

Effect of Cl^- on the corrosive wear of AISI 321 stainless steel in H_2SO_4 solution

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Abstract. The effect of Cl^- on the corrosive wear behaviour of AISI 321 stainless steel in H_2SO_4 solution was studied via the corrosive wear rate, the load bearing capacity of passive film and the relationship between pitting and corrosive wear. There is a critical load at natural potential, below which the corrosive wear rate is slightly lowered by Cl^- , while above which is increased. At natural potential there are more pits at low load than that at a higher one in the wear tracks and the pits are also deeper. The load bearing capacity is lowered by Cl^- at passive region and then the corrosive wear rate increased.

Keywords. Chloride ion; corrosive wear; stainless steel.

1. Introduction

In many industries such as oil, chemical etc, machining and components are subject to the effects of sliding wear under corrosive conditions and extensive studies have been carried out in this direction. The study of corrosive wear is diverse and the effect of Cl^- is one such parameter investigated.

The effect of Cl^- on the corrosive wear of stainless steel in H_3PO_4 and H_2SO_4 solutions at comparatively high loads was studied according to the practical conditions in factories (Jiang *et al* 1992; Zhang *et al* 1993, 1994). It was found that the accelerating effect of Cl^- on corrosive wear was caused by the Cl^- assisted surface film cracking. In addition, there are controversies about the role of surface film in corrosive wear. In this work, the effect of Cl^- on the corrosive wear behaviour of AISI 321 stainless steel in H_2SO_4 solution was studied via the corrosive wear rate, the load bearing capacity of passive film and the relationship between pitting and corrosive wear. Neville and Hodgkiess (1999) made a study of the erosion–corrosion behaviour of two nominally corrosion resistant alloys. The experiments comprised of exposure to an impinging jet of 3.5% sodium chloride solution. It was found that the passive film on the corrosion resistant materials remained essentially intact under solids-free impingement but that these alloys exhibited active corrosion under liquid–solid impingement, i.e. the passive film played a role in corrosive wear. In order to clarify the role of surface films, experiments were performed under comparatively lower loads in the current study.

2. Experimental

The material studied was commercial grade AISI 321SS (UNS S32100) with the chemical composition (wt.%) C 0.079, Cr 17.75, Ni 9.31, Mn 1.19, Si 0.53, Ti 0.56, P 0.030, S 0.0064 and Fe balance. The specimens used for corrosive wear loss tests were discs of 12 mm in thickness and 48 mm in diameter. For the polarization measurements, the electrodes were AISI 321 SS plates with 1 cm² exposed to the test solution. The electrodes were immersed in the test solution first and when the steady natural potentials were reached, the polarization swept from cathodic to anodic direction with a scan rate of 0.16 mV/s. All the potentials were reported vs saturated calomel electrode (SCE). The transient specimen used for the observation of current decay after scratching was a pin 1 mm in diameter embedded in a polytetrafluoroethylene (PTFE) disc of 12 mm thickness and 48 mm in diameter. All the working surfaces of specimens were polished to 700-grit finish with emery paper, rinsed in acetone and then dried. The test solutions were 0.5 mol/l H_2SO_4 with different Cl^- concentrations prepared with A. R. grade chemicals.

The corrosive wear tests were carried out on an indigenously made multi-functioning corrosive wear machine (Huang *et al* 1998) which is shown in figure 1. A sliding speed of 0.12 m/s was used for all the wear experiments. For the weak corrosive wear tests, the load range was 1.0–10.0 N and the rider was a Al_2O_3 ball 12.7 mm in diameter. In order to facilitate comparison, experiments were also performed at higher loads with a load range of 20–60 N and a rider of Al_2O_3 ball 6 mm in diameter was used to increase the pressure. The potential of the specimen was controlled by Princeton-273 potentiostat. The

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corrosive wear experiments were conducted at free corrosion potential and passive potential 500 mV (vs SCE). The corrosive wear loss was measured by 2201 Type shape measurement device with a precision of 10^{-4} mm³. The testing period was 1 h for the corrosive wear loss measurement. The friction coefficient was calculated from the friction force recorded 15 min after the beginning of the experiment. For the observation of current decay after scratching, the specimen and rider were changed (also shown in figure 1) and the specimen was controlled at a constant potential of 500 mV (vs SCE). The rider was a Si₃N₄ knife for the scratching experiments. For the experiments under natural potential, the tests began after steady potential were reached. For those at the passive potential (500 mV vs SCE), the tests began 30 min after the potential was applied.

Electrochemical experiments were carried out on electrochemical 332 system. The corrosive wear tracks of two specimens under natural potential were examined by scanning electron microscopy (SEM).

