

Degradation of the mechanical integrity of steam turbine steels due to stress-corrosion cracking in acidic water

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Abstract

Low-pressure steam turbines are susceptible to stress-corrosion cracking (SCC). The use of alternative water sources in steam/water cycles involves an increased amount of organic compounds, leading to higher concentrations of organic acids in the aqueous environment of steam turbine steels. The impact of this environmental change on the mechanical integrity of steam turbine materials and the role of organic acids in the SCC mechanism are yet not fully understood.

This review paper provides an overview of the main factors influencing SCC of low-pressure steam turbines, i.e. material properties and the role of the acidic aqueous environment and stresses. Due to SCC, the mechanical properties of conventional NiCrMoV steels are deteriorated. However, their corrosion behaviour in current environments is reasonably understood and under control. Nevertheless, they have to be re-evaluated due to continuously changing environments. Therefore, the impact of the water chemistry, especially of organic acids, at certain temperatures and flow rates, during both operation and shutdown conditions, still must be investigated. Stresses must be minimized and crevices must be avoided, in which steam turbine design plays a major role.

A lot of industrial cases have been reported where cracking probably not solely occurred by stress-corrosion, but also hydrogen embrittlement was involved. Hydrogen might play a key role in the SCC of low-pressure steam turbines, but further research is required to determine its contribution and evaluate the influence of organic acids.

Keywords

low-pressure steam turbines; stress-corrosion cracking; organic acids; hydrogen embrittlement

Introduction

In low-pressure steam turbines, the steam cools down during its adiabatic expansion and a complex mixture of vapour and liquid phases is present [1]. The first (early) condensate can cause significant corrosion damage to the steam turbines, including stress-corrosion cracking (SCC) of rotors, discs and blades, which might lead to an unexpected stop of the power plant and hence produce important operating losses [2, 3, 4, 5]. SCC is a process of metal degradation caused by corrosion and a simultaneous sustained tensile or torsional stress. One of the first catastrophic SCC-related failures of steam turbines took place in 1969 at the nuclear plant Hinkley Point A in Great Britain [6]. From then onwards, turbine failure accidents have been reported continuously, amongst others in France [7], Taiwan [8, 9], South Africa [10], USA [11]. Since these low-pressure steam turbine failures - most of them related to SCC - frequently occur and result in huge costs (e.g. in excess of € 100M due to a catastrophic failure in South Africa [10]), SCC prevention of low-pressure steam turbines is of major importance.

In order to convert large amounts of heat energy into mechanical work, water is used in steam turbines. Hence, the steam turbine materials come into contact with an aqueous environment. Ideally, the chemistry of the water would be constant in place and time. However, water scarcity induces the need for an increased use of alternative water sources, such as municipal or industrial wastewater, for many different water-demanding processes, including steam/water cycles. Such alternative water sources may have a deviating water quality compared to typically used ground water sources, often due to the higher amounts of organic matter (total organic carbon, TOC) in these water types, and thus require a cost- and energy intensive treatment to meet the water quality standards, for example for boiler feed water [12]. Complete TOC removal is not realistic and when such water types are fed into a boiler system, the elevated temperatures in the boiler induce a breakdown of the organic compounds by hydrothermolysis, leading amongst others to the formation of organic acids, such as formic acid and acetic acid [13, 14, 15]. These organic acids significantly decrease the pH at the metal surface, i.e. typically at regions where steam condensates [16, 17]. The oxide layer of the metal, which normally allows keeping the corrosion rate under control, can therefore lose its protective nature, leading suddenly to an exponential growth in corrosion rate [18].

The influence of the acidic aqueous environment on the mechanical integrity of low-pressure steam turbines is not yet fully understood. In addition, the role of organic acids in the stress-corrosion cracking mechanism still needs to be clarified. Tackling these research questions is not self-evident, since stress-corrosion cracking is a very complex phenomenon, influenced by many factors, such as material properties, environment and stresses present [19]. In the following three sections each of these main factors is treated. Finally, a fourth section deals with the crack formation itself, in which hydrogen might play a key role.

