occurrences of caustic SCC with respect to geographic location (Fig. 4, Ref 5) revealed that occurrences of caustic SCC were concentrated in areas where the local water supply had certain chemical characteristics, specifically, water rich in sodium bicarbonate and lacking in sulfates. Over time, sodium bicarbonate in boiler water decomposed to sodium carbonate, which then hydrolyzed to form sodium hydroxide (Ref 5). Sodium hydroxide would then concentrate in crevices, such as between rivets and the boiler plate. (Often, a buildup of solid sodium hydroxide was observed on the outside surface of the boiler plates at the rivet hole locations.) Residual tensile stress from fabrication (i.e., riveting) in conjunction with concentrated sodium hydroxide at elevated temperatures resulted in caustic SCC of both the rivets (Fig. 5, Ref 5) and the steel plate (Fig. 6, Ref 5).

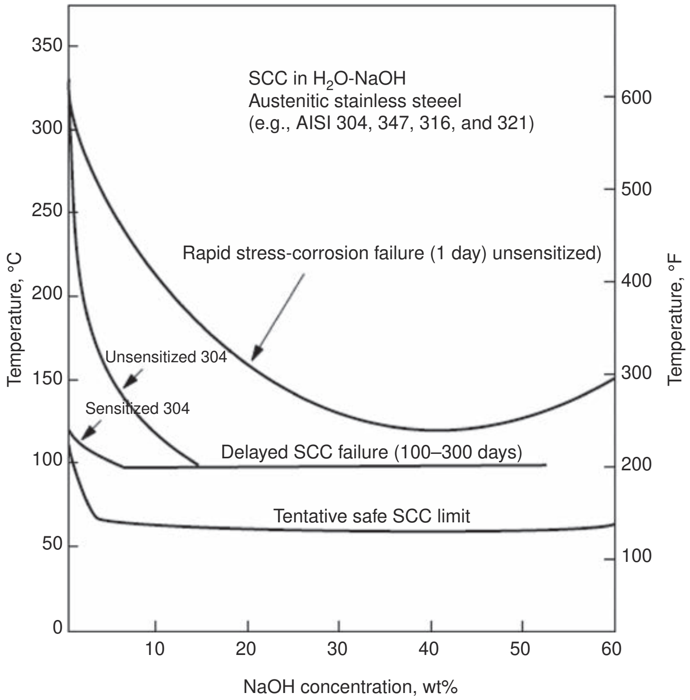

Fig. 3 Plot demonstrating the susceptibility of some austenitic stainless steels to caustic stress-corrosion cracking (SCC) with respect to temperature and caustic concentration. Stress-corrosion cracking has not been observed in these austenitic stainless steels exposed to conditions corresponding to the region below the line identified as "Tentative safe SCC limit." Source: Ref 10

Fig. 4 Map of the United States with red circles identifying the locations of wells whose water was linked to caustic stress-corrosion cracking in boilers in the early 20th century. Source: Ref 5

Chloride Stress-Corrosion Cracking of Insulated Austenitic Stainless Steel

Austenitic stainless steels are susceptible to SCC in chloride-rich environments. While some environments are obviously rich in chlorides, such as marine environments or indoor saltwater pools, a chloride-rich environment may also develop unintentionally, such as when chlorides leach from some wet or moist insulation material. Process piping and vessels are insulated to minimize temperature variations, improve energy efficiency, and for protection of personnel. Because of the high volume fraction of air found in insulation, water can be absorbed and retained in contact with the surface of process piping and vessels when the weatherproofing breaks down/becomes ineffective. Chloride and other halide ions can be leached from the insulation in the presence of moisture from rainwater, which can enhance general corrosion and result in SCC if the piping/vessel material is susceptible. Chlorides then become concentrated at the surface of the vessel from intermittent wetting and drying cycles. Residual stresses from fabrication provide the tensile stress, and SCC develops on the outside surface of the vessel.

Stress

As noted previously, SCC requires the presence of a tensile stress. Furthermore, the magnitude of the tensile stress must be above a certain minimum value. The minimum stress required for SCC has been studied both in terms of a threshold stress and, using a linear elastic fracture mechanics approach, a threshold stress intensity.

Threshold Stress

The stress below which SCC will not occur in a specimen or component is called the threshold stress. The threshold stress depends on temperature, the composition and metallurgical structure of the metal/alloy, and the composition of the environment. For example, in laboratory tests, SCC occurred for one metal-environment combination when the applied stress was as low as approximately 10% of the yield strength, while SCC did not develop for a different metal-environment combination until the applied stress was approximately 70% of yield strength (Ref 7).

An example of the effect of alloy composition on threshold stress is provided by the graph in Fig. 7, which illustrates the relationship between applied stress and time-to-fracture in boiling 42% magnesium chloride solution for various austenitic stainless steel alloys. As indicated by the nearly horizontal portions of the curves, the threshold stress in this environment is approximately 241 MPa (35 ksi) for the higher-alloy stainless steel alloys, types 310 and 314, and approximately 83 MPa (12 ksi) for the lower-alloy stainless steel alloys, types 304 and 304L.

Threshold Stress Intensity

The linear elastic fracture mechanics approach to the study of SCC is focused on the growth of stress-corrosion cracks in specimens

Fig. 5 Photographs of a cracked rivet (top) and dislodged rivet heads (bottom) from a boiler that experienced caustic stress-corrosion cracking. Source: Ref 5

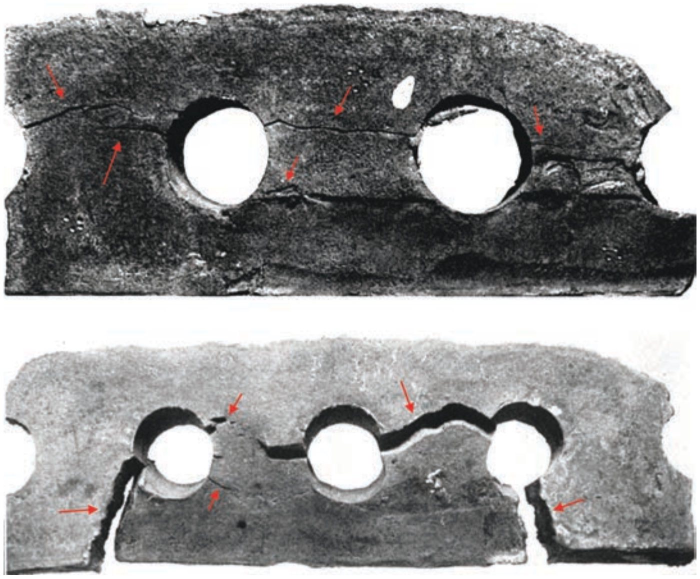

Fig. 6 Photographs of boiler plates exhibiting caustic stress-corrosion cracking (arrows). Source: Ref 5

that contain a small preexisting crack. It uses the stress-intensity factor at the crack tip, K_{I}, to represent the mechanical driving force for SCC. The stress-intensity factor, K_{I}, is related to both the stress level, σ, and the crack size, a, and has units of MPa$\sqrt{\text{m}}$ (ksi$\sqrt{\text{in.}}$). There are different formulas used to calculate K_{I} depending on crack location and geometry. For an edge crack in a component of depth a, $K_{\text{I}} = 1.12\,\sigma\sqrt{\pi a}$.

Figure 8 (Ref 12) is a schematic diagram showing the rate of crack propagation as a function of crack tip stress-intensity factor. An important concept illustrated by this diagram is the threshold stress-intensity, K_{ISCC}, below which SCC does not occur. K_{ISCC} varies for different metal/alloy-environment combinations and also for the same metal/alloy subjected to different thermomechanical processing in the same environment. For example, three pieces of 4340 steel cut from the same plate and heat treated to strength levels of 896, 1241, and 1517 MPa (130, 180, and 220 ksi) exhibited K_{ISCC} values of 122, 28.5, and 11.5 MPa$\sqrt{\text{m}}$ (111, 26, and 10.5 ksi$\sqrt{\text{in.}}$), respectively (Ref 13). For austenitic stainless steel in hot chloride solutions, K_{ISCC} values as low as 0.16 MPa$\sqrt{\text{m}}$ (0.15ksi$\sqrt{\text{in.}}$) have been reported (Ref 14, 15).

