

Effect of solution pH, Cl^- concentration and temperature on electrochemical behavior of PH13-8Mo steel in acidic environments

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ABSTRACT

The effect of solution pH, Cl^- concentration and temperature on the electrochemical corrosion behavior of PH13-8Mo steel in acidic solution was investigated by using the electrochemical tests, scanning electron microscopy and X-ray photoelectron spectroscopy. The PH13-8Mo martensitic precipitation hardened stainless steel is in the passivity state when the pH value is above 3.0, below which the anodic polarization curves of the steel are actively dissolved. The corrosion current density gradually decreases with increasing the solution pH and decreasing Cl^- concentration and solution temperature. Pits are initiated on the sample surface in the presence of the Cl^- and gradually developed into uniform corrosion with increasing the Cl^- concentrations. Moreover, the corrosion is more serious with an increase in solution temperature.

1. Introduction

Precipitation hardened stainless steels are usually used in high performance aerospace and atomic energy application, which requires a combination of high strength and excellent corrosion resistance. The high strength of these steels is attributed to their low carbon content and the existence of carbide as well as the precipitates formed during heat treatment^[1-3]. The excellent corrosion resistance of these steels is ascribed to their high chromium content which can form compact passive film. Among them, PH13-8Mo martensitic precipitation hardened stainless steel can develop the lowest yield strength of 1458 MPa after proper heat treatment. Therefore, it is widely applied in the aerospace industry owing to its excellent mechanical properties, welding and molding performances. Previous study on PH13-8Mo steel mainly focused on the relationship between heat treatment, precipitation hardening phase and its mechanical properties^[4-7]. However, few studies have been conducted to investigate the corrosion resistance of the PH13-8Mo steel. Generally, the Cl^- concentration^[8-19] and the solution pH^[20,21] were found to have a remarkable effect on the corro-

sion behavior of stainless steels.

The aim of this work was to investigate the effects of the solution pH, Cl^- concentration and temperature on the electrochemical corrosion behavior of PH13-8Mo steel in a 0.5 mol/L ($\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$) solution by electrochemical tests, including the electrochemical impedance spectroscopy and the polarization curves. The morphology was characterized by scanning electron microscopy (SEM) and the composition of the corrosion product of the steel was measured by X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Sample and electrolyte

The PH13-8Mo stainless steel was supplied by the Central Iron and Steel Research Institute, China. Its chemical composition is given in Table 1. The PH13-8Mo steel was quenched at 950 °C, cooled in air for 1 h and subsequently tempered at 510 °C for 4 h. The final microstructure was composed mainly of martensite as shown in Fig. 1. Fig. 2 shows that the martensite under this condition consists of lath structure containing a very high density of dislocations.

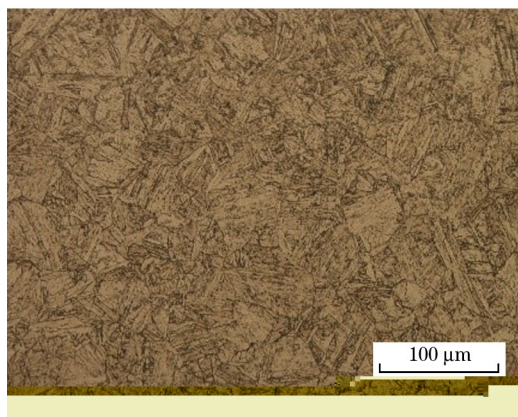
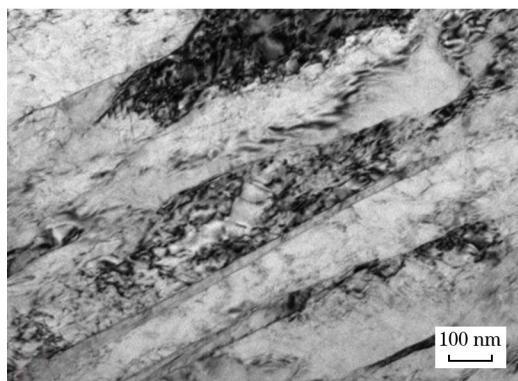
The sample was prepared with dimensions of 10 mm ×

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Table 1

Composition of experimental steel (mass%)

C	Mn	Si	P	S	Cr	Ni	Mo	Fe
≤0.05	≤0.10	≤0.10	≤0.01	≤0.002	12.25–13.25	7.50–8.50	2.00–2.50	Balance

**Fig. 1.** Optical micrograph of PH13-8Mo steel.**Fig. 2.** Transmission electron microscope image of PH13-8Mo steel.

10 mm × 5 mm. One end surface of the sample was soldered to copper wires and sealed with epoxy resin, and a working surface of 1 cm² was left. The working surface was ground using SiC papers up to 1500 grit, cleaned with deionized water and acetone, and then dried.

The test electrolyte was 0.5 mol/L (Na₂SO₄ + H₂SO₄) solution prepared from deionized water^[22,23]. H₂SO₄ was used to adjust the pH value of the solution. By adding NaCl, the Cl⁻ concentration in the solution was adjusted to 1.0, 3.5 and 7.0 wt. %, respectively.

2.2. Electrochemical measurements

A typical three-electrode system was applied. The counter electrode was a platinum plate, and the reference electrode was a saturated calomel electrode (SCE). All of the potentials were tested against the SCE. The electrochemical tests were operated by using an Autolab PGSTAT 302N electrochemical system. Before the electrochemical experiment, the stainless

steel surface was cathodically polarized at -1.3 V *vs.* SCE for 3 min to remove the passive film^[24-27], and then relaxed for 60 min to ensure steady state condition. The polarization curve tests were conducted at a potential scanning rate of 2 mV · s⁻¹. The electrochemical impedance spectroscopy (EIS) test was carried out at open circuit potential (OCP), over the frequency range of 10⁻² Hz to 10⁴ Hz, using a 10 mV sinusoidal potential modulation. The EIS data were analyzed using ZSimpWin software.

3. Results and Discussion

3.1. Effect of solution pH

3.1.1. Morphology of corrosion

Fig. 3 shows the SEM images of the PH13-8Mo steel in 0.5 mol/L (Na₂SO₄ + H₂SO₄) solution with different pH values after 7 d immersion at (25 ± 1) °C in a water bath.

Fig. 3(a, b) shows that the sample surface presents the uniform corrosion morphology. In the pH 0.5 and pH 1.0 solutions, a large number of corrosion products were covered in the sample surface. There are only a small amount of corrosion products absorbed on the sample surface in the pH 2.0 solution (Fig. 3(c)). With the increase of solution pH, fewer corrosion products with clear and smooth surfaces are observed in the pH 3.0 solution than in the pH 0.5, pH 1.0 and pH 2.0 solutions, and no corrosion products are found in the pH 4.0 and pH 5.0 solutions. This is owing to the presence of H⁺, which makes the solution penetrate the passive film, decreases the rate of reaction with Fe, and inhibits the occurrence of pitting corrosion when the concentration of H⁺ in the solution is not too high. The SEM images indicate that activation/passivation occurred on the surface of PH13-8Mo steel under different H⁺ concentrations.

3.1.2. Polarization curve and EIS measurements

Fig. 4 shows the polarization curves of PH13-8Mo steel measured in 0.5 mol/L (Na₂SO₄ + H₂SO₄) solutions at different pH values. It can be seen that the solution pH affects remarkably the electrochemical corrosion behavior of PH13-8Mo stainless steel. The corrosion potential moves to the positive direction and the corrosion current decreases significantly with the increase of pH value. In particular, the cathodic polarization current density decreases obviously. The limiting diffusion current density appears at pH equal

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