Hydrogen Effect on Fatigue Crack Initiation Behavior of Structural Materials

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Abstract Hydrogen effect on fatigue crack initiation behavior of structural materials related to the internal hydrogen embrittlement and hydrogen environment embrittlement is reviewed. Mechanisms of hydrogen effect on fatigue crack initiation behavior of structural materials are briefly summarized. The emphasis is focused upon the hydrogen related corrosion fatigue crack initiation behavior of structural materials in aggressive gas and sour crude oil environments. Finally recommended researches in hydrogen effect on fatigue crack initiation of structural materials are touched on briefly.

Keywords Hydrogen, Fatigue, Corrosion fatigue, Corrosion pit, Crack initiation

1. Introduction

Hydrogen effect has been investigated on structural materials used for important machinery components in oil and energy related industries so far. It is well recognized that hydrogen drastically accelerate crack propagation rate of structural materials [1]. However hydrogen effect on crack initiation behavior of structural materials is not well understood. Prevention of hydrogen related fatigue crack initiation of structural materials is indispensable for safety use of fuel cell vehicle and hydrogen fueled internal combustion engine yet to come[2,3]. In this paper hydrogen related fatigue crack initiation behavior of structural materials is reviewed mainly on the basis of the author’s experimental results. First the proposed mechanisms of hydrogen effect on fatigue crack initiation and propagation behavior of structural materials are briefly summarized. Then the corrosion related fatigue crack initiation behavior of structural materials in steam, humid air and aqueous solution including industrial gas such as H2S, SO2 and CO2 are summarized. Hydrogen related corrosion fatigue crack initiation behavior of ship hull structural steels in sour crude oil environment is also emphasized. Finally recommended studies in hydrogen effect on fatigue crack initiation behavior of structural materials are touched on briefly.

2. Mechanism of hydrogen effect on fatigue crack initiation behavior of structural materials

It has been well recognized that fatigue strength of structural materials is affected by oxygen and humidity in air. Therefore oxygen effect on fatigue crack initiation of structural materials has been well investigated. The mechanisms for oxygen effect on fatigue crack initiation such as the oxygen intake mechanism with dislocation motion [4] were proposed so far. However the decisive mechanism for hydrogen effect on fatigue crack initiation has not yet proposed so far. Hydrogen effect on fatigue strength of mild steel with round notched plate specimen was not significant as compared with effect of oxygen and humidity [5]. Suzuki et al. conducted low cycle fatigue tests for normalized S45C round bar specimens with different purity with P,S,N,O and Al in order to investigate the pre-charged hydrogen effect [6]. The pre-charged hydrogen effect on low cycle fatigue life was not significant for high purity S45C steel. On the contrary low cycle fatigue life of low purity S45C steel was 50 to 90 % lower than that of conventional normalized S45C steel. They concluded that cyclic softening reduce the dislocation density in S45C steel with high purity and make the steel insensitive to hydrogen. Low cycle fatigue tests were also conducted for 21/4 Cr-1Mo steel in high temperature and...
high pressure hydrogen environment (P_{H2}:24.5MPa,733K) [7]. The low cycle fatigue life was 50% lower than that in nitrogen environment. The low cycle fatigue life in hydrogen environment was dependent on loading frequency and the hydrogen effect on crack initiation was observed. In order to ensure the safety of pipe and vessel used in high pressure hydrogen gaseous environment Nakamura et al. conducted cyclic pressurization fatigue tests for plane and pre-cracked austenitic stainless steels such as SUS304 steel, SUS316 steel, 32% cold worked SUS316 steel, precipitation hardening A286 steel and SCM435 low alloy steel with different tensile strength in hydrogen environment (P_{H2}:35MPa) [8]. The stable austenitic stainless steel SUS316 showed no reduction of fatigue life in high pressure hydrogen gaseous environment. In contrast significant reduction of fatigue life was observed on metastable SUS304 steel, precipitation hardening A-286 steel and SCM 435 steels. They concluded that hydrogen condensation at austenitic phase for metastable 304 steel and hydrogen trapping at cementite for A286 steel is the cause of fatigue life reduction in high pressure hydrogen embrittlement.

