welds. This partial pressure value is based primarily on oilfield experience and is not exact. The H_2S partial pressure to cause SSC will vary depending on other contributing factors, including steel strength and hardness, pH, and stress level.

d) pH.

1. Hydrogen permeation and diffusion rates in steel have been found to be minimal at pH 7 and increase at both higher and lower pH.

2. Decreasing pH below 7 increases the potential for wet H_2S damage. At pH < 4, only a small amount (ppm levels) of H_2S is needed. However, wet H_2S damage can also occur at pH above 7. If an environment with an alkaline pH is corrosive and contains H_2S, e.g. ammonium bisulfide, wet H_2S damage can still occur.

3. Increasing levels of ammonia may push the pH higher into the range where cracking can occur.

4. Rich amine solutions are also an alkaline environment where wet H_2S damage can occur. See 3.3.

e) Contaminants.

1. Salts or other species in the water phase that decrease the pH or increase the corrosion rate will increase the hydrogen charging rate and, therefore, the severity of the wet H_2S damage environment.

2. HCN in the water phase can cause increased corrosion rates, which significantly increases hydrogen permeation in alkaline (high-pH) SW and thereby increases the potential for all forms of wet H_2S damage. For example, at pH > 7.6 with 20 ppmw dissolved HCN in the water, as little as 1 ppmw total sulfide content in the water can cause SSC.

f) Temperature.

1. Blistering, HIC, and SOHIC have been found to occur between ambient temperature and 300 °F (150 °C) or higher.

2. SSC potential is greatest at about 70 °F (20 °C) and decreases with increasing or decreasing temperature. This is likely related to the rate of diffusion of hydrogen and its behavior in steel at different temperatures. SSC is generally a concern below about 200 °F (95 °C); however, the limiting temperature above which SSC is no longer a concern will depend on the situation, i.e. on the hardness of the steel involved and the severity of other environmental factors such as pH.

   — If susceptible metals become charged with hydrogen during high-temperature exposure [e.g. above 200 °F (95 °C)], they can subsequently crack when cooled back down to ambient.

g) Microstructure.

1. Blistering and HIC are strongly affected by the presence of inclusions and laminations, which provide sites for diffusing hydrogen to accumulate.

   — Flat, elongated manganese sulfide (MnS) inclusions produced by ordinary steel plate rolling practices are particularly detrimental. However, steel chemical composition and manufacturing methods can be tailored to produce HIC-resistant steels. (See Reference 6.)

   — Improving steel cleanliness and processing to minimize blistering and HIC damage may still leave the steel susceptible to SOHIC.

2. HIC is often found in so-called “dirty” steels with high levels of inclusions or other internal discontinuities from the steel-making process.

h) Hardness.

1. Hardness is primarily an issue with SSC. Blistering, HIC, and SOHIC damage are not related to steel hardness. Typical carbon steels used in refinery applications are not expected to be susceptible to SSC because their strength and hardness is sufficiently low. Welds in carbon steel should be controlled to produce weld hardness < 200 HB, and they will typically achieve this without any special precautions. Carbon steel welds are not susceptible to SSC unless localized zones of hardness above 237 HB are present.

   — The welds in submerged-arc-welded steel pipe where an acid flux and high welding voltage were used can have hard zones sufficiently hard to cause SSC.

2. High-strength steels (generally those with hardness greater than 22 HRC) or steels that can be hardened by welding, such as Cr-Mo steels, can be susceptible to SSC, and steps need to be taken, such as limiting the hardness of the material or applying PWHT to reduce the hardness of the welds, to prevent SSC. (See Reference 8.)

i) Tensile stress level.

1. Blistering and HIC damage develop without applied or residual stress. PWHT will not prevent them from occurring.

2. The tensile stress needed to cause SOHIC typically comes from weld residual stresses, which, in the absence of thermal stress relief, are typically very high, i.e. approaching the yield strength. High local stresses or notch-like discontinuities such as shallow sulfide stress cracks can serve as initiation sites for SOHIC. PWHT is somewhat effective in preventing or reducing SOHIC damage.

3. The tensile stress needed to cause SSC in a susceptible material can come from applied stress or residual stress.

— High-strength components are typically used in the non-welded condition and, therefore, are most likely to fail from applied stress. A highly susceptible material, e.g. one with very high hardness, needs relatively little tensile stress to cause SSC.

