JOURNAL OF MATERIALS SCIENCE 40 (2005) 2911–2917

Electrochemical repairing of pitted 18-8 stainless steel

H. P. DUAN, Y. C. LI, C. W. YAN*
State Key Laboratory for Corrosion & Protection, Institute of Metal Research Chinese Academy of Sciences, Graduate School of the Chinese Academy of Sciences, 62 Wencui Rd, Shenyang 110016, People's Republic of China
E-mail: hpduan@imr.ac.cn, cwyan@imr.ac.cn

In order to clarify the reaction essential of electrochemical repairing method, which was developed to repair the passive film on pits and suppress pitting corrosion on passive 18-8 stainless steel (18-8ss) after occurrence of pitting, the electrochemical characteristics, morphology and composition of passive film after different treatments were investigated by electrochemical impedance spectroscopy (EIS), Cyclic Voltammogram (CV), Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The dynamic behavior of reactions occurred at lower potential ($E_L = -200$ mV) and higher potential ($E_H = 1000$ mV) of alternating electric filed was discussed respectively and the correlation between those reactions was analyzed. Based on above results, reaction essence of electrochemical repairing for pitted 18-8ss electrode was proposed: during the periodic action of alternating current, recycle reactions take place on the surface and the pit area of pitted electrode, i.e., metal dissolves into cations (occurs at E_L) and form hydrous hydroxide, the hydrous hydroxide turns into metal oxide (occurs at E_H), a 'bipolar mode' passive film forms and Cr content is increased in repaired passive film. At the pit area, enclosed state of the pit is destroyed by the perturbing effect of alternating current in 1.0 M H_2SO_4 solution, thus the pit area will be repaired through above-mentioned process.

1. Introduction

Application of stainless steel is extensive gradually due to its favorable corrosion resistance and general properties. Studies on stainless steel, more attention was paid to improve corrosion resistance [1], to study the semi-conductive properties [2] of passive film and to illuminate pitting behavior [3] and formation mechanism of passive film [4] in recent years. But the applications of stainless steel in some Cl^- containing environments were limited for appearance of local corrosion, principal pitting corrosion. Currently, many kinds of pitting corrosion inhibitor [5, 6] were used to restrict further pitting corrosion, but this method didn't meliorate the surface damaged by pitting corrosion. So studies on the repassivation behavior of pit and searching for effective repairing technique of pitted surface are of great meaning.

The alternating current technique as an effective surface modification method, although it can subdue passive ability and increase corrosion rate of stainless steel in some conditions [7–9], its application to surface modification showed remarkable effects, such as improvement of corrosion resistance and stability of passive film [10–12], and formation of color passive film [13, 14]. However, its application to repair a destructed surface, especially pitted surface has seldom reported.

Integrating the feature of pitting corrosion with the characteristic of alternating current technique, an electrochemical repairing technique, which had controllable alternating current parameters, was put forward to repair pitted passive alloys, most stainless steel. Using the perturbing effect of electrochemical repairing process, the oxidation and reduction reaction was maintain, the half-occluded structure was destroyed, and the inner local concentrated corrosion intermediates in pits were disturbed and exchanged with the repassive intermediates. Then, the pitted surface and substrate of pits were repassivated by the reactions between repassive intermediates and substrate occurred at electrochemical repairing process. Thus, pits can be repaired by repassivation simultaneously with controlling pits developed further. So far, the optimal conditions of electrochemical repairing technique were discussed for certain solutions and satisfied results had been obtained in our results, for example, after electrochemical repairing in dilute H_2SO_4 solution, the breakdown potential (E_b) of pitting corrosion is increased by 300 mV and polarization resistance (R_P) is increased by 10 times for a pitted 18-8ss electrode

---

*Author to whom all correspondence should be addressed.

in 3.5% NaCl solution rather than those for untreated sample.

For the purpose of developing and directing the application of the electrochemical repairing technique, we extend our previous work to further demonstrate the essential of reactions occurred during electrochemical repairing on pitted 18-8ss electrode in 1.0 M H_2SO_4 solution by studying the effect of higher potential (E_H) and lower potential (E_L) on the electrochemical repairing process respectively. Before and after electrochemical repairing treatment, the electrochemical characters and composition of passive film on 18-8ss were detected by electrochemical and spectroscopic methods. At the same time, SEM was used to compare morphologies of pits before and after electrochemical repairing treatment.

2. Experimental

2.1. Electrodes and electrolytes

The samples for electrochemical treatment were cut from 18-8ss rod (wt%, C:0.07, Mn:1.19, Si:0.57, S:0.01, P:0.029, Ni:9.41, Cr:17.66, Ti:0.51) and the edges of the working electrode were coated with epoxy resin, leaving only the polished disk surface with area of 1 cm^2. Before experiment, the specimens were successively polished with 400, 600, and 800 grit emery papers and rinsed with distilled water and ethanol. Solutions were made of analytical grade reagents and distilled water.

