

Corrosion Fatigue Behavior of Duplex Stainless Steel in 3.5% Sodium Chloride Solution

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Abstract: The corrosion fatigue behavior of duplex stainless steel (DSS) was studied at different cyclic stress levels in 3.5%NaCl (mass fraction, so as the follows) solution (pH=7) at 50 °C. The results showed that DSS was susceptible to pitting corrosion and corrosion fatigue. Both intergranular corrosion cracking and transgranular corrosion cracking initiated at the bottom of pitting holes. Furthermore, the corrosion fatigue properties of DSS in 3.5%NaCl solution may be related to complex electrochemical and mechanical coupling effects between the three phases (austenite, ferrite and martensite), where martensite and ferrite were anodic in the corrosion cell and could be prone to cracking under certain condition.

Key words: corrosion fatigue; duplex stainless steel; sodium chloride solution

In general, the initiation of corrosion fatigue cracks is enhanced by pitting which forms stress raisers [1], by preferential dissolution of deformed areas that are more anodic than the surrounding matrix [2] and by rupture of protective film [3]. Sometimes this led to the matrix dissolution and crack formation. The differences between the corrosion potentials of inclusions and the matrix also may lead to preferential corrosion, hence, to the initiation of cracking [4]. The propagation of corrosion fatigue cracks depends not only on the stress intensity factor and the composition of the bulk environment, but also on the local electrochemical conditions and the properties of the material at the crack tip [5, 6].

1 Experimental Procedures

1.1 Specimen preparation

Cold-rolled commercial DSS sheet of 3 mm thick was used in the experiment. The chemical composition was (mass fraction in %) C, 0.002; Si, 1.40; Mn, 1.12; P, 0.029; S, 0.006; Cr, 18.29; Ni, 5.02; Mo, 2.50; and Fe, balanced. The material was solution annealed under the protection of argon at constant temperature 1050 °C for 20 min and then water quenched. The specimen was machined to the shape as shown in figure 1. Their gauge lengths were polished to 1000 grit finish.

1.2 Experimental conditions

Cyclic frequency in the study was 3 Hz, and the R -value ($\sigma_{\min}/\sigma_{\max}$) of -1 was employed. The surface of specimens was subjected to corrosion fatigue tests in 3.5%NaCl(mass fraction, so as the follows) solution (50 °C) under different loads ($\sigma_{\max}=2.98.2, 337.9,$

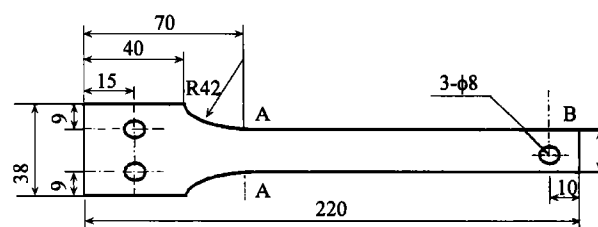


Figure 1 Corrosion fatigue specimen configuration, the stress was maximal at point A and decreases to its minimal value at point B during the experiment. Unit: mm.

359.8, 377.7, 417.4, and 437.3 MPa).

2 Results and Discussion

2.1 Corrosion fatigue $S-N$ curve of duplex stainless steel

The results show that the fracture life of the specimen decreases with increasing applied stress (figure 2). The failure of the material is referred to the synergy effect of corrosive environment and applied stress. It is found that the corrosion fatigue testing for DSS in air environment extends to very high number of cycles (number of cycles $> 9\ 987\ 800$, $\sigma_{\max} = 437.3$ MPa) without fracture, whereas fracture has occurred in 3.5% NaCl solution under the same stress level at lower number of cycles (number of cycles = 30 900). This shows that corrosion fatigue cracking is accelerated due to the existence of chloride solution.

2.2 Fracture morphology of duplex stainless steel after corrosion fatigue testing

The results show that the microstructure of the steel consists of elongated islands of austenite phase (white

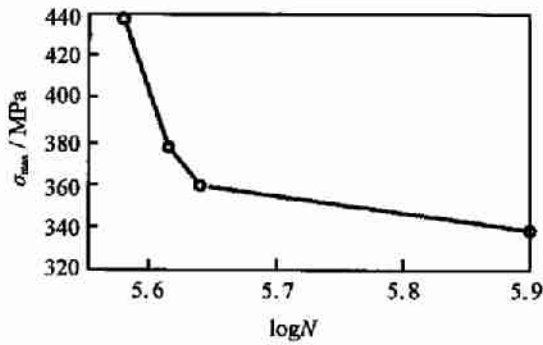


Figure 2 Corrosion fatigue $S-N$ curve of duplex stainless steel used in the experiment.

area) distributed randomly in the matrix of ferrite phase (black area), see figure 3. The SEM results of the fracture surface reveals that the crack initiates on the surface at the ferrite phase, especially at small pits and propagate along phase boundary adjacent to austenite phase in ferrite phase in transgranular "cleavage" mode, see figure 3 and figure 4.