— Hardenable steels that are welded need to be PWHT'd to reduce hardness in order to avoid SSC, and the PWHT will also relieve residual stresses. PWHT (for stress relief) of carbon steel is normally not necessary, but if there is concern for localized hard spots in the HAZ due to the chemical composition of the steel, PWHT will relieve the weld residual stresses even if it does not reduce the hardness of the hard spots, and relief of the residual stresses will help minimize the likelihood of SSC.

3.67.4 Affected Units or Equipment

a) Blistering, HIC, SOHIC, and SSC damage can occur throughout the refinery wherever there is a wet H_2S environment present.

b) In hydroprocessing units, an ammonium bisulfide concentration above 2 % increases the potential for blistering, HIC, and SOHIC.

c) Cyanides, particularly in the vapor recovery sections of FCC and delayed coking units. significantly increase the probability and severity of blistering, HIC, and SOHIC damage. Typical locations include fractionator overhead drums, fractionation towers, absorber and stripper towers, compressor interstage separators and knockout drums, and various heat exchangers, condensers, and coolers.

d) SWS and amine regenerator overhead systems are especially prone to wet H_2S damage because of generally high ammonia or ammonium bisulfide concentrations and cyanides.

e) SSC is most likely found in hard welds and HAZs and in high-strength components including bolts, relief-valve springs, 400 series SS valve trim, and compressor shafts, sleeves, and springs.

3.67.5 Appearance or Morphology of Damage

a) All four forms of wet H_2S damage are best illustrated though the photos and diagrams shown in Figure 3-67-1 to Figure 3-67-10.

b) Hydrogen blisters appear as bulges, most often on the ID surface of the steel, but can be found anywhere in the shell plate or head of a pressure vessel. Blistering has been found on rare occasions in seamless pipe; however, large-diameter seam-welded pipe, which is typically made from plate, similar to a pressure vessel, will have susceptibility comparable to pressure vessels. Blistering has even been seen in the middle of a weld, but this is very rare.

c) Late-stage HIC or SOHIC will create surface-breaking cracks.

d) In pressure-containing equipment, SOHIC and SSC damage are most often associated with weldments.

e) Blisters and HIC typically are not associated with welds but rather occur within and sometimes throughout a shell plate or course. However, they can grow toward and intersect a weld, which increases the likelihood for SOHIC in the HAZ and development of a thru-wall crack.

3.67.6 Prevention/Mitigation

a) Effective barriers, including alloy cladding and coatings, that separate the surface of the steel from the wet H_2S environment can prevent blistering, HIC, and SOHIC. Barrier coatings can also prevent SSC of the underlying material, but they are often considered a temporary measure until a more permanent solution can be put in place.

b) Process changes that affect the pH of the water phase and/or ammonia or cyanide concentration can help to reduce blistering, HIC, and SOHIC. A common practice is to utilize wash water injection to dilute the HCN concentration, e.g. in FCC gas plants. Cyanides can be converted to harmless thiocyanates by injecting dilute streams of ammonium polysulfides. Injection facilities require careful design.

c) HIC-resistant steels can be used to minimize the susceptibility to blistering and HIC damage. Detailed materials and fabrication guidance can be found in Reference 6.

d) PWHT can help minimize susceptibility to SOHIC.

e) PWHT will not prevent blistering or HIC, because they are not initiated by stress and usually occur away from and not associated with welds.

f) SSC in welds can generally be prevented by limiting the hardness of carbon steel welds and HAZs to 200 HB maximum. Similar, but slightly higher, maximum hardness limits are normally applied to Cr-Mo steels for which high hardness is prevented by using preheat, PWHT, and welding procedure control.

g) High-strength materials should be selected in accordance with NACE MR0103/ISO 17945.

h) Specialized corrosion inhibitors can be used.