Low-pressure steam turbine materials

Early steam turbine wheels in the 19th century were commonly made of cast iron [19]. A number of early wheel failures, attributed to mechanical design factors, occurred during the 1920s [20]. Then, nickel alloyed steel was implemented as the primary wheel material. The addition of nickel to steel increased both toughness and hardness [21]. During the early 1930s, the effect of chromium and molybdenum on high temperature properties was fairly understood and accepted, permitting a significant increase in steam temperature [19]. Within the same timeframe, the stresses in the wheels began to approach a significant fraction of the yield strength of the available steels due to the increase in rotor speed [19]. Therefore, also vanadium was added to the steel's chemical composition, resulting in NiCrMoV steam turbine steels.

By subjecting the alloyed carbon steel to a quench and temper heat treatment, chromium, molybdenum and vanadium based precipitates can be introduced, resulting in a high strength material with increased fracture toughness due to secondary hardening. However, these steels are potentially susceptible to tempered martensite embrittlement (TME) [22]. TME, also known as low-temperature temper embrittlement or 350°C embrittlement is the loss of toughness which may occur on tempering a martensitic steel in the 250 to 400°C temperature range [22]. Therefore, only a small amount of tramp elements, such as phosphorus, is allowed [23, 24, 25]. Amongst others Holdsworth et al. [26] and Lyle et al. [27] reported that phosphorus and other residual elements also influenced stress-corrosion crack growth kinetics. In contrast, according to Speidel et al. [28, 29], neither the steel cleanliness, nor the base composition influenced the growth of stress-corrosion cracks in low alloy steels when exposed to hot water. The plausible independence of base element content, such as molybdenum, on the SCC crack growth is remarkable, as Gras et al. [7] indicated later on that general corrosion of Mo-containing steels could generate molybdic acid, which might play a role in the SCC mechanism.

During the 1960s, the mechanical properties of the low-pressure steam turbines were even more enhanced, by lowering the austenitizing temperature to achieve a finer grain size, as such improving strength and toughness [19]. In order to obtain an improved transformation structure, the content of nickel, which is an austenite stabilizing element, was increased, whereas the ferrite stabilizing molybdenum content was reduced [19].

In the 20th century, extensive research in the area of steam turbine material's susceptibility to cracking in turbine environments has been conducted, resulting in several NiCrMoV steels, which are nowadays still used. Especially 3.5NiCrMoV steel is often used for steam turbine rotors and discs, while 12Cr stainless steels are often used for blades [10]. Generally, these steels have a martensitic structure, because austenitic steels are not appropriate due to their low damping capacity and relatively high thermal expansion coefficients [30]. Sometimes also precipitation hardened stainless steels are used for steam turbine blades, although they may be difficult to weld and be prone to selective dissolution, as such forming pits which can act as crack initiation sites [31].

Besides the conventional NiCrMoV steels, also developments concerning improved aerodynamics of the last row blades increased the necessity of higher strength alloys [32]. However, with increased yield strength of high strength steels usually the susceptibility to environment induced cracking increases and crack propagation is much faster [4, 32, 33]. The crack growth rate at higher yield strength can even be several orders of magnitude larger than for lower yield strength materials. For this reason, many power plants had to replace their steam turbine discs with a lower strength material because of the danger for SCC failure [31]. The yield strength is reported to be the dominant material factor governing SCC [34]. Consequently, applicable steels for especially rotors, discs and blades seem to be limited in yield strength.

However, in the meantime, some turbine materials with higher strength have been developed. For example, the use of titanium alloy blades, e.g. Ti-6Al-4V, for the last stages of low-pressure steam turbines are used and some others are under investigation [31, 35, 36]. Such titanium blades can have similar yield strength as the steels, are a lot lighter and would have a better corrosion resistance, including a better behaviour regarding SCC during operation in wet steam [36, 37, 38]. However, they are significantly more expensive, difficult to machine, more brittle, have a low material damping and might be more prone to scratches [31, 37]. Protective coatings for steam turbines are also sometimes used [39, 40, 41, 42, 43]. The behaviour of advanced steam turbine steels in steam/water conditions still needs thorough investigations before actual implementation in industry is possible. Even the corrosion behaviour of the currently used steam turbine steels still needs to be investigated, because of possible variations in the environments in which they are used.

