

Critical Chloride Concentration for Stress Corrosion of 304 Stainless Steel

Lv Guocheng, Xu Chunchun, Cheng Haidong

(School of Materials Science and Engineering, Beijing University of Chemical
Technology, Beijing 100029, China)

Abstract: The relationship between the stress corrosion susceptibility of 304 stainless steel and the concentration of Cl in the solution was obtained by slow tensile experiment, and the fracture morphology of the tensile specimen was analyzed by scanning electron microscope. The fracture morphology of the tensile specimen was analyzed by scanning electron microscope, and the critical chloride ion concentration for stress corrosion of 304 stainless steel was obtained. The use of self-designed A self-designed device was used to apply tensile stress to the 304 stainless steel specimen, and electrochemical in situ testing under constant strain conditions was used to study the rupture potential of the passivation film of 304 stainless steel. Stainless steel passivation film rupture potential and chloride ion concentration of the relationship. The relationship between the Cl⁻ concentration leading to the sudden change of rupture potential of passivation film and the critical Cl concentration for stress corrosion rupture was found to be the same as that of the rupture potential. It was concluded that the Cl⁻ concentration leading to the rupture potential of the passivation film and the critical Cl⁻ concentration for stress corrosion rupture are basically the same.

Keywords: 304 stainless steel; passivation film; stress corrosion; critical chloride ion concentration

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1 Introduction

304 stainless steel has been widely used because of its good corrosion resistance. However, under the action of chloride ions, 304 stainless steel will undergo stress corrosion rupture [1-21], resulting in equipment running, bubbling, dripping and

leaking, which often brings disastrous consequences. Moreover, the equipment in the cold Moreover, the chlorine ions in the medium such as cooling water in the equipment will be gradually concentrated, increasing the corrosion of the equipment. A large number of scientific research work reveals the occurrence and development of stress corrosion¹⁴⁶. Stress corrosion of stainless steel is related to Cl^- concentration, temperature, pH value and other ions in solution ⁷, when the Cl^- concentration reaches the critical value, the stress corrosion of stainless steel is related to Cl^- concentration, temperature, pH value and other ions in solution ⁷. Cl^- concentration reaches a critical value, 304 stainless steel will occur stress corrosion rupture, but for the critical value did not reach a unanimous conclusion 18-101, and can not be proposed to completely avoid or eliminate stress corrosion. Can not be proposed to completely avoid or eliminate the boundary conditions of stress corrosion.

In certain conditions of stainless steel passivation film rupture formed by etching holes often become a source of stress corrosion, so the structure and performance of the passivation film Affect the corrosion resistance of stainless steel. The corrosion resistance of the stainless steel passivation film is largely determined by the rupture of the metal in the medium of the film. potential [12]. Therefore, the study of 304 stainless steel passivation film rupture potential E_0 , can reflect the stability of the stainless steel passivation film, and further And study the stress corrosion behavior of 304 stainless steel.

In this paper, the critical Cl^- concentration of 304 stainless steel for stress corrosion was obtained by slow tensile experiment and corresponding fracture analysis; in-situ electrochemical analysis under constant deformation was used to study the stress corrosion behavior of 304 stainless steel. In this paper, the critical Cl^- concentration of 304 stainless steel for stress corrosion was obtained by slow tensile test and corresponding fracture analysis; the relationship between the rupture potential of 304 stainless steel passivation film and the Cl^- concentration was investigated by in-situ electrochemical test under constant deformation. The stress corrosion mechanism of 304 stainless steel in Cl^- containing media was further analyzed.

2 Experimental method

The experimental material is 304 stainless steel sheet, composition (mass fraction): Cr 17.080%, Ni8.010%, Mn 1.380%, Si 0.490%, C 0.050%, S 0.001%, P 0.020%, the remaining Fe.

Si 0.490%, C 0.050%, S 0.001%, P 0.020%, and the rest is Fe. All the specimen in this study were subjected to high-temperature solid solution treatment (1050 °C, 0.020%).

treatment (1050 °C, 30 min, water cooling). The surfaces of the specimen were polished with water sandpaper, degreased with acetone, rinsed with deionized water, and dried. Rinse with deionized water, dry and spare. Different concentrations of NaCl solutions were prepared with deionized water and analytically pure NaCl, and the pH value was adjusted to 7°C with NaOH or HCl solution. The pH value was adjusted to 7 ± 0.1 with NaOH or HCl solution. The test temperature was 60 ± 0.1 °C.

2.1 Slow strain rate method

The slow tensile test was performed using a dumbbell-type specimen with a spacing section of (20mm×3mm×2mm). The slow tensile experiments were carried out at a 10 kN stress corrosion testing machine, tensile strain rate 2×10^{-6} s⁻¹.

