

Effect of Chemical Passivation Treatment and Flow on the Corrosion of 304 Stainless Steel in Hydrochloric Acid Solution

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Effects of passive film quality by chemical passivation and solution flow on the corrosion behavior of 304 stainless steel in HCl solution were investigated using a coloration indicator, and by corrosion weight loss, electrochemical polarization and element dissolution measurements. A high redness degree suggests a low passive-film integrity for 304 stainless steel following air exposure, while the minimum redness degree for the samples after chemical passivation suggests a high passive-film integrity. In the static condition, samples subjected to air exposure exhibited a high corrosion rate and preferential dissolution of Fe. Chemical passivation inhibited the corrosion rate due to the intrinsically high structural integrity of the passive film and high concentrations of Cr-rich oxides and hydroxide. Solution flow accelerated corrosion by promoting both the anodic dissolution reaction and the cathodic reaction. Solution flow also altered the preferential dissolution to fast uniform dissolution of metal elements.

Keywords : *stainless steel, chemical passivation treatment, flow, corrosion, metal element dissolution*

1. Introduction

Stainless steels are materials frequently used in overflowing facilities in petrochemical industry and power plants. In flowing acceleration corrosion environment, stainless steels are considered as good choice of replacement of carbon steel due to the intrinsic high corrosion resistance. However, solution flow still causes corrosion of stainless steel. In multiphase flowing environment, corrosion-erosion damages the surface of stainless steel¹⁻⁴. Even in one-phase flowing condition, the acceleration of pitting by solution flowing was also been reported⁵. Therefore, the corrosion of stainless steel in flowing environment arouses many researchers' interest. Many researchers have studied the flow corrosion of stainless in salt and marine solution, but rare studies have been reported in the acid solution.

Excessive dissolution of metal elements into solution could impose a risk to environment and human health. Attentions have been received for dissolution of stainless steel in acid food solution and body fluids^{6,7}. It has been recognized that corrosion behavior of stainless steel directly influence the dissolution of metal elements⁶. Many factors that involve the corrosion properties, such as surface roughness, temperature and solution concentration

have been examined in acid food solution. However, the metal dissolution under flowing environment has not yet been studied.

In the present paper, the corrosion behavior and metals dissolution of 304 stainless steel was studied in flowing hydrochloric solution. The hydrochloric acid solution is one typical industrial solution. Many published literatures have reported the corrosion of stainless steel in hydrochloric solution⁸⁻¹⁰; such experimental data can be utilized to extensively realize the corrosion of stainless steel in flowing solution. Moreover, various processes could results in different quality of surface passive film and then effect on corrosion resistance. Therefore the role of passive film quality and solution flowing during the corrosion of 304 stainless steel has been our focus. The passive film quality was firstly evaluated by X-ray photoelectron spectroscopy (XPS) and color indicator. The corrosion behavior was examined by immersion test, electrochemical polarization. And also the dissolution of metals was discussed.

2. Experimental procedure

A commercial AISI 304 stainless steel plate was used. The plate was cut into pieces with size of $\phi 10$ mm \times 3 mm. The samples were ground up to 1200 grit size using SiC paper. Passivation treatment was then conducted by air exposure and chemical passivation. Chemical passi-

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vation was carried out by immersing the samples in 20 vol.% HNO₃ solution at 45 °C for 30 min.