Acidic aqueous environment

Over the last few decades, a gradual change in the environment in which steam turbine steels are used has occurred, due to for instance new water treatment practices and the ongoing shift towards alternative water sources. Steam turbine steels acting as high-performant in certain environments, may fail in other environments. Indeed, minor changes in the environment can have a large impact on the corrosion behaviour. Factors of major importance concerning the environment are, amongst others, its chemistry, temperature and flow rate. In this section, first the chemistry of the environment is treated, including the presence of dissolved gases and impurities. Subsequently, SCC dependence on temperature and flow rate is discussed. The last part of this section deals with the importance of shutdown conditions.

Dissolved gases

Several dissolved gases, such as O₂, CO₂ and H₂S, might influence the stress-corrosion cracking of steam turbine steels. In the late 20th century, the contradicting impact of dissolved gases on SCC of steam turbine materials was reported. Stress-corrosion crack growth rates of rotor disc steel measured by Speidel et al. [28] showed no dependence on oxygen concentration or on CO₂ level. In addition, calculations of Liu et al. [5] showed that the initiation and propagation of stress-corrosion cracking was not very sensitive to the oxygen content of the steam. In contrast, McMinn et al. [44] reported a strong relationship between cracking and the concentration of oxygen in the steam/water system of power plants. According to Schleithoff [45], CO₂ had an important influence on the crack development.

In the beginning of the 21st century some more insight was gained on the influence of dissolved gases on SCC of steam turbines. Maeng et al. [46] noted an increase of the SCC susceptibility of typical 3.5NiCrMoV steam turbine steels in environments with higher dissolved oxygen content, by performing constant elongation rate tests in high temperature water of various dissolved oxygen concentrations. However, Dooley [47, 48] reported that oxygen does not concentrate in the first condensate, i.e. oxygen levels in the first condensate might be lower than 1 ppb for steam inlet oxygen levels of 30-250 ppb. This low oxygen content in the first condensate is due to the partitioning of oxygen between the steam and liquid phases [48]. In terms of corrosion research this had an impact on the potential corrosion mechanisms of steam turbines. Consequently, the main thinking in scientific research shifted from steam turbine corrosion caused by high oxygen levels towards other factors of the environment that are dominant for the corrosion of steam turbine materials, especially steam purity, temperature, flow rate and shutdown conditions.

Guidelines for industry nowadays recommend a maximum oxygen concentration of a few hundred ppb [49, 50]. Deoxygenation can be done by use of e.g. deaerators and oxygen scavengers, such as hydrazine. However, at some places the use of hydrazine was abandoned to enhance the resistance of the magnetite layer to flow-accelerated corrosion (FAC) [51]. It is recommended to also remove other dissolved gases, such as H₂S. Especially in geothermal steam turbines, a non-negligible amount of H₂S most often is present, leading to corrosion of turbine materials [42, 43, 52, 53].

Impurities

A lot of contaminants, such as hydroxides, sodium, chlorides, carbonates, acids, hydrogen, sulphur, etc. may be present in the steam/water cycle, originating from multiple sources. Besides entering the steam/water cycle along with the feed water, originating from condenser leaks or from condensate polishers, they could also be present due to manufacturing, storage, installation or inspection of steam turbine parts [31].

NaOH is referred to be the most corrosive contaminant with respect to SCC of low-pressure steam turbines [54]. It may have originated from high boiler carryover while improper boiler water control and from malfunctioning condensate polishers and makeup systems [31]. According to Lyle [55], addition of small amounts of NaCl reduced the concentration of NaOH necessary to produce SCC of 3.5NiCrMoV steam turbine steel.

Besides the impact such contaminants can have on the corrosion behaviour of steam turbines, a lot of them also can thermally decompose into acids such as organic, carbonic, sulphuric, hydrochloric and molybdic acid [31]. Molybdic acid can be formed from MoS₂, often used as thread lubricant, and might cause SCC of NiCrMoV shrunk-on discs [7]. Consequently, such corrosive lubricants have to be eliminated from use in steam/water cycles.

