Effects of Hydrogen on Passivity and Stress Corrosion Cracking of Stainless Steels

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Abstract

It is known that the stress corrosion cracking (SCC) susceptibility of austenitic stainless steel (SS) is dominated by the mechanism of anodic path cracking (APC) and is enhanced by the passivity degradation. Experimental observations show that ingress of hydrogen into austenitic SSs reduces the stability of passive films and enhances the susceptibility to SCC. The hydrogen-promoted SCC is well demonstrated by lower crack initiation lifetime and higher crack propagation rate, as well as high frequency of passive breakdown at crack tip. The hydrogen-induced passivity degradation is indicated by the low breakdown potential, high passive current density, declined repassivation ability and low critical chloride concentration to induce breakdown of passive films. It is found that the action of static tensile stress in elastic deformation regime can also affect the passivity of material, as indicated by the high passive current density, low breakdown potential and low critical chloride concentration to induce breakdown of passive films. The results imply that the hydrogen-promoted SCC of austenitic SSs is likely to be related to the hydrogen-induced passivity degradation which resulted from the highly defective film structure caused by ingress of hydrogen. The hydrogen effects was also observed for the SCC and passivity degradation of Alloys 690 and 800 in high temperature water containing lead species.

1. Introduction

Two categories of mechanisms are proposed to interpret stress corrosion cracking (SCC) behavior, namely, hydrogen-induced cracking (HIC) and anodic path cracking (APC or anodic dissolution)[1,2]. The SCC of austenitic stainless steels (SSs) and nickel-based alloys in aqueous solution containing chloride ions is generally recognized to be dominated by the APC mechanism. Experimental evidences have indicated that dissolved hydrogen could reduce the facture time and the threshold stress-intensity factor of 310SS [3] and the hydrogen-charged 310SS was less resistant to general corrosion [4]. As predicted by a hydrogen-facilitated anodic dissolution model [5,6], the active dissolution at a crack tip would be accelerated significantly owing the interaction of local stress field and hydrogen [5,6]. A recent research showed that the interactive effect of dissolved hydrogen and local stress field at crack tip on active dissolution is very limited [7]. Therefore, hydrogen is likely to affect SCC via an alternative way. In recent years, the authors' research group conducted a series research on effects of hydrogen on passivity and found that the hydrogen could reduce the stability of passive films [8,9,10,11]. Hydrogen dissolved in the metallic substrate changed the film composition, structure and properties [4,12,13,14,12,14]. In addition, dissolved hydrogen may lead to martensite phase transformation in austenitic SS and have profound impact on passivity and SCC behavior [15,16]. It was reported that the hydrogen incorporation into passive films of Fe- and Ni-based alloys when they are exposed to high temperature water with lead contamination, accompanying with passivity degradation and high susceptibility to SCC **[**17]. In this paper, our findings on the effect of hydrogen on passivity and SCC will be summarized. The hydrogen-induced passivity degradation will be correlated to hydrogen-promoted SCC phenomena.

2. Hydrogen-Promoted SCC Phenomena

SCC tests of 304 SS were conducted in the boiling 42% $MgCl_2$ solution at 143 ^{0}C under constant tensile load. The crack initiation lifetime, t_i, of 304 steel was determined using taper specimens with a tape angle 3^0 under a constant load. After the specimens were broken after a period of time t_f, they were sectioned along their centerline in longitudinal direction. The distribution of crack size on a sectioned surface along the longitudinal direction of tapered specimen was measured using a microscope. Then the position and depth of each crack, a_{SCC}, were measured on the sectioned surface. It was found that the dependence of a_{SCC} upon local stress corresponding to each crack position, σ, can be approximately expressed with the following equation:

$$a_{SCC} = \lambda(\sigma - \sigma_i) \tag{1}$$

where λ is an experimental constant and σ_i can be regarded as the critical stress to initiate SCC at the given test duration, t_f, since $a_{SCC} = 0$ if $\sigma \le \sigma_i$. The test duration can approximately represent t_i under the action of the applied stress of σ_i. The crack propagation lifetime t_p is equal to the difference between t_f and t_i. A lower crack growth lifetime results from a high crack propagation rate.

