Enhancing the Stability of Passive Film on 304 SS by Chemical Modification in Alkaline Phosphate–Molybdate Solutions

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Abstract

The purpose of this work was to enhance the corrosion resistance of the passive film on 304 stainless steel (SS) by chemical modification in alkaline phosphate–molybdate solutions. The 304 SS was passivated in both phosphate and phosphate–molybdate mixed solutions to investigate the effect of molybdate on its corrosion resistance. The experimental results indicated that the passive film showed better corrosion resistance in Cl−-containing solutions after modification in phosphate–molybdate solutions than in phosphate-only solutions. Energy-dispersive spectroscopy analyses revealed that the passive film formed in phosphate–molybdate solutions contained Mo and P after modification, which is the reason for the enhanced corrosion resistance.

Keywords Passive film · 304 SS · Corrosion · Phosphate · Molybdate

Introduction

304 stainless steel (SS) is extensively used as an engineering material due to its superior corrosion resistance, good appearance, and mechanical properties [1]. The passive film formed on 304 SS, with a thickness of several nanometers, plays a major role in protecting it from corrosion [2, 3]. However, 304 SS cannot be used for extended periods of time in marine environments, which are rich in Cl− [4]. Cl− can adsorb onto the surface of the passive film and may penetrate into the film and reach the film/substrate interface, thereby causing stress at the interface and film breakdown [5]. The mechanism of passive film breakdown induced by Cl− is still a matter of debate [6–9], but is believed to be highly dependent on the nature of the materials [10–13]. Regardless of the specific mechanism of passivity breakdown, it is of great importance to develop surface modification methods to inhibit Cl− attack.

Various methods have been developed to enhance the stability of this passive film, including chemical modification [14, 15], electroless plating [16, 17], electroplating [18], diffusion and infiltration technology [19], laser surface modification [20], and ion implantation [21]. Of these, the chemical modification method is favored for its flexibility and minimal consumption of electrical energy. The composition, thickness, and structure of a passive film can be modified by adjusting the chemical conditions of the solution, such as the pH and concentration of inorganic ions. Mo- or P-containing passive films are beneficial to passivity, leading to an increased corrosion potential [22–24]. Phosphate and molybdate have been considered to be beneficial passivators for carbon steel, aluminum alloy, and zinc [25, 26]. However, passivation in molybdate-only solution has resulted in a film with cracks [27]. Phosphate and molybdate have been reported to possibly have a synergistic effect on the passivation process, leading to the formation of a surface film with superior corrosion resistance [28, 29].

Here, we describe our surface modification experiments in alkaline phosphate–molybdate solutions. The corrosion resistances of the resulting passive films were evaluated by electrochemical impedance spectroscopy (EIS), and their compositions were determined by energy-dispersive spectroscopy (EDS).
Experimental

Material

The 304 SS, which was provided by Taiyuan Iron and Steel Co., was cut into plates with a dimension of 10 mm × 10 mm × 2 mm. They were then welded to a copper wire and embedded in epoxy resin, exposing a surface with 1 cm² in area. The prepared samples were abraded with 2000-grit SiC paper, cleaned with distilled water, acetone, and ethanol, and then dried with a hair drier.

Acid Picking

Prior to the passivation tests, we removed the surface oxide layer by immersing the specimens in a solution containing HNO₃ (4%) and HCl (36%) at 40 °C for 5 min and then washing them in a solution containing HNO₃ (7%), H₂SO₄ (9%), and HF (5%), at 25 °C for 1 min (concentration listed in mass fractions). All the solutions were exposed to air.

Passivation of 304 SS

After acid picking, the specimens were immediately placed in the passivation solutions. In this work, two solutions were used to modify the composition of the passive film formed on the 304 SS, as shown in Table 1. Solution A included NaOH, NaNO₂, and Na₃PO₄. Na₂MoO₄ (1%) was added to solution B to investigate the effect of molybdate on the corrosion resistance of the passive film. For comparison, a blank sample was used that had not been subjected to acid picking or passivation processing. Both solutions were exposed to air, and the passivation time lasted for 20–40 min. After the passivation process, the specimens were taken out, cleaned with distilled water, and blow-dried with a hair drier.

Electrochemical Impedance Spectroscopy

EIS measurement was taken at a VersaSTAT 3 electrochemical workstation (Princeton Applied Research, USA). To obtain a stable corrosion potential, after chemical passivation, we immersed the prepared specimen in a 3.5% (mass fraction) NaCl solution for about 20 min. The frequency used in the EIS measurement was set to range from 100 kHz to 10 mHz, with a peak-to-peak amplitude of the potential sinusoidal wave of 20 mV. With nine points for each frequency decade, the total number of data points was 63. The EIS data were fitted using ZSimpWin software.

Scanning Electron Microscopy (SEM) and EDS

SEM and EDS were performed using a Su1510 SEM (Hitachi, Japan) equipped with a model 550i energy-dispersive spectrometer.

