Short Communication

Study on Passivation Treatment of 304 Steel and its Corrosion Resistance in Simulated Concrete Pore Solution

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304 steel as construction material is passivated from nitric acid and the mixed solution containing nitric acid and potassium dichromate. The surface morphology, structure, composition, roughness and corrosion resistance of 304 steel and passivated 304 steel in simulated concrete pore solution is studied. The passivation of 304 steel is accompanied by the formation and dissolution of passivation film. The passivation film is composed of Fe_3O_4, FeO and Cr_2O_3. Compared with the 304 steel, the content of chromium in the passivation film increases obviously, but the content of iron decreases. The 304 steel after passivation treatment has compact surface with small roughness. Moreover, the 304 steel passivated from the mixed solution of nitric acid and potassium dichromate has the most positive corrosion potential and the smallest corrosion current density. After 8 days of immersion in simulated concrete pore solution, the passivation film obtained from nitric acid and potassium dichromate still has a corrosion current density of 13.27 μAcm^{-2}, which is only 30% of that of 304 steel.

Keywords: 304 steel; Construction material; Passivation film; Corrosion resistance; Simulated concrete pore solution;

1. INTRODUCTION

Steel is a kind of iron based alloy with excellent and comprehensive performance. Due to its high chemical stability and optimal mechanical performance, steel is widely used in construction field, mechanical equipment, automobile, aerospace and so on [1-4]. Especially, a large number of steel materials are used in construction field as pipe, holder, square tube, etc in the concrete environment. General speaking, steel can be divided into martensitic steel, ferrite steel and austenitic steel. In addition, according to the chemical composition, steel can also be divided into chromium steel, chromium and nickel steel and so on. As a kind of chromium and nickel steel, 304 steel is commonly used in construction field due to its many advantages [5-9]. The corrosion resistance of 304 steel is mainly from the addition of chromium and nickel alloy elements, which will be oxidized in the air to

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generate oxidation film and isolate the corrosion medium. However, the oxide film formed on the surface of steel under natural conditions is loose, uneven and very thin, so the protection performance is poor. If the steel is exposed to the corrosive medium for a long time, due to a large number of defects on the surface of loose oxide film, the corrosion resistance will be reduced obviously.

There are many ways that can effectively improve the corrosion resistance of steel. At present, the commonly used methods reported in literature include electrodeposition, chemical deposition, passivation and corrosion inhibitor addition [10-15]. Among them, steel passivation is a very effective surface treatment technology to improve the corrosion resistance of steel. According to relevant literature, passivation can effectively improve the corrosion resistance of steel mainly due to three aspects. Firstly, after passivation, the corrosion potential of steel moves positively, which weakens the corrosion tendency. Secondly, steel passivation can eliminate the potential active points on the surface of steel to weaken local corrosion. Finally, the passivation of steel helps to dissolve the oxide impurities on the surface of steel. At present, high concentration of nitric acid is often used to passivate steel to improve its corrosion resistance [16-18]. However, high concentrations of nitric acid can be hazardous and wasteful. It has been found that steel can be passivated from a mixed solution with nitric acid and metal salt at a lower concentration of nitric acid. In this paper, 304 steel is passivated from the solution with a mixture of nitric acid and a small amount of potassium dichromate to greatly improve the corrosion resistance of 304 steel as construction material in simulated concrete pore solution. The direct relationship among the corrosion resistance, the composition and the structure of passivation film is revealed.

2. EXPERIMENTAL

2.1 Chemical agents and technological parameters

The composition and technological parameters of passivation solutions for 304 steel are presented in Table 1 below.

Table 1. Composition and technological parameters of passivation solutions for 304 steel

Composition and condition	Nitric acid passivation	Nitric acid and potassium dichromate passivation
68% HNO_3	400 ml/L	200 ml/L
$K_2Cr_2O_7$	-	30 g/L
Temperature	50 ℃	50 ℃
Time	30 min	30 min

The 304 steel plate (3 cm×3 cm×0.1 cm) is used as the substrate. Pretreatment is needed before the passivation treatment. Firstly, the 304 steel plate is polished and immersed into the alkali solution (30 g/L NaOH, 50 ℃, 10 min) and acid liquid (10% hydrochloric acid, 25 ℃, 3 min) respectively to get rid of oils and rusts. Secondly, two cleaned 304 steel plates are immersed into two

kinds of passivation solution respectively to do the passivation treatment for 30 min at 50 °C. The specific information associated with two kinds of passivation solution is listed in Table 1. After the passivation is finished, the passivated 304 steel is cleaned and dried.