2.1 Passive film inspection

Quality of passive film was evaluated through two procedures: the coloration reaction by color-change indicator and subsequent color measurement by a colorimeter. The phenanthroline solution, which was composed of 0.1 g/L C₁₂H₈N₂·H₂O, 1.954 g/L to 0.109 g/L C₆H₈O₇·H₂O and 0.206 g/L to 2.735 g/L of C₆H₅O₇Na₃·H₂O, was employed as the indicator. A piece of white test paper saturated with the solution was attached on the samples for coloration reaction. Fig. 1 shows the schematic of the coloration reaction that occurred on the surface of stainless steel. Once the indicator reacted with stainless steel, ferrous ions released from the matrix through the defects or porosity of passive film. The phenanthroline solution showed good complexation ability with ferrous to form deep red coloured ferriin, whereas the passive film can inhibit the release of Fe ions and retard the reaction. The quality of passive films was indirectly characterised by the redness degree of the ferriin¹¹). It is noted that the ferriin indicator has been used extensively for several years in solution titration analysis of iron¹²), but no research has been reported on the application of passive film inspection before. After 3 min of coloration reaction, the redness degree of produced ferriin was evaluated by colour measurement. A colour reader (Konica Minolta, CR-10) was used to measure the redness in the CIE Lab space.

XPS measurement was carried out using an XPS spectrometer (Thermo ESCALAB 250Xi) without any sputtering technique. The X-ray source employed was a monochromator Al-K_α (1486.6 eV, 15 kV, 14.9 mA). The spectrometer was operated with constant pass energy of 20 eV.

2.2 Immersion corrosion and element dissolution measurement

300 ml of 0.36 M HCl solution for each specimen was employed in immersion corrosion. A stirring hot plate was used to control the solution at room temperature and 50

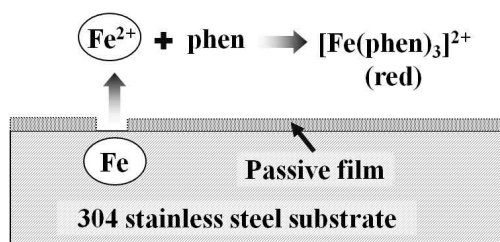


Fig. 1. Schematic of coloration reaction during examination on the passive film integrity by color-change indicator.

°C in water bath. Since this paper only compared two conditions (the flowing and static) on the corrosion, a rotator stirring rate of 700 r/min was employed for the flowing condition. The flowing velocity around the rotator calculated about 2.4 m/s. However, the flow velocity on the samples surface is much lower than the calculated velocity because the distance from the string is 50 mm. Weight variation was measured by using electronic balances with accurate to 0.1 mg (Sartorius, BS 124S). The corrosion morphologies of the samples after corrosion were analysed by SEM (JSM5600-LV). The concentration of Fe, Ni, Cr in the solution after corrosion was analysed using SOLAN 969 Atomic Absorption Spectrophotometer, and the dissolution amounts per surface area of specimens were calculated, respectively.

2.3 Electrochemical test

Electrochemical measurements were performed in 0.36 M HCl solution with a conventional three-electrode cell, and a saturated calomel reference electrode (SCE) and a Pt plate for a counter electrode were used. The exposed area of the samples that made contact with the NaCl solution was a circle with a diameter of 10 mm. The potentiodynamic polarisation was scanned from -0.6 V and ended at 0.1 A·cm⁻² with a scan rate of 0.5 mV/s. Before potential scanning, initial delaying of more than 20 min was carried out to achieve a stable open potential.

3. Results and discussion

3.1 Passive film analyses

Fig. 2 shows the XPS spectra of Cr 2p_{3/2} and Fe 2p_{3/2} detected for passive films on 304 stainless steel after 1 h air exposure and chemical passivation treatment. The

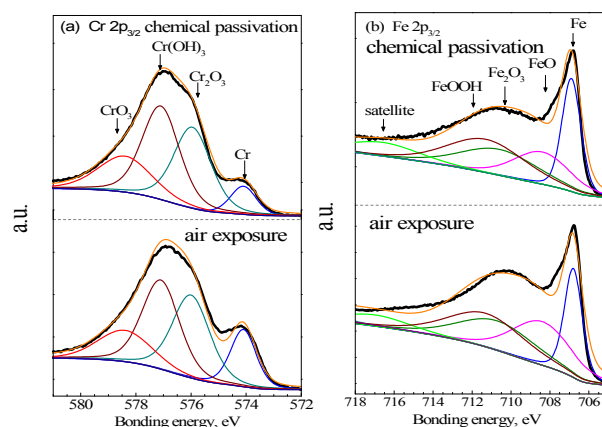


Fig. 2. XPS spectra for passive films on 304 stainless steels after 1 h air exposure and chemical passivation in HNO₃ solution: (a) Cr 2p_{3/2}, (b) Fe 2p_{3/2}.