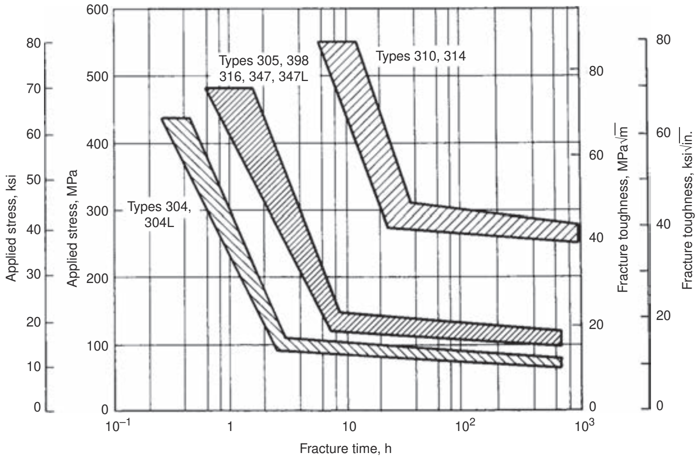

Fig. 7 Relative stress-corrosion cracking behavior of austenitic stainless steels in boiling magnesium chloride. Source: Ref 11

Sources of Stress

Stress-corrosion cracking will occur when the cumulative tensile stress (applied plus residual) in the metal/alloy exceeds the threshold stress/threshold stress intensity. An important role of tensile stress is related to the rupture of protective films during both initiation and propagation of cracks. These films may be tarnish films, such as those on brasses; thin oxide/hydroxide films; films richer in the more noble element of an alloy, such as a copper-gold alloy; or other protective films.

The types of stresses that can contribute to the magnitude of the overall tensile stress in a component include residual stress from welding, manufacturing, or fabrication, installation stresses, and operating stresses. While many, if not all, of these stresses are generally considered during the design of equipment and components, additional, unexpected stresses can result in SCC failures. Examples of unexpected stresses include:

- Misalignment during fabrication and installation
- Thermal expansion/contraction due to unexpected heating/cooling (e.g., doors left open, insufficient insulations, etc.)
- Deformation due to mechanical damage (e.g., component was dropped or hit)
- Rotating equipment that is out of balance
- Imposing loads beyond what is specified by the original equipment manufacturer's specifications
- Misalignment of gears, splines, or couplings

With respect to the prevention or mitigation of SCC, or the investigation of an SCC failure, it is important to not only understand the obvious loading conditions but to also investigate unexpected loading conditions that may occur and result in the initiation and propagation of SCC.

Stages of Stress-Corrosion Cracking

The development of stress-corrosion cracks involves both crack initiation and crack propagation.

Crack Initiation

Stress-corrosion cracks generally initiate at surface irregularities that may exist before or develop after the surface is exposed to the environment. Figure 9 (Ref 16) illustrates common crack-initiation sites for SCC. Stress-corrosion cracking can initiate at locations subjected to pitting corrosion (if the pits are sufficiently elongated), crevice corrosion, intergranular corrosion, or dealloying. (It is generally accepted that the pit depth should be more than 10 times the width of the lateral corrosion/opening of the pit for SCC to occur, Ref 12.) A more in-depth discussion of these types of corrosion can be found in *Corrosion: Fundamentals, Testing, and Protection*, Volume 13A of the *ASM Handbook*, 2003, and in the article "Forms of Corrosion" in this Volume.

Likewise, SCC can initiate at surface-connected porosity, surface-connected inclusions, coarse machining marks, and fatigue cracks. Some of these features are conducive to the concentration of injurious ions. The geometry of many of these surface features can act to locally concentrate the stress and thereby encourage the initiation of SCC.

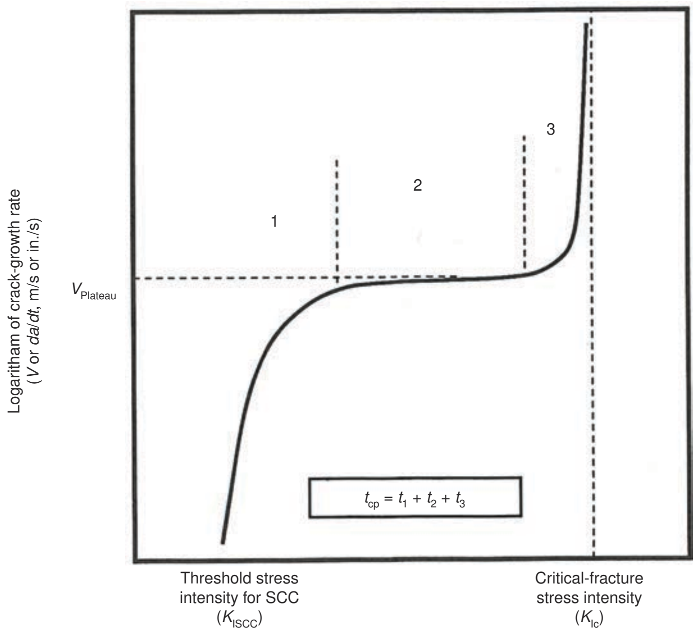

Fig. 8 Schematic diagram of typical crack-propagation (cp) rate as a function of crack tip stress-intensity behavior illustrating the regions of stage 1, 2, and 3 crack propagation. SCC, stress-corrosion cracking. Source: Ref 12

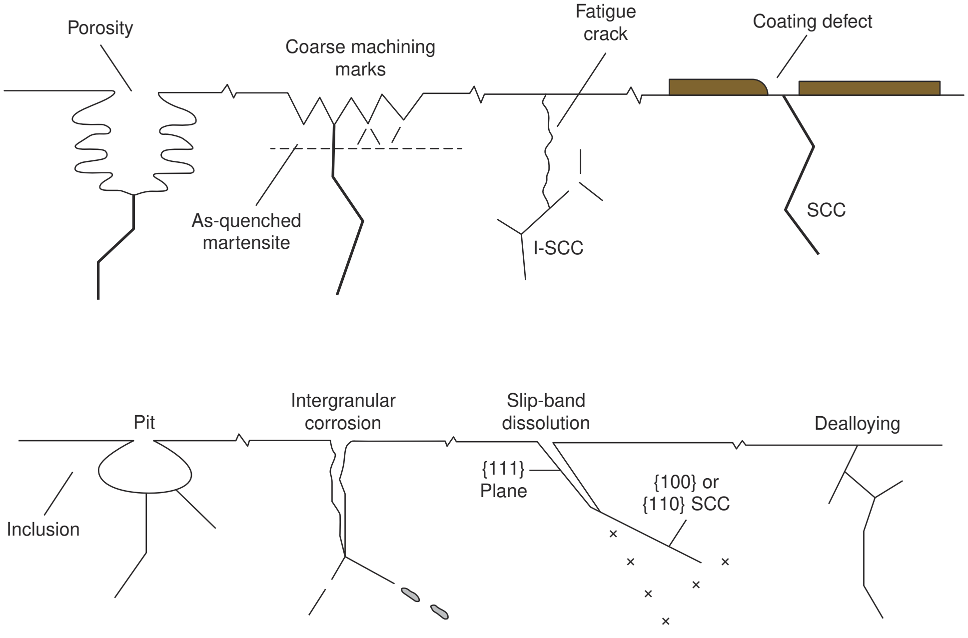

Fig. 9 Schematic diagrams illustrating common crack-initiation sites for stress-corrosion cracking (SCC). Adapted from Ref 16

Crack Propagation

As noted earlier, the linear elastic fracture mechanics approach to the study of SCC is focused on the growth of stress-corrosion cracks in specimens that contain a small preexisting crack. In other words, it focuses on the propagation of SCC cracks. Figure 8, which is a schematic diagram showing the rate of crack propagation as a function of crack tip stress-intensity factor, shows three stages of SCC crack propagation. (The crack-propagation rate is depicted by da/dt, the change in crack length per unit of time. The stress intensity factor, K, represents the intensification of stress at the tip of a crack of a known size and shape. For more information, refer to the appropriate sections of *Fatigue and Fracture*, Volume 19 of the *ASM Handbook*, 1996.) Stage 1 involves a rapidly increasing crack-growth rate once the crack tip stress-intensity factor exceeds the threshold stress intensity, K_{ISCC}. Stage 2 represents a plateau at intermediate values of crack tip stress-intensity factor. In stage 2, the crack growth is essentially constant over a range of crack tip stress-intensity factors. The actual crack-growth rate during stage 2 crack propagation is a function of the particular alloy/environment combination and may vary by orders of magnitude, depending on the alloy composition, heat treatment, degree of cold work, pH, and electrochemical potential. The lack of dependence of the crack-growth rate on stress intensity indicates that the crack-growth rate in stage 2 is controlled by chemical factor(s) rather than mechanical conditions. Stage 3 involves increasing crack-growth rates until failure occurs.