To get rid of a lot of contaminants, the feed water must be subjected to an appropriate water treatment before entering the steam/water cycle. Also during operation the water must be treated adequately, such as with condensate polishers and by performing boiler blowdowns. However, steam/water cycles are most often under pH control for protection of preboiler and boiler equipment. Consequently, it might be that this does not match with the requirements of the steam turbine surfaces. Care must be taken that the removal or addition of certain species in the water is reasoned for the sake of the whole steam/water cycle.

Nowadays, film-forming amines are often used as barrier inhibitors to slow down the corrosion rate. Van Lier et al. [51] stated that in a film-forming amine treated steam/water cycle not only caustic gouging and acid phosphate corrosion did not occur, but also that the risk of hydrogen damage was vastly reduced by the continuous removal of deposits. Moreover, film-forming amines might have a mitigating effect on both flow-accelerated corrosion and corrosion-fatigue, based on evidence presented by Lister et al. [56] and Povarov et al. [57], respectively. Although these film-forming amines form a protective layer against corrosion by adsorption on the wall, it is still unknown what the exact protection mechanisms are and whether these amines also are a source of corrosive organic acids themselves when they thermally degrade [58].

A good control of water chemistry is vital in preventing problems in a steam/water cycle system. However, very dilute solutions in the steam/water cycle can become concentrated during operation. As shown in Figure 1 [59], a steam turbine is normally part of a steam/water cycle. When certain species get concentrated, even due to very small incremental increases in each cycle, the chemistry of the environment of the steam turbines can be significantly changed and corrosion can be promoted. Dooley et al. [60] stated that “cycle chemistry is responsible for about 50% of the failures in fossil plants and about 70% in combined cycle units with HRSG” [51].

Not only concentrating of impurities due to the cyclic process must be taken into account, but also locally impurities can concentrate, e.g. in the first condensate. Indeed, the exhaust pressure of low-pressure turbines is often designed to be sub-atmospheric, in order to gain the maximum energy output [61]. When the steam, flowing through the low-pressure steam turbine, expands and crosses the saturation line (Wilson line), moisture droplets nucleate. Although the properties of such first condensate droplets are yet not fully understood, some things can be said about the steam-water partitioning. Ionic impurities, which are usually present in low concentrations in the steam, can concentrate by factors of more than one hundred in the liquid phase [17, 62]. Also anionic impurities might be concentrated in the liquid phase, leading to a reduced pH of the first condensate [48]. For example organic acids can transport from the vapour to the liquid phase due to their low distribution coefficients [63].