Results

Passivation Behavior in Alkaline Phosphate Solution

Figure 1 shows the EIS measurements for the 304 SS after passivation in solution A at various temperatures (90 °C, 100 °C, 110 °C). The Nyquist plots show the variation of impedance with frequency, and the Bode plots illustrate the variation of phase angle with frequency. The data were fitted using ZSimpWin software.

Table 1 Composition of passivation solution and other conditions

| Solution | NaOH (wt%) | NaNO₂ (wt%) | Na₃PO₄ (wt%) | Na₂MoO₄ (wt%) | Temperature (°C) | Immersion time (min) |
|----------|------------|-------------|--------------|---------------|------------------|----------------------|
| A        | 14         | 0.2         | 3            | 0             | 90–110           | 20–40                |
| B        | 14         | 0.2         | 3            | 1             | 40–110           | 30                   |
100 °C, and 110 °C. All the original data are depicted as points, and the corresponding fitting results are shown as lines. For passive metal covered by a layer of oxide film, an electrochemical equivalent circuit (EEC) of $R_s \cdot (Q \cdot R_t)$ can be used to simulate the electrochemical interface [30, 31], where $R_s$ is the solution resistance, $Q$ is the interface capacitance and is the constant phase element (CPE) related to the capacitance of the barrier layer ($n$ is the dispersion coefficient for the CPE), and $R_t$ is the charge transfer resistance, which is equal to the polarization resistance. We note that the most suitable EEC remains a matter of debate. For instance, Hien et al. [32] and Nam et al. [33] used an EEC that has two time constants. However, fitting the EIS data using their EEC generated huge errors in this work; therefore, we used a simple EEC that has been extensively used and reported in Refs. [30, 31].

Table 2 lists all the fitting results, including the fitting errors. All the Nyquist plots shown in Fig. 1a are characterized by an incomplete capacitance arc due to the very high polarization resistance of the electrochemical system. The diameter of the capacitance arc is approximately equal to $R_s$, and it can be seen that the diameter increases as the temperature increases from 90 to 110 °C. In this work, we did not use temperatures higher than 110 °C because a glass electrolytic cell works well only at temperatures less than 110 °C. The Bode plots in Fig. 1b indicate that as the temperature continues to increase, the impedance module values increase and the value of phase angle also increases. All the values of phase angle are negative because the imaginary part of the impedance is negative. The interface capacitance does not vary to a great extent, possibly because the number of adsorbed anions on the film surface alters just slightly. Nahali et al. [34] claimed that PO$_4^{3-}$ can interact with Fe$^{3+}$ and Fe$^{2+}$ to form non-soluble FePO$_4$ and Fe$_3$(PO$_4$)$_2$, respectively, which is beneficial to the passivation process. Table 2 shows that as the temperature elevates, $R_t$ increases accordingly and reaches $1.365 \times 10^6 \, \Omega \text{cm}^2$ at 110 °C, which is ~6 times higher than that of the blank sample. The reason that a high temperature is beneficial for the corrosion resistance of the passive film is possibly due to the increase in the film thickness at high temperature [35].

In the last section, we describe our determination of the optimal condition and further investigate the impact of passivation time on the corrosion resistance of 304 SS. Figure 2 shows the measured EIS data for various passivation times, and Table 3 lists the fitting results obtained using the EEC shown in Fig. 3. As shown in Fig. 2a, the diameter of the capacitance arc increases as the passivation time is prolonged from 20 to 30 min. Further increasing the passivation time from 30 to 40 min has little impact on film resistance. The Bode plots show trends similar to those of

Table 2

| Condition (°C) | $R_s$ (Ω cm$^2$) | $Q$ (Ω$^{-1}$ cm$^{-2}$ s$^{-n}$) | $n$ | $R_t$ (Ω cm$^2$) |
|---------------|-----------------|-------------------------------|----|-----------------|
| Blank         | 3.468 (2.211%)  | 7.774 $\times$ 10$^{-3}$ (1.751%) | 0.8874 (0.400%) | 2.309 $\times$ 10$^5$ (9.708%) |
| 90            | 3.260 (3.321%)  | 5.809 $\times$ 10$^{-5}$ (2.544%) | 0.8951 (0.555%) | 2.650 $\times$ 10$^5$ (12.220%) |
| 100           | 2.833 (3.100%)  | 5.728 $\times$ 10$^{-5}$ (2.289%) | 0.9012 (0.493%) | 3.889 $\times$ 10$^5$ (14.860%) |
| 110           | 4.704 (1.549%)  | 7.626 $\times$ 10$^{-5}$ (1.229%) | 0.8922 (0.294%) | 1.365 $\times$ 10$^6$ (35.240%) |

Fitting errors are listed in parentheses.
the Nyquist plots. These results indicate that the formation of passive film in passivation solution A reached a stable state after 30 min. The interface capacitance $Q$ decreased along with the passivation time, which demonstrates that a well-passivated film inhibits the adsorption of Cl$^-$.