Brief Overview of Proposed Stress-Corrosion Cracking Propagation Mechanisms

Despite approximately a century of research, there is no consensus among researchers as to a single, universal mechanism by which all SCC propagates. It is likely that there are different mechanisms, or a combination of mechanisms, that are metal- and environment-specific. For example, the mechanism for caustic SCC of carbon steels may be different from that which occurs for ammonia SCC of brass or even caustic SCC of austenitic stainless steels.

Stress-corrosion cracking mechanisms, however, must account for the characteristics of SCC including:

- The requirement of both a tensile stress and a corrosive environment
- The initiation and propagation of brittle cracks in an otherwise ductile metal
- The initiation and propagation of cracks at stress levels below the fracture toughness or yield, tensile, and fatigue strengths of the metal
- The discontinuous nature of the crack propagation
- The morphology of the cracking (e.g., inter- or transgranular cracking, presence or lack of crack tip branching)
- The specificity of the metal-environment combination
- The (potential) lack of corrosion product

Currently, there are four general categories of SCC propagation mechanisms: anodic dissolution, film-induced cleavage, adsorption-based mechanisms, and hydrogen embrittlement. Each mechanism is described briefly. For a more in-depth discussion, the reader is referred to the articles “Introduction to Environmentally Induced Cracking” and “Introduction to Forms of Corrosion” in *Corrosion: Fundamentals, Testing, and Protection*, Volume 13A of the *ASM Handbook*, 2003, as well as the Selected References at the end of this article.

Anodic Dissolution/Slip-Step Dissolution

The anodic dissolution mechanism theorizes that metal present only at the crack tip will dissolve by anodic electrochemical reactions. A protective film forms on the metal surface when it is exposed to a corrosive environment. Slip steps form at the crack tip because of the concentration of tensile stress. Eventually, these slip steps can cause an opening in the protective film, exposing bare metal to the corrosive environment. The bare metal at the slip step will then corrode, which advances the crack, until the protective film is reestablished and the process begins again.

Film-Induced Cleavage

Depending on the material and environment involved, a brittle protective film forms on a metal surface when it is exposed to a corrosive environment. Because of the brittle nature of the protective film, the tensile stress will initiate a crack in the protective film that will propagate through the protective film and into the ductile metal underneath. Once it penetrates the ductile metal, the crack tip is blunted and the propagation ceases. The protective film begins to form on the newly exposed metal surface, and the process begins again.

Adsorption-Based Mechanisms

When exposed to a specific corrosive environment that contains material-specific injurious ions and is at the conducive temperature and pH, either the protective film becomes unstable and breaks down at discrete locations (likely at crystallographic defect sites), leaving bare metal exposed to the environment, or the injurious ions diffuse through the protective film to the metal surface.

Injurious ions will chemisorb on the metal surface, forming a bond between the ion and the metal atom. There are several proposed mechanisms that describe how the adsorbed injurious ions facilitate crack propagation. The specific steps involved in each mechanism vary widely and are not discussed here. For an in-depth discussion of these mechanisms, the reader is directed to Chapter 1 of Ref 16. Regardless of the specific mechanisms, the chemisorbed ions result in the propagation of cracks in a brittle fashion at stresses below the fracture strength of the metal.

Hydrogen Embrittlement

Hydrogen embrittlement occurs when atomic hydrogen diffuses into a metal, embrittling it. Although it is a considered a distinct and separate mechanism from SCC, it is also the mechanism by which stress-corrosion cracks propagate for certain metal-environment combinations. Hydrogen is generated during the cathodic reaction associated with electrochemical corrosion. These nascent hydrogen atoms diffuse interstitially through the metal, driven by stress-concentration gradients, and collect along grain boundaries and precipitate or inclusion boundaries, facilitating fracture at those locations. Stress-corrosion cracks in high-strength steel alloys and martensitic stainless steels can propagate by hydrogen embrittlement.

Diagnosing Stress-Corrosion Cracking

The methodology employed to investigate an SCC failure is the same as for any failure analysis investigation. The general structure of a failure analysis investigation is discussed in the Section “Practice of Failure Analysis” in this Volume. The main purpose of this section is to discuss characteristics indicative of SCC that can be revealed during the examination and testing phase of a failure analysis investigation and to discuss the types of data, information, and samples that should be collected and analyzed to determine how and why SCC occurred.

Often, it is not the presence of a single characteristic that will identify an SCC failure but the observation of multiple characteristics. The analysis of service conditions and other process- and environment-related data is often the key to understanding why SCC occurred.

Detection of Stress-Corrosion Cracking

Stress-corrosion cracking failures do not always result in catastrophic failures. The purpose of mechanical integrity and other inspection programs is to detect, and correct or mitigate, the presence of detrimental conditions prior to complete failure or fracture. Inspection methods commonly used to detect SCC include surface techniques such as visual examination, magnetic-particle inspection, and liquid penetrant inspection in addition to volumetric inspection techniques such as ultrasonic inspection.

Once cracking is found, an investigation can determine if the cracking is SCC and identify the conditions responsible for its development.

Investigation

A failure analysis investigation begins with the identification of a failure either because of an unexpected fracture, leak, or other service disruption or process fault, or through routine nondestructive examinations.

Sometimes it may not be possible to complete all of the steps discussed here, due to the specific circumstances of the failure. Many of the SCC failures that are investigated occur in industrial facilities where the initial focus after the failure is to limit/stop the release of chemicals or process fluids, reduce hazards to life and property, and/or return the system to service as quickly as possible. It is possible that evidence important to the failure investigation is lost as a result of these activities or the manner in which the failure occurred. Each failure investigation presents a unique set of circumstances, and an investigator must collect the available information, data, and samples for analysis.

Once SCC has been discovered, the failed component should be secured in such a way that minimizes handling and prevents further damage. Ideally, the component should be left in place for examination by the failure investigator. Often, however, this is not practical. In such cases, prior to the removal of the failed component:

- The component and surrounding environs should be documented with sketches, photographs, and/or videos prior to removal.
- If a site visit cannot be performed prior to removal, the failure investigator should review the previously described documentation and advise what samples, in addition to the failed component, should be taken. This could include samples of deposits or debris related to the failure.
- Care should be taken to protect fracture surfaces (if apparent) and minimize impact on the component due to the removal process. (Prior to removal, fracture surfaces can be covered in clean bubble wrapping, foam padding, or other appropriate material to prevent inadvertent damage during removal. If a breach is present, and a complete fracture has not occurred, the clean padding or other appropriate material may be inserted between the crack surfaces to prevent the rubbing of these surfaces during removal. Further, appropriate structural support should be used to prevent/reduce deformation.) Note that fractured components should never be reassembled in such a way that the fracture surfaces come into contact with each other. This can damage or obscure fracture features that may aid in the determination of the failure mechanism.

Once removed, the component and collected samples should be secured so that they are not exposed to environments that will degrade the samples, such as extreme temperatures or adverse weather conditions, or will disturb evidence such as corrosion products or other deposits that may be attached to the samples. Ultimately, all samples should be shipped to a laboratory facility for examination and testing as soon as possible after collection.

In addition to the samples collected for the laboratory examination and testing, information and data related to the service conditions of the component should also be requested and collected. These data should include:

- A description of the environment to which the component was exposed at the time of the failure, specifically, the environment to which the surface where the SCC initiated was exposed
- A description of the service in which the component was placed. (This information may be quite simple, as would be expected for a clamp or structural support, or require a review and understanding of the process conditions, as would occur in a chemical plant or power plant.)
- A history of the component, process unit, and/or service conditions. (Because SCC failures generally do not immediately occur upon exposure to the environment/stress, the source of the corrosive environment may be the result of a transient condition, poor process control, or a process upset that occurred at some time previous to the discovery of the failure. Historical data regarding process conditions, for example, temperature, conductivity, composition, pressure, and so on, can be informative when determining how/why SCC developed and should be requested.)
- Material and fabrication specifications of the component
- Details regarding what occurred just prior to, during, and immediately after the failure
- A description of maintenance performed on the component and inspection reports related to the component

While the diagnosis of SCC as a failure mechanism is dependent on the results of examination and testing, as discussed later, the information described earlier can be used to determine the material and condition that made it susceptible to SCC, the environment, and the stress state, which are prerequisites for SCC.