3.67.7 Inspection and Monitoring

a) Process conditions should be monitored and evaluated by process engineers and corrosion or materials specialists to identify equipment where conditions are most likely to promote wet H_2S damage. Field sampling of the free water phase should be performed on a periodic or as-needed basis to monitor conditions or changes in conditions, particularly if water washing or polysulfide injection is used.

b) Inspection for blistering is normally done by internal VT.

c) Inspection for SOHIC typically focuses on weld seams and nozzles. For details of inspection plans including methods, coverage, and surface preparation, as well as repair, see Reference 1.

d) Cracks from SOHIC or surface-breaking HIC may be seen visually. However, to enable crack detection at an early stage, WFMT, ECT, or ACFM techniques can be used. Surface preparation by grit blasting, high-pressure water blasting, flapper wheel cleaning, or other method is usually required for WFMT but not for ACFM or ECT. PT cannot find tight cracks and is not reliable for finding SOHIC or HIC.

   1. It has become increasingly common to inspect welds on new pressure vessels intended for sour service using WFMT or another high-resolution NDE method. This is done to ensure there are no remaining flaws associated with the welds that would not have been found using standard fabrication inspection protocols when the vessel is first put into service. However, this was not done for most vessels currently in service in refineries. Because of this, extensive inspection on in-service equipment, when similar, high-resolution inspection has not been performed in the past, often leads to finding small, non-growing flaws that likely have been present since initial fabrication and are likely not H_2S damage. Therefore, caution and careful assessment need to be applied.

2. SOHIC occurs in the base metal alongside the weld. If the NDE applied for wet H_2S inspection of welds, i.e. for SOHIC, finds indications in the weld metal, they are likely fabrication weld flaws rather than SOHIC.

e) Angle beam UT techniques including external SWUT and PAUT can be used. These techniques are especially useful for volumetric inspection and crack sizing.

f) Electric resistance instruments are not effective for measuring crack depth.

g) Internal HIC can appear to be deep, clearly defined, individual, sharp-cornered pits when using straight beam UT for thickness measurements on vessel shells or heads. This is caused by the reflection of the ultrasonic sound wave off the internal separation. Practitioners need to be aware of this when interpreting thickness readings on equipment in wet sour service in order to not misinterpret internal HIC as ID pitting.

h) AET can be used to locate cracks and monitor crack growth.

i) If cracking or failure due to SSC is not visually apparent, the cracks can normally be found using MT if they are surface breaking and there is access to the surface, or angle beam UT (SWUT or PAUT) if they are subsurface or on an inaccessible internal surface.

3.67.8 Related Mechanisms

HE (3.40), hydrogen stress cracking in HF acid (3.41), and DMW cracking (3.26). Amine cracking (3.3) and carbonate cracking (3.12) can also occur in wet H_2S environments and may be similar in appearance. They are sometimes confused with wet H_2S damage.

3.67.9 References

1. NACE Standard SP0296, Detection, Repair, and Mitigation of Cracking in Refinery Equipment in Wet H_2S Environments, NACE International, Houston, TX.

2. "Fitness-For-Service Evaluation Procedures for Operating Pressure Vessels, Tanks, and Piping in Refinery and Chemical Service," Materials Properties Council, FS-26, Draft No. 5, Consultants Report, NY, 1995.

3. G.M. Buchheim, "Ways to Deal with Wet H_2S Cracking Revealed by Study," *Oil and Gas Journal*, July 9, 1990, pp. 92–96.

4. R.B. Nielson et al., "Corrosion in Refinery Amine Systems," Paper No. 571, *Corrosion/95*, NACE International, Houston, TX.

5. NACE SP0472, *Methods and Controls to Prevent In-service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments*, NACE International, Houston, TX.

6. NACE Publication 8X194, *Materials and Fabrication Practices for New Pressure Vessels used in Wet H_2S Refinery Service*, NACE International, Houston, TX.

7. R.D. Kane, R.J. Horvath, and M.S. Cayard, editors, *Wet H_2S Cracking of Carbon Steels and Weldments*, NACE International, Houston, TX, 1996.

8. NACE MR0103/ISO 17945, *Petroleum, petrochemical and natural gas industries—Metallic materials resistant to sulfide stress cracking in corrosive petroleum refining environments*, NACE International, Houston, TX.

9. D.J. Kotecki and D.G. Howden, *Submerged-arc-weld Hardness and Cracking in Wet Sulfide Service*, WRC Bulletin 184, Welding Research Council, Shaker Heights, OH, 1973.