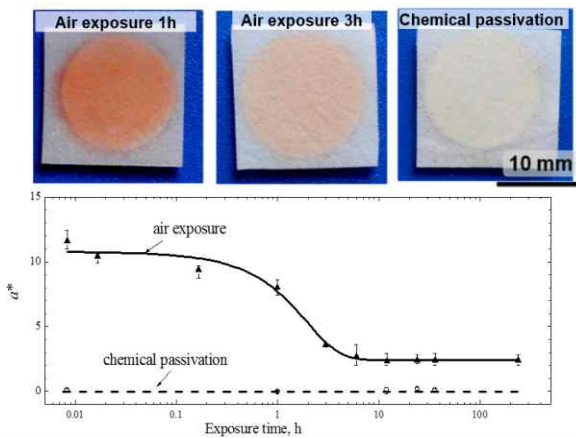


Fig. 3. Optical photograph and the measured redness degree during coloration reaction of indicator with 304 stainless steel after air exposure and chemical passivation in HNO_3 solution.

spectra of Cr $2p_{3/2}$ for the passive films show a broad distinct peak that can be attributed to the presence of Cr^{3+} oxides [$\text{Cr}^{3+}(\text{ox})$ 576 eV], Cr^{3+} hydroxides [$\text{Cr}^{3+}(\text{hyd})$ 577.3 eV] and Cr^{6+} oxides [$\text{Cr}^{6+}(\text{ox})$ 578.4 eV], with a small shoulder-related Cr metal [$\text{Cr}(\text{met})$ 574.1 eV]. The Fe $2p_{3/2}$ ionizations reveal the presence of metallic Fe [$\text{Fe}(\text{met})$ 706.8 eV], Fe^{2+} oxides [$\text{Fe}^{2+}(\text{ox})$ 708.6 eV], Fe^{3+} oxides [$\text{Fe}^{3+}(\text{ox})$ 710.6 eV] and hydroxides [$\text{Fe}^{3+}(\text{hyd})$ 711.8 eV]. Based on the XPS spectra, the ratio of $\{[\text{Cr}_{\text{ox}}]+[\text{Cr}_{\text{hyd}}]\}/\{[\text{Fe}_{\text{ox}}]+[\text{Fe}_{\text{hyd}}]\}$ was calculated. It was found that the ratio value is 0.5 in the samples subject to air exposure, while close to 1.8 for the samples subjected to chemical passivation, respectively. This result suggests the Cr-rich oxide and hydroxide of the high content form in the passive film after the chemical passivation. Fig. 3 shows the optical photograph and the measured redness degree during coloration reaction of indicator with 304 stainless steel. The optical graphs reveal the red-colored circles in the samples exposed to air for 1 and 3 h. The intensity of redness is higher in the samples exposed to air for 1 h than in those exposed to air for 3 h. However, the color of the test paper is still white on the samples subjected to chemical passivation. Correspondently, the measured a^* value was used to characterize the redness degree. Significant differences between the samples subjected to air exposure and chemical passivation are observed. The highest a^* value corresponds to the sample exposed to air for 0 h. The inspected a^* values decrease as the thin passive films grow during air exposure. The measured a^* values in the samples exposed to air for more than 3 h are close to 2, indicating that more passive films have formed. Compared with the samples exposed to air, the samples subjected to chemical passivation have a^* val-