Laboratory Examination and Testing

The main purpose of laboratory examination and testing is to determine the fracture/cracking mechanism and to collect physical data that can be used to determine how the conditions (material, environment, stress) developed that resulted in the fracture/cracking.

It is worth taking a moment here to define what is meant by the use of the terms *crack* or *cracking* versus the use of the term *fracture*. *Crack* or *cracking* refers to a localized fracture without complete separation of the component. *Fracture* refers to the complete separation of a component into two or more parts. In practical terms, the fracture surface should be visible and easy to examine, while a crack surface must be liberated from the failed component and opened before it can be examined. However, both fracture and crack surfaces will exhibit the same general characteristics and morphology of the fracture mechanism by which they were formed. The characteristics and morphology of SCC are discussed in detail later.

A detailed description of the types of testing and analyses used as part of a failure analysis investigation can be found in the articles "Examination of Damage and Material Evaluation," "Nondestructive Evaluation Applications for Failure Analysis," "Bulk and Microscale Composition Analysis," "Microfractography and Metallography for Failure Analysis," and "Mechanical Testing in Failure Analysis" in this Volume. The discussion in this section is limited to how testing and analyses can be used in the determination of SCC and the conditions required for its development.

The types of examination and testing include:

- Visual examination
- Nondestructive examination
- Microscopic examination of fracture/crack surface using a stereomicroscope and/or scanning electron microscope
- Collection and analysis of corrosion product or other deposits
- Metallographic examination
- Hardness testing and/or other mechanical tests
- Chemical analysis of the component to identify the bulk chemical composition and possibly composition gradients within the component

The initial step is a visual examination and documentation of the fractured/cracked component. Other nondestructive examination techniques may be used to identify all locations that exhibit cracking and to determine the exact location and depth of the cracks detected. Once all of the crack locations have been identified and documented, cracks can be opened for examination as a means to determine the cracking mechanism (i.e., to determine if they are stress-corrosion cracks). Often, the fracture surface or primary crack surface may be covered with corrosion product or other deposits that can obscure or destroy fracture features that are informative with respect to the fracture mechanism. Fracture features may also be obscured or destroyed as a result of the failure (e.g., erosion from escaping process fluids). Under these circumstances, it is often necessary to open secondary cracks that appear to be of the same orientation and morphology as the fracture/primary crack. The surfaces of these opened cracks are generally not as degraded by the environment and can provide data that have been obliterated on the fracture/primary crack surface. It must also be noted that the presence and location of secondary cracks can be instructive when determining a failure mechanism.

Opening secondary cracks is commonly achieved by making a saw cut from the surface opposite the cracked surface to the tip of the crack and mechanically forcing the crack to continue to propagate to complete fracture. Figure 10 provides a view of an opened secondary crack with the laboratory-induced fracture and cut surfaces identified.

Macroscopic Characteristics of Stress-Corrosion Cracking

As discussed previously, one of the characteristics of SCC is the development of brittle cracks in a normally ductile material. Given the brittle nature of SCC, a component exhibiting SCC will have the same general dimensions regardless of the presence of cracking.

Thinning or plastic deformation that is normally associated with ductile cracking and fracture will not be observed adjacent to the fracture surface (Fig. 11). Because of this, it may be prudent to measure key dimensions for comparison to the component drawing or, if drawings of the component are not available, comparison to an exemplar component of the same design.

In general, the fracture/crack surface will have a crystalline or fanlike appearance (Fig. 12). A crystalline appearance is indicative of intergranular SCC, while a fanlike appearance indicates crack branching for both intergranular and transgranular cracking. The SCC fracture surfaces have also been described as having a "woody" appearance. The fracture surface may be covered in corrosion product or exhibit beach marks associated with discontinuous crack propagation (Fig. 13). (Beach marks are macroscopic features on a fracture surface that indicate discontinuous and intermittent crack propagation.) Further, because it is common for multiple cracks to initiate due to SCC, ratchet marks may be present on the fracture/crack surface where the cracks linked up. (Ratchet marks are lines or markings on the fracture surface that represent the location where multiple cracks intersect and link up. Ratchet marks will be oriented parallel to the direction of crack propagation and are visible macroscopically.)

Cracking observed on the component surface will appear jagged and discontinuous and may exhibit crack branching (Fig. 14).

Because the fracture/crack surface may be covered in corrosion product/deposits, it may be necessary to clean these surfaces after the initial examination has been completed. Cleaning, however, should not be performed until the fracture/crack surface has been microscopically examined using a scanning electron microscope (SEM) and samples of the corrosion product or other surface deposit have been collected for further testing and analysis.

The fracture/crack surface can be cleaned after corrosion deposits have been collected and an initial microscopic examination of the surface has been completed. Cleaning should be completed in an incremental fashion, starting with the most benign cleaning agent before progressing to more aggressive cleaners, using an ultrasonic bath if possible. The surfaces may also be gently scrubbed with a soft nylon or bristle brush, such as a toothbrush, to help loosen and remove the deposits.

Microscopic Fracture Characteristics

To determine the fracture morphology, fracture/opened-crack surfaces should be examined using an SEM. In most cases, the size of the cracked/fractured component is too large to fit into an SEM, and areas of interest must be removed. The sections selected for removal and the location of the cuts will be determined based on the results of the visual and, if applicable, nondestructive examination of the component. Removal should be performed by mechanical cutting rather than through the use of heat (such as torch cutting), and care should be taken during the removal process so that the surface features of interest are not damaged and any corrosion product present is not contaminated with cutting fluid. In fact, if possible, cutting should be performed without the use of cutting fluid.

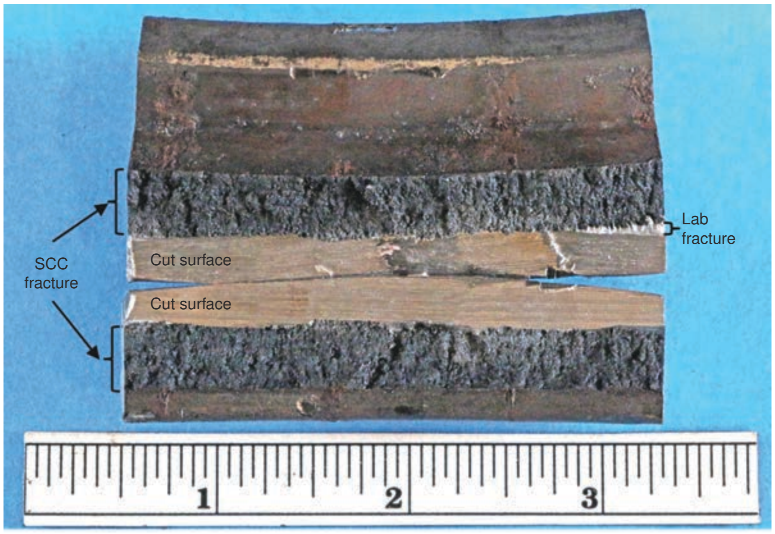

Fig. 10 Photograph of an opened stress-corrosion crack in a steam turbine rotor disk. SCC, stress-corrosion cracking

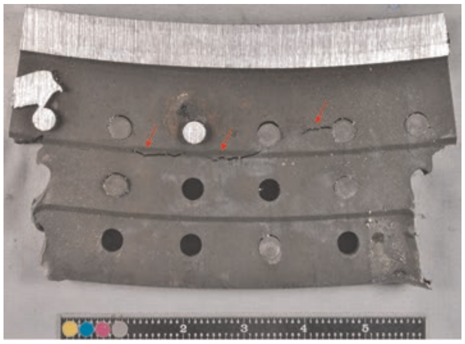

Fig. 11 View of stress-corrosion cracks (arrows) on the upstream side of a steam turbine disk. Plastic deformation or thinning was not observed adjacent to the stress-corrosion cracks.

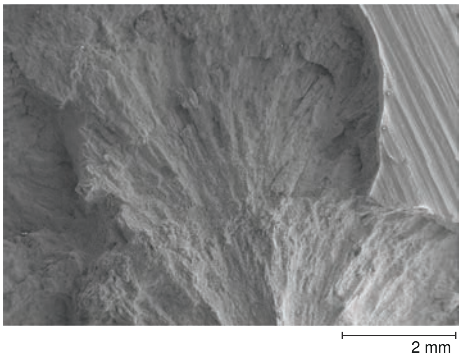

Fig. 12 Scanning electron microscopy image of an opened stress-corrosion crack in a secondary urea reactor exhibiting a feathery surface morphology

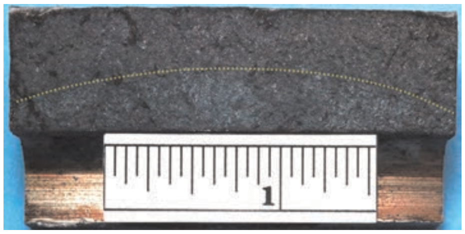

Fig. 13 Photograph of an opened stress-corrosion crack in a steam turbine disk. Dashed line highlights the crack-arrest mark observed on the fracture surface.

