Corrosion behavior of 316L stainless Steel under Cl⁻ corrosion medium

xiejunjun¹,a, ningyuheng²,b, sunxu³,c, yangzhanjun⁴,d

¹Datang Northeast Electric Power Test and Research Institute Co., Ltd., No. 3195, Ulsan Road, High-tech Zone, Changchun City, Jilin Province, China
²Datang Northeast Electric Power Test and Research Institute Co., Ltd., No. 3195, Ulsan Road, High-tech Zone, Changchun City, Jilin Province, China
³Datang Northeast Electric Power Test and Research Institute Co., Ltd., No. 3195, Ulsan Road, High-tech Zone, Changchun City, Jilin Province, China
⁴Datang Northwest Electric Power Test and Research Institute Co., Ltd., No.155, Fengcheng 7th Road, Economic Development Zone, Xi'an, Shaanxi, China

a1271165624@qq.com, bnyh3570@sina.com
c380541075@qq.com, d617578204@qq.com

Abstract. 316L stainless steel is widely used in the fields of thermonuclear industry and petrochemical industry due to its excellent comprehensive mechanical properties and corrosion resistance. Especially in the petroleum industry, 316L stainless steel is commonly used as oil pipelines and storage tanks because of its high corrosion resistance to media such as CO₂. However, 316L stainless steel will pitting in a high Cl⁻ concentration environment, posing a potential risk to these devices. At present, there is not enough data to show that whether 316L stainless steel will bring about pitting or stress corrosion cracking under the synergistic effect of high stress and high Cl⁻ concentration, this brings higher risks to the application and promotion of this material. In response to this phenomenon, the paper uses constant stress corrosion cracking method, and analyzes the fracture by scanning electron microscope (SEM). Researching 316L Stainless Steel corrosion behaviors and corrosion creeps in different Cl⁻ concentration solutions.

1. Introduction
Austenitic stainless steel has been widely used in many traditional industries such as petrochemical industry, hydrometallurgical industry, nuclear industry and so on because of its excellent comprehensive mechanical properties good weldability and corrosion resistance. As a typical austenitic stainless steel, 316L stainless steel is widely used in thermal nuclear industry, petrochemical industry and other fields, due to long-term work in harsh environments, the combined effects of temperature, corrosive media, and mechanics will cause corrosive damage to these devices [¹-³]. At present, there is not enough data to show that whether 316L stainless steel will bring about pitting or stress corrosion cracking under the synergistic effect of high stress and high Cl⁻ concentration, this brings higher risks to the application and promotion of this material, which requires us to conduct further research on it.
2. Method for preparation and test of sample

The test material is 316L stainless steel, it is an austenitic stainless steel from the point of view of the metallurgical organization, the standard grade of our country is 022Cr17Ni12Mo2. The specific chemical composition is shown in Table 1, and the mechanical properties of 316L stainless steel are shown in Table 2.

| Element | C   | Cr   | Mn   | Ni   | Si  | P      | S     | Ti    | Fe   |
|---------|-----|------|------|------|-----|--------|-------|-------|------|
| percent | 0.097 | 17.75 | 1.19 | 9.31 | 0.53 | 0.03 | 0.0064 | 0.56 allowance |

Table1. 316L stainless steel chemical composition (wt%)

| Mechanical property | Tensile strength (MPa) | Yield Strength (MPa) | Elongation rate (%) |
|---------------------|------------------------|----------------------|---------------------|
| Index               | 660                    | 360                  | 30                  |

Table2. 316L stainless steel mechanical properties

The sample preparation method is mainly based on GB/T 15970[1].4-1995 stress corrosion uniaxial tensile sample preparation, its shape and size shown in Fig1. Before the test, the sample was polished to 400# by using a metallographic sandpaper, and then washed with an ethanol-acetone mixture, rinsed with deionized water, and dried.

Fig1. Configuration and dimension of the specimen

The test method adopts a constant - load stretching pattern method, and the test medium is NaCl solution at different concentrations under room temperature. In order to speed up the progress of the experiment and shorten the experimental period, a certain amount of FeCl₃ was added to the corrosion solution. Table 3 shows the corrosive media parameters for corrosion and mechanical behavior of 316L stainless steel under constant stress conditions.

| group indication | Cl⁻ potency (ppm) | Fe³⁺ potency | pH value |
|-----------------|------------------|--------------|----------|
| 1               | 141480            | 1%           | 5        |
| 2               | 70740             | 1%           | 5        |
| 3               | 14148             | 1%           | 5        |

Table3. 316L stainless steel Corrosive media parameters under constant stress corrosion and Conditions of the mechanical behavior

3. Test results and discussion

3.1 Stress corrosion cracking of 316l stainless steel under constant stress

The indicators of stress corrosion cracking susceptibility are diverse. The first indicator used to
evaluate is the fracture time of the sample. There are some deficiencies in this evaluation index, such as the fracture toughness of the material, the number of crack initiation, and the width and thickness of the sample, affect the fracture time. This section mainly evaluates the stress corrosion cracking susceptibility of 316L stainless steel by three aspects of fracture time and elongation, and the morphology of corrosion fractures. Fig2 shows the deformation-time curve of 316L stainless steel in different Cl$^-$ concentration NaCl solutions, Fig3 shows the fracture time and elongation curves of 316L stainless steel in different Cl$^-$ concentration NaCl solutions.