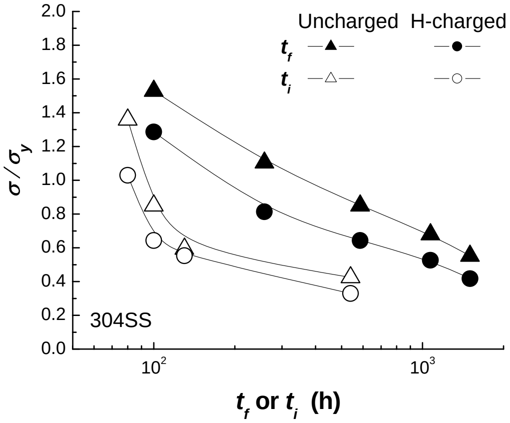


Fig. 1. Effect of hydrogen on SCC lifetime of 304SS in boiling 42% $MgCl_2$ solution at 143 °C [18].

The curves of SCC lifetime vs. stress for 304SS are shown in Fig. 1 [18] where the hydrogen-promoted crack initiation is well demonstrated. The data in Fig. 1 indicate that the values of t_p for the charged specimens were much less than those of uncharged ones and the impact of hydrogen-charging was more pronounced on the crack growth process than on the crack initiation. This is due to the hydrogen enrichment at the crack tip resulting from the diffusion driven by the stress field around the crack tip. The cracking is expected to be promoted with increasing hydrogen concentration. Since the SCC of austenitic SSs in chloride ion-containing solution has been recognized to be controlled by an anodic dissolution mechanism, the experimental results in Fig. 1 show clearly the impact of dissolved hydrogen on the SCC process for the SCC system controlled by APC.

3. Hydrogen-Enhanced Effects of Chloride on Passivity

It is well known that chloride ion is the primary contributor to passive film breakdown in aqueous environments. Generally, the stability of passive film is often evaluated by the breakdown potential determined from potentiodynamic curve. The result in Fig. 2 [14] shows that the breakdown potential of 304SS decreases with increasing chloride ion concentration in aqueous solution and the breakdown potential of hydrogen charged steel is much more sensitive to chloride than uncharged one does.

When a critical quantity of chloride was added under potentiostatic condition, the passive film breakdown can be detected by monitoring a sudden rise of current density after a period of time and the period required to breakdown the passive film decreases with increasing chloride concentration in solution and hydrogen charge current density. The critical concentration of chloride to induce the passive breakdown of passive film decreases with hydrogen charge current density, an indicator of dissolved hydrogen in steel increasing.

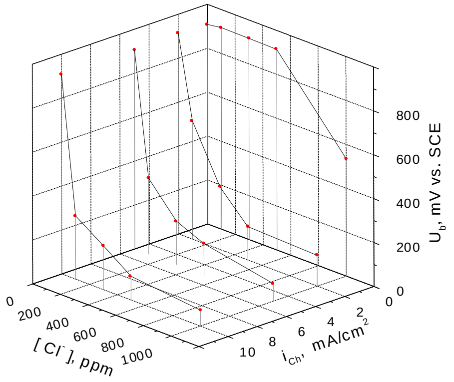


Fig**.** 2. Effects of hydrogen and chloride on breakdown potential of 304SS in borate buffer solution [14].

According to Point Defect Model proposed by Macdonald et al. [21], the passive current density is proportional to diffusion rate of point defects within passive films. The Mott-Schottky and photoelectrochemical measurements have indicated that the incorporation of hydrogen results in a high defective structure of passive film. Experimental data show that both high dissolved hydrogen concentration in SS and high chloride ions in solution increased the passive current density. The synergistic impact of hydrogen and chloride on the passive current density contributed significantly to the total current density, indicating a strong synergistic effect of hydrogen and chloride on passivity.

Theoretical analysis and many experimental observations indicated that the incorporation of hydrogen could increase oxygen vacancies in passive films, giving rise to a high passive current density. It is recognized that the oxygen vacancy is prone to react the adsorbed chloride ion and becomes the weak site of passive film. Hence the ingress of hydrogen leads to the formation of passive film vulnerable to localized breakdown.