Fig. 14 Photograph of stress-corrosion cracking (arrows) observed on the outside surface of a steam turbine rotor disk

One important area to examine is the crack-initiation location. Examination of the initiation location can provide data related to how/why SCC developed. Areas associated with the later stages of crack propagation can also provide useful information, because corrosion products, if present, are generally thinner at these locations and less likely to be contaminated.

A stress-corrosion crack/SCC fracture surface exhibits a brittle fracture morphology. For intergranular SCC, the surface exhibits a faceted appearance, sometimes referred to as a "rock-candy" structure (Fig. 15). Transgranular SCC exhibits a flat, cleavage appearance. For those metal-environment combinations that exhibit crack branching, the branched cracks can be observed oriented at an angle with respect to the fracture/crack surface (Fig. 16). (Crack branching can occur with transgranular and intergranular SCC.) Both trans- and intergranular fracture features may be observed on the same fracture/crack surface.

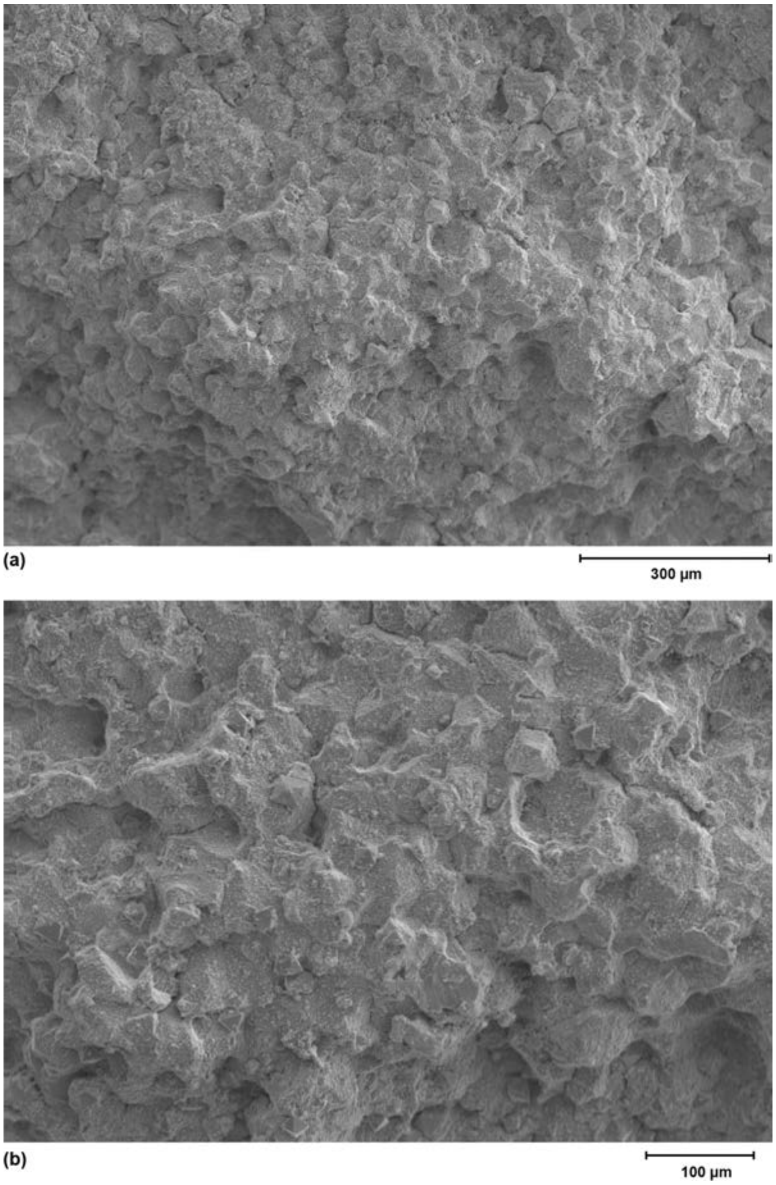

Fig. 15 Scanning electron microscopy images of an opened stress-corrosion crack in a secondary urea reactor exhibiting intergranular fracture ("rock-candy" morphology)

Corrosion Product/Surface Deposit Collection and Analysis

As discussed earlier, it may be useful to clean the surface in order to obtain a clearer view of the underlying fractographic features. However, prior to cleaning, a sample of corrosion product or surface deposits, if present, should be collected for analysis or analyzed while adhered to the fracture/crack surface.

Typically, energy-dispersive spectroscopy (EDS), also known as energy-dispersive x-ray spectroscopy and energy-dispersive x-ray spectrometry, is performed to identify chemical species that are present in the corrosion product/deposit in order to investigate the nature of the environment to which the component was exposed. Energy-dispersive spectroscopy can be performed on the corrosion product/surface deposits adhered to the fracture/crack surface, or it can be performed on samples removed from the fracture/crack surface.

One of the best ways to collect corrosion product/deposits from a surface is through the use of replication media. Acetate replication tape used for field metallography provides good results, although other replication media, such as the silicone-based media used for fracture-surface replication, may also be used. Once the corrosion product is collected, it can be prepared for and subjected to EDS. Energy-dispersive spectroscopy is performed in an SEM, so the collected sample will be subjected to vacuum conditions and must be rendered conductive, generally through carbon or sputter coating.

While EDS is a useful tool that is commonly available, caution must be exercised when analyzing and interpreting EDS data, for several reasons:

- The injurious ions associated with SCC for a given metal-environment combination may be present in quantities below the detection limit of the spectrometer.
- Some injurious ions cannot be distinguished from other elements in the corrosion product. Energy-dispersive spectroscopy can detect only the presence of an element while not providing information regarding what compound (if any) that element is a part of. For example, EDS may detect the presence of sulfur on a surface, but it cannot distinguish between a sulfate compound, a sulfide compound, or elemental sulfur.
- Some injurious ions cannot be detected; EDS cannot detect light elements, such as hydrogen or lithium. Thus, hydroxyl ions (OH^-), for example, cannot be detected using EDS.
- Some injurious ions may not become entrapped by or form the corrosion product.
- The injurious ions may be removed as a result of the fracture (e.g., surface erosion due to the release of process fluids, fire damage) or during removal of the component.
- The surface may have been contaminated because of subsequent activities (e.g., fire suppression or nondestructive examination).

Regardless, EDS is a useful tool that can be used to test for the presence of SCC-inducing elements in the environment and can provide useful data to determine why a particular environment is conducive to SCC.

Other analytical techniques can be used to characterize corrosion product/surface deposit samples, although their usage is less common than EDS. These include x-ray photoelectron spectroscopy, x-ray diffraction,

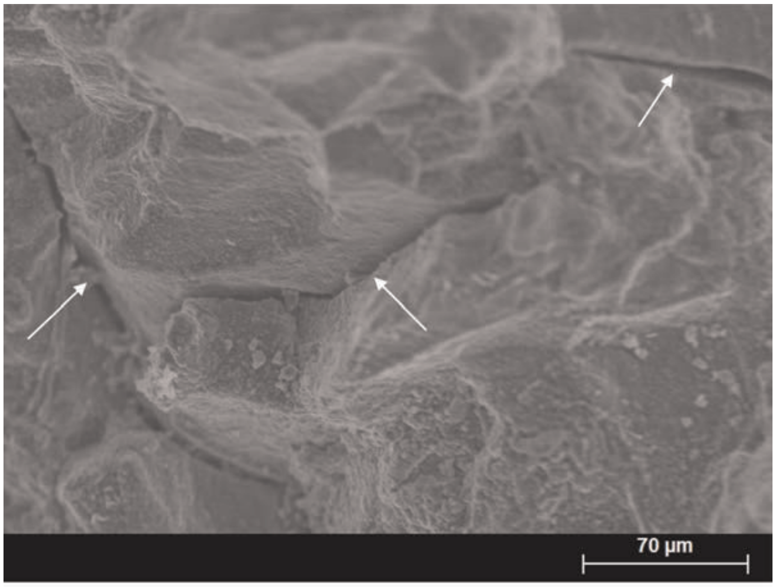

Fig. 16 Scanning electron microscopy image of an opened stress-corrosion crack in a steam turbine rotor disk. Arrows identify crack branches.

x-ray fluorescence, Auger electron spectroscopy, and wavelength-dispersive spectroscopy. For details about these techniques, the reader is directed to *Materials Characterization*, Volume 10 of the *ASM Handbook*, 2019.