Before repair treatment, pitting is induced by Potentiodynamic polarization on 18-8ss electrode in 3.5% NaCl solution at a scan rate of 0.5 mV/s. And the potential sweep was stopped when the corresponding polarized current density up to 1 mA/cm^2, which is enough to induce pitting corrosion and to make surface dissolved for trans-passivation on 18-8ss electrode in 3.5% NaCl solution. With the purpose of avoiding repassivated during replace electrolyte after pitting was induced in 3.5% NaCl solution, the electrode was reduced for one minute in 1 M H_2SO_4 solution before electrochemical treatment.

2.2. Electrochemical measurement

The electrochemical measurements were performed with a Princeton Applied Research (PAR) EG&G potentiostat/galvanostat model 273 with model 352/270 corrosion software and EG&G 5210 lock-in amplifier with M398 testing software. All electrochemical measurements were conducted by using a conventional three electrodes electrochemical cell with a platinum auxiliary electrode and a saturated calomel reference electrode (SCE).

Four types of experiments were carried out: (i) electrochemical repairing with alternating current parameters of $E_H = 1000$ mV, $E_L = -200$ mV, Frequency = 10 Hz and Ratio = 1, was used to repair the pitted 18-8ss electrode in 1 M H_2SO_4 solution; (ii) Potentiodynamic polarization was to induce pitting in 3.5% NaCl solution, as well as to investigate the passive conditions of 18-8ss electrode in 1 M H_2SO_4 solution at a scan rate of 0.5 mV/s; (iii) EIS was used to analyze dynamic process of reactions at E_H and E_L respectively. The signal amplitude was 10 mV and frequency ranged from 1.5E-3 to 1.0E5 and (iv) Because oxidation and reduction processes taken place on electrode surface alternately during electrochemical repairing treatment at alternating filed, the favorable redox reversibility of passive film will maintain reactions occurred at E_H and E_L continuous and determine the repairing effect for pitted 18-8ss electrode. In order to explain this property and correlation of reactions at E_H and E_L during electrochemical repairing treatment, cyclic voltammogram (CV) was carried out at a scan rate of 50 mV/s.

2.3. Morphology and composition analyses

The surface morphologies of pitted electrode before and after electrochemical repairing treatment were observed by scanning electron microscopy (SEM) (XL-30FEG, PHILIPS).

For analyzing chemical composition of pitted electrode surface with different treatments, XPS analyses were performed with a VG Esca Lab MK II spectrometer equipped with a non-monochromatic Mg X-ray source. Survey scans of all samples were obtained using a 600 μm X-ray spot size and 150 eV pass energy. All spectra were referenced to the C1s signal at 284.6 eV.

3. Results

3.1. Electrochemical characteristics

As the Potentiodynamic polarization experiment described in Fig. 1, the range from around −200 to 0 mV is the active range, and 200 to 950 mV is the stable passive range of 18-8ss in 1.0 M H_2SO_4 solution. When potential is over 1000 mV, the electrode was transpassivated and presented as the Tafel behavior [15]. According to the corrosion electrochemical characteristic of the material, the parameters of alternating current were chosen as E_H is 1000 mV at the edge of transpassive range and E_L is −200 mV in active range.

In order to explain the electrochemical repairing mechanism of the pitted electrode, reactions taken at E_H and E_L were studied respectively by CV and EIS technique as following. During CV experiment, the pitted electrode was polarized at static potential, −200 mV

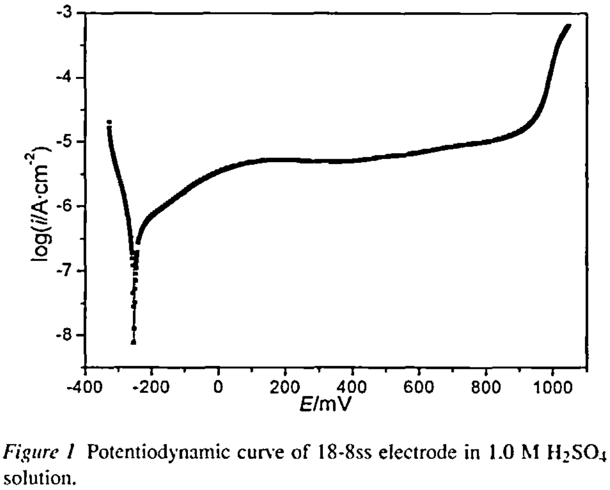


Figure 1 Potentiodynamic curve of 18-8ss electrode in 1.0 M H_2SO_4 solution.

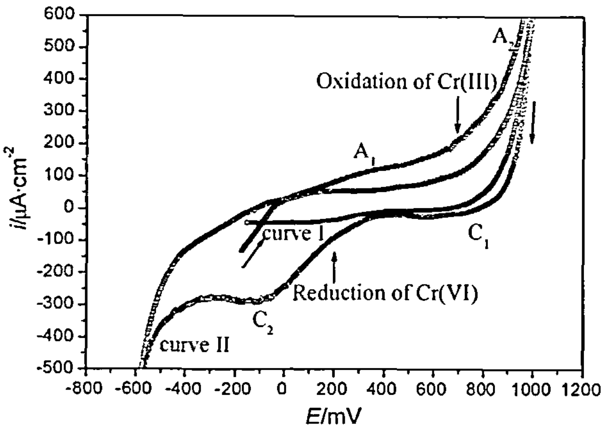


Figure 2 Cyclic voltammograms of 18-8ss electrode in 1.0 M H_2SO_4 solution action in different way (curve I: pre-polarization at static potential (Estatic) = −200 mV for 1000 s,then scanning in positive direction, curve II: pre-polarization at Estatic = 1000 mV for 1000 s,then scanning in negative direction).

