View from the Penthouse

The DNFM Technical News Letter

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Stress-corrosion-cracking (SCC) is a well-defined failure mechanism in metals. In order to have SCC, three conditions must be satisfied: the material must be susceptible, the susceptible environment must be present, and the tensile stresses must have reached the threshold necessary for SCC to develop. Different names have been given to SCC based on the susceptible material and environment. For instance: cracking of high-strength low-alloy steels in hydrogen-enhanced environments is known as hydrogen embrittlement (not to be confused with hydrogen damage); cracking of brass in an ammonia environment is known as season cracking; cracking of austenitic stainless steels in a chloride environment is known as chloride stress-corrosion-cracking; and cracking of carbon steels in a strong alkali environment is known as caustic cracking or embrittlement.

Stress-corrosion cracking can be either intergranular (along the grain boundaries), **Figure 1**, or transgranular (across the grains), **Figure 2**, or both, depending on the conditions. If a crack is induced by the brittle film in the ductile material then the crack will be arrested by ductile blunting. The film reinitiates by the corrosive species and propagates by the residual or applied stresses and this process repeats, resulting in transgranular cracking. Austenitic stainless steels exhibit either transgranular or intergranular cracking. The presence of sensitized austenitic grains may lead to intergranular cracking. Sensitized grain boundaries are less corrosion-resistant due to the depletion of chromium adjacent to the sensitized grains. Whether these SCC cracks are intergranular or transgranular with branching, as shown in **Figure 2**, they always exhibit brittle, thick-edged failures without any significant plastic deformation or wastage. Austenitic stainless steels, as well as austenitic super alloys containing large amounts of Ni, are made resistant to hydrogen embrittlement by cathodic reactions, due to a lower diffusion coefficient and higher ductility. But austenitic stainless steels are very susceptible to chloride SCC at room temperature and are severely susceptible at elevated temperatures. Ferritic carbon steels are susceptible to caustic SCC when exposed to hydroxides. These hydroxides concentrate on discontinuities such as scratches, pits and geometric details in the components.

Intergranular SCC failures in high-temperature superheater/reheater tubes should not be confused with creep failures. In creep failures, intergranular creep voids are present at higher magnifications; this is not the case with intergranular SCC failures. Intergranular SCC typically exhibits the fallen grains on the affected area during polishing, as shown in **Figure 1**. Load swings and low-load conditions may promote SCC in superheaters and reheaters. Attemperator sprays likely introduce the contaminants and load swings or low-load conditions may cause the accumulation of condensate at the bottom of the loops are contributing to chloride-induced SCC, as shown in **Figure 3**. Ferritic steel tubes in boilers may experience caustic embrittlement, but austenitic steels are very susceptible to chloride-induced SCC.

