Electrochemical Studies on Local Corrosion Behavior Mechanism of Super Ferrite Stainless Steel in Low-temperature Geothermal Water Environment

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Abstract. Super ferrite stainless steel as a new material in heat transfer equipment has applied widely in foreign coastal power plants because of its high strength, low coefficient of thermal expansion, and corrosion resistance. In this paper, stainless steel materials with S44660 super ferrite and 316L were selected as research objects. The corrosion and scaling of S44660 and 316L in model geothermal water (environmental conditions of geothermal water in the central plain of China) were studied by the electrochemical tests, weight loss method. The electrochemical results show that the corrosion resistance of S44660 is better than that of 316L in geothermal water. Weight loss tests and microscopic analysis indicate that S44660 is easier to form scale than 316L.

1. Introduction
In recent years, because of conventional energy crisis, environmental pollution and climate warming, geothermal energy development and utilization have been a bright investment in the new green low-carbon economy following solar and wind power [1-2]. However, there are some technical challenges that seriously restrict the efficient and economical use of geothermal energy. One of the key issues is the local corrosion of metals in geothermal water environment [3-5]. Harsh corrosive environment, such as high salinity and high concentration of Cl-, causes most low-cost metals, such as carbon steel, even 316L stainless steel, corrosion failure during the application sand pose a threat to the safety of the geothermal facilities. The resistant materials such as Titanium alloys, nickel-based alloys, zirconium increase the reliability of geothermal systems, but the high cost limit their applications.

Super ferrite stainless steel as an emerging heat exchanger material, because of its good resistance to pitting corrosion, inter-granular corrosion and reasonable price, has won extensive applications in heat exchangers in foreign coastal power plants. More than 100 facilities at coastal power plants have been using super-ferrite materials in the USA [6]. Since the geothermal environment is similar to the seawater environment (high concentration of Cl- and corrosive), the United States has begun to test the corrosion properties of Super ferrite stainless steel materials and has completed experimental replacements of some materials [7]. At present, the application of super ferrite is still stalled in China. The main reason is lacking comprehensive evaluations of the heat exchanger applications of the material with independent production of super-ferrite stainless steel. Based on the analysis of the traditional testing
technology, this test studies the local corrosion of super-ferrite stainless steel in geothermal water. The impact of the surface environment on the local corrosion process is clarified [8].

In this paper, the test condition is the typical geothermal water environment in central China and the research objects are S44660 super-ferrite stainless steel and 316L stainless steel. The comparative study of corrosion, scaling of product morphology, composition in the model geothermal water, and the difference in the process of electrochemical corrosion of the three materials was conducted. This paper provides certain theoretical and technical recommendations to prevent metal pipelines from corrosion and scale formation in geothermal water.

2. Experimental

2.1 Materials and pretreatment

The S44660 and 316L Stainless Steel, with chemical composition shown in Table 1, were used in this study. The specimens were machined into a size of 10mm×10mm×1mm as working electrode (WE). Copper wire was welded to WE to ensure electrical contact for electrochemical measurements, and then WE was embedded in epoxy resin with exposed working area of 10×10mm². Prior to the tests, the working surface of WE was abraded with silicon carbide paper of decreasing roughness (up to 1200 grit), rinsed with deionized water and degreased with acetone.

The specimens were machined into a size of 50mm×10mm×1mm and 50mm×10mm×5mm. Prior to the tests, the working surface of each specimen was abraded with silicon carbide paper of decreasing roughness (up to 1200 grit), rinsed with deionized water, and degreased with acetone. After that, the specimen was weighed using an electronic balance with a precision of 0.1 mg, and then stored in a desiccator.

The test solution, a simulated geothermal water solution in Table 2, was made up from analytical grade reagents and deionized water. The solution was purged with N₂ (99.99%) for at least 4 h, and then WE was immersed into the solution while N₂ gas purging was maintained at a low flow rate to ensure no oxygen throughout test.

