ENVIRONMENTAL EFFECTS ON THE FATIGUE BEHAVIOR OF AN AUSTENITIC STAINLESS STEEL

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ABSTRACT

The influence of environmental factors, including pH, chloride ion, and pitting inhibitor, on the corrosion fatigue properties of type 347 stainless steel was investigated. Both high-cycle fatigue (HCF, S-N curves) and fatigue crack growth (FCG, da/dN-ΔK curves) tests have been conducted in air and several aqueous environments. Results showed the HCF strength was markedly reduced in an acid solution and in a chloride-containing solution, as compared to the air value. An addition of pitting inhibitor could restore the HCF strength in salt water back to the level in atmospheric air by preventing the formation of corrosion pits and decreasing the corrosion rate. However, the corresponding stage II FCG rates in all given environments were almost equivalent. These results indicated that the variation of chemistry in bulk environment exerted more influence on the fatigue crack nucleation than on the growth of long fatigue cracks.

1 INTRODUCTION

Type 347 stainless steel (SS) was developed to improve the resistance of 304 grade austenitic SS to intergranular stress corrosion cracking (IGSCC) by adding niobium (Nb) plus tantalum (Ta) to form niobium and tantalum carbides in preference to Cr-rich carbides so that the depletion of chromium at grain boundary regions could be reduced [1]. As the fracture behavior under cyclic loading in aggressive environments might be different from the one under static loading such as IGSCC, it is important to study the corrosion fatigue (CF) properties of type 347 SS so as to better assess and predict the service life of the components made of this alloy. However, only limited work has been done on the fatigue strength of type 347 SS [2] and there is still lack of systematic studies on the CF properties of 347 grade austenitic SS. The present work was therefore planned to characterize the environmental effects on the fatigue crack initiation and propagation stages in type 347 by conducting systematic experiments, including both high-cycle fatigue (HCF) and fatigue crack growth (FCG), in air and several aqueous environments.

2 EXPERIMENTAL PROCEDURES

The 347 SS, with nominal wt% composition of 17.28 Cr, 10.23 Ni, 1.67 Mn, 0.63 Nb, 0.59 Si, 0.08 Cu, 0.05 Co, 0.05 C, 0.035 N, 0.025 S, 0.023 P, < 0.01 Ta and Fe (balance), was tested in solution-annealed conditions. The mechanical properties have an ultimate tensile strength of 658 MPa, a yield strength of 310 MPa, an elastic modulus of 190 GPa, an elongation of 61.4% (in 25 mm), and a hardness value of 42 HRb. Both HCF and FCG tests were carried out at room temperature in laboratory air and four aerated aqueous environments: (1) deionized water (pH = 6.5); (2) 50 ppm H_2SO_4 solution (pH = 3.0); (3) 3.5 wt% NaCl solution (pH = 6.5); (4) 3.5 wt% NaCl + 3000 ppm methoxypropylamine (MPA) solution (pH = 11.1). The addition of MPA in NaCl solution was intended to study the effect of pitting inhibitor on the CF properties of the given alloy. All CF tests were conducted under freely corroding conditions, i.e. no external potential was applied to the specimens. HCF tests were conducted as per ASTM E466 on axial smooth-surface specimens, with a cylindrical gage section of 6 mm in diameter and 18 mm in length, to determine the stress-life (S-N) curves. FCG experiments were performed in

accordance with ASTM E647 on 6.35-mm-thick compact tension (CT) specimens to determine the fatigue crack growth rate (FCGR) curves in terms of da/dN-ΔK relationship. Details of the specimen geometry and experimental set-up for such CF tests were described elsewhere [3]. All fatigue tests were performed on a closed-loop, servohydraulic machine under a sinusoidal loading wave form with a load ratio of R = 0.1 and a frequency of f = 5 Hz. The corrosion rate (I_{corr}, corrosion current density) in each alloy-aqueous-environment system was determined by extrapolation of the anodic and cathodic Tafel slopes from the anodic and cathodic polarization curves obtained in an standard electrochemical measurement. Details of this electrochemical measurement technique can be found in Ref. [4]. Characterizations of the fracture surface morphology were made by scanning electron microscopy (SEM).

