

the Conduit

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Stress Corrosion Cracking in Turbine Rotors

By David Daniels

Stress corrosion cracking can occur in a variety of metals from high strength steels to copper alloys. In this article, we will focus on the mechanism as it occurs in turbine materials (Figure 1).

Stress corrosion cracking is a corrosion process where corrosion weakens the structure and stress causes cracking along or through grain structures in the metal. It requires the convergence of three separate factors, namely: a susceptible material, a corrosive environment, and stress or strain (Figure 2).

If the cracking progresses through the metal grains, it is referred to as *transgranular cracking*. If it progresses around the grain boundaries, it is designated as *intergranular cracking*. In either case, some level of stress (operating or residual) is required for the cracking to progress. Laboratory testing has shown

that the stress needed for cracking to advance is well below that required for mechanical yielding of metal, proving that a corrosion process at the crack tip must play an active role in the crack initiation and growth rate. Whether the cracking is trans- or intergranular depends on the material, corrodent, and

stresses applied (Figure 3). In specific combinations of these three factors, the cracking may be mixed-mode, containing both transgranular and intergranular cracks. (Continued on page 2)

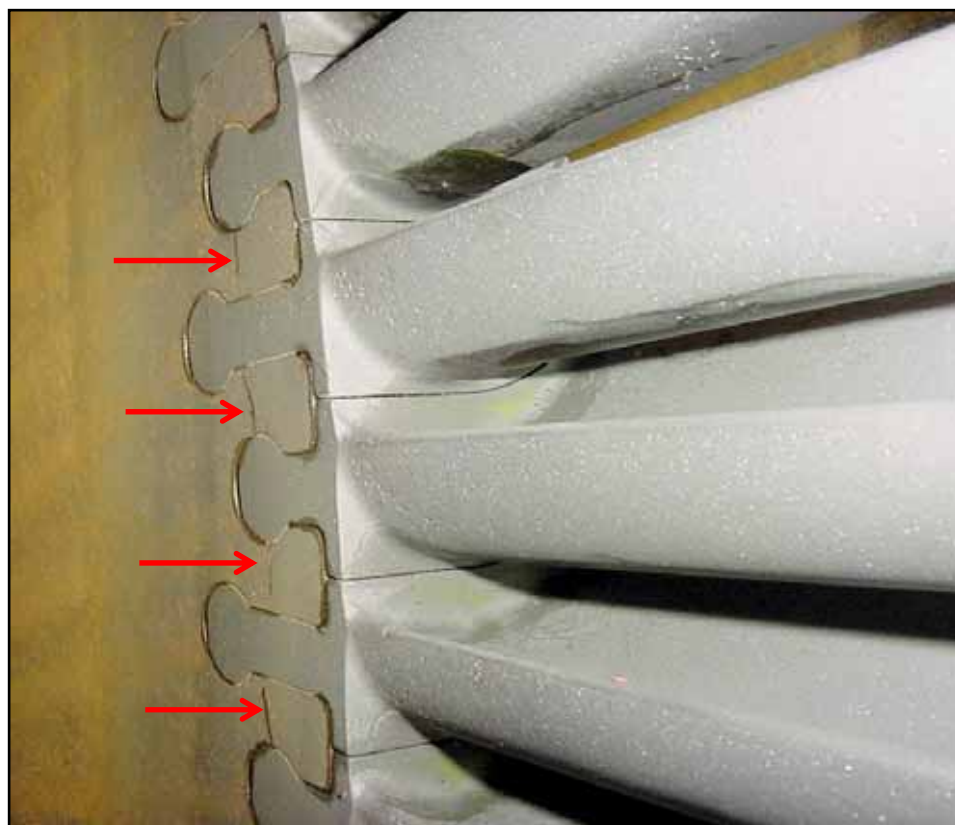


Figure 1. Stress corrosion cracks in a turbine rotor .

Proposed Mechanisms of Stress Corrosion Cracking

Two major theories have emerged describing the mechanism of stress corrosion cracking. Both mechanisms begin with the formation of a defect or break in this protective oxide layer which exposes the electrolyte or liquid layer to fresh metal. This break might be the result of stress or chemical attack by a number of chemical species including chloride, hydroxide, and sulfide. For stress corrosion cracking to occur, there must be a liquid layer that exists on the metal surface. This liquid coating contains contaminants that precipitate from the steam. In some cases, the "liquid" may have a very high concentration of salts such as sodium chloride or caustic.