4. Interactive Effect of Hydrogen and Stress on Passivity

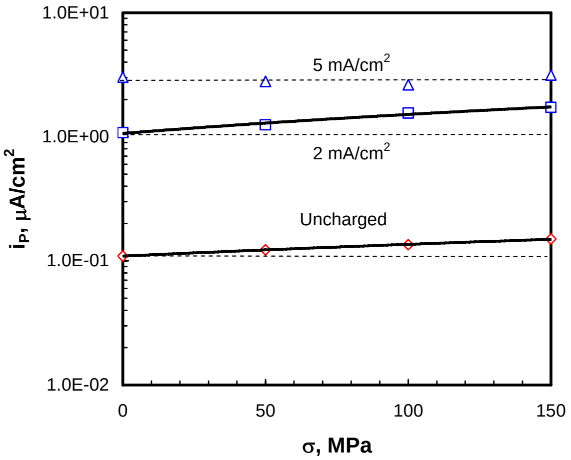


Fig.3. Effects of hydrogen and tensile stress on passive current density of 304SS in borate buffer solution containing 100 ppm chloride [19].

The stability of passive film is also affected by applied stress in elastic deformation regime, where the applied stress is no more than 50% of yield strength [19,20]. This effect is enhanced by the ingress of hydrogen, as indicated by the breakdown potential determined by potentiodynamic measurement. This effect is also demonstrated by a potentiostatic measurement similar to those shown in Fig. 3. The critical chloride required to induce passive film breakdown in hydrogen-charged SS is about 100 times lower the uncharged one and the effect of stress is more pronounced in the hydrogen-charged steel.

A linear relation is approximately held between the breakdown potential and applied tensile stress when the material is hydrogen-charged under a constant current density. The effect of tensile stress increases initially with the hydrogen charge current density, peaks at 1 mA/cm^2, declines with a further increase of hydrogen charge current density and ceases when the hydrogen charge current density reaches 10 mA/cm^2.

Similar to the breakdown potential, the passive current density is also affected by tensile stress and this effect depends on hydrogen concentration in steel. The effect of stress increases initially with increasing the hydrogen charge current density reaches a maximum at the current density around 2 mA/cm^2 and then decreases with a further increasing hydrogen charge current density, as shown in Fig.3. The tensile stress can also retard the repassivation after passive film breakdown, although the impact is not so pronounced [19].

As described by Point Defect Model of passive films developed by Macdonald et al. [21], in chloride–containing environments, the absorbed chloride ion can desorb along with a surface cation to form a vacancy-pair. This process is favored in the case where the anion tends to complex with the cation rather than forming an insoluble compound. The cation may submerge into barrier layer by outward movement of a cation through vacancy self-diffusion, resulting in a cation vacancy at the film/substrate interface and the regeneration of an isolated surface oxygen vacancy at the film/solution interface. This is an autocatalytic process since the oxygen vacancy can then absorb another anion like Cl^-, and it can be promoted by the action of tensile stress because the self-diffusion of vacancies can be facilitated by the tensile stress. When the oxygen vacancy density in passive film is low, such as in the uncharged steel, and the chloride concentration in solution is low, the probability of oxygen vacancy to be occupies by chloride ion is very low and the impact of tensile stress on the stability of passive film is small. When the oxygen vacancies increase due to ingress of hydrogen or chloride concentration of solution is high, the action of tensile stress may increase the supply of oxygen vacancies at the film/solution interface, leading to the passivity degradation, and the passivity degradation is enhanced due to the increase of oxygen vacancy by ingress of hydrogen. When the hydrogen charge current density exceeds certain critical value, the effect the applied stress is reduced. Two reasons may account for this phenomenon: (1) the oxygen vacancy diffusion is no longer a rate-determining step of corrosion reaction because the vacancy density in passive film has been sufficiently high and/or (2) the impact of applied stress is overrated by the high stresses caused by the hydrogen-induced martensite phase transformation that will be mentioned later.

5. Hydrogen-Incorporation in High Temperature Water Containing Lead Contamination

The ingress of hydrogen into metals is facilitated by some ‘poison’ species present in aqueous environments, such as As^{3+}, S^{2-} etc, by hindering the combination of hydrogen atoms to form hydrogen molecules. The hydrogen embrittlement or hydrogen-induced cracking of pipelines in the aqueous environments containing H_2S, as a typical example, has been well documented [22]. It is generally recognized that the SCC of steam generator tubing alloys in high temperature water, as in the cases of nuclear power generation systems, is dominated by APC mechanisms [23,24]. The steam generator tubing alloys are normally Fe- or Ni- based alloys. Lead contamination is almost unavoidable in the steam generators of nuclear power plants and has been found to be a primary contributor to SCC of steam generator tubing alloys. The experimental evidence has indicated that the SCC induced or promoted by lead contamination, PbSCC, may be correlated to the passivity degradation induced by the lead contamination [17] but the roles of lead species in PbSCC and Pb-induced passivity degradation are still poorly understood [23].