(or 1000 mV) for 1000 s respectively, then passed higher (or lower) potential region in positive (or negative) direction and scanned to lower (or higher) potential region finally. These results were presented in Fig. 2. There is a weak oxidation region around A1 (300 mV) in oxidation branch of curve I, which is the result of formation of lower valence oxide or hydroxide of Fe, Ni and Cr [16]. When potential is over 600 mV, the oxide of Cr(III) is oxidized with current increasing sharply [16] and dissolved for transpassivation around A2 (1000 mV) in curve II. And there is a weak cathodic reductive peak (C1) in reduction branch of curve II, which is corresponded to the reduction of higher valence oxide in the surface diffused layer of electrode [16]. With reduction current decreasing around 200 mV, Cr(VI) was reduced [17]. The reduction of higher or middle valence mixture (of Cr, Fe and Ni) in the film is occurred around −200 mV (C2). The most distinction between two curves is that there is higher oxidized current in curve I, and the reductive current is more evident in curve II.

Dynamic behavior of 18-8ss electrode at E_H and E_L of alternate current in 1.0 M H_2SO_4 solution were investigated respectively by EIS. There are two time constants in Fig. 3a, which correspond to a capacitive arc and diffusion process respectively. This capacitive arc at high frequency in Fig. 3a and b is related to the relaxation process of interface duplex layer and reaction transfer resistance, and at low frequency in Fig. 3a, the diffusion process is evoked by the diffusion of dissolved corrosion product from electrode surface into electrolyte or ions transfer from electrolyte to electrode surface. There is an inductive arc at low frequency in Fig. 3b, which indicated that the reaction at E_H might be occurred as adsorption of intermediate or solid phase reaction [18].

The redox characteristic of 18-8ss electrodes with and without electrochemical repairing treatment was shown as Fig. 4. Compared to curve II, there are two reduction regions around −200 and 900 mV and an oxidization region around 100 mV in curve I, which are respectively similar to points C2, C1 and A1 in Fig. 2. That is to say, after electrochemical repairing treatment, the electrode surface has dual characteristics of oxidation and reduction, i.e., the composition of surface film can be oxidized and reduced in given conditions, that is the surface film repassivated by electrochemical technique on the pitted 18-8ss electrode is composed of mixture of higher and lower valence products which were respectively produced at E_H and E_L.

3.2. Structure characteristic of pitting

Scanning electron microscopy (SEM) was used to observe the structure transformation of pitting before and after electrochemical repairing treatment. After pitting induced (shown in Fig. 5a), the pitting was half-occluded by corrosion product, which deposited around the pit and formed salt film. There were many pores for corrosion dissolving distributed around the pit randomly in the corrosion product, and these pores with light-white border have tendency to dissolve sequentially. But after electrochemical repairing treatment, due to the perturbing effect of alternating current and dissolving effect of dilute H_2SO_4 solution, the above mentioned corrosion product was dissolved, and the bottom and side of the pit were exposed as an open mouth shape. At the same time, the tendency to dissolve of every pore was eliminate, the bottom and side of the pit were repassivated as the rest surface. As far

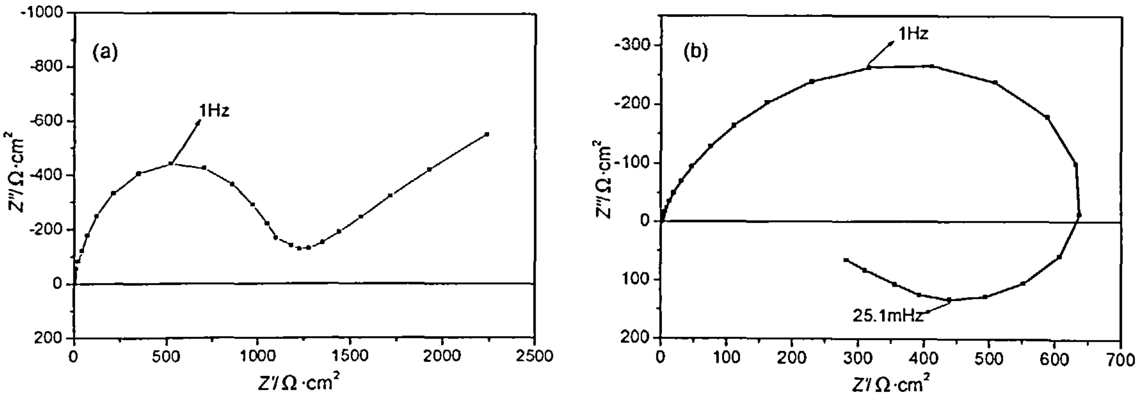


Figure 3 EIS of 18-8ss electrode in 1.0 M H_2SO_4 solution at different potential, (a) −200 mV, (b) 1000 mV.