There are two paths for crack propagation when the tip of crack meets the boundary of austenite phase. One way is a void formed in the boundary to arrest crack propagation, as shown in figure 4(b), or if stress is high enough, the austenite phase is broken in dimple mode.

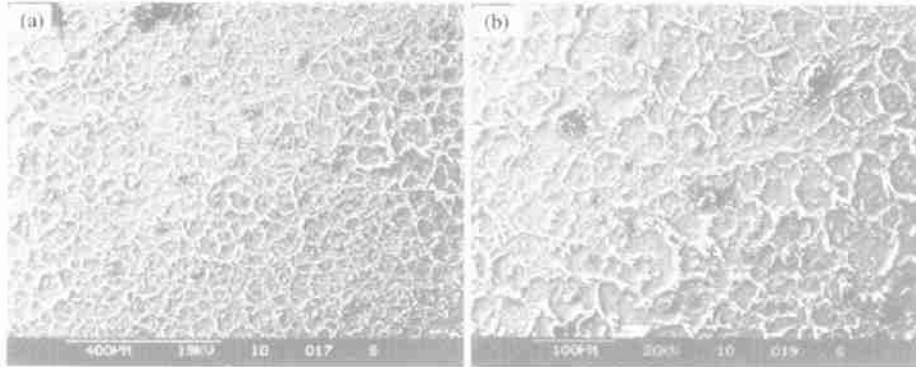


Figure 3 Microstructure of DSS to reveal ferrite between austenite islands in 3.5%NaCl solution, (a) austenite islands in ferrite matrix; (b) α -ferrite corroded preferentially.

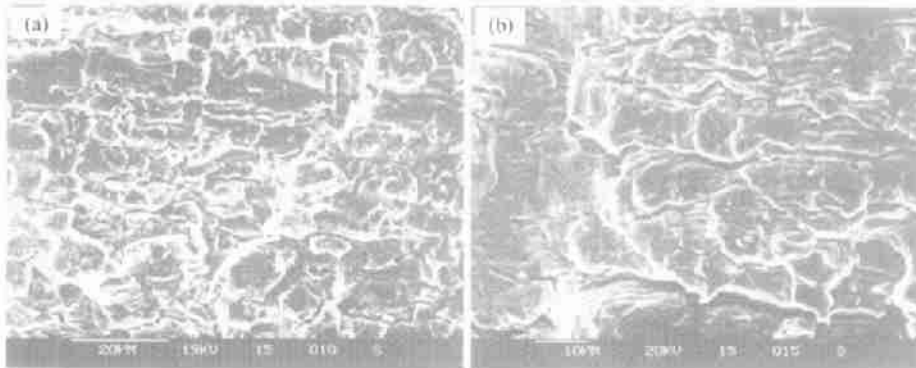


Figure 4 Corrosion fatigue cracks initiated at the ferrite phase and propagated along phase boundary adjacent to γ -phase in ferrite phase by transgranular "cleavage" mode, (a) crack propagated along grain boundaries; (b) transgranular cleavage mode.

The other way is that the crack passes through austenite phase in "cleavage" mode involving martensite phase (figure 5).

The fracture behavior of DSS is generally dominated by the presence of high portion of ferrite phase. Not only does the ferrite provide easier crack nucleation but also a path by which crack easily passes through the ferrite phase. Ferrite phase is fractured in a transgranular "cleavage" mode, and the islands of austenite phase acted as the effective barriers to crack propagation can be fractured in a "dimple" of plastic deformation mode. But under certain conditions (if stress was high enough, or it induced martensite transformation resulted in selective corrosion) the austenite phase can be fractured also by a transgranular cleavage mode.

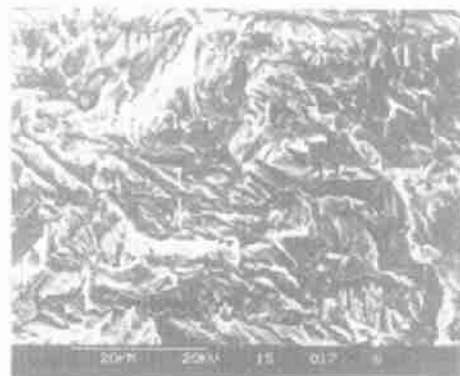


Figure 5 Corrosion fatigue cracks propagated through martensite laths (3.5%NaCl, 50 °C, 3 Hz, σ_{max} = 298.2 MPa).