3. Results

3.1 Polarization behaviour of 321 stainless steel in Cl⁻ + H₂SO₄ solution

Polarization curves of specimens in Cl⁻ + H₂SO₄ solution are shown in figure 2. The free corrosion potential (E_{corr}) of the specimen in 0.5 mol/l H₂SO₄ was -140 mV (vs SCE). When Cl⁻ was added, the E_{corr} decreased. When the Cl⁻ concentration was 0.6 mol/l, E_{corr} decreased to -370 mV (vs SCE). As the Cl⁻ concentration increased, the passive region shrank and the current to preserve passive state increased. The passivation current oscillates tremendously due to the coexistence of passive and active ions in the solution with 0.2 mol/l Cl⁻.

3.2 Corrosive wear behaviour of 321 stainless steel in Cl⁻ + H₂SO₄ solution at free corrosion and passive potentials

The relationship between corrosive wear rate and Cl⁻ concentration of specimens in H₂SO₄ solution at free corrosion and passive potential is shown in figure 3. The corrosive wear rate increased with the increase in Cl⁻ concentration at passive region (figure 3c).

It should be noted that when the rider was 12.7 mm in diameter the corrosive wear rate decreased slightly with the increase in Cl⁻ concentration at free corrosion potential (figure 2a). When the rider was 6 mm in diameter the corrosive wear rate remained almost unchanged as the Cl⁻ concentration changed under 35.4 N. The corrosive wear rate increased with the increase of Cl⁻ when the load exceeded 43.4 N.

Table 1 shows the friction coefficient of stainless steel in 0.5 mol/l H₂SO₄ with different Cl⁻ concentrations at

free corrosion and passive potential. At free corrosion potential, the friction coefficient decreased generally with increase in Cl⁻, while at the passive potential (500 mV), it increased with increase in Cl⁻.

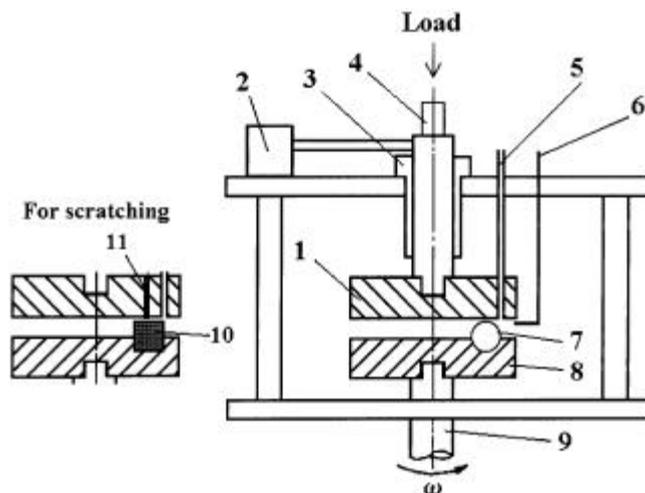


Figure 1. Schematic diagram of corrosive wear apparatus. (1. Specimen (steel plate); 2. friction force sensor; 3. sliding bearing; 4. loading axis; 5. capillary; 6. pt counter electrode; 7. abrading rider (Al₂O₃ ball); 8. rider holder; 9. rotating shaft; 10. rider for scratching (Si₃N₄ knife); 11. steel pin (the holder of the pin is nylon block)).

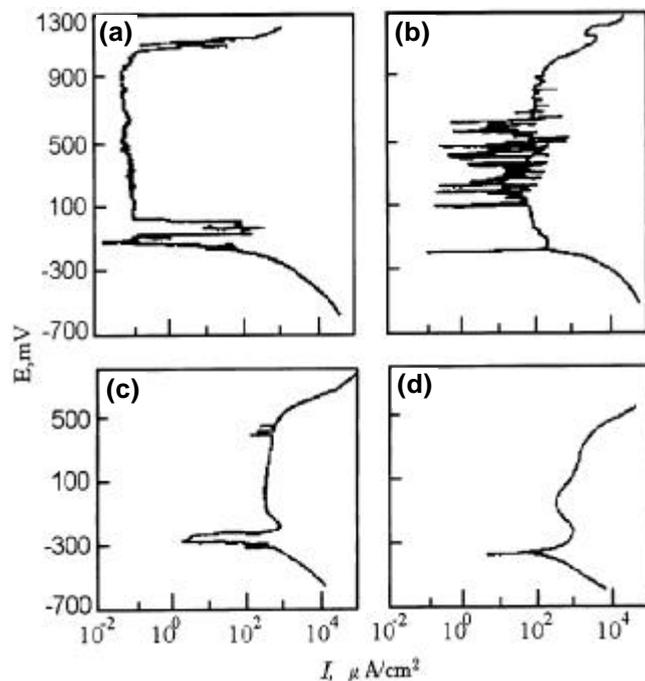


Figure 2. Polarization curves of 321 stainless steel in 0.5 mol/l H₂SO₄ solution with various Cl⁻ concentrations. (a) H₂SO₄, (b) 0.2 mol/l NaCl + 0.5 mol/l H₂SO₄, (c) 0.4 mol/l NaCl + 0.5 mol/l H₂SO₄ and (d) 0.6 mol/l NaCl + 0.5 mol/l H₂SO₄.