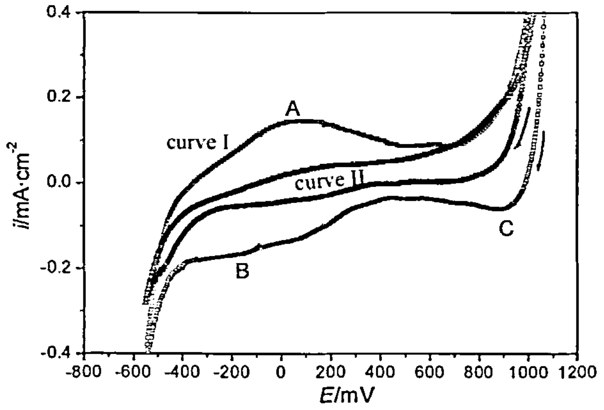


Figure 4 Cyclic voltammograms of 18-8ss electrode in 1.0 M H_2SO_4 solution in different surface condition. Curve I: with electrochemical repairing treatment; Curve II: Blank sample.

as morphology is concerned, the opening structure pit is suitable for maintaining passivation property of pitting because it enabled ions transfer to be easy, so it might hinder condensation of the corrosion intermediates. From above analysis, it follows that the electrochemical repairing treatment can improve the passive property of the pitted 18-8ss electrode, as well as repair the pitting area.

3.3. Chemical composition of passive film on pitted 18-8ss by different treatments

In order to display the superiority of electrochemical repairing technique for the pitted 18-8ss electrode, the chemical composition of passive film by different treatments on the pitted 18-8ss electrode was detected by X-ray photoelectron spectroscopy.

Full spectrum of each passive film of the pitted 18-8ss electrode treated by different ways as shown in Fig. 6, consisted of more or less the same elements, i.e., chromium, oxygen and iron, but there is more evident iron in line (a) which is disposed at E_L. And the content of Cr is higher in Fig. 6c than that in Fig. 6b and a. This result can be seen clearly by the quantitative statistic result of atom ratio between Fe, Cr and O (shown in Table I). This indicated that the passive film with lower potential treatment consisted of compounds of Fe and Cr, however, after higher potential or electrochemical repairing treatment, the passive film mainly consisted of components of Cr. The enriched Cr level is consistent with the formation of a Cr-rich passive film as is observed conventionally on steels under conditions where Fe is active [19].

TABLE I Atoms ratio evaluated by peak areas of each element in surface layer with different treatment

Different treatment	Atoms ratio (Fe/Cr/O)
Polarized at E_L	0.96/1.0/10.4
Polarized at E_H	0.29/1.0/6.1
Electrochemical repairing	0.29/1.0/4.6

The separated peaks (shown in Fig. 7) of Cr $2p^{3/2}$ indicated the presence of Cr(III) and Cr(VI), and O 1s indicated the presence of OH^-, O^{2-} and H_2O in all of the films studied. But the constituents of the passive films are different after different treatment, that is the passive film disposed at E_L mainly consisted of component of Cr(III), such as Cr_2O_3, $Cr(OH)_3$ and little CrO_4^{2-}, the passive film polarized at E_H mostly consisted of Cr(VI), such as CrO_4^{2-}, CrO_3 and Cr_2O_3, and the passive film after electrochemical repairing treatment consisted of Cr_2O_3, $Cr(OH)_3$, CrO_3 and CrO_4^{2-}. That is to say, the electrochemical repairing treatment can produce higher and lower valance oxides and hydroxides of Cr simultaneously.

4. Discussion

4.1. Reactions at lower potential (E_L)

Based on the above-mentioned results, the formation process of passive film under electrochemical repairing treatment will be discussed as following. Metal atoms dissolved into lower valence cations and transferred into solution at E_L(−200 mV), and such dissolution may mainly be Fe, coupled with dissolution of Ni and Cr [20]. With the carrying through of reactions at E_L, metal cations gathered in the liquid layer nearby the electrode surface and hydrolyzed into hydroxide when the concentration of hydrous cations is saturated, then hydroxide were adsorbed on the electrode surface for its increasing concentration. The process can be described