3   RESULTS AND DISCUSSION

3.1   *Fatigue behavior in various aqueous environment*s

Fig. 1 shows the S-N curves in air, deionized water, 3.5% NaCl solution and 50 ppm H_2SO_4 solution. The straight solid and dash lines represent the best-fit S-N curves. The estimated fatigue strengths corresponding to a fatigue life of 10^6 cycles for each environment are given in Table 1. Fig. 1 clearly demonstrates deleterious effects of the three aqueous environments on the HCF response of type 347 SS, as a marked reduction of fatigue life was found in each aqueous solution compared to atmospheric air. The counterpart results of the FCG tests were plotted as (da/dN) vs. (ΔK) in Fig. 2 where FCGRs in air were not significantly different from those in the given three corrosive aqueous media, namely deionized water, salt water and sulfuric acid solution. Apparently, these three aqueous media did not generate as severe damage on the FCG resistance of pre-cracked CT specimen (stage II cracking only) as they did in the case of smooth-surface HCF specimen (including crack initiation, stage I and stage II cracking) under a cyclic load of 5 Hz. In this way, S-N curve comparison provided a good indication of the effect of environment on fatigue crack initiation. Note that any results related to the environment of 3.5% NaCl + 3000 ppm MPA solution will be discussed in next section.
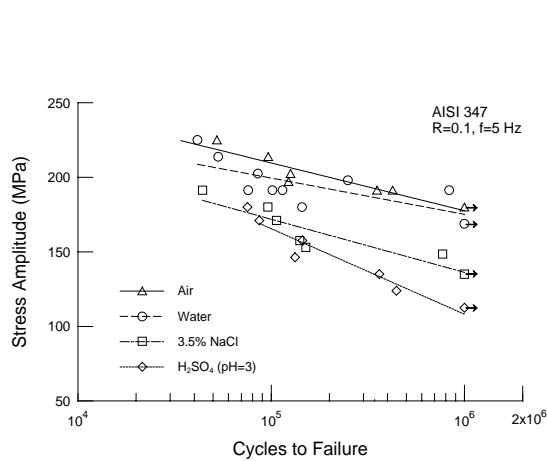

Fig. 1   S-N curves in different environments.
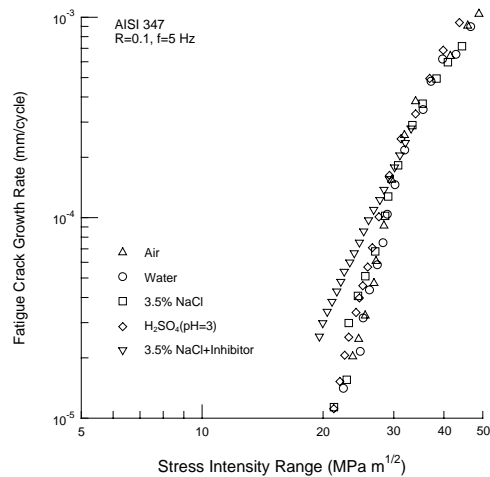(Arrows designate runout tests.)

Fig. 2   FCGR curves in different environments.

Table 1   Corrosion rate and fatigue strength for type 347 SS in different environments

Environment	Corrosion Rate, I_{corr} ($\mu A/cm^2$)	Fatigue Strength at 10^6 Cycles (MPa)
Air	-	182
Deionized water (pH = 6.5)	0.107	179
3.5 wt% NaCl (pH = 6.5)	0.246	140
50 ppm H_2SO_4 (pH = 3)	0.641	111
3.5 wt% NaCl + 3000 ppm MPA (pH = 11.1)	0.00459	191

The above comparisons between HCF and FCG results showed the HCF life depended primarily on crack nucleation stage and the environmental effect on the CF resistance of 347 SS was exerted mainly on the phase of crack initiation and stage I crack growth rather than on the phase of stage II crack growth.   The possible governing CF processes include pitting, preferential dissolution, stage I crack growth and transition from stage I-to-stage II crack growth [5].   It was generally recognized that corrosion pits and/or accelerated dissolution at emerging slip steps or extrusion, somehow induced by CF process, prematurely initiate fatigue cracking or reduce the applied stress required to initiate fatigue cracks [5-7].