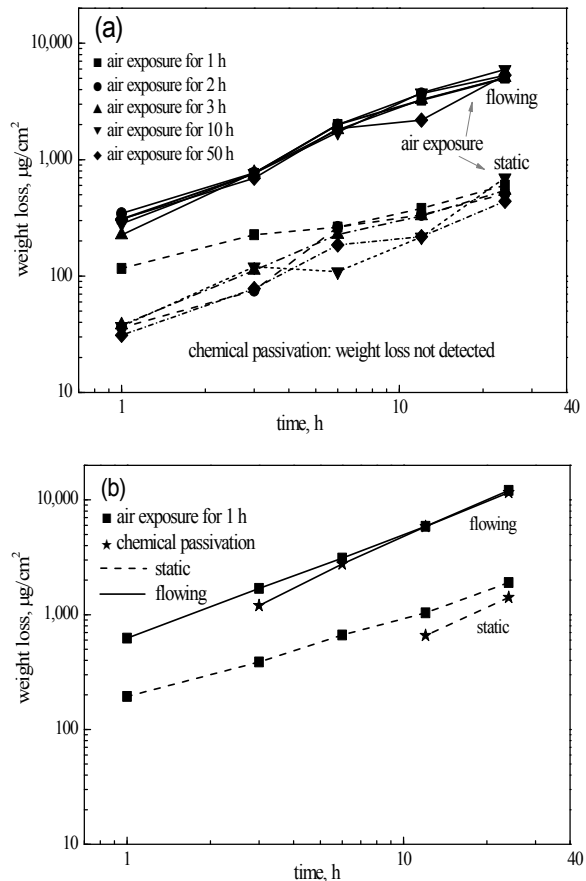


Fig. 4. Weight loss of 304 stainless steel after corrosion in 0.36 M hydrochloric solution under static and flowing condition at various temperature: (a) at room temperature, (b) at 50 °C.

ues close to 0. This finding suggests that the optimum film quality can be found in the samples subjected to chemical passivation.

3.2 Corrosion weight loss and surface morphology

Fig. 4 shows the weight loss of 304 stainless steel after corrosion in 0.36 M HCl solution at different temperatures and flowing conditions. At room temperature, the weight loss decreases with increasing air exposure period. Under solution flowing condition, the corrosion of stainless steel was accelerated but no obvious difference between the samples after various periods of air exposure, suggesting weak protectiveness of passive film formed in air under flowing condition. Notably, no obvious weight loss was evidenced in the sample after chemical passivation, as shown in Fig. 4(a). At the elevated temperature of 50 °C, the corrosion weight loss was boosted. In such condition the sample subject to chemical passivation also corroded after immersion of 12 h, as shown in Fig. 4(b). Moreover, weight loss of specimen subject to air exposure and that

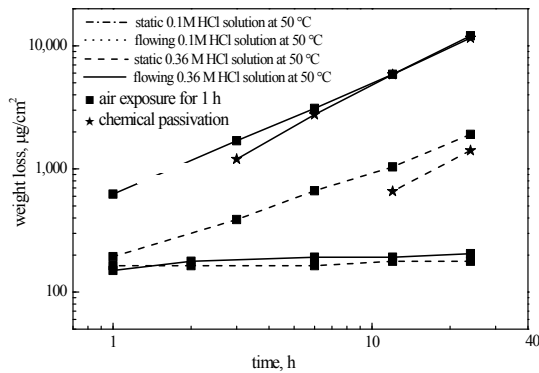


Fig. 5. Weight loss of 304 stainless steel after corrosion in 0.36 M and 0.1 M hydrochloric solution under static and flowing condition at 50 °C.

subject to chemical passivation is similar in the flowing condition. But, there is difference in the weight loss in the stagnant condition.

Fig. 5 shows the weight loss of 304 stainless steel after corrosion in different concentration of HCl at 50 °C. Compared with the weight loss in 0.36 M HCl solution, the corrosion of 304 stainless steel was decreased and the effect of flowing was apparently diminished in 0.1 M HCl solution. No obvious weight loss was observed for the samples subject to chemical passivation.