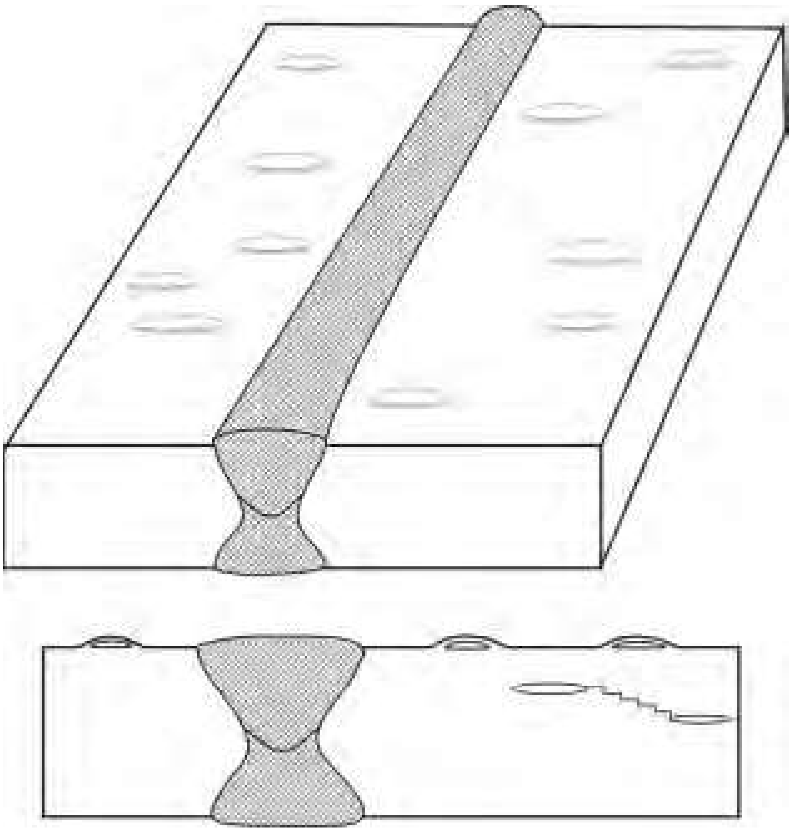

Figure 3-67-1—Illustration showing hydrogen blistering and HIC damage.

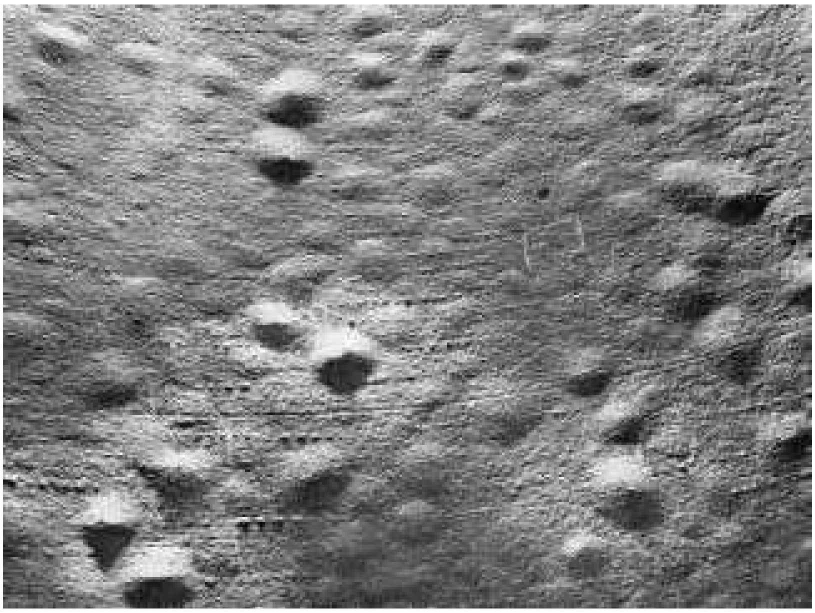

Figure 3-67-2—Extensive hydrogen blistering on the ID surface of a steel pressure vessel.

Figure 3-67-3—HIC damage as shown in the cross section of the shell of a trim cooler that had been cooling vapors off a hot high-pressure separator (HHPS) vessel in a hydroprocessing unit.