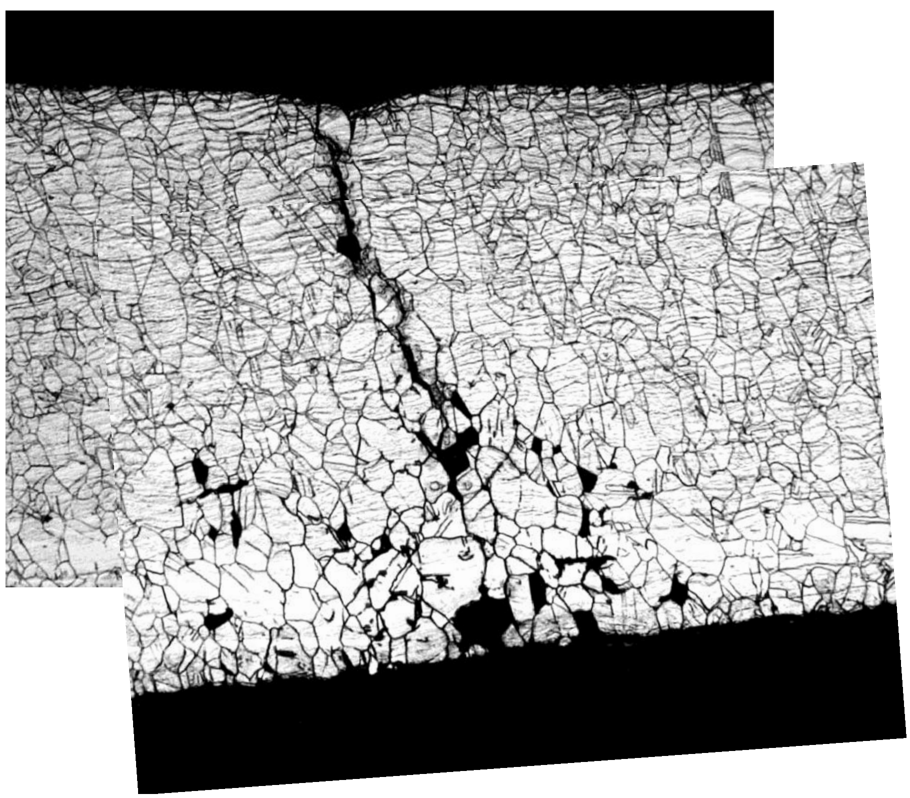

Figure 1. Chloride SCC in austenitic stainless steel tube, 100x.

Figure 2. Severe branching of transgranular cracks in 304H stainless steel flange. 50x.

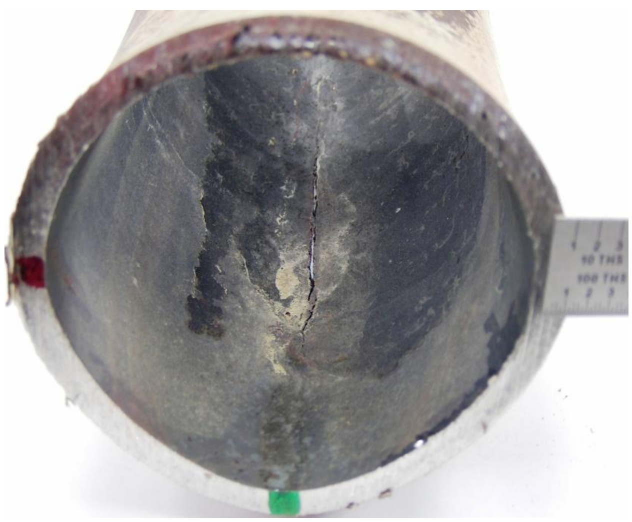

Figure 3. Stress-corrosion cracking at the bottom of a reheater tube bend.

Caustic embrittlement was a significant factor in ferritic steels during the early 1900s due to caustic contamination associated with the riveted joints. Sodium hydroxide (NaOH) was once used for controlling pH of the boiler feedwater. The conditions for caustic embrittlement are concentrated hydroxide, tensile stress and elevated temperature. Nowadays, caustic SCC failures in the ferritic steels of superheaters/reheaters, **Figure 4,** may be the result of caustic introduction in the attemperator or desuperheater spray.

Hydrogen embrittlement is another form of SCC. When high-strength low-alloy steels with enough tensile stress are exposed to hydrogen, they may be subject to brittle failures, as shown in **Figures 5 and 6**. Hydrogen embrittlement is often the result of unintentional introduction of hydrogen into susceptible metals during forming or finishing processes, or during a corrosion reaction. Atomic hydrogen may be generated during a corrosion reaction and may diffuse into the steel, causing hydrogen embrittlement. Stress raisers due to geometric inequalities, manufacturing defects and service-related degradations increase the susceptibility to embrittlement. High-strength, low-alloy steels are very susceptible to this condition. Alternatively, austenitic stainless steels provide better resistance to hydrogen embrittlement. Steels with tensile strength of less than 140 ksi are not susceptible to hydrogen embrittlement. Hydrogen embrittlement is different from hydrogen damage, which is more often seen in boilers operating above 1500 psi. Hydrogen damage occurs without any tensile stress. In hydrogen damage, the atomic hydrogen is trapped underneath thick deposits and diffuses into the steel along the ferrite grain boundaries. Iron carbide in the steel reacts with diffused hydrogen to form a large molecule of methane. This large methane molecule cannot diffuse through the grain boundaries, so collects there and develops significant pressure, leading to grain boundary cracks and, eventually, a thick-edge, low-ductility failure. Depending on the extent of the damage, a complete decarburization may also occur in the microstructure. Hydrogen damage is more prevalent in acidic environments, but it can also occur in strongly basic environments.