2.2 Fracture analysis of slow tensile specimen

After the specimen fracture, remove it immediately and protect the fracture. The corrosion products adhered to the surface were first rinsed with deionized water, and then blown dry with nitrogen. Blow dry. In the ultrasonic cleaner using acetone to clean the fracture, nitrogen blow-drying using Cambridge-S250 scanning electron microscope to observe the fracture morphology. The fracture morphology was observed using a Cambridge-S250 scanning electron microscope.

2.3 In-situ electrochemical testing at constant strain

In order to study the effect of Cl concentration on the surface passivation film of 304 stainless steel under tensile stress, an in-situ electrochemical test setup under constant strain was designed. The in situ electrochemical testing device was designed under constant strain, see Fig. 1. It is known from the pre-test that when the strain is greater than 30%, the increase of strain has less effect on the rupture potential of the passivation film. Therefore, a strain of 30% was used in this study.

The electrochemical test specimen was of dumbbell type, and the dimension of the spacing part was (20mm×2mm×2mm). The self-designed device shown in Fig. 1 was used to apply tensile stress to the specimen. The tensile stress was applied to the

specimen with 30% deformation (without unloading) using the self-designed device shown in Fig. 1. The center portion of the specimen was left bare for 1 cm² and the rest of the specimen was sealed with silicone rubber adhesive. The rest of the specimen was sealed with a silicone rubber adhesive.

The electrochemical tests were carried out using a three-electrode system, with the specimen as the study electrode, a platinum electrode as the auxiliary electrode, and a saturated calomel electrode as the reference electrode. The scanning speed of the kinetic potential was 20 mV/min.

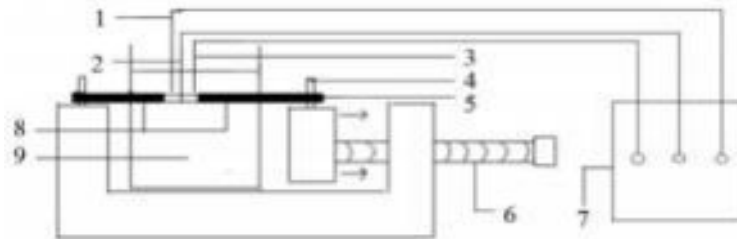


Fig. 1 Constant strain in-situ electrochemical test setup

1. reference electrode
2. working electrode
3. auxiliary electrode
4. pin
5. dumbbell specimen
6. screw
7. electrochemical workstation
8. silicon rubber
9. solution

3 Results and Discussion

3.1 The effect of changes in Cl⁻ concentration on the stress corrosion susceptibility of 304 stainless steel

Table 1 for the specimen in the solution containing different Cl⁻ concentration of slow strain tensile test obtained test data. Elongation is the specimen Elongation is the ratio of the elongation between the specimen markings and the original markings after pulling off, and the elongation of the specimen tensile in air and solution is δ_0 and δ . The test measured that the 8.5 mm of 304 stainless steel is the same as the original specimen. 8. of 304 stainless steel was measured as 71.44%. The plasticity loss l_b was used as a characterization parameter for the stress corrosion susceptibility of the material [13], the i.e.

$$l_b = (1 - \delta / \delta_0) \times 100\%$$

The values of l_b for specimen stretched in different concentrations of Cl⁻ solutions are shown in Table 1

Table 1 Effect of chloride ion concentration on stress corrosion susceptibility

氯离子浓度/mg·L ⁻¹	δ_f /%	I_{sc} /%
60	69.85	2.226
90	63.80	10.69
120	61.70	13.63
300	60.60	15.17
600	60.03	15.97
900	59.43	16.81

Figure 2 shows the relationship of I_{sc} to Cl^- concentration. As can be seen from the figure, when the Cl^- concentration is less than 90 mg/L, with the increase of Cl^- concentration, the stress corrosion susceptibility increases significantly; when the Cl^- concentration is greater than 90 mg/L, the stress corrosion susceptibility is larger but changes slowly. Curve turns at point g, so this point is the stress corrosion sensitivity with the Cl^- concentration of the mutation point, that is, the critical Cl^- concentration of stress corrosion occurs.