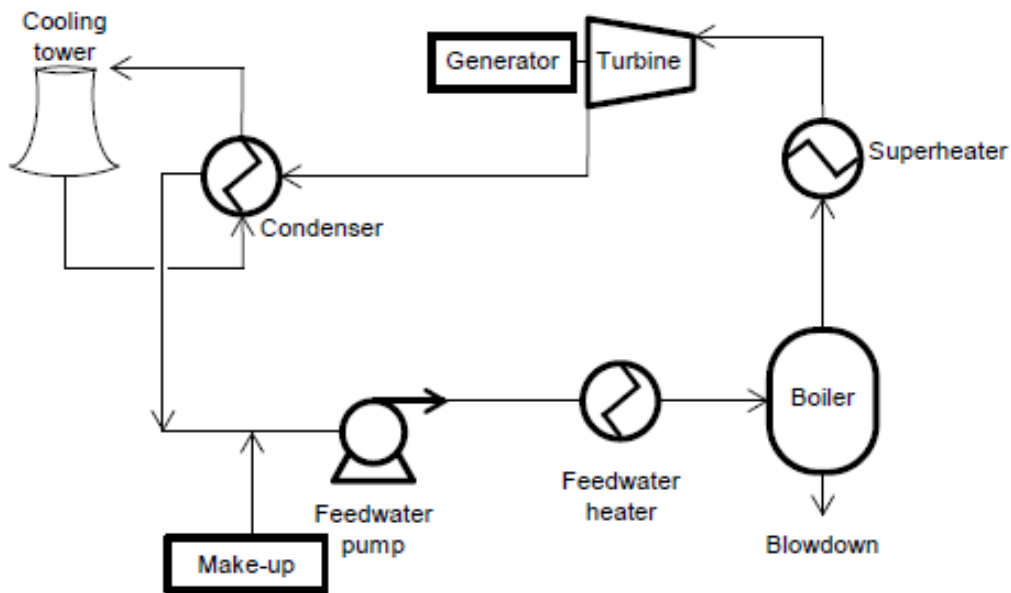


Figure 1. Schematic drawing of a steam/water cycle [59].

A common organic acid found in the first condensate is acetic acid. Concentrations of about 600 up to 6000 ppb of acetate were found in the first condensate by performing first condensate sampling experiments [3, 17]. According to Wei et al. [63], the concentration of acetic acid in the first condensate is more than 1000 times higher than that in the inlet steam, resulting in a lowered pH of the liquid phase. Maeng et al. [64] showed that the presence of acetic acid facilitates SCC of typical 3.5NiCrMoV steam turbine steel by performing constant extension rate tests in hot water. However, at very high concentrations SCC susceptibility was again lowered because excessive dissolution induced crack blunting [64]. Also in first condensates containing chloride ions, acetic acid would play a key role in the initiation and propagation of pits by decreasing the pitting resistance and increasing the corrosion rate of 2Cr12MoV steam turbine steel [63]. Other organic acids can be formed as well. For example ethanolamine, often used as pH-conditioner and chelating agent in low-pressure steam turbines, can thermally decompose to organic acids, such as acetic acid, formic acid and galactic acid [64].

Besides steam-water partitioning during condensation, also deposition due to exceeding of steam solubility limits during steam expansion or even local evaporation of moisture, might lead to increased impurity concentrations [19, 31]. After all, a lot of parameters controlling corrosion, such as pH and temperature, can change within a broad range in the steam turbine.

Temperature

The temperature can have a large impact on the stress-corrosion cracking of low-pressure steam turbines. Maeng et al. [46] reported that the SCC susceptibility of 3.5NiCrMoV steel increased with increasing temperature. The elongation and maximum stress of the steel decreased as temperature increased. The temperature would speed up the rate-controlling step of the SCC of steam turbine steels [46]. Test results of Lyle [55] indicated that the minimum sodium hydroxide concentration required to produce detectable SCC decreased with increasing temperature.

Flow rate

Also the relative velocity of the environment with respect to steam turbine material affects the corrosion behaviour. Especially in stagnant areas, solutions can concentrate and remain for long periods during operation [19, 46].

Beside regions without or with hardly any flow, too high flow velocities can also be problematic. Indeed, the flow velocity of the wet steam may not exceed the allowable velocity specific to the turbine materials and moisture chemistry, in order to avoid flow-accelerated corrosion. Therefore, regions of high turbulence must be avoided. Another way to avoid FAC might be the use of steels containing enough chromium – and maybe also other alloying elements - to form a protective oxide layer which keeps its integrity in such circumstances [31, 65]. Also the control of the water chemistry, e.g. reducing organic acids and as such increasing the pH of the first condensate, could result in less FAC [31].

Another flow rate related problem is water droplet erosion, particularly in the last stage of the low-pressure steam turbines. The blades, rotating with high velocity, get damaged because they hit condensed water droplets. The pH, amongst others influenced by the concentration of acids, was found to have a large impact on the erosion rate [66, 67].