2.2 Performance testing

The surface morphology of the sample is observed by Olympus BX53M metalloscope and the composition of passivation film is analyzed by Skyray EDX3000. Moreover, Smartlab X-ray diffraction is used to characterize the structure of samples from 30° to 80° at the scanning rate of 3°/s. The roughness of passivation film is tested by SJ5700 surface profiler in the range of 3000 μm at 10 μm/s scanning rate and 5 mg applied force. Finally, the corrosion resistance of samples immersed in simulated concrete pore solution (saturated $Ca(OH)_2$, 6 g/L NaOH and 3 g/L NaCl) for different times at room temperature is evaluated by CHI660E electrochemical station based on potentiodynamic polarization curve at the scan rate of 1 mV/s. Meanwhile, the sample with surface area (1 cm×1 cm) is as the working electrode and the pure platinum (3 cm×3 cm) is as the counter electrode. The saturated calomel electrode is used as the reference electrode.
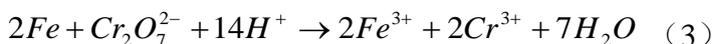
3. RESULTS AND DISCUSSION

3.1 Surface morphology and structure of 304 steel and passivated 304 steel
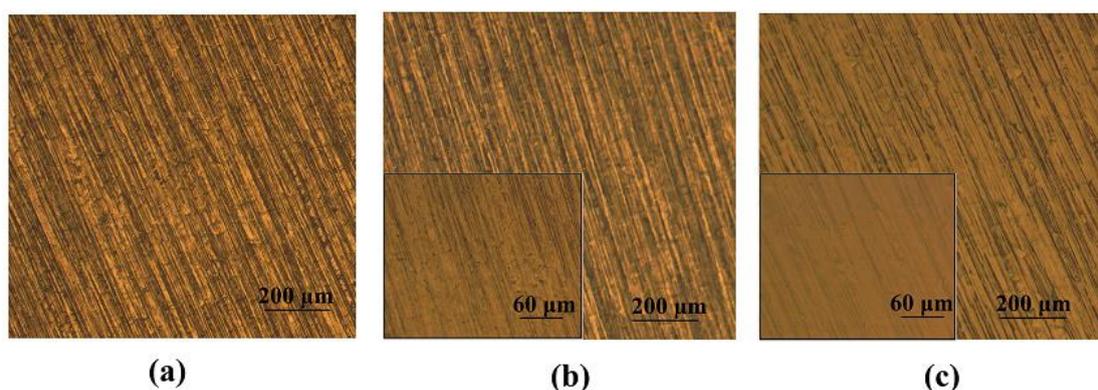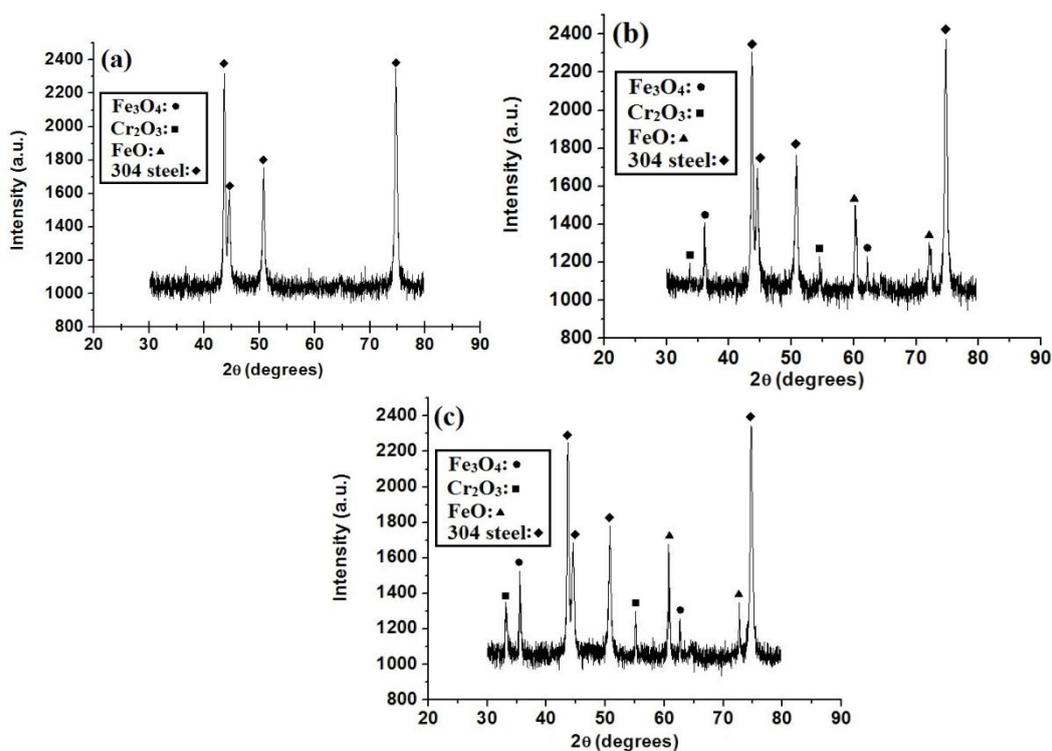