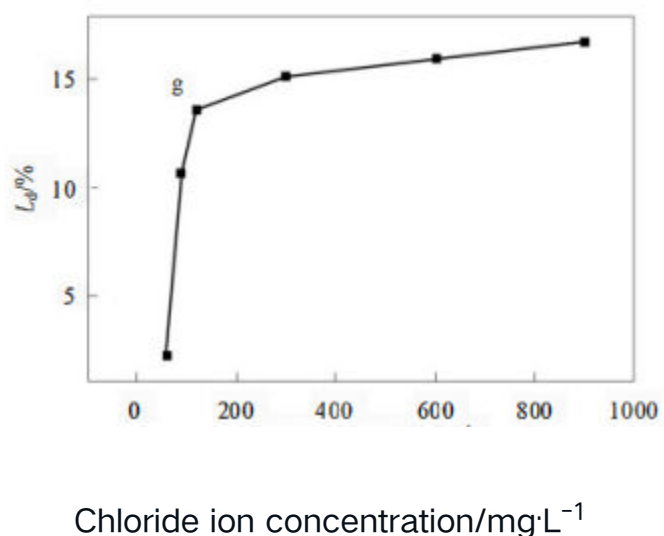


Figure 3 shows the SEM morphology of the fracture of 304 stainless steel after slow stretching in Cl^- concentrations of 60 mg/L, 90 mg/L, 300 mg/L, and 900 mg/L solutions.

As can be seen in Fig. 3, when the Cl^- concentration is 60 mg/L, there are a large number of tough nests on the fracture surface, which is a typical tough fracture morphology, see Fig. 3 (c); when the Cl^- concentration is 90 mg/L, there are a large number of tough nests on the fracture surface. When the Cl^- concentration was 90 mg/L, small secondary cracks began to appear on the fracture surface, but the number was very small, see Fig. 3 (b); when the Cl^- concentration was 300 mg/L, the

size and number of secondary cracks on the fracture surface increased significantly compared with Fig. 3 (b), see Fig. 3 (c); when the Cl^- concentration was 900 mg/L, the size and number of secondary cracks on the fracture surface increased significantly compared with Fig. 3 (c); and when the Cl^- concentration was 900 mg/L, the size and number of secondary cracks on the fracture surface increased significantly. When the Cl^- concentration was 900 mg/L, the number of secondary cracks on the fracture surface increased compared with Fig. 3(c). The number of secondary cracks on the fracture surface increased at a Cl^- concentration of 900 mg/L compared with that in Fig. 3(c), but the change in crack size was not significant, see Fig. 3(d).

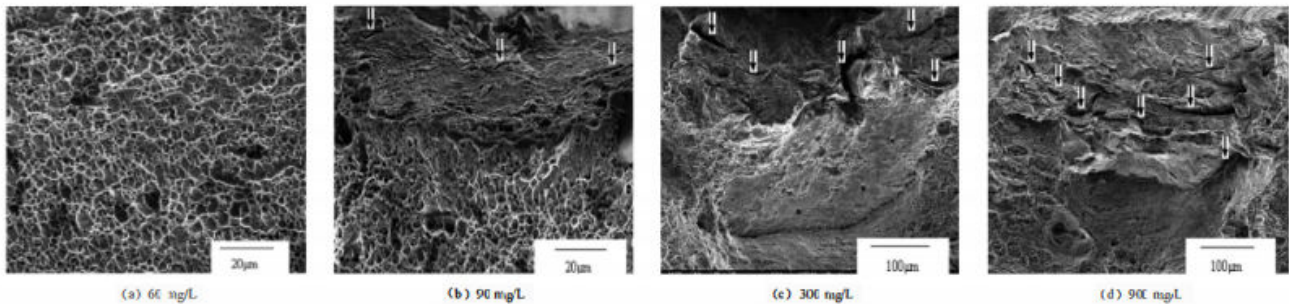


Fig. 3 Fracture morphology (SEM) of tensile specimens in different Cl^- concentrations.

From Fig. 2 and Fig. 3, it can be seen that 90 mg/L is the mutation point of stress corrosion sensitivity with the change of Cl^- concentration, i.e., 90 mg/L is the critical Cl^- concentration for the occurrence of stress corrosion under the test conditions. When the Cl^- concentration is greater than or equal to this value, secondary cracks will appear on the fracture surface, and stress corrosion will occur; when the Cl^- concentration is less than 90 mg/L, there is no secondary cracks on the fracture surface, and the stress corrosion sensitivity is small.

3.2 Effect of Cl^- concentration on rupture potential of 304 stainless steel passivation film under tensile stress

Figure 4 shows the anodic polarization curves of specimens with 30% strain in different concentrations of Cl^- solution. The corrosion current density is very small in the passivation zone, about $2 \mu\text{A}/\text{cm}^2$ (known from experimental data), and the passivation film shows good protection. When the potential exceeds the rupture potential of the passivation film, the corrosion current density increases rapidly, 304 stainless steel was severely corroded. Therefore, the rupture potential of the passivation film is a very important parameter that can be used to evaluate the stability of the passivation film in solution. The more positive the rupture potential, the more stable the passivation film; the more negative the rupture potential, the less

stable the passivation film. Corrosion current density of $10 \mu\text{A}/\text{cm}^2$ when the corresponding potential for the passivation film rupture potential E_b ^[14], that is, Figure 4, the potential of each curve at the turn.