Fatigue crack propagation process in structural materials is significantly affected by hydrogen. It has been reported that fatigue crack propagation rate was significantly accelerated by hydrogen for various kinds of structural materials such as Nickel base alloy, Inconel 718 and Waspaloy for space shuttle engine[9], 21/4Cr-1Mo steel[10], mild steel, HT790 steel[11], low alloy steel, super dual phase stainless steel, super ferritic stainless steel[12,13] and BS4360 steel[14]. R.P. Wei proposed hydrogen embrittlement mechanism at local stressed area ahead of crack tip [15]. Hydrogen by transportation process diffused into the local processed area (fracture zone) where embrittlement reaction occurs. Quantitative relation of plastic zone size during fatigue crack propagation and hydrogen embrittlement fracture zone size is recommended to evaluate. The potential hydrogen trap site might be martensite laths, carbides, sulfides or oxy sulfides[16]. Certain gaseous activities to a hydrogen atmosphere can stop a running crack in 4340 steel[17]. The hydrogen-metal interactions was prevented by the addition of gaseous specie such as O_2, CO_2 and N_2O[18]. In the results of accelerated fatigue crack propagation rate by hydrogen fracture surfaces such as intergranular, cleavage and quasi cleavage are predominantly observed [18,19 and 20].

Hydrogen effect on fatigue crack initiation in structural materials seems not to be prominent as compared with that on fatigue crack propagation. Nagumo explained that hydrogen embrittlement fracture surface is characterized by hydrogen assisted nano scale failure such as vacancy defect and dislocation interaction in ductile fracture process [21]. Hydrogen embrittlement is deeply related to plastic slip [22, 23]. The microscopic mechanism related to dislocation motion is recommended to investigate in order to understand hydrogen effect on fatigue crack initiation of structural materials more in detail.

3. Hydrogen related corrosion fatigue crack initiation behavior of structural materials

In order to determine the design stress of machinery components in oil and energy related industries it is indispensable to consider the effect of gaseous environment such as H_2, H_2S, SO_2 and CO_2, and sour crude oil on fatigue strength of structural materials. However, these environments are aggressive and injurious to human health. Therefor corrosion fatigue data under such aggressive environments are very few to find because of difficulty to conduct corrosion fatigue testing.

3.1 Effect of aggressive gas in steam and humid air
Fig. 1 shows S-N diagrams of plain bar specimens for 12Cr stainless steel and Ti-6Al-4V alloy in steam containing industrial gases such as H₂S and CO₂[24]. Reduction of corrosion fatigue strength in 12 Cr stainless steel is 87.5% in steam containing 20ppm H₂S gas, while the reduction of corrosion fatigue strength in Ti-6Al-4V alloy is only 4%. The SO₂ gas effect in humid air was as same as that of H₂S gas in humid air. The CO₂ gas effect in steam was not remarkable as compared with that of H₂S gas in steam. In the results of fatigue crack propagation tests with frequency of 30 Hz for 12 Cr plate specimen the effect of 20ppm H₂S gas containing in humid air on corrosion fatigue crack propagation rate of 12 Cr stainless steel was scarcely noticeable. Therefore it can be concluded that the major cause of the reduction in corrosion fatigue strength of 12Cr stainless steel is acceleration of corrosion fatigue crack initiation by H₂S gas in steam and humid air. In fact fracture surface observations revealed that crack initiated at a corrosion pit with about 10 μm depth and propagated in association with intergranular fracture as shown in Fig. 2.

Figure 1. Influence of industrial gas in steam on fatigue strength of SUS410J1 and Ti-6Al-4V[Ebara[24]].
Rotating bending, 60Hz, R=−1

Figure 2. Corrosion fatigue fracture surface of 12 Cr stainless steel in 20ppm H₂S and 4000ppm CO₂ in steam[Ebara[24]].
171.6MPa, 2.36X10⁷ cycles
a) Corrosion pit at initiation area
b) 2mm from initiation
The corrosion pit initiated in the result of reaction between 12Cr stainless steel and H₂S gas in humid air. Intergranular fracture surface was induced by hydrogen occurred in the corrosion reaction. Fig. 3 also shows plane bending corrosion fatigue testing results for T type welded joints of high 17-4PH stainless steel 5000ppm H₂S and 99.9% CO₂ gas in a humid air [25]. The remarkable reduction of corrosion fatigue strength of T type welded joints can be observed. The similar results were obtained on AISI410 and AISI4330 steel [26]. The higher the ultimate tensile strength of the steel, the larger the influence of H₂S gas environment was. In 5000ppm H₂S and 99.9% CO₂ environment corrosion fatigue crack initiated from corrosion pit at welded toe. Striation was predominant at crack propagation area. Typical fracture surface of 17-4 PH steel in humid H₂S gas environment is shown in Fig. 4. The following reaction can be considered.