Figure 1. Surface morphology of 304 steel and passivated 304 steel: (a) 304 steel; (b) 304 steel passivated by nitric acid; (c) 304 steel passivated by nitric acid and potassium dichromate;

Figure 1 shows the surface morphology of 304 steel and passivated 304 steel. It can be found from Figure 1(a) that 304 steel has a small amount of fine scratches on its surface, which may be caused by polishing. In addition, there are some uneven areas on the surface of 304 steel. Figure 1(b) shows the surface morphology of 304 steel after passivation by nitric acid. It can be found that passivation film uniformly covers the surface of 304 steel, with shallower scratches. According to the Figure 1(c), the surface of 304 steel after passivation by a mixed solution of nitric acid and potassium dichromate has the fewest scratches. It is found that the passivation film mainly consists of iron oxide and chromium oxide, which can uniformly cover the surface of 304 steel to improve the compactness

and corrosion resistance [19-21]. The detailed information about the passivation film forming mechanism can be explained in the equations below [22-23].

$$HNO_3 \rightarrow O + HNO_2 \qquad （1）$$

$$HNO_3 \rightarrow O + NO_2^- + H^+ \qquad （2）$$

$$2Fe + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Fe^{3+} + 2Cr^{3+} + 7H_2O \qquad （3）$$