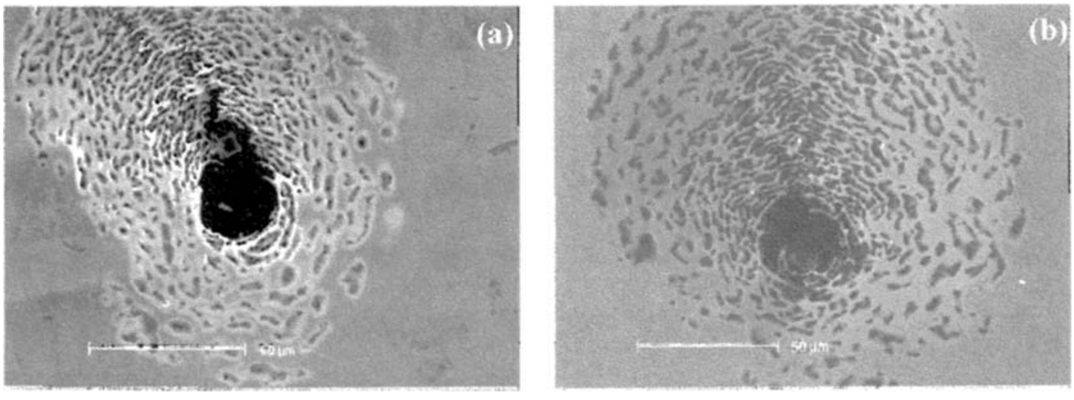


Figure 5 SEM morphology of pitting with different treatment. (a) After pitting induced, (b) after electrochemical repairing.

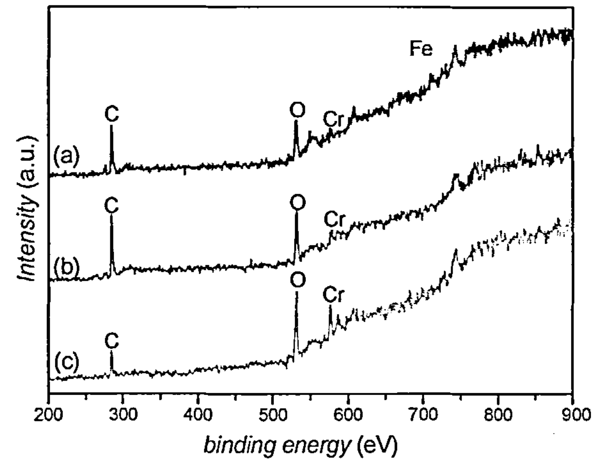
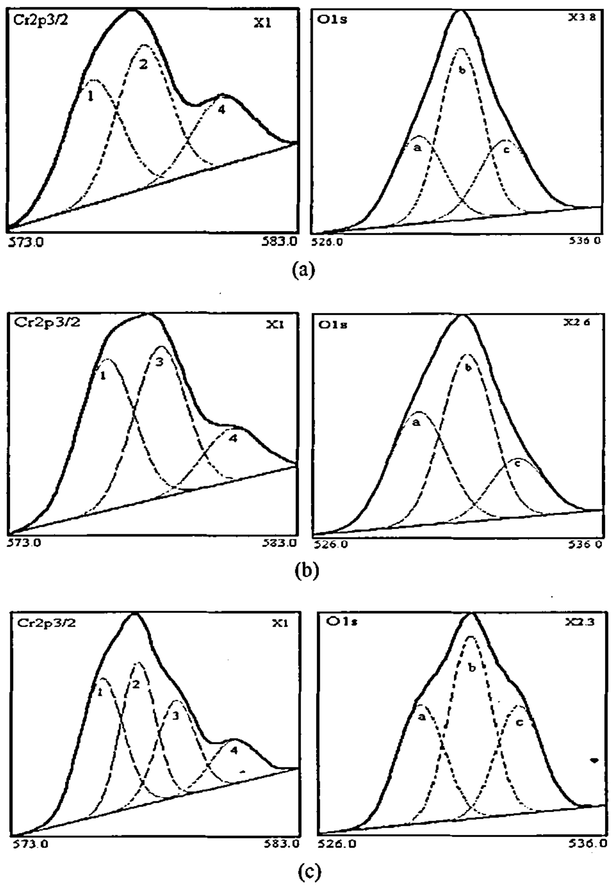


Figure 6 XPS spectra of passive films after different surface treatments on 18-8ss electrodes: (a) with lower potential polarization, (b) with higher potential polarization, and (c) with electrochemical repairing treatment.



(a)

(b)

(c)

Figure 7 Cr 2p3/2 and O 1s photoelectron spectra obtained from passive film of 18-8ss electrode after different treatments, (a) with lower potential polarization, (b) with higher potential polarization, (c) with electrochemical repairing treatment. 1. Cr_2O_3: 576.3 eV, 2. $Cr(OH)_3/CrOOH$: 577.4 eV, 3. CrO_3: 578.3 eV, 4. CrO_4^{2-}: 580.5 eV; a. O^{2-}: 529.9 eV, b. OH^-: 531.2 eV, c. H_2O: 533.1 eV.

as following:

$$\mathrm{Me} \rightarrow \mathrm{Me}^{z+} + z\mathrm{e}^- \quad (\mathrm{Me: Cr, Ni, Fe}) \tag{1}$$

$$\mathrm{Me}^{z+} + (z+y)\mathrm{H_2O} \rightarrow \mathrm{Me(OH)}_z \cdot y\mathrm{H_2O} + z\mathrm{H}^+ \tag{2}$$