Shutdown conditions

During shutdown the environment can be totally different with respect to the environment during operation, leading to alternative forms of corrosion. During unprotected layup, corrosive deposits can be present due to an increased humidity and oxygen content present in the aqueous environment in contact with the steam turbine materials. This can lead to pitting of especially disc-blade attachments and steam turbine blades, particularly in the phase transition zone (salt zone) [31]. Little pitting is observed on wet stages because impurities can be washed away. In contrast, at places where impurities can almost not be removed, such as in blade tenon-shroud crevices, pitting is frequently observed [31]. Pitting can be the precursor to more extensive damage such as SCC and corrosion fatigue [48]. To reduce the chances of pitting during shutdowns, specific equipment can be installed, such as recirculation systems for pressure sections, nitrogen generators, dehumidification systems and gas-transfer membrane skids [68]. In addition, the selection of titanium alloy blades is recommended, due to their good resistance against pitting.

Concerning the corrosive impact of the environment on steam turbine materials, as well the environment during operation as the environment during shutdown needs to be taken into account. For both environments, steam purity is of major importance and has to be kept under control. Although it is not possible to remove every single impurity (organic contaminants which form organic acids can still be present) at all times the steam/water composition should be known. A real-time appropriate water treatment should be performed based on the instantaneous steam/water chemistry. Also awareness of local temperatures and flow rates is recommended. In addition, the currently used steam turbine materials need to be re-evaluated, taking into account their changing environments. For this, a better understanding of the role of different features of the material microstructure in the mechanical degradation of low-pressure steam turbine steels due to SCC may be evaluated by performing experiments based on the methodology developed by Depover et al. [69, 70, 71, 72, 73, 74]. They characterized the impact of an environment, in their case the presence of hydrogen, on the mechanical integrity of several steels by performing constant extension rate tests with in-situ hydrogen charging.

Stresses

Besides the corrosive environment, stresses are also needed for a steam turbine to suffer from SCC. A first aspect related to the stresses in steam turbine materials is the design of the steam turbines. For example steam turbine blade root designs have geometries with stress concentrations that promote SCC. In order to minimize local tensile stresses, those steam turbine parts can be shot-peened. As a result, compressive residual stresses are generated at the surface, which can resist crack initiation [10, 42, 43]. However, tensile stresses are consequently present in the subsurface region. When the compressive layer gets damaged up to the region of these induced tensile stresses, corrosion might even be enhanced.

Although design parameters may be well advanced for material behaviour and aerodynamics, they might also induce undesirable impurity concentrations. Especially crevices can act as impurity traps and in addition they also facilitate the formation of oxygen concentration cells and generate high stresses. Therefore, crevices must be avoided as much as possible. For this purpose, it might be better to use large parts instead of a lot of small parts assembled together, e.g. solid turbine parts instead of built-up or shrunk-on parts. In addition, a large advantage of one-piece-parts is that they are made of only one material, because combination of dissimilar materials in contact can produce galvanic corrosion and must therefore better be avoided. Another advantage of solid turbine parts, e.g. solid rotors, is that they do not suffer from disc bore SCC as shrunk-on discs do [31].

A third possible type of low-pressure rotors are welded rotors, as shown in Figure 2 [75]. These are also a good option in order to eliminate the high stresses in disc keyways of shrunk-on discs [76]. Besides welding of steam turbine parts, also weld repair with amongst others 12Cr steel is often performed [65]. However, welding influences the properties of the base material in the heat affected zone and may introduce internal stresses [77]. In this way also the corrosion behaviour of the steels can be changed [78]. In addition, welding is a possible cause for the entry of hydrogen into the material, leading to metal degradation [79, 80]. Hydrogen can be picked up in the molten weld pool because of dissociation of hydrogen gas, water or hydrocarbons [81]. Upon solidification, the hydrogen remains trapped in the material and consecutively causes a degradation of the material [82].

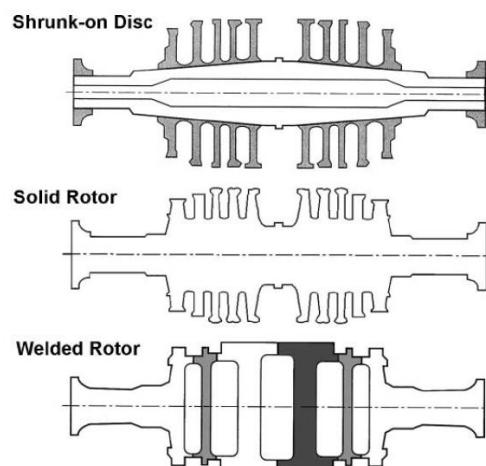


Figure 2. Three types of construction for low-pressure rotors [75].