3.3 Load bearing capacity of passive film and Cl^- concentration

The current variation of specimens in Cl^- containing H_2SO_4 solutions was recorded at the controlled potential of 500 mV. If the passive films of specimen failed after the scratch by the rider, a current ramp could be observed. Table 2 shows the value of current ramp amplitude.

The current ramp could not be seen in 0.5 mol/l H_2SO_4 + 0.005 mol/l Cl^- solution under extremely low load of 1.2 N, i. e. the surface shear stress was not high enough to break the passive film in this condition. But as the Cl^- concentration and load increased, the current appeared and the value of current ramp increased with increase in Cl^- concentration and load.

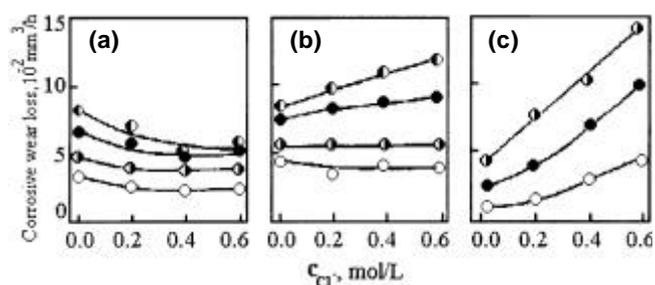


Figure 3. Relationship between corrosive wear loss and Cl^- concentration (C_{Cl^-}) for 321 stainless steel in 0.5 mol/l H_2SO_4 with different Cl^- concentrations. (a) Natural potential, Al_2O_3 ball dia 12.7 mm (O, 2.8 N; \odot , 4.8 N; \bullet , 7.8 N; \bullet , 9.8 N), (b) natural potential, Al_2O_3 ball dia 6 mm (O, 23.4 N; \odot , 33.4 N; \bullet , 43.4 N; \bullet , 53.4 N) and (c) passive potential (500 mV vs SCE), Al_2O_3 ball dia 12.7 mm (O, 2.8 N; \bullet , 7.8 N; \bullet , 13.4 N).

Table 1. Friction coefficients of stainless steel in 0.5 mol/l H_2SO_4 with different Cl^- concentrations.

C_{Cl^-} (mol/l)	Load (N)						
	at natural potential				at passive potential		
	2.8	4.8	7.8	9.8	2.8	7.8	13.4
0.0	0.33	0.37	0.30	0.32	0.35	0.23	0.18
0.2	0.26	0.35	0.31	0.31	0.45	0.32	0.21
0.4	0.26	0.33	0.30	0.28	0.45	0.42	0.29
0.6	0.27	0.25	0.27	0.31	0.46	0.43	0.31

Table 2. The maximum value of current decay, I_0 , transients for stainless in H_2SO_4 and $\text{H}_2\text{SO}_4 + \text{Cl}^-$ solution (μA).

C_{Cl^-} (mol/l)	Load (N)				
	1.2	2.2	4.2	7.2	12.2
0.00	0	12	163	260	445
0.05	0	136	348	367	520
0.10	41	147	321	497	613
0.20	86	230	375	550	681

3.4 Morphology of wear tracks

Figure 4 shows the morphology of wear tracks by SEM of two specimens under different loading conditions at natural potential. Pits existed in wear tracks. The pits in the wear tracks of specimen under low load are deeper and the number is larger than that under higher load.

4. Discussion

The corrosive wear loss shown in figure 3a was measured at low loads. The corrosive wear rate decreases slightly as Cl^- concentration increases. The results are somewhat different from that under low load when the pressure is increased. The corrosive wear loss remains unchanged with the increase in Cl^- concentration under load of 33 N and increases above it, i.e. there exists a critical load above which the corrosive wear loss of stainless steel increases with the increase in Cl^- concentration.