Reaction (1) is an overall equation, which can be described by BBD model [21], taking Fe for example:

$$\mathrm{Fe} + \mathrm{H_2O} \rightarrow (\mathrm{FeOH})_{\mathrm{ads}} + \mathrm{H}^+ + \mathrm{e}^- \tag{3}$$

$$(\mathrm{FeOH})_{\mathrm{ads}} \rightarrow (\mathrm{FeOH})^+ + \mathrm{e}^- \tag{4}$$

$$(\mathrm{FeOH})^+ + \mathrm{H}^+ \rightarrow \mathrm{Fe}^{2+} + \mathrm{H_2O} \tag{5}$$

Metal atoms dissolved from crystal lattice of substrate into solution under effect of adsorbed water on electrode surface. On the other hand, metal cations were adsorbed on electrode surface and didn't diffuse into solution rapidly for linked function between adsorbed water and electrode surface [22]. The coverage of adsorbed intermediate ($(\mathrm{FeOH})_{\mathrm{ads}}$) was kept in a certain value under the effect of competitive actions of adsorption and diffusion, and the active adsorbed intermediate was passivated when the coverage reached to a critical value. This reaction can be described as following:

$$(\mathrm{FeOH})_{\mathrm{ads}} + \mathrm{H_2O} \rightarrow \mathrm{Fe(OH)_2} + \mathrm{H}^+ + \mathrm{e}^- \tag{6}$$

Many studies indicated that active dissolution of Ni [23] and Cr [24] also follow the above mechanism and impedance graphs of Cr, Ni, Fe are similar in their active range [23–26].

4.2. Reactions at higher potential (E_{H})

The selected higher potential ($E_{\mathrm{H}} = 1000$ mV) is at the edge of transpassive region of 18-8ss. Thus Cr and Ni are dissolved for transpassivation but Fe is passivated at this potential [22]. For this reason, the passive film formed in this region mainly consists of oxide of chromium; hence the ratio of Fe/Cr in passive film formed at E_{H} is less than that at E_{L} as the result of XPS experiments represent in Fig. 6 and Table I. Similarly, the electrochemical impedance spectroscopy characteristic at E_{H} mainly reflects the transpassive dissolution behavior of Cr, which was supported by studies on impedance characteristic of pure Ni and Cr [27].

The signal of Cr(III) and Cr(VI) can be found in the passive film formed at E_{H} by XPS and Cr(III) may represents as Cr_2O_3 and Cr(VI) may represents CrO_3 and CrO_4^{2-}, because the higher potential($E_{\mathrm{H}} = 1000$ mV) locates in the transpassive range of pure Cr. Near the interface of film/crystal lattice Cr(III) may transform to Cr(VI) in solid state as following:

$$\mathrm{Cr_f^{III}} \rightarrow \mathrm{Cr_f^{VI}}(\text{in film}) + 3\mathrm{e}^- \tag{7}$$

$\mathrm{Cr_f^{VI}}$, as the precondition of transpassive reaction, exists in the film may induce formation of the adsorbed intermediate, thereby the EIS characteristic in low frequency is an inductive arc (Fig. 3b). Under sustained effect of higher potential, concentration of $\mathrm{Cr_f^{VI}}$ is increased and $\mathrm{Cr_f^{VI}}$ is dissolved for transpassivation when its concentration over certain critical value.

$$\mathrm{Cr_f^{VI}} \rightarrow \mathrm{Cr_{aq}^{VI}}\ (\text{in aqueous phase}) \tag{8}$$

Thus a CrO_4^{2-} containing film was formed through the following solid-state reaction:

$$Cr(OH)_3 + H_2O \rightarrow CrO_4^{2-} + 5H^+ + 3e^- \quad (9)$$

Because the above reaction mainly taken place on solid surface layer of passive film and CrO_4^{2-} species form insoluble salts with Cr in the $Cr(OH)_3$ layers [28], CrO_4^{2-} appears on surface layer of passive film but not dissolves into solution, and it can be detected on the film surface. Certainly, reactions taken place at E_H also include dehydrogenation and dehydration of hydroxide of Cr that produced at E_L in inner layer of passive film, and form oxide of Cr. For the above reasons, the passive film on stainless steel is layered, i.e., the inner layer is Cr_2O_3 and the outer layer is $Cr(OH)_3$ or CrOOH mainly. Hence, the main transpassive reaction is $Cr(OH)_3$ transformed into CrO_4^{2-}, then CrO_4^{2-} in outer layer formed a bipolar structure which is of benefit to formation of Cr_2O_3 and keeping passive film stable [28].

4.3. Correlation of the reactions at higher and lower potential

The electrochemical repairing process of the pitted electrode, which is composed of reactions taken place at E_H and E_L, isn't simple combination of those reactions. Therefore, investigation of mutual effect of reactions occurred at E_H and E_L is of great benefit to understand clearly the essential of electrochemical repairing of the pitted electrode based on the investigation about reactions occurred at E_H and E_L respectively.