### Passivation Behavior in Alkaline Phosphate–Molybdate Solution

To investigate the effect of molybdate on passivation, a 304 SS specimen was immersed in solution B at various temperatures, after which the corrosion resistance was measured in the NaCl solution (Fig. 4). The passivation time for all experiments was 30 min. As shown in Fig. 4a, the capacitance arcs first increase and then decrease as the temperature increases from 40 to 110 °C. The Bode plots shown in Fig. 4b exhibit similar trends. The fitting results shown in Table 4 reveal that $R_s$ first increases and then decreases, and $Q$ shows the reverse trend. The decreased corrosion resistance at 110 °C is possibly because the thick film that formed at high temperature may have had more defects, which degraded the corrosion resistance [36].

### Surface Morphology and Composition of the Passive Film

The morphology and composition of the passive film were determined using an SEM equipped with EDS, the results of which are shown in Figs. 5 and 6. The untreated 304 SS had a uniform surface with some scratches due to abrading that can be clearly seen. Figure 5b shows the EDS results of the region highlighted by the red box in Fig. 5a. The passive film contains O (2.009%), P (0.088%), S (0.015%), Cr (19.165%), Fe (70.833%), and Ni (7.755%). Figure 5c, d shows the element mapping results for Fe and P, respectively. We can see that P was distributed uniformly on the surface, and that the passive film is an oxide layer successfully modified by P. P may play a major role in enhancing the stability of the passive film.

Figure 6c–e presents the element mapping results of Fe, P, and Mo. After passivation in solution B, the P content increased by a factor of five relative to that of the untreated sample (Fig. 6b). The passive film contains O (0.017%), P (0.478%), S (0.001%), Cr (18.814%), Fe (71.962%), and Ni (8.568%). In addition, Mo (0.161%) is detected on the
Table 4  Fitted electrochemical parameters of passivated 304 SS in 3.5% NaCl solution (304 SS specimens were passivated in phosphate–molybdate solution at different temperatures)

| Condition (°C) | $R_s$ (Ω cm$^2$) | $Q$ (Ω$^{-1}$ cm$^{-2}$ s$^{-n}$) | $n$ | $R_t$ (Ω cm$^2$) |
|----------------|------------------|-------------------------------|-----|------------------|
| Blank          | 3.468 (2.211%)   | 7.774×10$^{-5}$ (1.751%)     | 0.8874 (0.400%) | 2.309×10$^5$ (9.708%) |
| 40             | 3.661 (1.686%)   | 6.556×10$^{-5}$ (1.299%)     | 0.9026 (0.294%) | 5.675×10$^5$ (13.410%) |
| 60             | 3.401 (1.970%)   | 5.759×10$^{-5}$ (1.573%)     | 0.9480 (0.344%) | 6.092×10$^5$ (13.770%) |
| 80             | 3.366 (2.044%)   | 4.457×10$^{-5}$ (1.561%)     | 0.9485 (0.332%) | 1.268×10$^6$ (21.470%) |
| 110            | 3.336 (2.126%)   | 5.896×10$^{-5}$ (1.581%)     | 0.9026 (0.350%) | 8.944×10$^5$ (22.760%) |

Fitting errors are listed in parentheses.
surface, which indicates that the passive film is modified by Mo. The effect of Mo on pitting corrosion has been well documented, but the mechanism remains a matter of debate. The role of Mo in enhancing the pitting potential is possibly based on one of the following reasons:

1. Mo-containing alloys resist pitting. This effect is likely provided by Mo$^{6+}$ locally enriched on the film surface [24, 37];

2. Mo slows the dissolution kinetics after the initiation of pitting [38].

Details of this mechanism were not determined or confirmed in this work because the chemical modification of the passive film that forms on 304 SS is at the nano- or atomic level. To clarify these changes at atomic level, advantage characterization techniques and atomic modeling are favorable. In future work, we may use a spherical aberration correction in a transmission electron microscope to observe the structure and composition of the passive film at very high resolution.

Conclusions

1. The corrosion resistance of the passive film was enhanced after passivation in alkaline phosphate solutions, as compared to that of the blank sample. P was detected and found to be uniformly distributed on the film surface, which is beneficial to passivity.

2. The solution temperature and passivation time of the alkaline phosphate solutions were found to have a significant effect on the corrosion resistance of passive film, whereby a higher temperature leads to a high-quality film. The best passivation time was determined to be ~ 30 min.

3. The addition of molybdate to the alkaline phosphate solution further enhanced the corrosion resistance of the passive film, as confirmed by EIS analysis.

4. EDS results indicated the detection of Mo and P in the passive film after passivation in alkaline phosphate–molybdate solutions. These results indicate that Mo is beneficial to the stability of the passive film.

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