| Table 1. Chemical compositions of test steels (wt.%) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Steel           | C               | Si              | Mn              | Cr              | Mo              | Ni              | S               | P               | N               | Ti+Nb           |
| S44660          | ≤0.03           | ≤1.0            | ≤1.0            | 25.0~28.0       | 3.0~4.0         | 1.0~3.5         | ≤0.04           | ≤0.04           | 6×(C+N)~1.0     |
| 316L            | ≤0.03           | ≤1.0            | ≤2.0            | 16~19           | 1.8~2.5         | 12~16           | ≤0.03           | ≤0.035          | -               | -               |

| Table 2. Composition and concentration of the simulated geothermal water(g/L) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Composition     | NaHCO₃          | Na₂SO₄          | MgCl₂           | KCl             | NaCl            | CaCl₂           | Na₂SiO₃         | pH              |
| Concentration   | 0.336           | 0.0650          | 0.110           | 0.180           | 3.60            | 0.280           | 0.0850          | 6               |

2.2 Electrochemical measurement

A solartron 1287 electrochemical interface/1255B frequency response analyzer was used for electrochemical measurements. A three-electrode electrochemical cell was used with a platinum plate as counter electrode and a saturated calomel electrode (SCE) as a reference electrode. All the potentials in this study were referred to this reference electrode. Before potentiodynamic polarization curve and EIS tests, WE was immersed in the solution for 15-30 minutes to obtain a stable open circuit potential (OCP). EIS was measured at OCP with a sinusoidal potential excitation of 10mV amplitude in the frequency range from 0.01Hz~105Hz. Potentiodynamic polarization curves were carried out in a range of -250mV~500mV with respect to the corrosion potential, and with a scan rate of 0.5 mV/s. The impedance value was fitted with Zview software using an equivalent circuit [9].
2.3 Weight loss test

Weight loss tests were carried out in a 1L beaker to investigate the corrosion rate and corrosion morphology of S44660 and 316L in simulated geothermal water solution. Four specimens were installed in the beaker. After the beaker was sealed, purging N2 was adopted to remove the oxygen for 2h. After the beaker was heated to 30°C, 40°C, 50°C, 60°C, 70°C. All the tests were carried out under static conditions. After each corrosion test the specimens were respectively taken out of the beaker, rinsed with deionized water, dehydrated with alcohol, and dried in the air. Three specimens were respectively descaled in the solution consisting of nitric acid (200ml, density is 1.42g/ml) and deionized water (800ml) at room temperature, and then rinsed with deionized water, dehydrated with alcohol and dried in the air. After that, the specimens were weighed again to determine the weight loss. The corrosion rate was calculated through the following equation:

\[ V_{CR} = \frac{8.76 \times 10^4 \Delta w}{5pt} \]  

(1)

Where \( V_{CR} \) is the corrosion rate, mm/a; \( \Delta w \) is the weight loss, g; \( S \) is the exposed surface area of specimen, g/cm²; \( t \) is the corrosion time, h; 8.76 \( \times \) 10⁴ is the unit conversion constant. The corrosion rate with error bars was averaged from the corrosion rates of the three parallel specimens [10].

3. Results and discussion

3.1 EIS and Polarization analysis

Geothermal fluid includes many corrosive components, and corrosion thus occurs easily in the heat exchanger and the fluid transfer pipeline. Therefore, it is necessary to investigate the corrosion resistance of the material. Metals AC impedance spectroscopy is one of the most efficient and informative methods for corrosion evaluation, which can detect the in-situ and non-destructive relaxation phenomena in a wide frequency range.

The impedance maps of S44660 in different simulated geothermal waters show the semicircular capacitive arc in the fourth quadrant of the complex plane, and just contain one-time characteristic constant. The above indicates that the capacitance of the electric double layer in the equivalent circuit present the "diffusion effect". In addition, the intersection of the semi-circular arc and the real axis in the high-frequency region is closer to the coordinate origin, which indicates that the solution resistance of the simulated hot water at different temperatures is small. The magnitude of these capacitive reactance arc radii reflects the difference in charge transfer resistance.

Fig.1 shows that \( R_s \) decreases with increasing temperature because the kinetic energy of the ions in the solution increases with increasing temperature. The movement of the ions is accelerated; hence, the resistance of the solution decreases, and the corrosion rate of S44660 increases. In addition, with increasing temperature, \( R_p \) decreases, the speed of the ions movement in the solution increases and the corrosion rate of the passivation film is accelerated. For the simulated geothermal water with different temperatures, the value of the charge transfer resistance (\( R_p \)) gradually decreases with increasing temperature. That is to say, the charge transfer resistance changes inversely with the temperature.