As presented in Fig. 8, compared with the CV behavior of blank sample presented in Fig. 4 curve II, in the curve I (in Fig. 2) which had polarized at E_L for 1000 s, the potential region with current increased sharply in oxidation branch is shifted in the more negative potential direction. It was shown that the oxidation reaction which occurred around 600–900 mV in curve I (Fig. 2) can be carried out at more negative potential than that in curve II (Fig. 4), and might be that the reaction product produced at E_L was oxidized by solid-state reaction. In this condition, the reaction at E_H is related to two different sub-reactions, i.e., transpassive dissolution of passive film (shown as reactions (7) and (8)), and oxidation of the reaction product produced at E_L on electrode surface. Because the selected potential E_H locates at the lower edge of the transpassive range of 18-8ss in dilute H_2SO_4 solution, the main reactions are oxidation and dehydrogenation of the lower valence oxide and hydrous product (shown as reaction (9)).

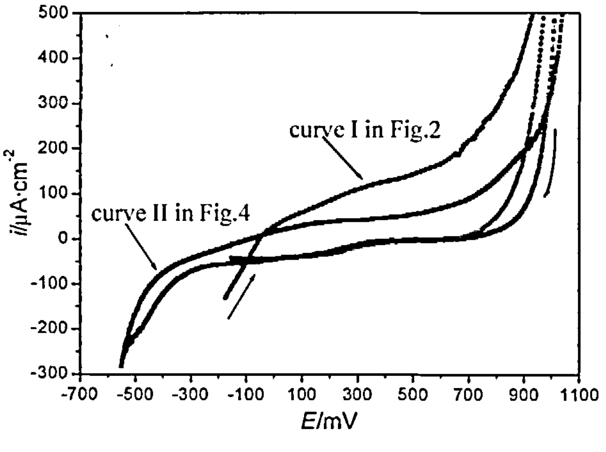


Figure 8 Cyclic voltammograms behavior comparison between curve I in Fig. 2 and curve II in Fig. 4.

Similar to the reactions at E_H, reactions occurred at E_L are also related to two processes, i.e., the metal dissolved into cations (reaction (1)) and the reaction product produced at E_H was reduced. Compared with the CV behavior of blank sample presented in Fig. 4 curve II, curve II in Fig. 2, which had treated at E_H for 1000 s, has two evident reductive regions which correspond to the reduction of higher and middle valence compounds respectively. From the above discussion, it can be concluded that once the reaction product produced at E_H gathered on electrode surface, it will be reduced at E_L, and metal substrate doesn't be dissolved if the time of reaction at E_L is controlled properly.

4.4. Repairing of pitting by electrochemical method

As for as repairing is concerned, the most important thing is to eliminate or reduce disadvantageous factors in geometry and circumstance and to improve the performance of passive film around pits and to reform passive film on pits.

With a view to the special geometrical environment around pits with many active pores shown as Fig. 5a, in which corrosion product piled and formed half-enclosed local environment, the repairing process must destroy the half-enclose structure and enable the repassivation intermediate to be inserted into the pits during the process. The electrochemical repairing treatment in dilute H_2SO_4 makes corrosion product around the pits dissolved, at the same time, perturbing effect of alternating current is beneficial for destroying half-enclosed structure and thus promotes interchanging the intermediate between inner and outer of the pits. When metal substrate in pits was soaked adequately by given repassivation intermediate, the repairing reaction would be occurred in the pits according to the repairing process on electrode surface.

4.5. Reaction mechanism of electrochemical repairing process

Summarizing the above discussions, the reaction mechanism of electrochemical repairing of the pitted 18-8ss electrode with typical parameters in dilute H_2SO_4 solution can be described as following:

The electrochemical repairing process consists of two correlative steps when E_H locates at the higher edge of the passive region or lower edge of transpassive region (800–1000 mV) and E_L locates in the active region ($-100 \sim -300$ mV) of 18-8 stainless steel. During the first step (at E_L), metal atoms dissolve away from substrate and form hydrates of Cr or Fe, those are known to be intermediate species for substrate dissolution and film formation. Then, many fine channels for ion transmission were formed in the intermediate for migration of metal atoms (most is Fe atom) away from the substrate. And during the second step (at E_H), lower valence hydrous hydroxide was dehydrated and dehydrogenate, and formed higher valence oxide or oxyhydroxides, at the same time, part of $Cr(OH)_3$ was oxidized into CrO_4^{2-}. Following recycle reactions, CrO_4^{2-} was reduced into hydrate of Cr accompanied with substrate dissolved into cations and formed hydrate at E_L. Simultaneously, the passive film was divided into two layers for the appearance of ion selective film with bipolar property of CrO_4^{2-} at E_H, and thus different reactions occurred at different spaces of passive film. In inner part, with increasing effect of passivation, dehydrate and dehydrogenation of metal hydrate can be easily formed, which becomes thin barrier layer in the passive film. In these conditions, transfer of metal cations from substrate was controlled by migration via lattice of the passive film. On the other hand, the formation of CrO_4^{2-} through the oxidation of $Cr(OH)_3$ will sustain the growth of passive film. By the above series of reactions, the passive film would grow to a certain thickness on stainless steel, and the corrosion resistance of the whole surface including the pits area both was increased evidently due to the formation of duplex layer structured passive film and the selective adsorption of CrO_4^{2-} on the surfaces including that of pits.