Figure 3. S-N curves of T type welded joints of 17-4PH T type welded joints in H₂S and CO₂ gas environment [Ebara et al. [26]].
Plane bending, 20Hz, R=0.05

Figure 4. Corrosion fatigue fracture surface of 17-4PH T type welded joint in humid air(353K, 90% relative humidity) containing 5000ppm H₂S gas [Ebara et al.[26]].
294.3MPa, 1.4x10⁷ cycles
a) corrosion pit at crack initiation area
b) 3mm from initiation area,
Arrow shows crack propagation direction
In humid H$_2$S gas environment
\[
\text{Fe} + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{H}_2 \quad (1)
\]
\[
\text{Fe} + \text{H}_2\text{S} + \text{H}_2\text{O} + \frac{3}{2}\text{O}_2 \rightarrow \text{FeSO}_4 + 2\text{H}_2 \quad (2)
\]
In humid CO$_2$ gas environment
\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \quad (3)
\]
\[
\text{Fe} + \text{H}_2\text{CO}_3 \rightarrow \text{FeCO}_3 + \text{H}_2 \quad (4)
\]
In the results of reaction between these steels’ welded joints and aggressive gas such as H$_2$S and CO$_2$ corrosion products such as FeSO$_4$ and FeCO$_3$ were formed and corrosion pit initiated at corrosion fatigue crack initiation area. H$_2$ also evolved in the result of reaction. However the role of hydrogen in fatigue crack initiation is not understood well. Corrosion fatigue behavior of structural steels in geothermal steam environment at Onikobe and Katayama have been reported on power plant steels such as 13CrMo, 12CrMoV, 3.7NiCrMo and CrMoV. Reduction rate of corrosion fatigue strength of these steels was dependent on Cr content in steel. It was concluded that the major cause of corrosion fatigue strength reduction was stress concentration at corrosion pit formed at corrosion fatigue crack initiation area [27]. Corrosion fatigue strength reduction was also reported on AISI 403, AISI422 steel at Geysers geothermal steam [28] and 13Cr, 2.5NiCrMoV steel at Otake geothermal steam [28]. Fatigue life decrease of a medium carbon steel for compressor valve springs and sucker rods was observed in hydrogen sulfide environment[29].Quasi cleavage fracture and FeS reaction product was observed on fracture surface[30]. Thus it is apparent that major cause of reduction of corrosion fatigue strength of structural steels and welded joints in humid aggressive gas such as H$_2$S and CO$_2$ can be attributed to corrosion pit formed at corrosion fatigue crack initiation area. Mechanism of hydrogen effect on corrosion fatigue crack initiation in structural materials is still veiled in aggressive gas in steam and humid air.

3.2 Effect of aggressive gas in aqueous solution

Corrosion fatigue strength decrease of plain carbon steel used for machinery of oil and gas production in brine with H$_2$S was due to hydrogen effect [31]. The similar findings were obtained by plane bending and axial corrosion fatigue testing on oil well sucker rods [32,33]. Tsukada et al. conducted corrosion fatigue life tests for a SAE4135 steel and a modified SAE 4135 steel in a 0.5% percent acetic acid solution in saturated with H$_2$S gas [34]. The modification of SAE4135 steel consists of an increase in molybdenum content of 0.20 to 0.75 percent and addition of 0.036 percent columbium. Corrosion pits and sub cracks were severely observed at the corrosion fatigue crack initiation area of these steels in H$_2$S gas environment. High cycle corrosion fatigue strength for the modified steel was 66 percent higher than that of the standard steel. They concluded that the improvement was attributed to an increase in resistance of hydrogen embrittlement brought about by a higher tempering temperature which reduces the amount of phosphorus on grain boundaries, as well as the beneficial scavenging effects associated with the increase in molybdenum content and the presence of columbium. They also conducted crack propagation tests for both steels. However crack propagation behavior of these steels were similar and hydrogen effect was significant at lower $\Delta K$ region. Fatigue life decrease of weathering steel in artificial sea water saturated with H$_2$S [35] and work hardened nickel in hydrogen sulfide saturated water [36] were also observed.