![Fig2. 316L stainless steel deformation-time curve in different Cl$^-$ concentrations](image)

Fig2. 316L stainless steel deformation-time curve in different Cl$^-$ concentrations

Fig2. shows that the deformation-time curves of 316L stainless steel in different Cl$^-$ concentration NaCl solutions are roughly divided into three stages: the first stage is the rapid deformation stage of 316L stainless steel at the beginning of the tensile stress, which is a short period of time; the second stage is the slow deformation stage of 316L stainless steel under the action of tensile stress and corrosive media; the third stage is the crack propagation process of 316L stainless steel under the synergistic action of tensile stress and corrosion medium, which accelerates the deformation of the specimen until the fracture stage.

![Fig3. 316L stainless steel fracture time and elongation curves in different Cl$^-$ concentrations of NaCl solutions](image)

Fig3. 316L stainless steel fracture time and elongation curves in different Cl$^-$ concentrations of NaCl solutions

It can be seen from Fig3. that when the concentration of Cl$^-$ in the corrosion solution is 14148 ppm, the fracture time of the 316L stainless steel sample is approximately 37 days, the variation is 29%, the
plastic loss is 4%, and the Cl\textsuperscript{-} concentration is 70740 ppm, the sample fractures. the time was about 23 days; the line variation was 23%, the shaping loss was 24%; when the concentration of Cl\textsuperscript{-} was 141,480 ppm, the fracture time of the sample was about 12 days, the line variation was 18%, the plastic loss was 40%; It can be seen that with the increase of the concentration of the corrosion solution Cl\textsuperscript{-}, the fracture time of the sample decreases and the plastic loss increases, indicating that the stress corrosion sensitivity of the 316L stainless steel is enhanced.

This is mainly due to the anodic dissolution of 316L stainless steel under the combined action of tensile stress and corrosive media. As the concentration of Cl\textsuperscript{-} in the solution increases, Cl\textsuperscript{-} can be preferentially adsorbed on the surface of the 316L stainless steel sample at some active sites, and binds with the metal ions to form soluble chlorides. These chlorides develop into small particles, the pitting corrosion will largely destroy the passivation film on the surface of the metal sample. And with the increase of Cl\textsuperscript{-} concentration, the more serious the passivation film cracks, pitting pits\textsuperscript{[4-5]}. The pitting pits form a large stress concentration under the action of tensile stress, which leads to a decrease in the plasticity of the material, the more pitting pits, the greater the depth and the greater the plastic loss.

### 3.2 Fracture morphology

An important means for studying the mechanism of metal fracture is micro fracture analysis. JMS-5600 scanning electron microscope was used to study the stress corrosion fracture morphology of 316L stainless steel under different Cl\textsuperscript{-} conditions. Fig.4 shows the fracture morphology of 316L stainless steel in air and different Cl\textsuperscript{-} concentrations of NaCl solution.

![Fracture morphology](image)

Fig4. 316L stainless steel fracture morphology in air and different Cl\textsuperscript{-} concentration of NaCl solutions

It can be seen from Fig.4 that the microscopic fracture morphology of (a) is composed of many small dimples, that is, 316L stainless steel is stretched in the air to be a pronounced ductile fracture, and (b) the microscopic fracture morphology is also more. The dimples and fractures are mainly ductile fractures, but compared to (a), the number of dimples is decreasing. (c) Microscopic fracture morphology. The dimples are larger, and the number of dimples is also decreasing. The dimple
fractures are still dominant, but the number of dimples in the (d) diagram is further reduced, the
dimples are further enlarged, and they resemble the patterns of river patterns, the fracture mode is
dimple fracture, but it also showed some quasi-clearance fractures. The above results show that with
the increase of Cl\(^-\) concentration of corrosion solution, the fracture mode of 316L stainless steel
changes from ductile fracture to brittle fracture, and the corrosion sensitivity increases. When the
concentration of Cl\(^-\) is 141480ppm, the fracture mode of the sample presents a certain quasi-solution
and show a certain degree of brittleness.