5. Conclusions

The electrochemical repairing process of the pitted electrode of 18-8 stainless steel in dilute H_2SO_4 solution is composed of reactions taken place at E_H and E_L of alternating current and the repassive film consists of a mixture of higher and lower valence products produced by E_H and E_L reactions respectively.

The reaction mechanism of electrochemical repairing of the pitted 18-8ss electrode may be as follows: recycle reactions take place on the surface and pitting area of electrode, i.e., metal dissolves into cations (occurs at E_L) and then form hydrous hydroxide; the hydrous hydroxide turns into metal oxide (occurs at E_H); thereafter a 'bipolar fixed charge mode' of passive film is formed. And the half-enclosed state of pits is destroyed by perturbing effect of alternating voltage during the electrochemical repairing process in dilute H_2SO_4 solution; accordingly, the opening surface of the mouth-like pits was repaired to become the same as the rest electrode surface, and therefore, the corrosion resistance of pitted 18-8ss electrode is re-gained due to the formation of double-layer structured passive film with the increasing content of Cr.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 50171074); Thanks to professor Wu for the revision of the paper.

References

1. C. M. ABREU, M. J. CRISTOBAL, X. R. NOVOA, G. PENA, M. C. PEREZ and R. J. RODRIGUEZ, *Sur. Coat. Technol.* 158/159 (2002) 582.
2. H. TSUCHIYA, S. FUJIMOTO and T. SHIBATA, *J. Electrochem. Soc.* 151 (2004) B39.
3. A. I. ALMARSHAD and D. JAMAL, *J. Appl. Electrochem.* 34 (2004) 67.
4. S. FUJIMOTO, K. TSUJINO and T. SHIBATA, *Electrochimica Acta* 47 (2001) 543.
5. D. GOPI and S. RAJESWARI, *Cim Bull.* 96 (2003) 93.
6. S. RAJENDRAN, B. V. APPARAO and N. PALANISWAMY, *Bull. Electrochem.* 13 (1997) 441.
7. J. L. WENDT and D.-T. CHIN, *Corrosion Sci.* 25 (1985) 889.
8. *Idem., ibid.* 25 (1985) 901.
9. D.-T. CHIN and S. VENKATESH, *J. Electrochem. Soc.* 126 (1979) 1908.
10. T. B. DU, *Brit. Corros. J.* 37 (2002) 18.
11. A. NEVILLE and T. HODGKIESS, *ibid.* 35 (2000) 183.
12. L. KWIATKOWSKI and F. MANSFELD, *J. Electrochem. Soc.* 140 (1993) L39.
13. R. CONRRADO, N. BOCCHI, R. C. ROCHA-FILHO and S. R. BIAGGIO, *Electrochimica Acta* 48 (2003) 2417.
14. S. FUJIMOTO, T. SHIBATA, K. WADA and T. TSUTAE, *Corr. Sci.* 35 (1993) 147.
15. M. BOJINOV, G. FABRICIUS, T. LAITINEN and T. SAARIO, *J. Electrochem. Soc.* 145 (1998) 2043.
16. T. PIAO and S. M. PARK, *ibid.* 144 (1997) 3371.
17. P. SCHMUKI, S. VIRTANEN, A. J. DAVENPORT and C. M. VITUS, *ibid.* 143 (1996) 3997.
18. R. D. ARMSTRONG and M. HENDERSON. *J. Electroanal. Chem.* 40 (1972) 121.
19. A. TURNBULL, M. RYAN, A. WILLETTS and S. Q. ZHOU, *Corr. Sci.* 45 (2003) 1051.
20. C. J. LIN and J. G. DUH, *Thin Solid Films* 287 (1996) 80.
21. O. M. JOHN, "Surface Electrochemistry" (Plenum Press, New York, 1993) p. 758.
22. G. OKAMOTO, *Corrosion Sci.* 13 (1973) 471.
23. I. EPELBOIN and M. KEDDAM, *Electrochimica Acta* 17 (1972) 177.
24. R. D. ARMSTRONG, M. HENDERSON and H. R. THIRSK, *J. Electroanal. Chem.* 35 (1972) 119.
25. R. D. ARMSTRONG and M. HENDERSON, *ibid.* 39 (1972) 222.
26. I. EPELBOIN, C. GABRIELLI, M. KEDDAM and H. TAKENOUTI, *Electrochimica Acta* 20 (1975) 913.
27. M. BOJINOV, G. FABRICIUS, P. KINNUNEN, T. LAITINEN, K. MAKELA, T. SAARIO and G. SUNDHOLM, *ibid.*, 45 (2000) 2791.
28. A. R. BROOCKS, C. R. CLAYTON, K. DOSS and Y. C. LU, *J. Electrochem. Soc.* 133 (1986) 2459.

Received 22 September
and accepted 16 December 2004