In corrosion fatigue testing, the appearance of ϵ -martensite is examined and evaluated using magnetometer-

testing machine. It was suggested that the transformation from γ to ϵ phase may occur under the appropriate strain or stress rate and provide a further process for cyclic stress induced cracking. Under this condition, there are no barriers for crack propagation, crack easily passes through the ϵ -martensite by transgranular "cleavage" mode.

2.3 Fractographic observation on microstructure

The fractographic observation results indicate that austenitic phase is little sensitive to corrosion fatigue on crack propagation in 3.5%NaCl solution. The presence of the austenitic grains acts to slow-down the crack propagation rate. Unbroken ligaments of austenite phase can exist behind the main crack front and the inter-striation spacing in the ferrite phase is variable and strongly influenced by the local presence of austenitic grains. On the other hand, in the corrosion fatigue tests, crack initiation is often associated with extrusion on the surfaces of austenitic grains as a result of the lower yield strength of the phase, see **figure 6**. Presumably, the initiation sites correspond to intrusion pairs (intrusion on the surfaces of ferritic grains). The crack initiation at such sites keeps with the negligible tendency to pitting under conditions similar to those of the fatigue endurance tests.

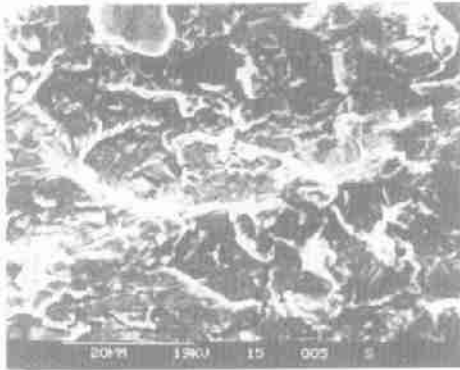


Figure 6 Crack initiation site corresponding to extrusions on the surface of austenitic grains (3.5%NaCl, 50 °C, 3 Hz, σ_{max} = 417.7 MPa).

Therefore it is concluded that the corrosion fatigue crack propagation rate is influenced by the microstructure of the material, where the austenite is beneficial to slowing down the corrosion fatigue crack propagation rate but do not have good resistance to crack initiation and propagation. The corrosive environment causes cleavage-like fracture with brittle striations in the ferrite phase as shown in **figure 7**. While the striations in the austenite phase remains ductile. The inter-striation spacing in the ferrite phase is influenced significantly by the localized presence of austenite grains, see **figure 8**. As cyclic stress intensity increases, brittle striations become less brittle and better delineated.

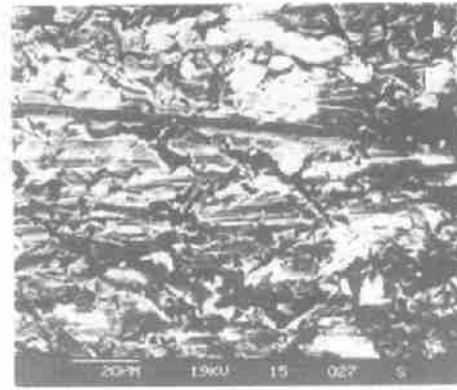


Figure 7 Cleavage-like fracture with brittle striation in phase and the ductile striations in phase.

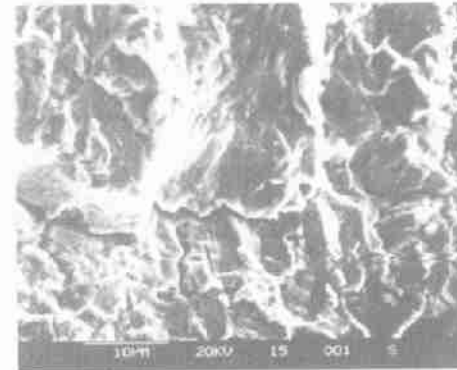


Figure 8 Inter-striation spacing in phase influenced significantly by the localized presence of phase grains.

2.4 Effect of phase structure on corrosion fatigue process

According to the explanation above, it is proven that corrosion fatigue properties of DSS in 3.5%NaCl solution may be related to complex electrochemical and mechanical coupling effects between the two phases (austenite and ferrite), where ferrite is anodic in the corrosion cell and can be very prone to cracking under certain conditions.