The incorporation of lead impurities alters the composition of passive films markedly and hinders the dehydration of hydroxides to transform into crystalline oxides film during passivation, giving rise to the formation of passive films with more defective structures [25]. Meanwhile, lead contamination promotes anodic dissolution and retards the repassivation after passive film breakdown (Fig. 4). This kind of changes in passive film structure reduces the film rupture ductility under action of tensile stress [17] and the resistance to breakdown demonstrated by lower pitting corrosion resistance [25]. The experimental investigation indicated PbSCC susceptibility of Alloy 800 was well correlated to the rupture ductility of passive films (Fig. 5) [17]. An interesting phenomenon is that the presence of lead contamination can promote to ingress of hydrogen into passive films, as indicated by the SIMS measurements showing in Fig. 6. Lead species seems to act as a ‘poison’ that facilitates hydrogen atoms to enter alloys. It is worthy to note that the phenomena of Pb-induced passivity degradation are quite similar to those of hydrogen-induced passivity degradation reported here and elsewhere [26]. It is worthy to investigate the roles of hydrogen in the PbSCC and Pb-induced passivity degradation.

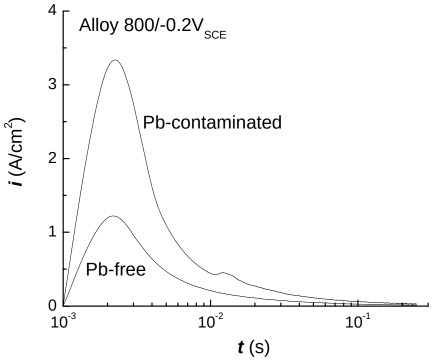


Fig.4. Retarded repassivation in alkaline crevice chemistry due to Pb contamination.

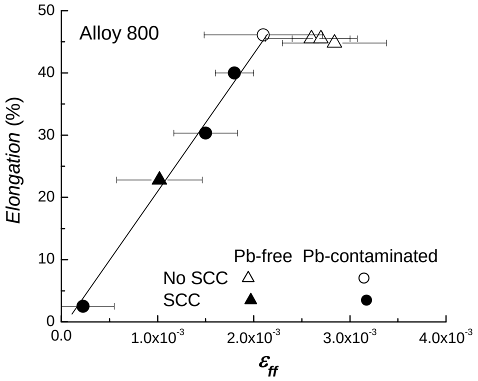
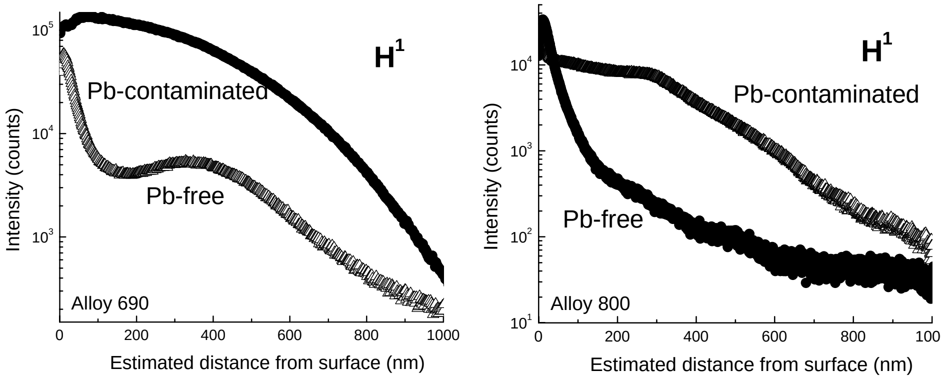


Fig. 5. Correlation between elongation measured by constant extension rate tensile test and film rupture ductility [17].