3.3 Effect of aggressive gas in crude oil

Fig.5 shows S-N diagrams of high strength steel (HT50,TMCP) notched round bar specimen with stress concentration factor of 4.02 in air and in sour crude oil with 400ppm H$_2$S[37]. The
Effect of sour crude oil on the fatigue life of round notched specimen is pronounced in high stress region and tends to decrease as decreasing the stress. At nominal stress of about 470MPa the fatigue life in the sour crude oil decreased to about 10% of the fatigue life in air. Decreasing the stress the effect of sour crude oil on fatigue life decreased. At nominal stress of about 200MPa specimen did not fail after $2 \times 10^6$ cycles. Fatigue life testing results on boxing fillet welded specimens in air and in sour crude oil are also shown in Fig 5. At axial stress of 150MPa specimen in sour crude oil did not fail even after 10 times of the number of cycles to fail in air. Macrophotography fracture surface observation for round notched bar specimen revealed that fatigue crack initiated at notched root as shown in Fig 6 a). It is apparent from SEM observation that corrosion pit was not observed at crack initiation area[Fig. 6 b)]. Britt striation was predominant at crack propagation area[Fig. 6 c)]. It is well understood that crack propagation rate of ship structural steels and line pipe steels is accelerated in sour crude oil environment[37,38 and 39]. Hydrogen effect on crack propagation rate of these steels and welded joints was drastically observed at high $\Delta K$ region. Cleavage fracture surface and brittle striation were predominant at crack propagation area. At axial stress of 196MPa a couple of small fatigue cracks initiated at notched root as shown in Fig. 7 a).Figure 7b) is one of the forced fracture surface from these cracks. The depth of the corrosion fatigue crack was 0.2mm and notched area was brown in color. But corrosion pit was not observed at fatigue crack initiation area [Fig. 7 b)]. Ductile striation was predominant at crack propagation area [Fig. 7c)]. This means that crack propagation rate was not affected by hydrogen in low stress region. After corrosion fatigue life test for 2393hrs crude oil exhibited less H$_2$O content (340 to 210ppm), lower pH value (7.3 to 4.3) and more total S content than those before test. All these facts suggest that hydrogen (H$_2$) was produced through the reaction of H$_2$O and H$_2$S in sour crude oil with steel. Thus, in high stress region it can be considered that atomic hydrogen (H) accumulated in the plastic zone at fatigue crack tip accelerate crack propagation rate and reduce the fatigue life of the specimen. In the low stress region, plastic zone size is small and hydrogen does not accelerate fatigue crack propagation rate. It is assumed that wedge effect [40] of crude oil retarded corrosion fatigue crack propagation rate of notched bar specimen and boxing fillet welded specimen. Corrosion fatigue mechanism in sour crude oil is schematically illustrated in Fig. 8. Corrosion fatigue behavior is a time dependent phenomenon. If corrosion pit formed at initiation area in

Figure 5. S-N curves of round notched HT50(TMCP) specimen in air and sour crude oil environment [Ebara et al.[37]]
Figure 6. Corrosion fatigue fracture surface of HT50(TMCP) steel in sour crude oil (H₂S 400ppm) [Ebara et al. [37]].
round notched bar specimen
294.2MPa, 2x10⁴ cycles
a) macroscopic fracture surface
b) crack initiation area
c) 1.8mm from initiation

Figure 7. Surface crack and fracture surface of HT50(TMCP) steel in sour crude oil (H₂S 400ppm) [Ebara et al. [37]].
round notched bar specimen
196.1MPa, unfailed after 1.66x10⁶ cycles
a) surface crack
b) macroscopic fracture surface
c) 0.12 mm from surface
lower stress level drastic reduction of corrosion fatigue strength may be anticipated. The long term corrosion fatigue test is expected to conduct in lower stress level.

4. Concluding remark

This paper has briefly summarized hydrogen effect on fatigue crack initiation behavior of structural materials. In aggressive gas such as H₂S, CO₂ and SO₂ in steam, humid air and aqueous solution corrosion fatigue crack initiation from corrosion pit reduce corrosion fatigue strength of structural materials. Under these environments it is stressed that corrosion pit initiated at fatigue crack initiation area drastically reduced fatigue strength of structural steels. On the contrary, in sour crude oil environment hydrogen from reaction of steel with H₂S accelerated corrosion fatigue crack propagation rate of steels. It can be concluded that hydrogen effect on corrosion fatigue crack initiation in sour crude oil is still veiled. For safety use of structural materials in hydrogen environment prevention of fatigue crack initiation is indispensable. Definite fatigue crack initiation mechanism in hydrogen environment is expected to propose. In order to evaluate the hydrogen related fatigue life of the structural components more precisely the following studies are recommended to investigate.

1) Microscopic crack initiation mechanism with dislocation motion
2) Quantitative evaluation of the relation between the plastic zone and hydrogen embrittlement zone size at the fatigue crack tip
3) Hydrogen effect on ΔK₁₀₀ and near ΔK₁₀₀ region in da/dN
4) Hydrogen resistant materials to prevent fatigue crack initiation

References