According to the equations above, nitric acid has a strong oxidation which can oxidize ferrous ions and atomic oxygen in the passivation liquid to be absorbed on the surface of steel. The oxygen can gain electron while metal is easy to lose electron. Therefore, the oxygen absorbs electron on metal surface to generate a series of metal oxides, thus forming compact passivation film on steel surface. In the mixed solution of nitric acid and potassium dichromate, the potassium dichromate can continue to react with iron to form chromium trivalent, which improves the chromium content in the passivation film. The passivation film covering the surface of the substrate is not constant, and the outer layer of the passivation film is easy to be dissolved in the acid passivation solution. It is found that he passivation film is growing and thickening under the action of oxygen adsorption. Only when the growth rate of the passivation film is greater than the dissolution rate, it is possible to effectively obtain uniform and compact passivation film. It is generally believed that under acidic conditions, the passivation film is mainly formed by the combination of metal oxides and water molecules adsorbed on the surface. However, under the alkaline conditions, the passivation film is mainly composed of metal hydroxide.
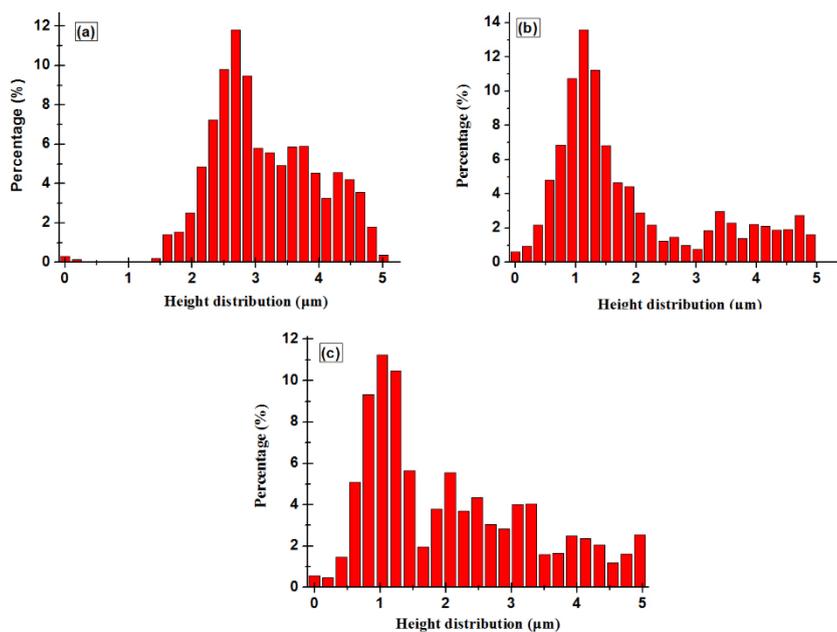

Figure 2. XRD patterns of 304 steel and passivated 304 steel: (a) 304 steel; (b) 304 steel passivated by nitric acid; (c) 304 steel passivated by nitric acid and potassium dichromate; The angle is from 30° to 80° at the scan rate of 3°/s.

The X-ray diffraction is used to characterize the structure of 304 steel and passivation films. As can be seen in Figure 2(a), the typical diffraction peaks of 304 steel can be observed at the position of $2\theta=43.8°$, $2\theta=44.2°$, $2\theta=50.8°$ and $2\theta=74.6°$ respectively. The XRD pattern of passivated 304 steel from nitric acid is different from that of 304 steel. Except for the diffraction peaks of 304 steel substrate, there are some small diffraction peaks can be observed which indicate the Fe_3O_4, Cr_2O_3 and FeO. It is verified that the passivation film on 304 steel obtained from nitric acid solution is mainly composed of iron oxide and chromium oxide [24]. For example, Ranganath prepares a kind of passivation film composed of FeO and Cr_2O_3 [25]. Barroux uses XPS to study the chemical composition of passivated steel which is similar to the result in the paper [26]. Moreover, regarding to Figure 2(c), the 304 steel passivated by nitric acid and potassium dichromate possesses stronger diffraction peak of iron oxide and chromium oxide than that of passivation film prepared by nitric acid. The main reason is that in the mixed solution of nitric acid and potassium dichromate, the potassium dichromate can continue to react with iron to produce chromium and iron trivalent, which is conducive to improving the content of metal oxides in the passivation film.

3.2 Roughness and composition of passivation film

Figure 3 shows the height distribution on the surface of 304 steel and passivated 304 steel. It can be seen from Figure 3(a) that the height fluctuation on the surface of 304 steel is mainly attributed to the polishing and pickling processes in the pretreatment.
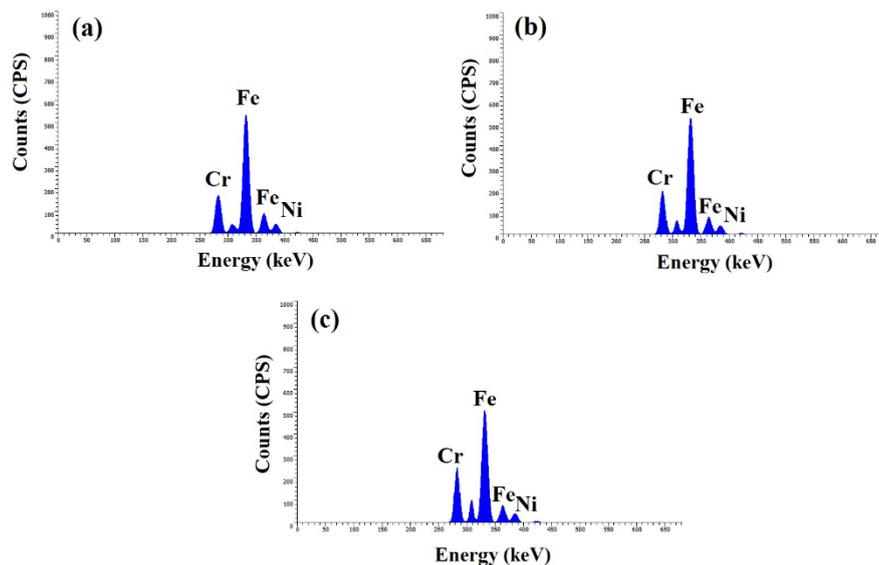