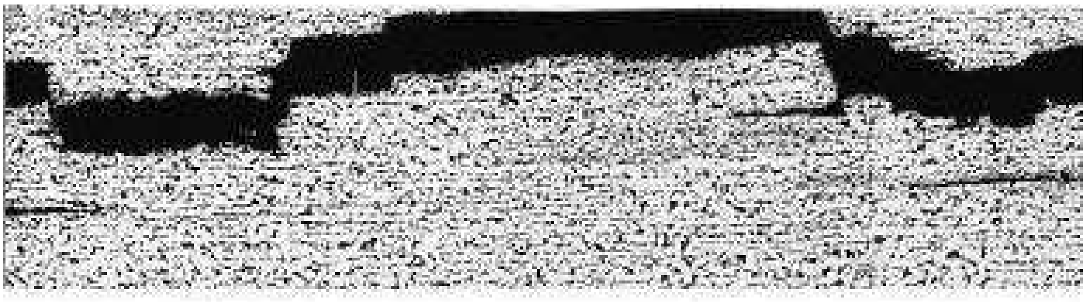

Figure 3-67-4—High-magnification photomicrograph of HIC damage.

Figure 3-67-5—High-magnification photomicrograph showing stepwise cracking nature of HIC damage.

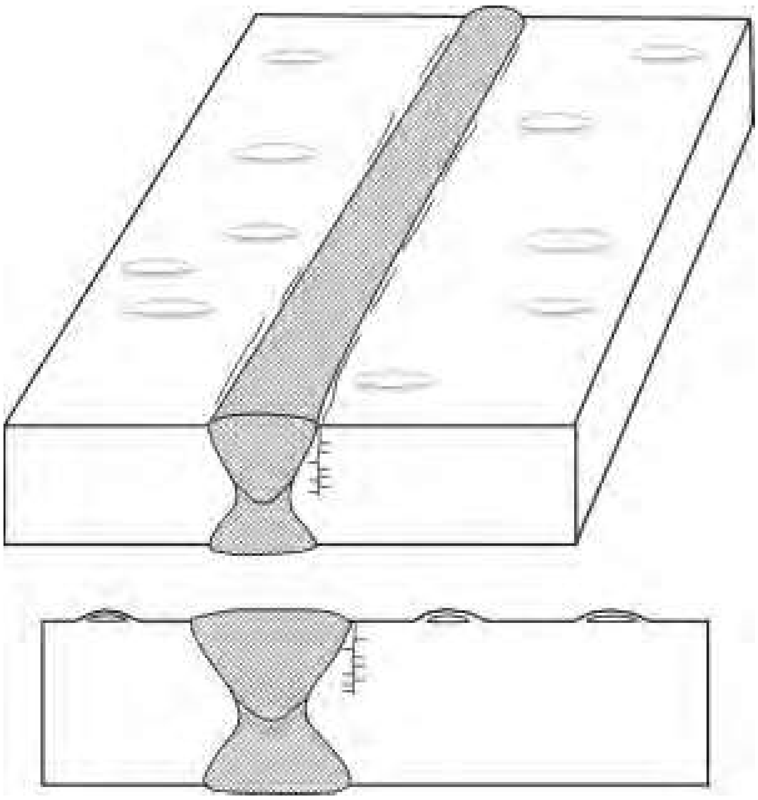

Figure 3-67-6—Illustration of hydrogen blistering that is accompanied by SOHIC damage at the weld.