Besides the design stresses, for example steam turbine discs can also have some residual stresses from machining, vibratory stresses and stresses due to centrifugal loads by rotor rotation. Minimization of stresses can have a large influence on the sensitivity to stress-corrosion cracking. A well-chosen design can make a huge difference in the SCC of steam turbines by amongst others minimizing stresses and avoiding crevices.

Cracking

The cracking of steam turbine steels occurs predominantly intergranularly and cracks are often branched [83]. McMinn [44], for instance, reported intergranular cracking along the prior austenite grain boundaries. Hodge and Mogford [84] also observed that cracking in UK steam turbines was mainly intergranular, although the crack initiation was usually transgranular. Fractures due to SCC are typically brittle [65] and several SCC mechanisms have been proposed: film-rupture mechanisms [85, 86], mechanically assisted chemical dissolution mechanisms [87], strain induced corrosion cracking mechanisms [88] and hydrogen (embrittlement) assisted cracking mechanisms [89, 90]. A key factor in the latter type of mechanisms is hydrogen, which might play an important role in stress-corrosion cracking. Hydrogen is able to absorb into the metal and diffuse to regions ahead of the crack tip, as such accelerating the crack propagation. Hydrogen embrittlement (HE), characterized by a hydrogen induced ductility loss, is known to cause unpredictable failure.

HE in steam turbines

During the 1950s already, the fracture of a low-pressure steam turbine rotor made of NiCrMoV steel was reported to be initiated from crack-like flaws, apparently caused by hydrogen damage [19]. When experts studied the cracks found in both burst and intact discs of the catastrophic SCC-related steam turbine failure at the nuclear plant Hinkley Point A in Great Britain, they concluded that cracking probably did not solely happen by stress-corrosion, but that hydrogen embrittlement might have had a relevant contribution as well [6]. Also after performing tests related to the steam turbine failure in France in the 1990s, Gras et al. [7] stated that the stress-corrosion cracking mechanism probably involved hydrogen embrittlement. Although hydrogen can readily enter steam turbine materials during processing, welding or in service, necessary precautions have not been taken so far [79, 80, 81, 82].

Bavarian et al. [91] reported that turbine rotors, discs and blades made of high strength steels suffered from both stress-corrosion cracking and hydrogen embrittlement. Speidel et al. [28] argued that the propagation of stress-corrosion cracking in high strength materials was significantly accelerated by the local presence of hydrogen. According to them [28], the embrittlement by hydrogen of low-pressure rotor steel can be interpreted as an ‘alloying effect’, changing the properties of the material and accelerating crack propagation [92, 93].

By fractographic analysis of linearly increasing stress tested 3.5NiCrMoV steam turbine steel in distilled water at 90°C, Ramamurthy et al. [94] proposed a strain induced anodic dissolution mechanism at these conditions. However, when performing similar tests at temperatures below 60°C, hydrogen, coming from the cathodic reaction, was believed to play a role in the mechanism by embrittling the region ahead of the crack tip [95, 96]. This was confirmed by Liu et al. [97], who detected hydrogen associated brittle fracture events after the onset of necking of 3.5NiCrMoV steel, when performing the same tests at room temperature and at negative applied potentials, as such isolating the cathodic reaction. Consequently, this indicated that hydrogen might play a role in the SCC mechanism of low-pressure steam turbine steels at room temperature. However, it must be clarified whether hydrogen also plays a role in the SCC mechanism at higher temperatures, i.e. around 90°C, since at those temperatures the most SCC low-pressure steam turbine problems have been reported.

In addition, the fundamental effect of several factors, such as water chemistry and flow rate, still needs to be investigated. Particularly, the impact of organic acids in nowadays changing aqueous environments on the (hydrogen assisted) SCC mechanism should be determined, taking into account the complex structure of the low-pressure steam turbine materials.

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