What happens next depends on which theory you follow and it is possible that both mechanisms could be active in the stress corrosion process in steam turbines.

One model is known as the anodic dissolution model. It proposes that, once the oxide layer has been broken, chemical species in the electrolyte layer create a soluble iron hydroxide species that prevents the break from repassivating. The key to whether or not repassivation occurs is the corrosion potential at the metal/electrolyte interface. This may be affected by a number of ionic species which can change the oxidation/reduction potential or the pH at the interface. For anodic dissolution to occur, the

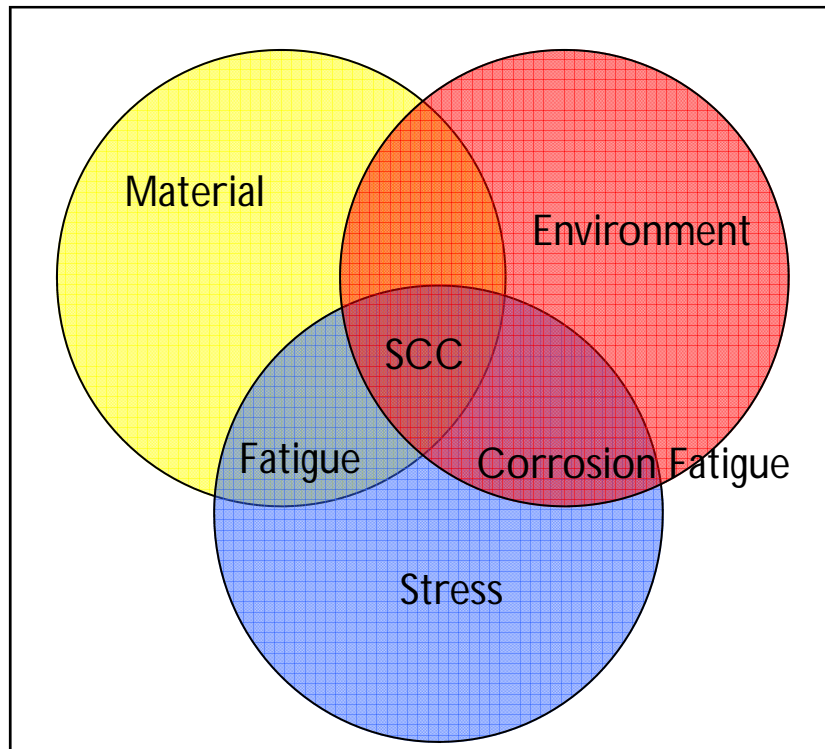


Figure 2. Stress corrosion cracking (SCC) requires the combined effects material, stress, and environment (chemistry).

environment must be oxidizing as oxygen forms the cathode of the reaction. Typically during operation, oxygen is not present in

steam. Therefore, shutdown conditions are a prime time for this corrosion process to progress via anodic dissolution.