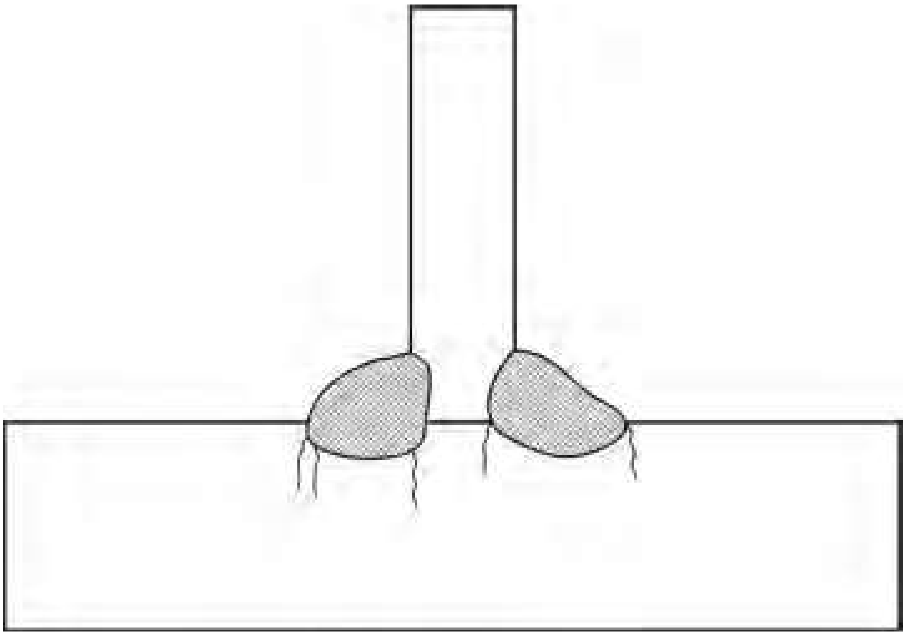

Figure 3-67-7—Illustration of SOHIC damage at a fillet weld that is usually a combination of SSC and SOHIC.

Figure3-67-8—Photograph showing WFMT indication of SOHIC damage.

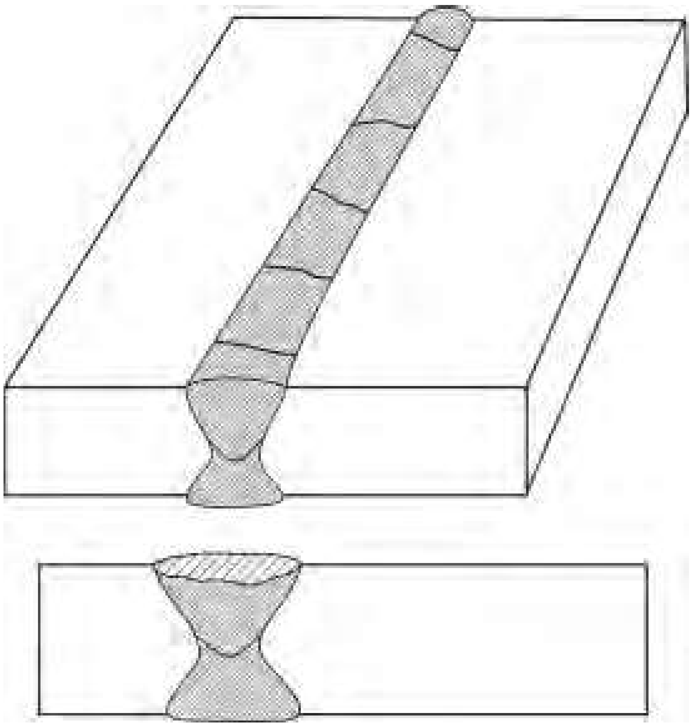

Figure 3-67-9—Illustration of SSC damage in a hard weld.

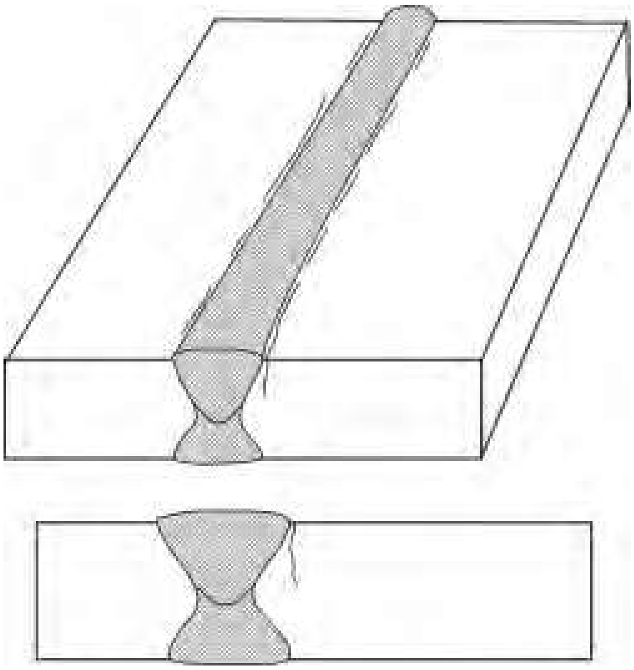

Figure 3-67-10—Illustration showing morphology of SSC in a hard HAZ.