Table 1 classified corrosion grades according to the weight loss, where S_{air} and S_{cp} was shortened for the sample subject to air exposure and chemical passivation, and

room temperature as RT, respectively. It is seen that S_{air} samples are easier to corrode than S_{cp} ones. Corrosion quantity decreases with increasing pH value, but increases with increasing temperature. Flowing accelerating corrosion becomes visible at high concentration of HCl and high temperature.

Fig. 6 chooses surface morphologies of S_{cp} after immersion in 0.36 HCl solution to illustrate the effect of temperature and flowing on corrosion morphology. Only scratches after ground was observed suggesting no serious corrosion occurred at room temperature. As the temperature was raised to 50 °C, corrosion and dissolution of stainless steel resulted in surface corrosion ditches. In the flowing condition, the surface corrosion degradation was further aggravated.

3.3 Potentiodynamic polarization

Fig. 7 shows the potentiodynamic polarization curves of 304 stainless steel subject to air exposure and chemical passivation in 0.36 M HCl solution. The polarization curve of the samples after air exposure shows an active dissolution from -0.4 V(SCE) to -0.25 V (SCE) and a passive region from approximately -0.1 V (SCE) to 0.1 V (SCE) in 0.36 M HCl solution at room temperature. Similar polarization were reported for 316L stainless steel in HCl solution⁹⁾. Under the flowing condition, a right forward shift of polarization curves and narrowed passive region were found as shown in Fig. 7(a). It is noted that although there exist passivation and pitting regions in the polar-

Table 1. Graded evaluation of weight loss of 304 stainless steel after corrosion

	0.36 M HCl		0.1 M HCl		0.01 M HCl		Corrosion extent
	flowing	static	flowing	static	flowing	static	
S_{air} at RT	corroded	corroded	slight	slight	No	No	small ↓ large
S_{air} at 50 °C	corroded	corroded	slight	slight	No	No	
S_{cp} at RT	No		No		No	No	
S_{cp} at 50 °C	corroded	corroded	No		No	No	

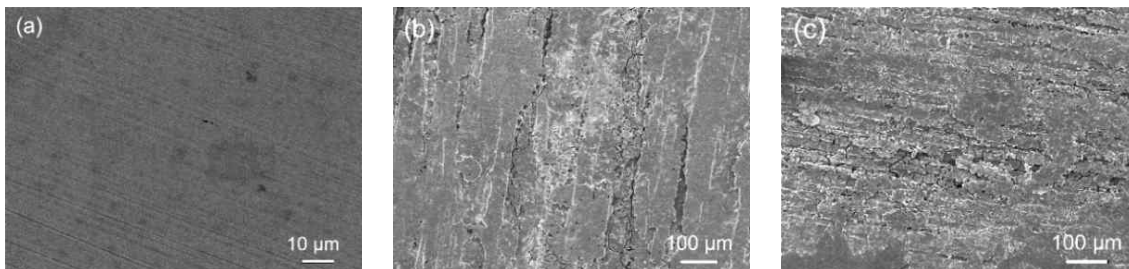


Fig. 6. Surface morphology of 304 stainless steel subject to chemical passivation after corrosion in 0.36 M HCl solution: (a) in solution at room temperature, (b) in static solution at 50 °C, (c) in flowing solution at 50 °C.