Metallographic/Microstructural Characteristics

Useful information can be obtained through a metallographic examination of the material adjacent to and containing stress-corrosion cracks. The following information can be determined through the metallographic examination of selected cross sections:

- It can be determined if the stress-corrosion cracks propagated predominantly along grain boundaries (intergranular cracks), through the grains (transgranular), around second-phase particles, or along twin boundaries. These features can be informative when identifying or confirming the environment responsible for the SCC.
- The presence, and extent, of crack branching can be observed, which can aid in the confirmation of SCC as the failure mechanism, especially when examination of the fracture surface is not possible.
- Surface microstructural features can cause or contribute to the conditions needed for SCC to occur. These include deformed or elongated grains, which can indicate the use of improper machining practices.
- For metallographic cross sections prepared through the crack origin, a metallographic examination may reveal surface conditions, such as pitting or intergranular corrosion, or manufacturing flaws/defects associated with the initiation of SCC.
- Microstructural features may be informative about the thermal/thermomechanical history of the component. For example:
    a. The presence of untempered martensite or excessive grain growth may indicate problems with the heat treatment of the material.
    b. The coincidence of SCC and a weld heat-affected zone may indicate high residual stresses due to welding, which may be the result of an improper welding procedure or postweld heat treatment.
    c. The presence of chromium carbides at the grain boundaries of austenitic stainless steels indicates sensitization.

Prevention and Mitigation

Stress-corrosion cracking can occur only when all three prerequisites are present. Conversely, lack of at least one of the prerequisites will prevent SCC. Thus, it is important to select a material resistant to SCC for a given environment, control the environment, and/or reduce the tensile stress.

Materials Selection

A detailed discussion about the materials selection process can be found in *Materials Selection and Design*, Volume 20 of the *ASM Handbook*, 1997. It is important to take into consideration the impact of operating conditions, manufacturing, and fabrication in addition to the environment when selecting the appropriate material and/or material condition. Material condition includes fabrication method, thermal treatment, thermomechanical treatment, and surface finish.

Control of the Environment

It is important to both fully understand the environmental conditions to which a component is exposed and to control that environment. When applicable (e.g., in chemical processing, power generation, petrochemical plants, refineries), key process variables such as temperature, pH, and composition should be monitored and controlled. With respect to boilers and steam turbines or process fluids, chemical additives and the removal of impurities can reduce or eliminate the presence of injurious ions. Further, the material can be separated from the environment via coatings.

Reduction of Tensile Stress

The tensile stress responsible for SCC can be a combination of applied and residual stress. Tensile stresses imposed by service conditions (i.e., applied stresses) are generally well understood and can be mitigated through design. Residual stress from manufacturing and/or fabrication may be more difficult to prevent or control. Components subjected to cold fabrication methods (such as cold rolling, crimping, deep drawing) should be annealed or subjected to local heat treatment to reduce residual stresses. Welding produces residual stress because of microstructural changes in the heat-affected zone and shrinkage of the weld metal during cooling and the constraint imposed by the adjacent solid metal and welding fixtures. Weld procedures that include appropriate weld preheat and interpass temperatures and postweld heat treatment can reduce residual welding stresses and prevent SCC. Thus, it is important to monitor and ensure that proper manufacturing and fabrication procedures are developed and followed to ensure that residual stresses are minimized.

Specific Alloy-Environment Combinations

In the remaining sections of this article, several engineering alloys are discussed with respect to their susceptibility to SCC. This includes a description of some of the environmental and metallurgical conditions commonly associated with the development of SCC, although not all, and numerous case studies. For a more in-depth discussion of SCC in these alloys, the reader is directed to the articles "Stress-Corrosion Cracking" and "Evaluating Stress-Corrosion Cracking" in *Corrosion: Fundamentals, Testing, and Protection*, Volume 13A of the *ASM Handbook*, 2003, and the References at the end of this article.

Stress-Corrosion Cracking of Carbon and Low-Alloy Steels

The susceptibility of carbon steels to SCC generally increases as carbon content decreases. However, decarburized steel and bulk pure iron are resistant to cracking; thus, susceptibility must be at a maximum at some concentration of carbon between 0 and approximately 0.10%. The exact carbon content at which cracking occurs most readily is not known, but the susceptibility to cracking is high in steels containing 0.05% C (Ref 17). The nature and concentration of other alloying elements in low-carbon steels have less of an effect on general susceptibility to SCC.

Surveys of the stress-corrosion behavior of high-strength low-alloy steels in a variety of environments have shown that the strength of the steel is the most important single indication of sensitivity to SCC. Steels with yield strengths of approximately 1379 MPa (200 ksi) or greater are especially susceptible to failure by SCC. However, SCC will also occur in mild steel and low-strength alloy steels.

Stress-Corrosion Cracking Environments

Caustic Stress-Corrosion Cracking of Steel

As discussed previously, caustic SCC is a serious stress-corrosion problem that has caused explosions and other types of failures, particularly in steam boilers, as discussed previously in this article. It has also been identified at welds in continuous digesters in the pulp and paper industry. Solutions that are of 5 to 40% caustic are also widely used in oil refineries and petrochemical plants to neutralize sulfuric, hydrochloric, and hydrofluoric acid streams. The general conditions that cause caustic SCC are reasonably well understood, but failure by such cracking remains a problem.

Caustic SCC failures frequently originate in riveted and welded structures because of residual stresses and in splash and wet/dry zones where soluble salts accumulate high local concentrations of caustic soda. Crack propagation is ordinarily intergranular. Stress-corrosion cracking failures have been produced at concentrations of sodium hydroxide (NaOH) as low as 5%, but a concentration of 15 to 30% NaOH plus a small amount of oxygen is usually required to induce caustic SCC. Failures take place at temperatures greater than approximately 75 to 110 °C (170 to 230 °F), as shown in Fig. 17 (Ref 18). The concentration of NaOH necessary to produce cracking generally increases as temperature decreases.

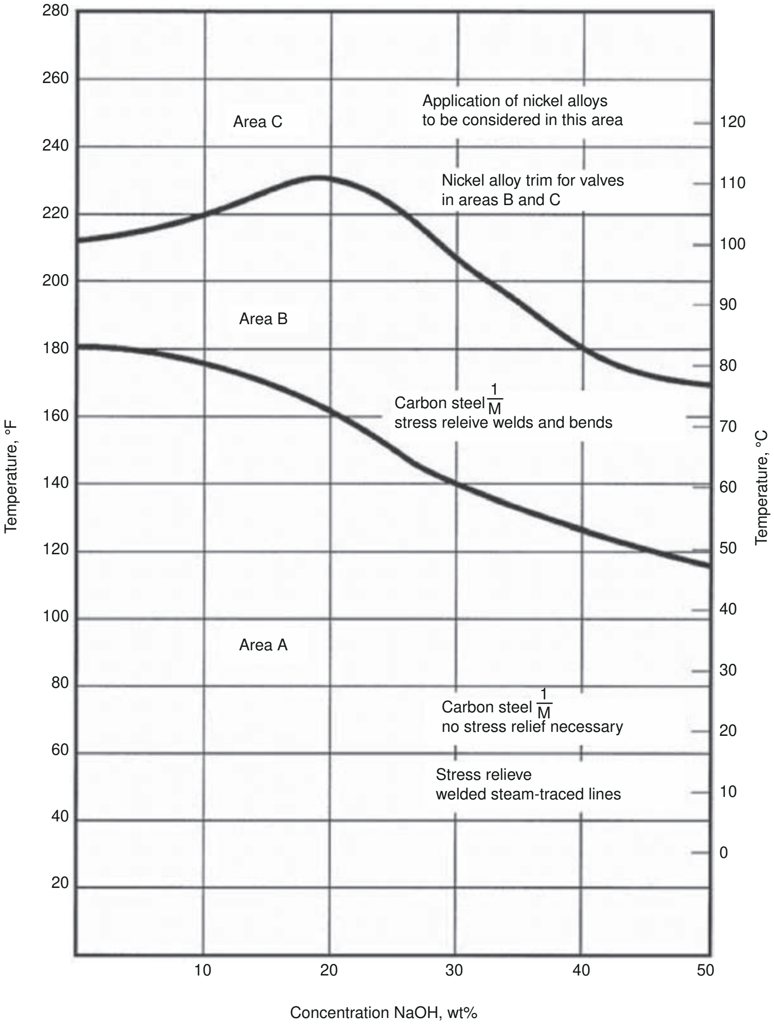

Fig. 17 Carbon steel caustic soda service chart. Source: Ref 18

Stress-corrosion cracking occurs where the corrosion potential is such that only part of the steel surface is covered with an oxide film. Stress-corrosion cracking can be prevented by anodic protection, which forms a continuous and more stable oxide film, or by cathodic protection, which shifts the potential and completely reduces the oxide film.