As can be seen from Fig. 4, with the increase of Cl^- concentration in the solution, the width of the passivation zone of 304 stainless steel becomes narrower, and the rupture potential of the passivation film becomes negative. potential becomes negative. It shows that the Cl^- concentration has a significant effect on the corrosion of 304 stainless steel under tensile stress.

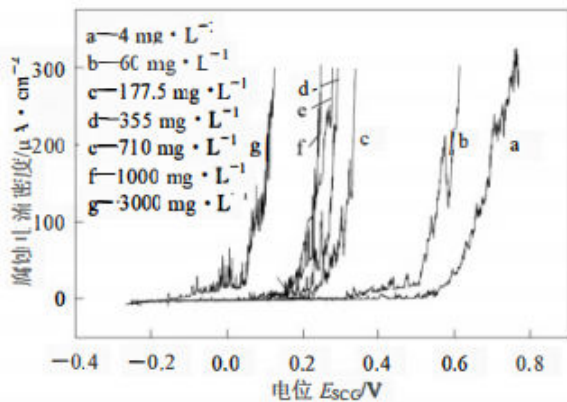


Fig 4. Potential E_{sc}/V

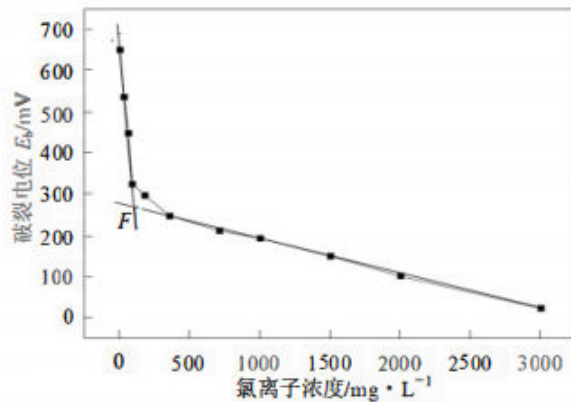


Fig 5. Chloride ion concentration/ $\text{mg}\cdot\text{L}^{-1}$

Figure 5 shows the rupture potential of passivation film of 304 stainless steel in different concentrations of Cl^- solution versus Cl^- concentration. In the Cl^- concentration is low, the passivation membrane rupture potential E_b with the increase of Cl^- concentration quickly negative shift, and linear relationship; when the Cl^- concentration is large, the passivation membrane rupture potential E_b , with the increase of Cl^- concentration slowly negative shift, also a linear relationship, the two straight lines intersected at point F (98 mg/L, 266 mV). That is, when the Cl^- concentration is greater than 100 mg / L, the rupture potential of the passivation membrane is more negative, and the change is not large, indicating that the passivation membrane has been damaged, increase the concentration of Cl^- , the impact has been small; when the Cl^- concentration of less than 100mg/L, with the decrease in the concentration of Cl^- , the rupture potential is rapidly positively shifted, that is, the passivation membrane of the protection of the rapid increase. Therefore, it can be considered, bear 30% of the tensile strain of 304 stainless steel in less than 100 mg/L of Cl^- solution, has a better stress corrosion resistance. This is consistent with the critical Cl^- concentration that leads to stress corrosion rupture of 304 stainless steel is consistent.

The mechanism of stress corrosion rupture in which anodic dissolution plays a controlling role has been extensively studied, but controversial. Many have suggested that the corrosion process promotes localized plasticity. that the corrosion process promotes localized plastic deformation leading to stress corrosion rupture of the material [15-18]. In this paper, we derived the results leading to the rupture of passivation film The agreement between the Cl^- concentration that leads to the potential mutation and the critical Cl^- concentration for the occurrence of stress corrosion rupture in this paper suggests that the rupture of the passivation film plays a significant role in the stress corrosion of 304 stainless steel. steel plays an important role in stress corrosion. After rupture of the film, localized anodic dissolution results in the formation of weak structures such as pitting corrosion.1191 Stress corrosion forms nuclei in the weak zones. Stress corrosion nucleates and expands in the weak zone.

4 Conclusion

(1) The critical Cl^- concentration for stress corrosion of 304 stainless steel in neutral solution at 60°C is about 90mg/L. The Cl^- concentration of 304 stainless steel in neutral solution at 60°C is about 90 mg/L.

(2) The constant strain in-situ electrochemical testing method can quickly measure the sudden change of Cl^- concentration that leads to the rupture potential of the membrane, and thus we can Preliminary judgment of the possibility of stress corrosion rupture of 304 stainless steel.

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