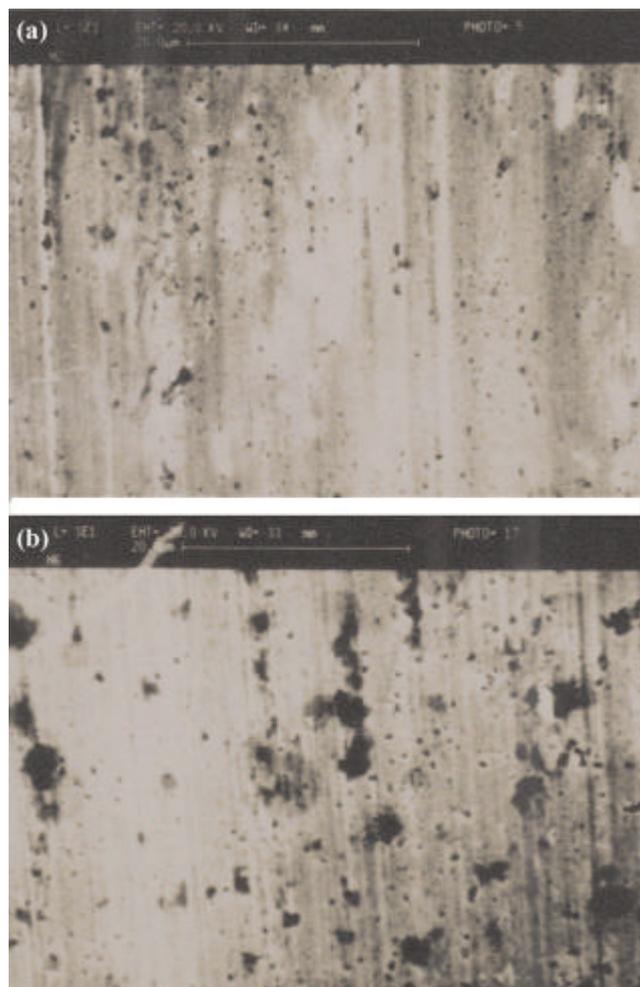


Figure 4. Morphology of wear tracks of 321 stainless steel at natural potential. (a) 0.2 mol/l NaCl + 0.5 mol/l H_2SO_4 , Al_2O_3 ball dia. 6 mm, load 43.4 N and (b) 0.2 mol/l NaCl + 0.5 mol/l H_2SO_4 , Al_2O_3 ball dia. 12.7 mm, load 13.4 N.

The results under higher loads are consistent with those reported previously by other workers (Jiang *et al* 1992; Zhang *et al* 1993, 1994). The results above the critical load can be explained as Cl^- induced embrittlement (Jiang *et al* 1992). Jiang *et al* (1992) found from their experiments that the friction fitters in solutions with and without Cl^- were different. The fitter in the solution with Cl^- was the same as that of brittle material and a concept of Cl^- induced brittleness was given (Jiang *et al* 1992). But this phenomenon can only occur under severe wear conditions. The presence of a thin corrosion film strongly influences the contact resistance, the friction and the degradation of the contact (Rudolphi *et al* 1997). The results below critical load can be possibly explained as the lubrication effect of corrosion product on the surface of 321 stainless steel at free corrosion potential. This was verified by the results of friction coefficient measurement shown in table 1.

Cl^- facilitates in forming and developing pits by destroying the surface film on the surface of stainless steel. But the phenomenon of pits development under surface shear stress should be noticed. Not only the pits developing opportunity was decreased due to the breakdown of surface film caused by the continuous surface severe shear stress, but also the pits pre-existed were made shallower or diminished. So the number of pits was less and the depth was shallow. But the material loss caused by shear stress was less under weak wear conditions, there was sufficient time for the pits to initialize and grow, so the pits were larger and deeper.

The load bearing capacity of the passive film under passive potential was decreased by Cl^- under the same loading conditions, which was verified by current ramp values shown in table 2. The current ramp was not observed in low Cl^- containing solution (0.05 mol/l) under very low load (1.2 N). When Cl^- concentration was increased to 0.1 mol/l, a current ramp was observed. This showed that the passive film could withstand slight surface shear stress without breaking down in the solution with no Cl^- or very low Cl^- concentration. The current ramp value was very high even in the solution with no Cl^- when the load was increased which showed the passive film had already broken down. It can be seen

from figure 1 that the current required to sustain passive state increased tremendously when Cl^- concentration was increased, the stainless steel was transformed from passive to active state and the corrosion component increased. Table 1 shows that the friction coefficient under passive potential increases as Cl^- content increases. This is due to the incomplete passive film due to Cl^- and the increase in surface roughness.

5. Conclusion

The effect of Cl^- on the corrosive wear behaviour of AISI 321 stainless steel in H_2SO_4 solution was studied and the following conclusions were drawn:

- (I) There is a critical load at natural potential, below which the corrosive wear rate is slightly lowered by Cl^- , above which it increases with the increase of Cl^- .
- (II) At natural potential the pits in the wear tracks of specimen under low load are deeper and the number of them is larger than that under higher one.
- (III) The stainless steel studied here can be used safely in weak corrosion media at natural potential under low loads.
- (IV) The passive film at passive potential can withstand slight mechanical wear in the solution with no or very low Cl^- content and this prevents the use of stainless steel in the combined condition of wear and corrosion at passive potential.

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