Figure 3. The height distribution on the surface of 304 steel and passivated 304 steel: (a) 304 steel; (b) 304 steel passivated by nitric acid; (c) 304 steel passivated by nitric acid and potassium dichromate; The scan length is 3000 μm at the scan rate of 10 μm/s and 5 mg applied force.
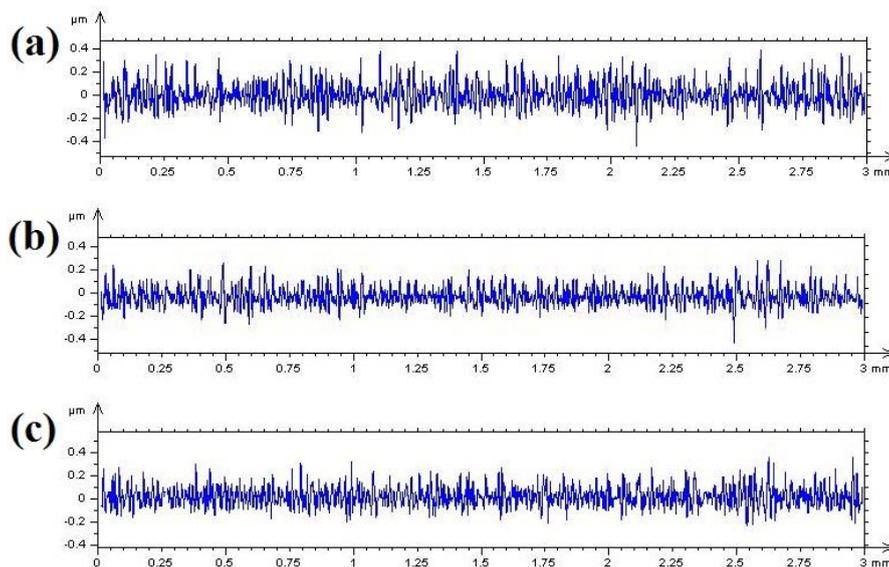
Figure 4. The roughness of 304 steel and passivated 304 steel; (a) 304 steel: (b) 304 steel passivated by nitric acid; (c) 304 steel passivated by nitric acid and potassium dichromate; $R_a \approx 0.282$ μm; $R_b \approx 0.246$ μm; $R_c \approx 0.219$ μm; The scan length is 3000 μm at the scan rate of 10 μm/s and 5 mg applied force.

After nitric acid passivation treatment, the height fluctuation of 304 steel surface tends to decrease. The main reason is that the metal oxide produced in the passivaton process of nitric acid uniformly covers on the surface of 304 steel, which improves the compactness to a certain extent. The surface height fluctuation of 304 steel passivated by nitric acid and potassium dichromate is the least. The passivation film obtained from nitric acid and potassium dichromate solution consists of more Fe_3O_4, FeO and Cr_2O_3 which are beneficial to cover the scratches and improve the compactness.

The roughness of samples is tested by surface profiler and shown in Figure 4. It can be seen that the roughness of 304 steel is about 0.282 μm due to some scratches on the surface. After the passivation treatment of nitric acid, the roughness of 304 steel decreases slightly to approximate 0.246 μm. The roughness of 304 steel passivated from the mixed solution with nitric acid and potassium dichromate is the smallest which is about 0.219 μm. After passivation treatment, the surface roughness of 304 steel decreases slightly. This is mainly because the metal oxides generated in the passivation process uniformly cover the surface of 304 steel, which improves the surface compactness to a certain extent. It is reported that there is a certain relationship between the roughness and corrosion resistance of materials [27-30].