Typical fracture surface morphology near the origins of fatigue cracks in HCF specimens tested in the three given corrosive aqueous environments is given in Fig. 3.   As shown in Fig . 3, fatigue cracks in deionized water, sulfuric acid solution, and sodium chloride solution appeared to initiate from the corrosion-induced defects on the surface passive film.   However, no evidence of such visible corrosion-induced damages on the surface passive film at fracture origin was found for the atmospheric air and 3.5% NaCl + 3000 ppm MPA solution.   As evidenced by the corrosion-induced damages on the specimens tested in deionized water and sulfuric acid solution (Figs. 3(a) and 3(b)), the metal-dissolution behavior for the given alloy in these two aqueous media appears to be general corrosion over pitting corrosion.   Although corrosion pits penetrating from surface were occasionally observed at fracture origins on the specimens tested in salt water (e.g. label p in Fig. 3(c)), the detrimental effects form these corrosion pits did not reduce the HCF life as much as the general corrosion effect caused by the acid H_2SO_4 solution.   This is supported by the fact that the HCF life was shorter in sulfuric acid solution than in salt water.   Therefore, the distinct reduction of HCF life in type 347 by the three given corrosive aqueous solutions over the atmospheric air could be attributed to an accelerated crack initiation and stage I crack growth caused by preferential dissolution mechanism.
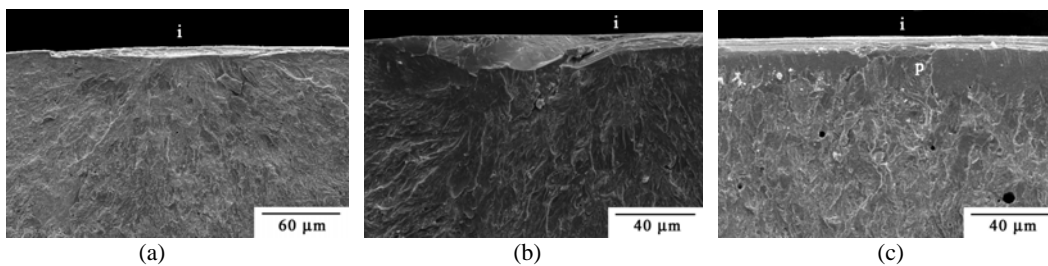

(a)   (b)   (c)

Fig. 3   SEM fractography in different environments: (a) deionized water; (b) 50 ppm H_2SO_4 solution; (c) 3.5% NaCl solution.   (i: crack initiation site;   p: corrosion pit.)

Apparently, the degree of the environmental effect on the HCF resistance of 347 austenitic SS is related to the nature of the corrosive environment. As indicated by the electrochemical data presented in Table 1, where type 347 showed the highest corrosion rate in sulfuric acid solution. The higher corrosion rate of type 347 in sulfuric acid solution over salt water and deionized water can be attributed to an increase in the hydrogen ion concentration and then an increase in metal dissolution. In this regard, the controlling CF mechanism such as preferential dissolution at slip bands in an acid medium would be more active in assisting the surface fatigue crack nuclei to overcome the microstructural barriers and accelerate the initial growth. As a result, 347 grade austenitic SS shows the greatest reduction of HCF lifetime in sulfuric acid solution compared to salt water and deionized water. Table 1 also shows, due to the presence of chloride, salt water is more aggressive than deionized water which explains why the HCF life was shorter in salt water than in deionized water.

As described above, preferential dissolution presumably played a very important role in determining the length of fatigue crack nucleation period and then the entire HCF life. However, this might not be the case for the extension of a long fatigue crack; otherwise the FCGR would have shown differences in the given environments as shown in the HCF results. It is generally believed that hydrogen embrittlement (HE) and active path dissolution are the two typical mechanisms responsible for the enhanced crack growth in an aggressive environment. As preferential dissolution was not likely to control the fatigue crack growth behavior for the given alloy-environment systems, it is suggested that HE played a major role for the stage II cracking in the current study. Note that the relative humidity of the given ambient air was between 60% and 70%. The atmospheric environment can therefore be seen as a moist gas with low water vapor pressure. However, a study [8] on a steel-water-vapor system indicated that the crack growth rate under static loading was increased with an increase in vapor pressure of the water vapor environment. Therefore, a loading frequency of 5 Hz might be too high to distinguish the degree of severity of HE effect on extension of long fatigue crack between the humid air and aqueous environments for the given type 347 SS.

If preferential dissolution were the controlling mechanism for stage II cracking, like the S-N curve results, 5 Hz cyclic loading could have generated differences in detrimental effects on the FCG behavior in these three aqueous environments according to the corrosion rate data in Table 1. On the contrary, comparable FCGRs were observed in these three aqueous media with different pH values and ionic species. These results imply that the key factor for the extension of long crack in aqueous environments is the presence of water regardless of the pH and ionic species in the bulk solutions. It is likely that similar electrochemical reactions might occur at the crack tip even though there are differences in pH and ionic species of the bulk solutions. Brown and co-workers [9,10] have shown that the pH of the occluded solution and the electrochemical potential within cracks differ significantly from the bulk solution characteristics. Under freely corroding conditions, crack-tip pH can be highly acidic (pH = 3.8) in Fe-based alloys for different bulk solutions with pH between 1 and 10 [9,10]. The solution within the crack-tip region could become acidified by the dissolution of Fe and subsequent hydrolysis. In view of the fact that crack-tip environmental conditions are generally recognized to be more crucial to subcritical crack growth than bulk solution properties, the coincidence of FCGRs in deionized water (pH = 6.5), 3.5 wt% NaCl (pH = 6.5) and 50 ppm H_2SO_4 (pH = 3) solutions (Fig. 2) suggests that the local conditions of pH and potential in these three aqueous environments are equivalent so as to produce the same amount of hydrogen at the crack tip on the premise that HE is the major feature of the corrosive FCG mechanism. In addition, it is highly possible that under a cyclic load of 5 Hz, the water vapor pressure level in the given humid air and the three given aggressive aqueous solutions generated equivalent HE effects in controlling the FCG behavior leading to comparable FCGRs.
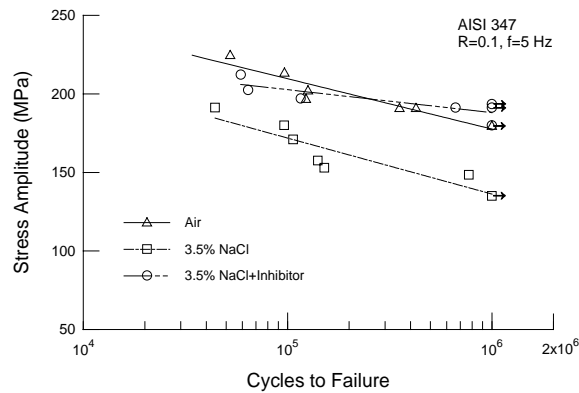
Fig. 4   Comparison of S-N curves in air and different salt water environments.
(Arrows designate runout tests)