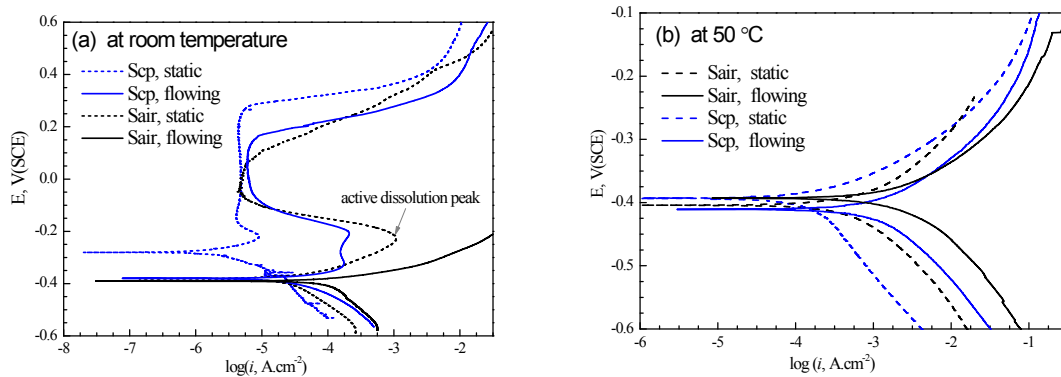


Fig. 7. Potentiodynamic polarization curves in 0.36 M HCl solution at different temperature for 304 stainless steel after air exposure for 1 h and chemical passivation in HNO₃ solution: (a) at room temperature, (b) at 50 °C.

Table 2. Electrochemical parameters calculated from the potentiodynamic polarization curves in Fig. 7

	air exposure room temperature		Chemical passivation room temperature		air exposure 50 °C		Chemical passivation 50 °C	
	static	flowing	static	flowing	static	flowing	static	flowing
-E _{corr} , mV(SCE)	394	390	349	391	404	393	394	410
I _{corr} , μA.cm ⁻²	83.1	145.3	5.4	43.4	952	3087	220	1784

ization curves, the presence of active dissolution peaks suggest a dissolution process during the immersion experiment. For the sample after air exposure of 1 h no passive region was observed, suggesting none existence of protective passive film under such condition. As solution temperature increased up to 50 °C, all samples exhibit active dissolution according to the polarization curves. This result indicates the degradation of passive film stability by the solution flowing and possibly gives a reason of different weight loss effect of chemical passivation under flowing and stagnant condition in Fig. 4.

The corresponding corrosion potential E_{corr} and corrosion current density i_{corr} can be obtained from potentiodynamic polarization curves (Table 1). Very low values of corrosion current at room temperature was achieved for the samples subjected to chemical passivation, which is according with the weight loss result (Fig. 4(a)). It is apparent that solution flowing boosted the value of i_{corr} . Moreover, such promotion effect increases with increasing temperature. Although the chemical passivation inhibited the corrosion of 316 L stainless steel, such inhibition can not prevent the fast corrosion in the presence of high value of i_{corr} .

3.4 Metal element dissolution

Fig. 8 shows the dissolution concentration of metal elements that remained in 0.36 M HCl solution after im-

mersion corrosion of 24 h at 50 °C. A large amount of Fe ions dissolved into solution after corrosion. Chemical passivation inhibited the dissolution of metal elements. Under the flowing condition, increment in dissolved Fe, Cr and Ni ions were evidenced, as shown in Fig. 8(a). The relative concentration percentage was calculated according to the following equation:

$$R_i = \frac{C_i}{C_{oi}} \times \frac{\sum C_{oi}}{\sum C_i} \times 100\% \quad (1)$$

Where C_i is the concentration of metal i , C_{oi} is the weight percentage of metal element i in 316L substrate. The value of R_i means the ratio of dissolution percentage of Fe, Cr or Ni in HCl solution to that in 316L substrate. It is easy to considered that element i would preferentially dissolved during corrosion when $R_i > 100$, while the dissolution of i may be inhibited when $R_i < 100$.