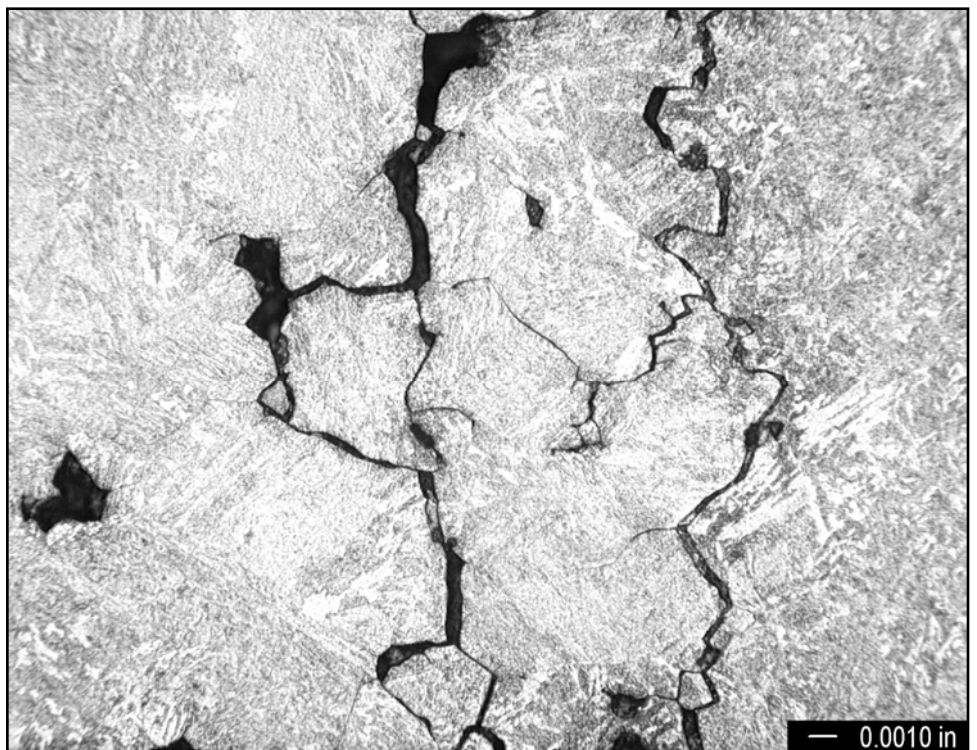


Figure 3. Intergranular cracking in a turbine rotor material.

Requirements for Fusion Welded Butt Joints

By **Bob Bruscato**

The strength, performance, and safety of most types of welded construction depend on the quality of fusion welded butt joints. Fusion butt welding is, by far, the primary joining method for boilers, pressure vessels, storage tanks, piping. Along with bolting, it is also the primary method for joining structural steel components together.

The satisfactory performance of fusion butt welds is dependent on three essential factors:

- the soundness of the weld metal,
- the strength of the weld metal, and
- the thickness of the weld.

Weld thickness is most important, because if the weld is under-thickness, the strength of the finished joint is likely to be compromised even if the weld metal itself is sound and has the proper strength. Because it is so fundamental, weld thickness requirements are discussed in this article.

Full Penetration Weld Requirements

The ASME Boiler and Pressure Vessel Code, ASME B31.1 Power Piping Code, and API Tank Standards (API 620, 650, 653) specifically require full penetration, full fusion welding of butt joints. This requirement applies to butt welding for all types of metals

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The second proposed mechanism is the hydrogen embrittlement model. In this model, corrosion processes in the crack generate hydrogen atoms that penetrate and accumulate in the metal structure just below the tip of the crack. These hydrogen atoms reduce the strength of the steel to the point where normal operational stresses cause the crack-front to move forward. In a steam turbine, sources of hydrogen could be a localized low pH condition. Hydrogen sulfide and other volatile hydrides can poison the metal surface preventing the recombination of hydrogen atoms to hydrogen molecules allowing hydrogen atoms the opportunity to be adsorbed. Since it is a cathodic process, it can occur during operation. Contamination events, such as a condenser tube leak, can contribute to a localized low pH on the turbine or conditions conducive to the adsorption of hydrogen.

In either case, it is clear that stress corrosion cracking is a corrosion process that forms cracks, and not purely a cracking process, such as a brittle failure.

SCC takes place in stages. The first, and probably least studied, is the incubation stage. There is often a significant lag between the presence of contamination on the turbine metal and the point where the first visible crack appears on a rotor disc, for example. Secondly, there is a propagation stage where corrosion at the crack tip, operating stresses and material properties are the driving factors.

Work has been done to measure the propagation rate of these cracks through rotor steels, with the object of determining if a rotor can safely remain in service while a replacement is built. It appears that the crack growth rate is related to stress intensity, yield strength, the type and level of contamination, and the temperature. With the exception of the type and level of contamination, these parameters are all determined by the manufacturer at the time of construction.

Where Does Stress Corrosion Cracking Occur?

Caustic is the most common contaminant that causes SCC in turbine rotors. Caustic has a very limited solubility in steam and is hygroscopic (absorbs water). For this reason, concentrated solutions of caustic can form over the entire superheat region of the turbine until the steam contains sufficient moisture to dilute the caustic beyond the point where it can cause damage, which may be a far back in the turbine as the L-1 row, depending on the operating conditions of the turbine. It has also been found as far forward in the turbine as the IP-LP crossover.



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including steels (carbon, alloy, stainless), and aluminum, nickel, titanium, etc., alloys.

Full penetration welding requires that the thickness of the weld be at least equal to the thickness of the base metals being joined together. Obviously, if a design calls for one-inch thick plate, then a full penetration (one-inch thick) weld must be deposited. This ensures that the thickness/strength of the welded plate assembly is equal to the thickness/strength of the individual sections.