3.2   Effects of inhibitor on the corrosion fatigue response

Fig. 4 shows the comparison of S-N curves in the environments of ambient air, 3.5% NaCl solution, and 3.5% NaCl + 3000 ppm MPA solution.   The addition of 3000 ppm MPA significantly increased the HCF lifetime of type 347 from the value in salt water, under a given cyclic stress level.   Moreover, the HCF strength at the long life regime (say around 10^6 cycles) in the salt water added with inhibitor was even greater than that in ambient air indicating that 3000 ppm MPA could effectively control premature crack initiation that was accelerated by the synergism between the aggressive salt water and the cyclic stresses.   This also implies that the atmospheric air is somewhat a minor corrosive environment.   Electrochemical data in Table 1 also indicated that an addition of 3000 ppm MPA could make the salt water become an alkaline environment and significantly reduce the corrosion rate to a very low value.   As discussed in the previous section, preferential dissolution at slip bands was considered as the controlling mechanism for HCF crack initiation and lifetime.   Therefore, addition of 3000 ppm MPA not only provided a means to prevent any formation of corrosion-induced surface defects serving as premature crack initiation sites in salt water but also minimized the activity of preferential dissolution at slip bands such that the crack nucleation was retarded and the fatigue life was extended.

On the contrary, the FCGRs shown in Fig. 3 indicated that the addition of 3000 ppm MPA did not produce any beneficial effect on the stage II cracking resistance in salt water.   The FCGRs in 3.5% NaCl + 3000 ppm MPA solution were comparable with (at high ΔK region) or even slightly higher than (at low ΔK region) those in other given environments.   The slightly higher FCGRs at low ΔK region in salt water added with MPA over the other environments might be attributed to a lesser crack closure effect, as corrosive products which were present on the fracture surfaces of CT specimens tested in other given environments were barely observed in salt water added with MPA.   As ΔK decreased, the crack tip opening became smaller and corrosive debris may wedge in the crack-tip region and cause oxide-induced crack closure to reduce FCGR.   As addressed in the previous section, the extension of a long fatigue crack was dominated by HE mechanism and localized acidification could occur at crack tip resulting in the comparable FCGRs in various bulk environments.   Apparently, such localized acidification at crack tip might also occur in 3.5% NaCl + 3000 ppm MPA solution such that the FCGRs in this environment were comparable with those in other given environments even though this alkaline bulk solution would

provide smooth surface with more resistance to general and pitting corrosion in salt water. The overall comparison of the HCF and FCG response of type 347 to the addition of 3000 MPA in salt water indicated that this adsorption type of inhibitor was effective as an inhibitor for pitting corrosion on smooth surface as well as for premature crack nucleation through preferential dissolution mechanism but not for stage II cracking controlled by HE mechanism.

4 CONCLUSIONS

(1) The HCF life of type 347 austenitic grade SS was dominated by crack initiation stage which was more susceptible to the variation of bulk environment than the phase of stage II crack growth.

(2) The degree of detrimentally environmental effect on the HCF response in the given aqueous media was of the order: sulfuric acid solution > salt water > deionized water. This was consistent with the trend of corrosion rate in metal dissolution suggesting that preferential dissolution at slip bands play an important role in facilitating premature fatigue crack initiation.

(3) Comparable FCGRs were observed in various given aqueous media implying a similar local crack-tip condition for crack extension associated with HE mechanism, regardless of the ion species and pH in the bulk solutions.

(4) Addition of a pitting inhibitor, 3000 ppm MPA, has been demonstrated to be effective to prevent premature fatigue crack initiation in salt water for type 347 SS and extend the HCF life.

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