Fig. 8(b) shows the calculated value of R_i for Fe, Cr and Ni element. The value of R_{Fe} is close to 120 %, indicating a preferential dissolution of Fe element during corrosion under static condition. The values below 70 % are achieved for R_{Cr} and R_{Ni} , which accord with the result in reported literatures⁶⁾. This result suggests the slow dissolution of Cr and Ni element during corrosion. Chemical passivation further decreased the dissolution of Cr element. Under the flowing condition, however, all values for those

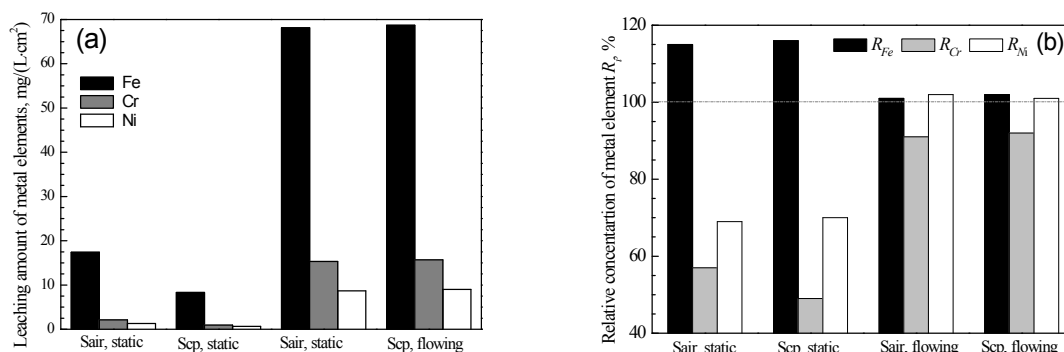


Fig. 8. Dissolution of metal elements from 304 stainless steel after corrosion in 0.36 M hydrochloric solution at 50 °C: (a) dissolution amount of metal elements, (b) relative concentration percentage of metal elements.

elements are close to 100 %, illustrating a fast and non-preferential dissolution.

The experimental results show that surface passive film and solution flowing affected corrosion of 304 stainless steel in HCl solution. As mainly two reactions involved during the corrosion, that is the oxidation of metal substrate and the reduction of hydrogen ion in the acid solution¹⁰, different role of passive film and solution flowing on those reactions is critical to the corrosion behavior. At room temperature, the low value of corrosion weight-loss (Fig. 4(a)) and the presence of passive region in the polarization curves (Fig. 7(a)) indicate that the corrosion of 304 stainless steel is controlled by the anodic oxidation reaction. The associated integrity of the passive films is thus importance in such condition. The passive film that formed during air exposure is non-protective due to its small amount of Cr-rich oxide (Fig. 2) and low level of film integrity (Fig. 3). On the contrary, the surface passive film that formed after chemical passivation processes large amount of Cr-rich oxide and exhibits high level of film integrity. The high quality passive film inhibits the anodic dissolution of metal substrate and thus nearly no corrosion weight-loss was observed (Fig. 4(a)). Solution flowing deteriorated the corrosion resistance by modifying the anodic reaction as shown in Fig. 7(a).

As the solution temperature increased up to 50 °C, the anodic dissolution was greatly promoted and the dissolved metal ions diffused fast into the solution, as illustrated by Fig. 8(a). A distinctive active dissolution was achieved at the high temperature (Fig. 7(b)). At the high temperature, it seems that the corrosion behavior is controlled by the cathode reduction reaction. Indeed a careful examination on the polarization curves in Fig. 7(b), the calculated anodic Tafel slop is about 99 mV/dec, which is much lower than the cathodic Tafel slop 155 mV/dec. Therefore, the effect of chemical passivation is weakened at 50 °C.

Moreover, solution flowing accelerated the corrosion by promoting cathodic reaction, as illustrated by the right shift of cathodic region in the polarization curves in Fig. 7(b).

4. Conclusion

- (1) Coloration indicator reveals that a low integrity of passive film for 304 stainless steel after air exposure and a high integrity of passive film formed after chemical passivation.
- (2) Immersion corrosion and polarization behavior show that solution flowing accelerated the corrosion of 304 stainless steel in HCl solution. Chemical passivation inhibited the corrosion due to high content of Cr-rich oxide and hydroxide and its high integrity.
- (3) Fe preferential dissolution occurred in the static solution during corrosion, but no apparent preferential dissolution in the flowing solution.

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