The finished weld joint must also be smoothly filled with weld metal completely through the thickness of the joint. Full fusion must be made between the weld metal and base metals and between the individual weld passes. Codes specify a maximum weld buildup (i.e., weld reinforcement) above the surface of the base metal and specifically exclude this reinforcement as a contributor toward the full penetration welding requirement. Thus, the reinforcement cannot be used to compensate for any internal lack of penetration in the weld.

The limitation on weld reinforcement (3/32-inches up to 1/4-inches in heavy thicknesses) is imposed to control the surface stress concentrations at the toes of the weld. High stress concentrations induced by excessive weld reinforcement adversely affect weld performance. For example, excessive reinforcement reduces the resistance of the welded joint to fatigue stresses and will significantly

reduce the fatigue strength of the welded joint.

Weld Quality by Design

It is essential that these welds be high quality particularly in equipment exposed to a high number of stress cycles induced by mechanical type loading (e.g., rotation, vibration or oscillation). Lack of penetration weld defects (such as underfill of the joint or lack of internal fusion) act as severe stress concentrations. Under repetitive fatigue type loading, such defects easily initiate fatigue cracking and can cause rapid, unexpected failure of the welded joint. Welded construction exposed to a significant number of thermal fluctuations also requires high quality, full penetration butt welded joints to preclude thermal fatigue cracking of the joints.

It is not unusual for Mechanical & Materials (M&M) Engineering to find butt welds with significant and even severe lack of penetration defects (Figure 1). There are a number of reasons for this. The necessity for a full penetration weld may not be completely understood and, consequently, welding requirements are not properly specified when the contract specifications are developed. Even when properly specified, inspection requirements and/or quality control procedures to verify proper welding during construction may not be developed, or if developed, they may not have been rigorously enforced.

It is essential to clearly specify welding (and other engineering/

fabrication) requirements in contract documents. In general, this can be accomplished by specifying an appropriate code for the design and construction of the particular piece of equipment. In some cases, an Engineering/ Construction Specification may have to be developed to clearly delineate these requirements.

M&M Engineering can provide assistance to our clients in specifying proper and adequate welding (and other) requirements. In addition, we can provide or even establish inspection procedures, evaluate, and monitor vendor capabilities/performance and, finally, provide onsite review and oversight of the construction to assure that welding is done properly in accordance with the specified requirements.



Figure 1. Example of Weld Porosity in a Superheater Weld



Organic Chemicals in the Steam Cycle

By David Daniels

For many years, there has been an active discussion on the place of organic (carbon-containing) chemicals in the steam cycle. On October 4-6 2005, a conference sponsored by EPRI and Power Plant Chemistry Magazine, was held in Stuttgart, Germany, to assess the state of knowledge in this area.

The critical area of discussion was the extent to which organic compounds such as acetic acid might create corrosion issues on steam turbines. Corrosion mechanisms in steam turbines typically take place in the low pressure area of the turbine. These corrosion mechanisms can include stress corrosion cracking, corrosion fatigue, and corrosion/erosion mechanisms such as flow accelerated corrosion. They can take place in the area called the Phase Transition Zone where saturated and superheated steam can coexist. This vacillation between a wet/dry environment creates areas where inorganic and organic chemicals can concentrate to levels that are or might be corrosive to blade or rim materials. The corrosivity of chloride and sulfate are well known. As they precipitate into the first condensate that forms in the LP turbine, they create a very low pH condition in the condensate. On the other hand, caustic creates an extremely high pH condition. Both pH extremes either directly cause or further contribute to corrosion processes

in the turbine. The question is, can carboxylic acids such as formic and acetic acid, and carbon dioxide act like chloride and sulfate.

Where do Organics in Steam Come From?

There are three primary sources of carbon-based molecules in a boiler or in the steam that it produces: compounds that come in with the makeup water; breakdown products from polisher resins; and, compounds that we purposefully add to the boiler as treatment chemicals.

The organic molecules we add include amines and oxygen scavengers added to the feedwater, and polymers added to the boiler. These are known quantities, and in many cases, their breakdown products have been studied extensively.

The organics that come in with the process water are a diverse group. They include large complex naturally occurring organic molecules such as humic acid (from plant degradation) and polysaccharides (generated by bacteria). These typically have no charge and any that are not adsorbed on to ion exchange resin passes through into the makeup water. Where steam goes to a host, particularly in a refining, chemical or other manufacturing process, there is the constant risk of organic contamination from any condensate returns.