(a) Alloy 690[17] (b) Alloy 800

Fig.6. Incorporation of hydrogen into passive films due to lead contamination

6. Implications to Hydrogen-Promoted SCC

SEM observations on fracture surface suggested incorporation of hydrogen did not alter the SCC mechanism of austenitic SS. Therefore, SCC of hydrogen charged austenitic steel may be still governed by a mechanism of APC type. Electrochemical (potential) noise created during SCC indicated that the dissolved hydrogen in steel reduced the crack initiation lifetime, which is in agreement with the test results in Fig.1, and the noise structure after crack initiation is characterized by a sharp drop followed by slow recovery. Similar noise structure for the charged and uncharged specimens indicated again that same mechanism operates in SCC of both hydrogen-charged and uncharged 304SS. A noise peak records a SCC event. The sharp drop of potential always accompanies a quick rise of transient current [27], which is resulted from a sudden exposure process of fresh metal produced by the breakdown of a passive film at the crack tip during SCC propagation. The slow recovery is due to the repassivation of fresh surface. The electrochemical noise suggests that cracking is likely to be dominated by the film rupture mechanism and crack propagation comprises the cycles of film rupture and repassivation.

The thermodynamic analysis and experimental observations have indicated the hydrogen and applied stress in elastic deformation regime have very limited effects on active dissolution [7]. Hence the hydrogen-promoted SCC of austenitic SS should be related to the hydrogen-induced passivity degradation and/or the promoted breakdown of passive film due to incorporation of hydrogen, as demonstrated by the increased film rupture frequency and the larger amplitude of transient current observed in the hydrogen-charged steel. It has been well recognized that, when cracking is dominated by the film rupture mechanism, the average crack growth rate $\overline{V}_C$ can be formulated by [24]

$$\overline{V}_C = \frac{M}{zF\rho}\frac{\overline{Q}}{\bar{t}_{ff}} = \lambda\frac{\dot{\varepsilon}_{ct}}{\bar{\varepsilon}_{ff}}\overline{Q} \qquad (2)$$

In Eq. (2) M the atomic mass of metal, z is the molar number of electric charge exchanged for oxidation of molar metallic atoms; F is Faraday's constant; ρ is the density of steel and λ is a constant independent of SCC mechanism. $\bar{t}_{ff}$ is the average time duration between the two adjacent events of passive film breakdown at the same location and inversed proportional to the frequency of noise peaks f_{Noise}. It is given by

$$\bar{t}_{ff} = \frac{\bar{\varepsilon}_{ff}}{\dot{\varepsilon}_{ct}} = \frac{\bar{t}_{Noise}}{\overline{A}_f} = \frac{1}{\overline{A}_f\, f_{Noise}} \qquad (3)$$

where $\bar{t}_{Noise}$ is the average time interval between the noise peaks; $\overline{A}_f$ can be regarded as the average surface area fraction at crack tip where passive film is breakdown; where $\bar{\varepsilon}_{ff}$ is the rupture ductility of passive film and $\dot{\varepsilon}_{ct}$ is the creep rate at crack tip. In Eq. (2) $\overline{Q}$ is the average of electric charge pass through the unit surface where passive film is breakdown

$$\overline{Q} = \overline{A}_f \int_0^{\bar{\varepsilon}_{ff}/\dot{\varepsilon}_{ct}} i(\tau)d\tau \qquad (4)$$

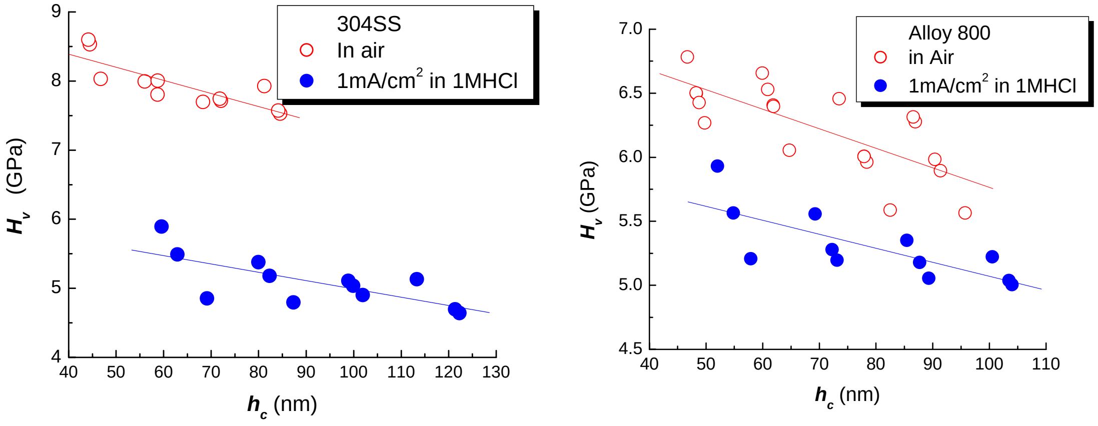
where $i(\tau)$ is the transient current density response over the surface where passive film is breakdown. In line with Eq. (2), the incorporation of hydrogen can accelerate the cracking via increasing $\overline{Q}$ and/or decreasing $\bar{t}_{ff}$. The later is determined by the film rupture ductility and crack tip creep rate.