Reducing pH and adding strong oxidizing agents to passivate the steel surface are common modifications of boiler water treatment that are used to prevent caustic SCC. Inhibitors such as nitrates, sulfates, phosphates, and tannins have also been added to boiler water. However adjustment of boiler water composition and the addition of inhibitors should be done only if the chemical behaviors of the metals involved are fully understood and only after suitable laboratory testing has been conducted, because adjustment of boiler water composition can destroy the effectiveness of some inhibitors/additives. Common practice for most steam boilers is to control pH and to monitor the water supply or maintain an effective concentration of inhibitors.

Reducing grain size has been found to be helpful in decreasing the susceptibility to caustic SCC of the low-carbon steels generally used in boilers. Minor changes in steel composition are of little value because they do not alter sensitivity at grain boundaries—areas that are preferentially attacked in caustic SCC. Stress-relief heat treatments after cold working or welding are often used to reduce residual stress.

Monoethanolamine/Diethanolamine Stress-Corrosion Cracking

Monoethanolamine and diethanolamine solutions (typically 20 to 25%) are used in gas fields and refineries to remove hydrogen sulfide and carbon dioxide from produced gas or light hydrocarbon streams. The "rich" solution (loaded with H_2S and CO_2) causes hydrogen stress cracking and hydrogen blistering, while the "lean" solution (stripped of gases) can cause a form of SCC called amine cracking or amine SCC. Stress-corrosion cracking has been experienced in both pressure vessels and piping at temperatures down to 40 °C (100 °F).

Stress-corrosion cracking in this environment is intergranular, with crack surfaces covered by a thin film of iron oxide (magnetite). Invariably, SCC is associated with welds that were not stress relieved, so new equipment is generally subjected to a postweld heat treatment after welding.

Stress-Corrosion Cracking in Nitrate Solutions

Stress-corrosion cracking of carbon and low-alloy steels in nitrate solutions has occurred in tubing and couplings used in high-pressure condensate wells and in storage tanks containing radioactive wastes. Stress-corrosion cracking in nitrate solutions is intergranular.

Boiling solutions of several nitrates, including NH_4NO_3, $Ca(NO_3)_2$, $LiNO_3$, KNO_3, and $NaNO_3$, have been found to produce SCC. In general, lower-pH (more acidic) solutions increase SCC susceptibility. The threshold stress necessary to produce cracking (which can be quite low) decreases with increasing concentration of the nitrate in the solution. For example, laboratory tests of carbon and low-alloy steels exposed to boiling 4 *N* solutions of the previously listed nitrates has produced cracking at tensile stresses lower than 69 MPa (10 ksi). The time-to-fracture increased with a decrease in temperature. By extrapolation of these test results, it can be estimated that failure would occur in approximately 1000 h at room temperature. Room-temperature tests of bridge cable wire in 0.01 *N* nitrate solutions resulted in SCC after exposure for several months. For reference, there are 720 h in a 30 day month.

Decreasing pH enhances nitrate-induced SCC, and resistance to SCC can be improved by raising the pH. Sodium hydroxide, which causes caustic SCC by itself, can be added to nitrate solutions to retard SCC. (It is also true that nitrate additions to caustic solutions retard SCC.) In addition to sodium hydroxide, several other inhibitors can be added to prevent SCC in nitrate solutions. Cathodic protection can prevent SCC in many nitrate solutions. However, anodic polarization is harmful.

In low-carbon steels, carbon content has a strong effect on susceptibility to nitrate-induced SCC. Initiation of SCC is minimized when carbon content is lower than 0.001 wt% (extremely low) or higher than approximately 0.18 wt%. The threshold stress for cracking is low at carbon contents of approximately 0.05 wt% but increases at carbon contents above approximately 0.10 wt%. Accordingly, decarburized steel surfaces can lead to SCC in nitrate solutions. This effect of carbon content applies primarily to crack initiation.

Tests performed on notched specimens have shown that preexisting cracks will propagate in steels of high carbon content. Stress-corrosion crack initiation and propagation in nitrate solutions appears to be closely related to carbon content and, possibly, to the amount of nitrogen at the grain boundaries. Changes in composition or processing history of the steel to alter carbon distribution can appreciably influence susceptibility to SCC. Strong carbide-forming elements, such as chromium, tantalum, niobium, and titanium, are generally helpful in improving resistance to SCC. Reducing grain size and cooling slowly after annealing also improve SCC resistance. Steels with pearlitic or coarse spheroidized carbide microstructures are usually less susceptible to cracking than steels containing fine carbides. Moderate cold working may increase susceptibility to SCC, but severe cold working appears to be beneficial. An appropriate post-weld heat treatment can prevent SCC of welded assemblies, which may contain fairly high residual stresses in the as-welded condition.

Stress-Corrosion Cracking in Ammonia

It has been shown that both plain carbon steels and quenched-and-tempered low-alloy steels are susceptible to SCC in ammonia. Both intergranular and transgranular SCC occurred in the quenched-and-tempered low-alloy steels, but generally only intergranular SCC occurred in carbon steels.

Carbon steel tanks containing anhydrous ammonia had developed leaks due to SCC. In one case, SCC developed in the interior surface of the head regions of tanks having cold-formed heads but not in tanks that had been stress relieved after fabrication. Residual tensile stresses, in combination with the applied stresses, were evidently sufficient for SCC to occur. Stress-corrosion crack growth in the tanks that failed was slow, and the average service time before detection of leaks was three years.

These failures were not produced in pure ammonia but occurred in ammonia mixed with air or mixed with air and CO_2. It is now known that the critical ingredient for SCC in ammonia is oxygen and that the presence of nitrogen can further promote SCC. It was discovered that the addition of water (approximately 0.2 wt%) to liquid anhydrous ammonia completely eliminated susceptibility to cracking. Water additions have become mandatory by a U.S. Department of Transportation ruling for interstate transportation of ammonia in high-strength steel vessels (steel with a yield strength greater than 620 MPa, or 90 ksi).

External Stress-Corrosion Cracking of Pipelines

This form of SCC is of major concern for gas-transmission pipelines. Two forms of SCC have been identified: classical, high-pH SCC and nonclassical, near-neutral-pH SCC. Stress-corrosion cracking generally occurs in older tape-wrapped pipe and coal-tar- or asphalt-coated pipe. Debonding of the coating, so that the metal surface is exposed to ground water, is a prerequisite for both forms of SCC. High-pH SCC develops when the pH of the moisture under the pipe coating is in the range of 8.5 to 11 and the carbonate/bicarbonate content of the water is high. On the other hand, low-pH SCC occurs in the pH range of 6 to 8.5 in dilute bicarbonate water. In general, high-pH SCC will be found within approximately 12 miles of a compressor station, but the near-neutral-pH SCC has been observed in pipelines as far as 75 miles from the nearest compressor, although it is typically considered to occur within 20 miles.

High-pH stress-corrosion cracks are intergranular. Low-pH stress-corrosion cracks are transgranular and exhibit corrosion product within the cracks. Historically, many of the pipeline failures were located in the first 16 km (10 miles) downstream of a gas compressor station, which is the high-temperature region on a gas pipeline because of the heat of compression.

As discussed earlier, one of the three conditions necessary for SCC must be eliminated to prevent it. With respect to high- and low-pH SCC, there is no simple way in which to achieve this. Keeping the cathodic potential outside of the critical range for cracking is difficult, if not impossible, at all points of a long pipeline. Keeping the temperature as low as possible helps to prevent SCC, but to do so, the thermodynamic effects due to the compression of gases must be overcome. The application of an appropriate coating to the pipe surface is a good deterrent when it is applied correctly and remains intact. Shot peening the pipe surface to remove mill scale and provide a good surface for the coating improves the efficacy of the coating. Operating conditions (e.g., temperature, pressure) can be controlled to reduce SCC susceptibility.