As mentioned earlier, the factors affecting SCC are susceptible material in the “right” environment and tensile stresses. Controlling SCC may start with the design process, when material is selected for the operating environment. Selection of material which is not susceptible to SCC plays very vital role in controlling the SCC, as does the fabrication process. On the other hand, we have to live with SCC and monitor the process and components to avoid catastrophic failures. The other requirement for SCC is the presence of tensile stresses. Eliminating or reducing the tensile stresses would eventually reduce the risk of SCC. But this is not always feasible. However, SCC failures resulting from residual stresses (cold working or welding) can be eliminated by appropriate heat treatment. Stress reliving in 300-series austenitic stainless steels may not provide satisfactory results because of the formation of undesirable changes in the steel, such as sensitization and sigma phase. Very high annealing temperature is required to counteract those undesirables. Careful attention is required when stress-relief annealing is performed on large structures. This may induce very high residual stresses in the newer regions if not done properly. Controlling environment, including adding corrosion inhibitors or isolating the susceptible material with coatings, may give satisfactory results. Metallic coatings with lower corrosion potential may protect the base metal, but there might be a possibility of hydrogen evaluation resulting in hydrogen embrittlement in low-alloy steels. However, corrosion inhibitors that reduce general corrosion may create favorable conditions for SCC.

Chlorides or hydroxides are the primary species that cause SCC in boiler tubes. Austenitic stainless steels are susceptible to chlorides and hydroxides, and ferritic steels are susceptible to hydroxides. These can be present from the carryover of volatile chemicals from water walls to the high temperature superheaters/reheaters or desuperheater/attemperator sprays, or can be due to contamination during chemical cleaning. Carryover from the waterwalls can be prevented by maintaining the right drum level. Maintaining the right water treatment can eliminate the possibility of entering these species into the superheaters/reheaters via attemperator sprays. Condenser leaks also contaminate the feedwater. Ingress of fireside species into the reheater tubes during tube failure promotes contamination.

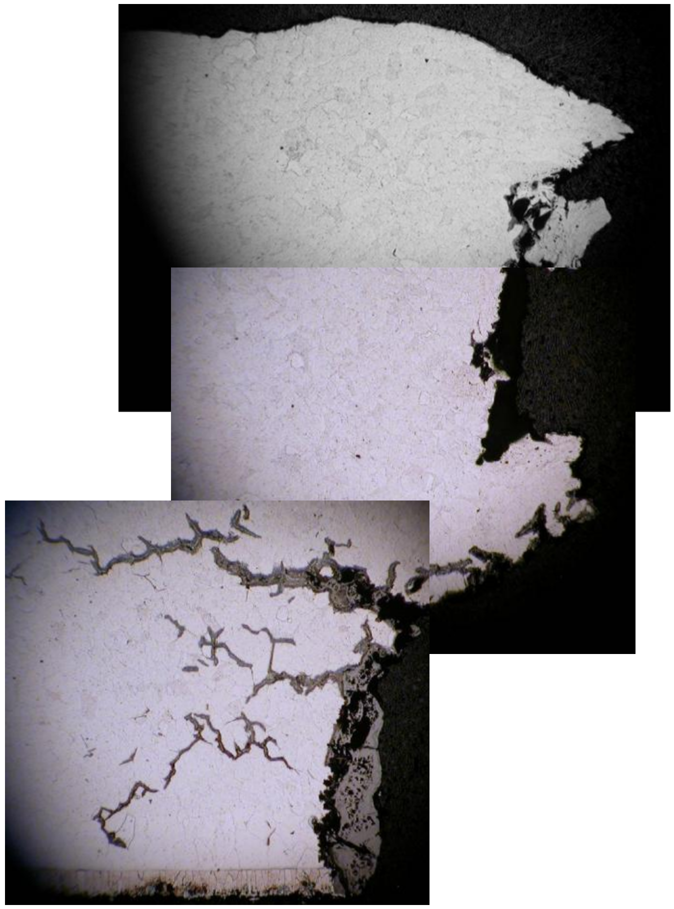

Figure 4. Caustic cracking in a reheater outlet tube, T22 Cr-Mo steel, intergranular cracking. 26x.