Scratch test results indicate that the ingress of hydrogen into SS retards the repassivation after the passive film breakdown. There is experimental evidence demonstrating that the tensile stress has same, but not significant, influence. It would give rise to an increase of $\overline{Q}$, the electric charge passing through the unit area of surface where the passive film is breakdown. This also agrees with electrochemical noise measured during SCC.

Reduced breakdown surface area fraction can lead to a decrease in electrochemical noise amplitude (or $\overline{Q}$) and an increase in the noise frequency. The ingress of hydrogen can raise both the noise peak amplitude and the noise frequency. Hence the later in $\overline{A}_f$ plays a minor role in hydrogen-promoted SCC.

The incorporation of hydrogen into passive film brings about certain changes in the passive film structure and results in degradation of resistance to the local breakdown [8]. This impact is enhanced by the action of tensile stress [19]. The changes in passive films caused by ingress of hydrogen and tensile stress are expected to have an effect on the mechanical properties of passive films, such as film rupture ductility. A recent research in our research group indicated that the presence of lead impurities in alkaline chemistry that was used to simulate the environment of crevices in nuclear power generation systems gave rise to an increase of hydrogen concentration as well as structural changes, in passive film of steam generator tubing alloys [25] The experimental measurements have indicated that this kind of changes in passive film structure can induce a decrease in rupture ductility of passive film [17] and degradation in resistance to both SCC and pitting corrosion [25].

Jani et al. [28] characterized the deformation substructure around the crack tip for 304 SS in 45% $MgCl_2$ at 155 °C using TEM and found that the stacking fault energy (SFE) of the material immediately ahead of the crack tip is lowered, with the deformation mode at the small distances (a few microns) in front of the growing crack being entirely coplanar while homogeneous at larger distance. They believed that the reduction in the SFE is attributed to absorbed hydrogen formed during the cathodic reaction. According to Magnin et al.[29] and Delafosse et al.[30], the localized plastic deformation at the crack tip is enhanced by the dislocation-hydrogen interaction. The hydrogen-induced plasticity effect can be demonstrated by nano-indentation measurements [31]. The effect would facilitate the crack tip creep and increase the likelihood of the passivity breakdown at crack tips. The hydrogen-enhanced anodic dissolution, as depicted by the retarded repassivation, may also facilitate the crack tip creep. According to non-equilibrium thermodynamics, the anodic dissolution-induced creep rate is proportional to the anodic current density [32,33]. The anodic dissolution-induced creep phenomenon has been experimentally observed [34,35,36,37,38]. The degradation of resistance to plastic deformation caused by anodic dissolution can also be demonstrated by the hardness measured by *in-situ* nano-indentation test [39], as shown in Fig. 7, where the hardness degradation induced by anodic dissolution is illustrated.



(a) 304SS (b) Alloy 800

Fig. 7. Comparison of in-situ hardness measured in air and 1MHCl while 1mA/cm^2 anodic current is applied.

The detrimental effects of hydrogen of SCC of metastable SS are further enhanced by the hydrogen-induced martensite phase transformation. The martensite phase transformation is more likely to occur at the stress concentrators like crack tip. Martensite has, comparing to austenite phase, poor corrosion resistance [15,16]. This would result in a high localized corrosion rate. The formation of martensite produces high local stress. It would increase the likelihood of passive film breakdown.

6. Summary

The incorporation of hydrogen into austenitic steel leads to formation of highly defective passive films that have poor resistance to localized breakdown. This effect may be enhanced by action of tensile stress. The ingress of hydrogen can induce the formation martensite in metastable austenitic steel. This results in a further degradation of corrosion resistance. The hydrogen-induced passivity degradation is an important contributor to hydrogen-promoted SCC of austenitic

SS in chloride-containing aqueous environments where the SCC is believed to be dominated by film rupture mechanism. Dissolved hydrogen in steel can facilitate SCC via reducing rupture ductility of passive film, promoting creep at stress concentrators and retarding repassivation after passive film breakdown.

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