There is a large difference in the diameter of the semi-circle of the capacitive reactance arc of 316L in the simulated geothermal water at different temperatures. The movement of the ions is accelerated. Hence, the resistance of the solution decreases and the corrosion rate of 316L increases. In addition, with increasing temperature, \( R_p \) also decreases, the speed of the ions movement in the solution increases, and the corrosion rate of the passivation film is accelerated. The corrosion rate of the S44660 is significantly higher than that of the 316L. Therefore, the simple equivalent circuit of
In order to study the impact of temperature on the corrosion performance of S44660, the polarization curves of S44660 and 316L at 30°C, 40°C, 50°C and 70°C were measured respectively. The polarization curves at different temperature are plotted in Figure 2.

Figure 2 presents the polarization curves of simulated geothermal water in different temperatures. It can be observed that the polarization curve of the anode region of S44660 displayed a platform in the region when the potential is greater than the self-corrosion potential at different temperatures, indicating that the surface of S44660 is blunt at this potential. S44660 electrode dissolution reaction Fe-2e─→Fe²⁺ was inhibited. The difference of the polarization curves of the samples in geothermal water with different temperatures is remarkable, which indicates that the difference in corrosion current density of the S44660 electrode in different temperature is distinguishable. The corrosion current density varies significantly with increasing anode polarization potential. The self-corrosion potential of S44660 decreases with increasing temperature, which indicates that the passivation film of S44660 is broken in the geothermal water. The corrosion rate accelerates continuously. On the whole, corrosion current density increases with increasing temperature. The corrosion rate considerably increases. The corrosion process is rapidly accelerated. The corrosion resistance of the material decreases significantly.

Compared with super-ferrite, 316L has a significantly lower corrosion potential and a lower corrosion current density. There is significant difference in the polarization curves of 316L in simulated geothermal water at different temperatures. For stainless steel, it is mainly due to the formation of an oxide layer on the surface which leads to the formation of the "passivation film". The electrochemical corrosion parameters of simulated geothermal water at different temperatures were calculated by Tafel extrapolation method. With the increase of temperature, the corrosion potential decreases and the...
corrosion current density increases remarkably, which indicates that the corrosion resistance of 316L decreases with increasing temperature. The self-corrosion potential of 316L increases with increasing temperature, and the self-corrosion potential of 316L decreases above 70°C. Compared with the self-corrosion potential of S44660, the self-corrosion potential of 316L is much bigger than that of S44660, which indicates that the corrosion tendency of 316L is much bigger than that of S44660. The self-corrosion current density of 316L increases with increasing temperature. Compared with the self-corrosion current density of S44660, the self-corrosion current density of 316L is much lower than that of and S44660. The corrosion tendency of 316L is great, but the rate of corrosion is low. The corrosion process is rapidly accelerated. The corrosion resistance of the material decreases significantly.

3.2 weight-loss tests and microscopic analysis

![Figure 3. Corrosion rate of S44660 and 316L at different temperature](image)

Figure 3 presents the average corrosion rates of tested steels after immersion corrosion tests in a geothermal water environment. It can be seen that the corrosion rate of S44660 was higher than 316L. This suggests that the corrosion resistance of S44660 cannot be improved by increasing Cr, Ti and Nb content in a geothermal water environment [11].

4. Conclusion

The self-corrosion potential of S44660 and 316L decreases with increasing temperature, and the corrosion tendency of sample increases with increasing temperature. The self-corrosion current density increases with decreasing corrosion potential. Compared with the self-corrosion potential of S44660, the self-corrosion potential of 316L is much higher than that of S44660, which indicates that the corrosion tendency of 316L is much smaller than that of S44660. Compared with the self-corrosion current density of S44660, the self-corrosion current density of 316L is much lower than that of and S44660.

The corrosion resistance of the S44660 and 316L decreases significantly with increasing temperature in geothermal water. The corrosion resistance of S44660 is less than that of 316L in the model geothermal water. The corrosion types of the samples are uniform corrosion and pitting. The pitting resistance of 316L is better than that of S44660. S44660 is more easily to scale than 316L in the model geothermal water; therefore, the scaling resistance of 316L is better than that of super-ferrite. The amount of scaling increases with increasing temperature. 316L is more preferred to be used in the geothermal water than Super-ferrite.

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