Furthermore, the role of ferrite can be emphasized which can promote the initiation evidently and propagation of corrosion fatigue cracking as well as cycling stress induced martensite transformation in the austenite phase, which lead to more complex electrochemical and mechanical coupling effects between the three phases. Martensite phase is selectively corroded by which the corrosion resistance of DSS decreases with the increase of the cycling stress in the corrosive medium. It may generally be accepted that corrosion fatigue cracking of DSS is dependent upon the competition of the kinetics of four processes, which can lead to localized corrosion:

- (1) Dissolution of the passive film of metal.
- (2) Depassivation of plastic straining.
- (3) Anodic dissolution of depassivated metal. The ferritic phase is more prone to corrosion than austenitic

phase. Also there is anodic dissolution of the martensite phase, which is formed after some period of cyclic stress. The martensite phase is very sensitive to pitting as well as crack initiation and propagation.

(4) Metal repassivation. It may also be emphasized that the corrosion fatigue cracking may be attributed to the localized slip within grains of the alloy caused by stress, or may be attributed to the removal of the barriers

of plastic deformation such as dislocations piling up at slip steps [7]. It is found that dislocation density at the sites adjacent to the fracture surface is much greater than that at the other surface, see **figure 9**. Also it is found that the pitting increases with the increase of the dislocation density and decreases with decreasing dislocation density, i.e., dislocation sites are more susceptible to pitting than other sites.

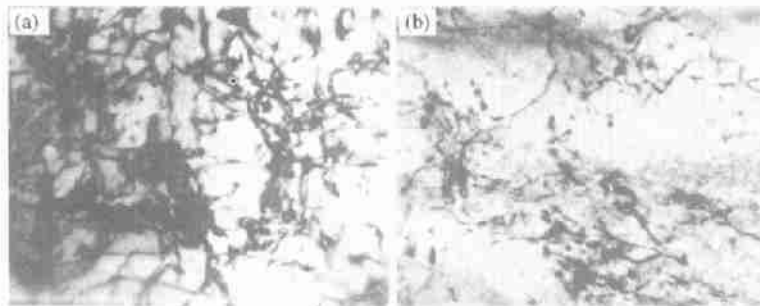


Figure 9 TEM investigation for corrosion fatigue specimen to reveal dislocations piling up at slip step (3.5%NaCl solution, 50 °C, 3 Hz, $\sigma_{max} = 417$ MPa), $\times 30\,000$, (a) dislocations piling up near fracture surface; (b) dislocations piling up far from fracture surface.

2.5 Initiation of corrosion fatigue cracks for duplex stainless steels

The results show that cracks initiate in the ferrite phase especially from small pits. Furthermore, cracks initiated in stress induce martensite phase, which is susceptible to pitting corrosion. Cracks initiate from the bottom of pits, which are formed in the early cycles during corrosion fatigue testing in 3.5%NaCl solution. These pits at the first stage are very small and then grow with increasing the applied stress and testing time.

Cyclic stress intensity inside the pits is enhanced with increasing the pit depth. That is because the pits have been considered as the sites of stress raisers. When the stress inside the pit become sufficiently high, corrosion fatigue cracking will initiate preferentially and propagate in the bottom of pits. It may be suggested that most of the cracks initiated and propagated in two different directions from pitting holes, probably with straight lines, where the pitting hole is the center point of the two straight cracks. The severity of corrosion fatigue cracking inside the pits increases with increasing the stress intensity factor. The stress inside the pitting hole distributes into two directions as a result of high concentration of stress inside the pitting hole. These pits initiate preferentially in the ferrite phase, where ferrite phase is anodic in the galvanic cell of two phases and can be very prone to cracking under certain conditions, whereas the cracks propagated around these pits are usually in the two ways, intergranular corrosion cracking and transgranular corrosion cracking.

3 Conclusions

(1) The corrosion fatigue cracks initiate from the bottom of pitting holes, which initiate at the ferrite phase.

(2) Corrosion fatigue cracking of DSS in 3.5%NaCl solution may be related to complex electrochemical and mechanical coupling effects among three phases, austenite phase, ferrite phase and stress induced martensite phase.

(3) The austenite is beneficial to slow down the corrosion fatigue crack propagation rate but do not provide good resistance to crack initiation and propagation, where ferrite phase is anodic in galvanic cell of two phases and can be very prone to cracking under certain conditions.

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