Figure 5. EDX spectrum of 304 steel and passivated 304 steel: (a) 304 steel; (b) 304 steel passivated by nitric acid; (c) 304 steel passivated by nitric acid and potassium dichromate; The voltage is 40 kV;

Table 2. Main composition of 304 steel and passivated 304 steel: (a) 304 steel; (b) 304 steel passivated by nitric acid; (c) 304 steel passivated by nitric acid and potassium dichromate;

Samples	Fe (%)	Cr (%)	Ni (%)
a	71.4	18.4	10.2
b	69.2	21.1	9.7
c	64.8	26.1	9.1

According to the XRD patterns, except for the main diffraction peak of 304 steel substrate, there are many diffraction peaks of Fe_3O_4, FeO and Cr_2O_3 could be observed on the XRD pattern of passivation film. Consequently, the EDX spectrum is used to check the main elements distribution on the surface of samples.

As can be seen from Figure 5 and Table 2, the main elements distribution on the 304 steel is Fe, Cr and Ni. After the passivation treatment, the iron element and nickel element both decrease slightly while the chromium element increases obviously. The 304 steel passivated by nitric acid and potassium dichromate has the highest content of chromium. The chromium content in passivation film mainly originates from the chromium oxide and potassium dichromate which is beneficial to improve the corrosion resistance [31-32].

3.3 Corrosion resistance of 304 steel and passivated 304 steel

The potentiodynamic polarization curves of 304 steel and passivated 304 steel in simulated concrete pore solution with different times are tested by electrochemical station. The corrosion potential and corrosion current density are calculated and listed in Table 3. According to the date, the corrosion potential and corrosion current density of 304 steel with immersion 0 day is about -0.57 V

and 11.87 μAcm^{-2} respectively. The 304 steel after passivation treatment shows more positive corrosion potential and smaller corrosion current density than that of 304 steel. Especially, the 304 steel passivated by nitric acid and potassium dichromate has the most positive corrosion potential and the smallest corrosion current density due to the chromium and chromium oxides which are reported that can extremely increase the corrosion resistance of materials [33-35]. With the increase of immersion times, the corrosion potential of 304 steel and passivated 304 steel all shifts slightly to negative position due to the corrosion products generated on the surface. Moreover, the corrosion current density of samples all increases with the increase of immersion times. However, when the immersion time is more than 4 days, the increasing rate of corrosion current density decreases gradually.