In addition to contaminating the feedwater directly, both naturally occurring and process contaminants can cause degradation of polisher resins. The resin breakdown product typically includes the sulfonate functional group on the resin. When this

enters the boiler, it breaks down further to organic acids and sulfate. It is not just makeup contaminants alone that cause polisher vessels to degrade. Neutralizing amines have long been associated with polisher resin breakdown in the nuclear industry.

If treated water sources are used for demineralizer makeup, such as potable water or a treated effluent water, the organic molecules may be chlorinated. These may pass through the ion exchange system or cause damage to the resins themselves.

Organics in the Boiler and Steam Tubing

When these organic compounds enter the boiler they are exposed to extreme temperature and pressure. If the compound is volatile, it is carried over into the superheater and reheater tubing. These are very harsh conditions and most organic compounds are oxidized in this process. Amines and nitrogen-containing oxygen scavengers often produce ammonia as a breakdown product. The carbon molecules forming carbon dioxide and one or more carboxylic acids such as formic, acetic, butyric, propionic, and glycolic acid. Chlorinated organic compounds can produce hydrochloric acid and organic sulfonates, from ion exchange resins, can produce sulfuric acid.

By in large, these breakdown products are volatile, particularly in the acid form. They may be less volatile as a sodium salt which is one advantage a phosphate treatment regime has over all volatile treatment.

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Organics in First Condensate

Of all the organic breakdown products, it turns out that carbon dioxide is the most innocuous. Research shows that at even relatively high concentrations, carbon dioxide at 212 F will not depress the at-temperature pH below that of pure water.

On the other extreme are chloride and sulfate which have a significant and well documented depressing effect on the pH of first condensate and the potential to cause, or at least facilitate, corrosion fatigue and stress corrosion cracking. Some have speculated that in cases where turbine damage has occurred in units with high levels of organics in the steam, it is the chloride and sulfate that were responsible for the damage and not the organic acids, per se.

In the middle are the carboxylic acids such as formic and acetic acid. These are produced by most of the organic treatment chemicals and naturally-occurring organic compounds. It is with these compounds that there is still a significant amount of question as to their potential to cause damage. It is clear that they have a slight depressing effect on the pH of early condensate. Some have also suggested that acetate has the ability to complex iron oxides. Maintaining the iron in solution and migrating it away from the corrosion tip may be key to continuing a particular corrosion mechanism.

Operational Experience with Organic Treatment Chemicals

All theories aside, there is a significant history of plants using carbon-based treatment chemicals that have operated for years with

no corrosion fatigue or stress corrosion cracking issues.

Neutralizing amines in particular are used extensively in industrial boilers and by the fossil and nuclear power industry. With the exception of elevated cation conductivity readings no one has presented firm evidence that the carboxylic acids produced by these compounds as they degrade is causing turbine blade failures. One of the reasons that has been suggested is that along with the carboxylic acid degradation product there is a commensurate production of ammonia which would increase the pH of the first condensate, negating the effect of the acids. Obviously this would not be the case with naturally-occurring organic molecules.

With oxygen scavengers, most power plants have an option to use hydrazine which contains no carbon, or carbohydrazide which only contains one carbon atom per molecule. Furthermore, testing shows that carbohydrazide breaks down into hydrazine and carbon dioxide, which does not affect the pH of first condensate.

The use of organic polymeric treatments for a boiler has an extensive history in industrial boilers and the treatment chemical manufacturers have formulations which are stable at higher pressures. The highest temperature and pressure units do not typically use polymers as part of their treatment and we are not aware of any turbine corrosion issues that could be attributed to polymer use.

Reducing Naturally Occurring Organics

Considering the potential for high

levels of organic breakdown products and chloride and sulfate contamination, the most important step most plants can take to reduce the potential for damage is to clean up the makeup water. Fortunately, reverse osmosis (RO) is excellent at removing many of the large organic molecules. The drop in membrane prices and the increase in caustic costs has made the economic justification of retrofit RO much .

While there is no set guideline or key parameter to measure, it makes sense to reduce the amount of naturally occurring organic matter in the feedwater.

Upcoming Events

HRSG Users Group Annual Conference

March 13-15

The Broadmoor Hotel
Colorado Springs, CO

Info at:

www.hrsgusers.org/events.php

Electric Utility Chemistry Workshop

May 9-11

Hawthorne Suites
Champaign-Urbana, IL
Contact: Elaine Wolff at:
wolff1@ad.uiuc.edu

International Water Conference

October 22-26, 2006
Omni William Penn Hotel
Pittsburgh, Pennsylvania

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