3.3 Corrosion creep of 316L stainless steel under constant stress
Material in the more corrosive medium and constant load under long-term plastic deformation will
occur slowly, that is, corrosion creep phenomenon. In this paper, the variation of corrosion creep rate
in NaCl solution of 316L stainless steel with different Cl\(^-\) concentration was studied. Fig.5 shows the
corrosion creep rate curve of 316L stainless steel in different Cl\(^-\) concentration NaCl solution.

![Corrosion creep rate curve](image)

Fig.5. 316L stainless steel corrosion creep rate curve

It can be seen from Fig.5 that the corrosion creep rate curves of 316L stainless steel in different Cl\(^-\) concentration NaCl solutions undergo three stages: deceleration creep stage—steady state creep stage—accelerated creep stage. When the Cl\(^-\) concentration of the solution is 141480ppm, the steady-state creep rate is about 4×10\(^{-7}\) m.s\(^{-1}\); when the Cl\(^-\) concentration is 70740ppm, the steady-state creep rate is about 2×10\(^{-7}\) m.s\(^{-1}\), and the Cl\(^-\) concentration At 14148 ppm, the steady state creep rate is approximately 1.8 x 10\(^{-7}\) m.s\(^{-1}\). It shows that the steady-state creep rate of 316L stainless steel decreases with the decrease of Cl\(^-\) concentration. It can also be observed that the steady-state creep phase increases when the Cl\(^-\) concentration decreases.

The main reason for the creep phenomenon is that 316L stainless steel undergoes anodic
dissolution and cathodic hydrogen evolution reaction under the action of stress and corrosive media.
And with the increase of Cl\(^-\) concentration, the more severe the passivation film cracks, pitting pits are
formed. The pitting pits form a large stress concentration under the action of tensile stress, which also
reduces the strength of the material and promotes corrosion creep. It is also theorized that the
vacancies produced by anodic dissolution promote dislocation climbs and promote corrosion creep.
Anodic dissolution will form a corrosion product film on the metal surface, and these corrosion
product films will produce an additional tensile stress, which is equivalent to increase the creep stress,
and further promote the corrosion creep process\(^{6-7}\).
3.4 Conclusions

(1) The deformation-time curves of 316L stainless steel in NaCl solution with different Cl\(^-\) concentration show that the fracture time decreases from 37 days to 12 days and the plastic loss increases from 4% to 40% with the increase of Cl\(^-\) concentration in the solution. The sensitivity of 316L stainless steel to stress corrosion is enhanced.

(2) The observation of fracture surface morphology shows that with the increase of Cl\(^-\) concentration in the corrosion solution, the dimple size of the micro fracture morphology increases, the number decreases, and the appearance resembles that of a river pattern, showing a brittle fracture trend. That is, the fracture mode of 316L stainless steel changed from ductile fracture to brittle fracture with the increase of Cl\(^-\) concentration.

(3) 316L stainless steel under the action of stress and corrosive medium occurs Corrosion creep phenomenon. Corrosion creep rate experiences three stages: deceleration creep stage, steady state creep stage and accelerate the creep phase. With the decrease of Cl\(^-\) concentration in solution, the steady-state creep rate decreased from 4×10\(^{-7}\) m.s\(^{-1}\) to 1.8×10\(^{-7}\) m.s\(^{-1}\), and the steady-state creep stage increased.

References

[1] R. K. Singh Roman, Wai Hoong Siew. Stress corrosion cracking of an Austenitic Stainless Steel in Nitrite-Containing Chloride Solutions[J]. Materials, 2014, 7:7799-7808.

[2] Rokuro Nishimura, Yasuaki Maeda. SCC evaluation of type 304 and 316 austenitic stainless steels in acidic chloride solutions using the slow strain rate technique[J]. Corr Sci, 2004, 46(3):769-785.

[3] Scully J C, Powell D T. Stress corrosion cracking mechanism of titanium alloys at room temperature[J]. Corr sci.1970,10(10):719–733.

[4] Parkins R N, Greenwell B S. Interface between corrosion fatigue and stress corrosion cracking[J]. Material science,1977,11(8):405~413.

[5] Wu Ying, Jiang Yiming, Liao Jiaxing, et al. Effect of Cl\(^-\) on critical pitting temperature of 304,316 stainless steel[J]. Corrosion Science and Protection Technology, 2007, 27(1):16-19.

[6] Revie R W, Uhlig H H. Further evidence regarding the dezincification mechanism[J]. Corr Sci, 1972, 12:669-671.

[7] Leinonen H, Hanninen H. SCC susceptibility of nitrogen alloyed stainless steels in 50% CaCl\(_2\) solution[J]. In: Hanninen H. High Nitrogen Steel 98. Switzerland: Trans Tech Pub Ltd, 1999:545-549.