immersion time 0 d

immersion time 2 d

immersion time 4 d
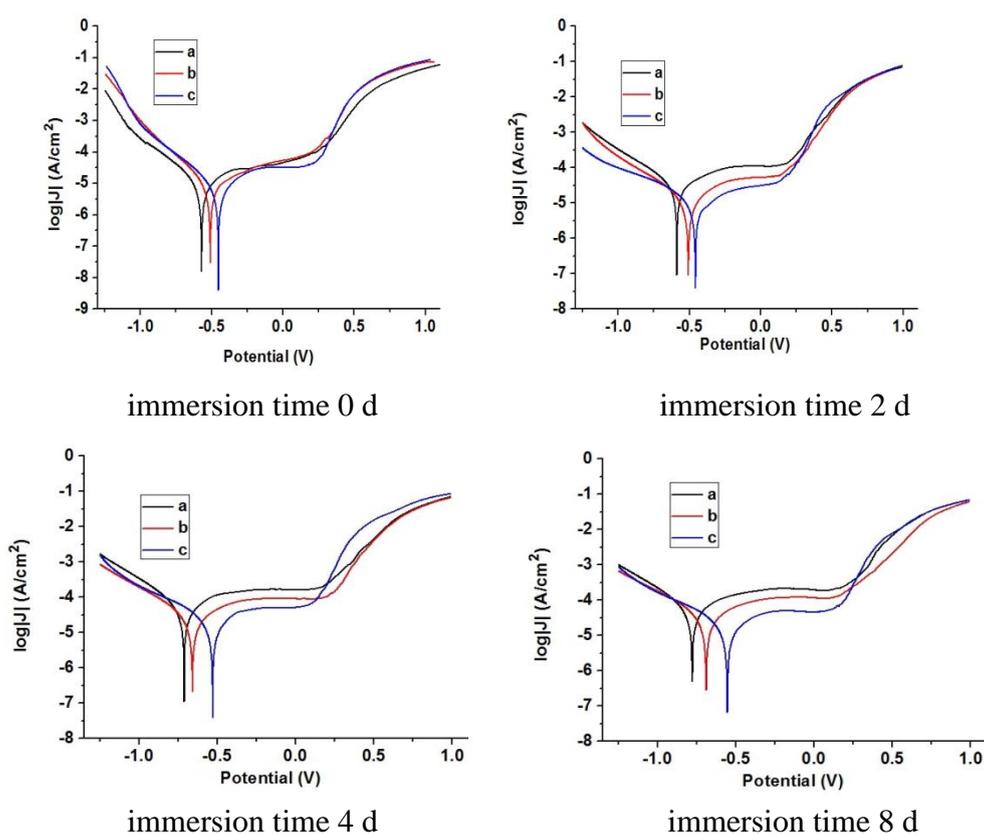
immersion time 8 d

Figure 6. Potentiodynamic polarization curves of 304 steel and passivated 304 steel in simulated concrete solution with different immersion time (0 d, 2 d, 4 d and 8 d): (a) 304 steel; (b) 304 steel passivated by nitric acid; (c) 304 steel passivated by nitric acid and potassium dichromate;

The corrosion current density of the sample immersed for 8 days is similar to that of the sample immersed for 4 days. At the initial stage of immersion, pore erosion occurred at the surface defect of the sample. The corrosive medium enters the hole and contacts the substrate, making the corrosion current density drop sharply. With the increase of immersion time, a large number of corrosion products covered the surface of the sample, which hinders the corrosion process to a certain extent. Therefore, with the increase of immersion time, the corrosion current density of the sample gradually

tends to be stable. Passivation film is mainly composed of iron and chromium oxide, especially chromium oxide has good corrosion resistance, and the corrosion products are very compact [36-37]. After 8 days of immersion, the passivation film obtained from nitric acid and potassium dichromate still has a corrosion current density of 13.27 μAcm^{-2}, which is only 30% of that of 304 steel.

Table 3. E_{corr} and J_{corr} of 304 steel and passivated 304 steel in simulated concrete solution with different immersion time (0 d, 2 d, 4 d and 8 d): (a) 304 steel; (b) 304 steel passivated by nitric acid; (c) 304 steel passivated by nitric acid and potassium dichromate;

Samples	Immersion 0 d		Immersion 2 d		Immersion 4 d		Immersion 8 d	
	$E_{corr}/$ V	$J_{corr}/$ μAcm^{-2}	$E_{corr}/$ V	$J_{corr}/$ μAcm^{-2}	$E_{corr}/$ V	$J_{corr}/$ μAcm^{-2}	$E_{corr}/$ V	$J_{corr}/$ μAcm^{-2}
a	-0.57	11.87	-0.59	24.75	-0.71	41.35	-0.78	45.38
b	-0.50	6.92	-0.52	10.38	-0.66	25.68	-0.69	25.98
c	-0.44	4.96	-0.46	7.83	-0.53	13.08	-0.55	13.27

4. CONCLUSIONS

In this paper, 304 steel used for construction is passivated with nitric acid and mixed solution containing potassium dichromate and nitric acid respectively, to greatly improve the corrosion resistance of 304 steel. It is found that the passivation process of steel is accompanied by the formation and dissolution of passivation film. Only when the formation rate of passivation film is greater than the dissolution rate, the passivation film will grow and thicken. Compared with 304 steel, the content of chromium in the passivation film is increased, while the content of iron is slightly reduced. The passivation film is mainly composed of iron oxide and chromium oxide. The 304 steel passivated by nitric acid and potassium dichromate has the most positive corrosion potential and the smallest corrosion current density.

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