Mitigation of SCC generally involves awareness of the nature of soils along the pipeline, close monitoring of the cathodic protection system, and, potentially, periodic nondestructive inspections. Nondestructive inspection using “smart pigs” passed through the pipeline may detect cracking.

Predictive methods related to SCC are reviewed in Ref 19.

Stress-Corrosion Cracking of Steam Turbines

Stress-corrosion cracking of carbon and alloy steel steam turbine components has occurred in cast steel casings, rotors, wheels, and bolting. The basic cause of SCC in steam turbines is the transfer of hydroxyl (i.e., caustic) and other ionic species (including chlorides, sulfates, carbonates, oxygen, and carbon dioxide) from the boiler water to the turbine. Some transfer of these injurious ions can occur by carryover, that is, the entrainment of water droplets in the steam. Evaporation of the water in the turbine results in concentrated deposits of these contaminants. Other impurities evaporate from the boiler water and concentrate in water that may condense in the cooler parts of the turbine. Alternate wetting and drying will lead to high impurity concentrations.

Leaks at bolted flanges or the turbine split line can lead to SCC of bolts, because the injurious ionic species can concentrate in those locations. Adequate control of steam purity is often difficult in industrial plants because of the variety of sources of make-up water. Further, SCC may be the result of upset conditions that occurred up to a decade or so prior to the discovery of SCC. Selection of more resistant metals and careful monitoring during operation are essential to reduce susceptibility to SCC in steam turbines.

Stress-Corrosion Cracking Case Studies

Failures of Carbon Steel Parts

Case Study: Intergranular Stress-Corrosion Cracking of Carbon Steel Pipe Welds in a Kamyr Continuous Digester Equalizer Line (Ref 20).

Background

Leaks were discovered at several cracks in and next to pipe welds in a Kamyr continuous pulp digester within 18 months of normal service. The pipe was schedule 80 low-carbon steel and was used to transfer kraft liquor at 175 °C (350 °F). The pipe ranged in diameter from 75 to 125 mm (3 to 5 in.) (NPS 3 to 5) and had been field welded using an E6010 electrode for root passes and E7018 electrodes for the cover passes.

Investigation

Both axial and circumferential cracks were found in the welds and heat-affected zones (Fig. 18a). The inside-diameter surfaces of the pipes were covered with a thin oxide film, but there was no evidence of general or pitting corrosion.

Scanning electron microscope examination showed that the cracks were primarily intergranular and EDS detected significant levels of sodium in the deposits at the crack tips. Metallographic examination of prepared cross sections revealed that the cracks had initiated at the inside-diameter surface and propagated through the weld metal to the outside-diameter surface (Fig. 18b). The intergranular cracks were branched in the ferrite/pearlite microstructure and oxide filled (Fig. 19). The hardness of the pipe base metal and the weld metal were in the range of 73 to 93 HRB.0

Discussion

Stress-corrosion cracking initiated on the inside-diameter pipe surface at welds and heat-affected zones. The most probable cause of the intergranular SCC in the pipe welds was high residual stresses from welding and the likely lack of postweld heat treatment. Welds that have not been subjected to postweld heat treatment are known to be susceptible to SCC in caustic environments such as the kraft liquor.

Corrective Measures

The weld procedure should include appropriate controls on the weld preheat and interpass temperatures and also include a postweld heat treatment to reduce residual stresses.

Case Study: Leaking Carbon Steel Weldments in a Sulfur-Recovery Unit (Ref 21)

Background

Two leaks were discovered in the sulfur-recovery unit of a refinery. The leaks were located at pipe-to-elbow welds in 152 mm (6 in.) (NPS 6) diameter piping that operated in lean amine service at 50 °C (120 °F) and 2.9 MPa (425 psig). Thickness measurements indicated a negligible loss of metal. The leaks were clamped, and production continued. A year later, 15 additional leaks were discovered, again at pipe-to-elbow welds in piping in lean amine service. Further nondestructive testing located other cracks, bringing the total to 35 cracked pipes. This piping had been in service for approximately eight years when the cracking was discovered.

Investigation

Examination revealed that the leaks were stress-corrosion cracks, which had originated at the pipe inside-diameter surface. Circumferential cracks were present in the weld metal, the heat-affected zones, and the base metal up to 5 mm (0.2 in.) away from the welds (Fig. 20).

The measured hardness values were 133 to 230 HB in the weld metal, 182 to 227 HB in the heat-affected zones, and 117 to 198 HB in the base metal. Hardness values were converted from Knoop readings.

The microstructures of the pipes and elbows were typical for the material. The observed cracking was intergranular and exhibited branching (Fig. 21, 22); cracks were oxide-filled.

Discussion

The observed cracking was characteristic of lean amine SCC. The location of the cracking indicates that the most probable cause of the intergranular SCC in the pipe welds was high residual stresses that resulted from welding. It is industry practice to postweld heat treat piping and pressure vessels in lean amine service if the temperature is expected to be above 95 °C (200 °F). It was decided that it was unlikely that these welds received such a postweld heat treatment, or the postweld heat treatment was not completed correctly.

Corrective Measures

It was recommended that all welds in the piping system be inspected using shear-wave ultrasonic inspection to identify any additional cracking. Further, all welds in lean amine service were subsequently subjected to postweld heat treatments.

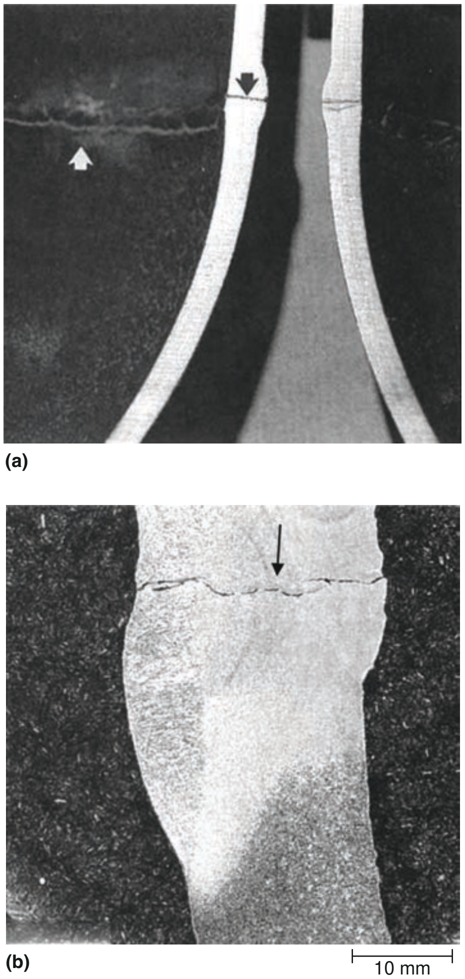

Fig. 18 Photographs of stress-corrosion cracking (SCC) (arrows) in a steel pipe weld. (a) Magnetic-particle enhancement of SCC in the weld of an equalizer line elbow section. (b) Stress-corrosion cracks initiated on the pipe inside-diameter surface (right side of photograph) and propagated through the weld.

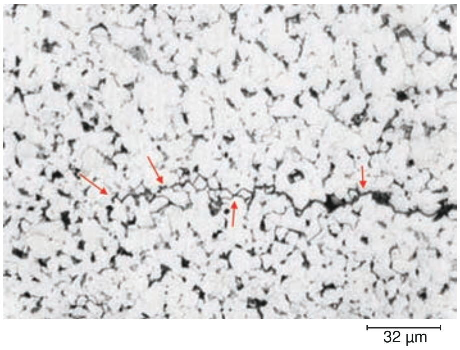

Fig. 19 Micrograph of an intergranular stress-corrosion crack (arrows) that partially penetrated the weld. The crack was filled with oxide.

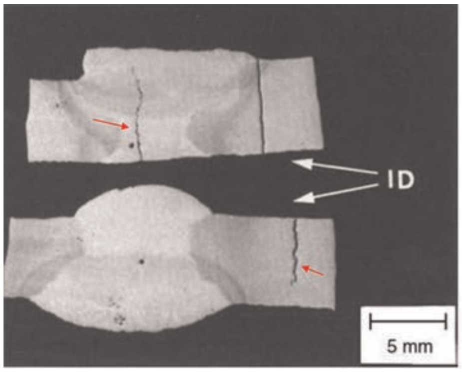

Fig. 20 View of metallographic cross sections of pipe-to-elbow welds showing stress-corrosion cracks (red arrows) originating from the inside surface of the weld metal and the base metal. ID, inside diameter