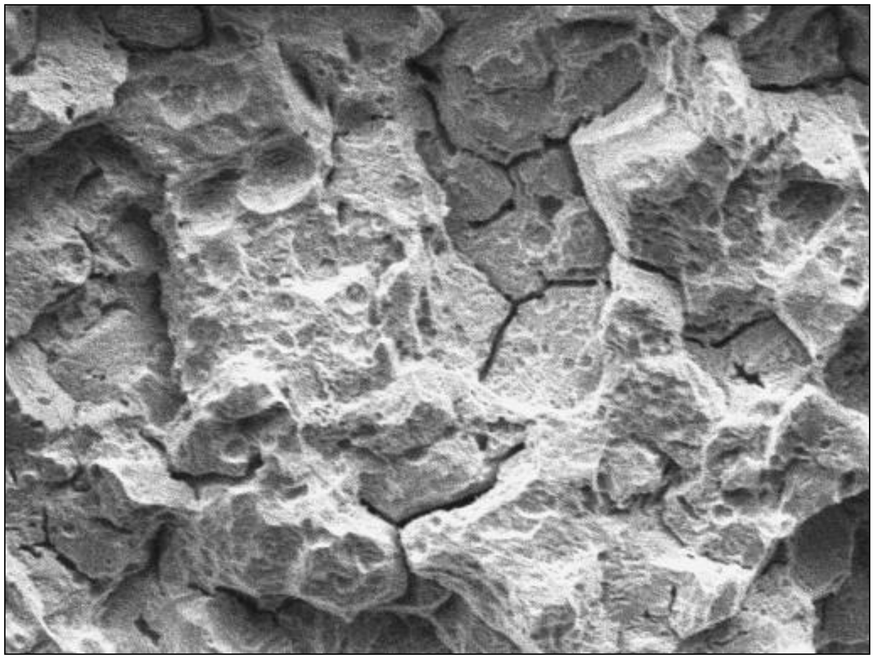

Figure 5. Hydrogen embrittlement, SEM image of intergranular voids in the high strength low alloy steel. 400x

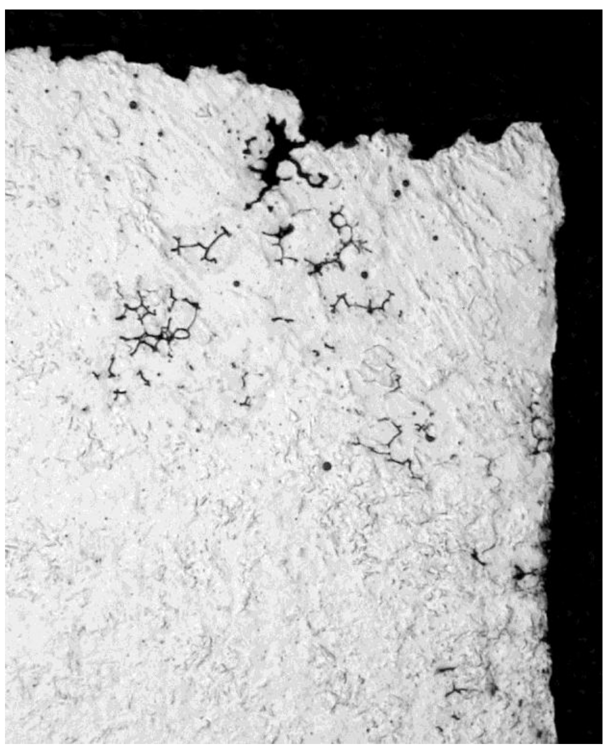

Figure 6. Hydrogen embrittlement damage in a chain link. 100x.