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Corrosion behavior of Tinplate in Aerated and Deaerated NaCl Solution

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The corrosion behavior of tinplate in aerated and deaerated sodium chloride solution was investigated by using polarization curve, electrochemical impedance spectroscopy (EIS) and immersion tests. The corroded surface of tinplate was characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) techniques, and the concentration of iron and tin ions dissolved in solution was determined by inductively coupled plasma mass spectrometer (ICP-MS). In aerated solution, tinplate has a higher corrosion current density and two time constants in EIS spectrum. The concentration of iron ions in solution is increased with immersion time, but the concentration of tin ions keeps almost unchanged. In deaerated solution, tinplate has a lower corrosion current density and one time constant in EIS spectrum. The concentration of iron and tin ions in solution is increased with the immersion time, but the concentration of tin ions is larger than that of iron ion. The corrosion process of tinplate in aerated solution is predominated by the dissolution of steel substrate, whereas in the deaerated solution the corrosion of tinplate is mainly by the dissolution of tin coating.

Keywords: Tinplate; corrosion; sodium chloride solution; deaerated condition

1. INTRODUCTION

Tinplate as the main packaging material is widely applied in canning industry because of its excellent formability, solderability and corrosion resistance with bright appearance [1-3]. However, there are still significant problems related to the use of tinplate in corrosive food products, such as corrosion failure, loss of seal integrity, discoloration, food safety, etc [4-6]. So it’s still essential to explore the corrosion behavior and mechanism of tinplate in canning environments so as to guarantee the quality of food and beverage.

The corrosion behaviors of tinplate depend many factors including can material (composition, grain size, surface morphology, base steel), nature of the organic coating (epoxy, polyester, acrylic resins), nature of the contacting medium (food and beverage matrix, acidity, presence of complexing agents) and storage conditions (duration, temperature)[3, 7-10]. Besides the above factors, can processing technology such as cleaning, canning, exhausting, sealing and sterilizing has also an important influence on the corrosion behavior of tinplate. Under the adequate processing parameters, abnormal content of oxygen and spoilage bacteria will be result in the can containers, and thus the shelf life of canned food will be shortened [11].

It's well known that the presence of oxygen has a detrimental influence on the corrosion resistance of materials owing to its cathodic depolarization effect. So canning producers are geared to reduce the presence of oxygen to a minimum [12]. It's evaluated that 10.6 mg tin or 4.9 mg iron in the tinplate will be dissolved owing to the existence of 1ml oxygen in the tinplate container [13]. Furthermore, the polarity of Sn-steel couple has been found to be different by the presence of oxygen [11, 12]. In deaerated citric acid solution, the corrosion of tinplate was dominated by the anodic dissolution of tin coating, which implies that tin is anodic to iron and has an electrochemical protective effect on the steel underlayer. Whereas in aerated citric acid solution, the corrosion of tinplate was mainly in the dissolution of steel, which means that tin is cathodic and acts as a simple barrier coating protecting the steel [14]. But few studies has been reported on the corrosion behavior of tinplate in NaCl solution under aerated and deaerated conditions.

In this work, the corrosion behavior of tinplate in 0.1 mol/L NaCl solution under aerated and deaerated conditions was investigated by using polarization curve, electrochemical impedance spectroscopy (EIS) and immersion tests. The corroded surface of tinplate was observed and determined by scanning electron microscopy and X-ray photoelectron spectroscopy, and the dissolution content of Fe and Sn elements in solution was determined. Based on these experimental results, the corrosion process and mechanism of tinplate under aerated and deaerated conditions were proposed and discussed.

2. EXPERIMENTAL

2.1 Materials

All the tinplate sheets used in this work were provided by the ORG Canmaking Company. The tinplate is composed by a low carbon steel and tin coating on both sides of steel by electrodeposition method. The thickness of steel and tin coating on both sides are 0.4 mm and 3 μm separately. The samples with the dimension of 70mm×70mm were degreased by ethanol and dried before exposed to NaCl solution.

2.2 Electrochemical measurements

The potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) of tinplate in 0.1 mol/L NaCl solution under aerated and deaerated conditions were carried out at room temperature in an electrolytic cell by using Autolab 302N electrochemical workstation. A three-electrode system with the tinplate by an exposed area of 19.6 cm^2 as working electrode, a saturated calomel electrode (SCE) as reference electrode and a ruthenium-titanium electrode as counter electrode was used. For the aerated solution, the compressed air was introduced into the electrolytic cell during the whole test. For the deaerated solution, the electrolytic cell was firstly put into a chamber, and then the chamber was vacuumized by vacuum pump and afterward filled with nitrogen until oxygen in the solution was taken out entirely before testing [14].

The potentiodynamic polarization experiments were performed at a scan rate of 0.1667 mV/s. And EIS measurements were carried out at the open circuit potential with a 10 mV amplitude signal and the applied frequency range from 100 kHz to 0.01 Hz. The electrochemical parameters for the EIS data were calculated by applying ZsimpWin software under the given equivalent circuits.

2.3 Immersion tests

Tinplate samples with the dimension of 70mm×70mm were immersed in 0.1 mol/L NaCl solution under aerated and deaerated conditions for 20 days. After immersion test, the surface morphology, composition and valence spectrum of corroded tinplate were characterized by Hitachi FE-SEM S4800 field-emission scanning electron microscopy and PHI5000 Versa Probe X-ray photoelectron spectrometer. The cross section morphology and element distribution of corroded tinplate were observed and determined by scanning electron microscopy and EDS Genesis XM2 energy dispersion spectroscopy.

Meanwhile, 1ml solution was taken from the immersion electrolyte at different immersion times, and the concentration of Fe and Sn ions dissolved in the solution was measured by Agilent 7700x inductively coupled plasma mass spectrometry (ICP-MS).

3. RESULTS

3.1 Polarization curve

The polarization curve of tinplate in 0.1 mol/L NaCl solution under aerated and deaerated conditions is shown in Fig. 1. It can be seen from Fig.1 that tinplate has almost the same corrosion potential (-410 mV_{SCE}) in aerated and deaerated NaCl solution. Compared with the polarization curve in deaereted solution, the polarization curve of tinplate in aerated NaCl solution is shifted to the higher polarization current under the same polarized potential, and there is a polarization platform found in the cathodic polarization branch owing to the diffusion of dissolved oxygen. The corrosion current density of tinplate in aerated and deaerated NaCl solution is 0.55μA/cm^2 and 0.06 μA/cm^2 respectively, which indicating that the presence of oxygen promotes the corrosion of tinplate in NaCl solution.

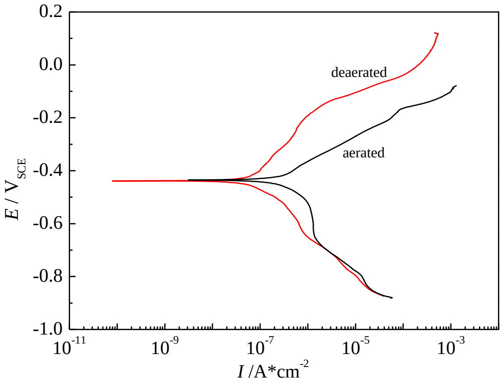
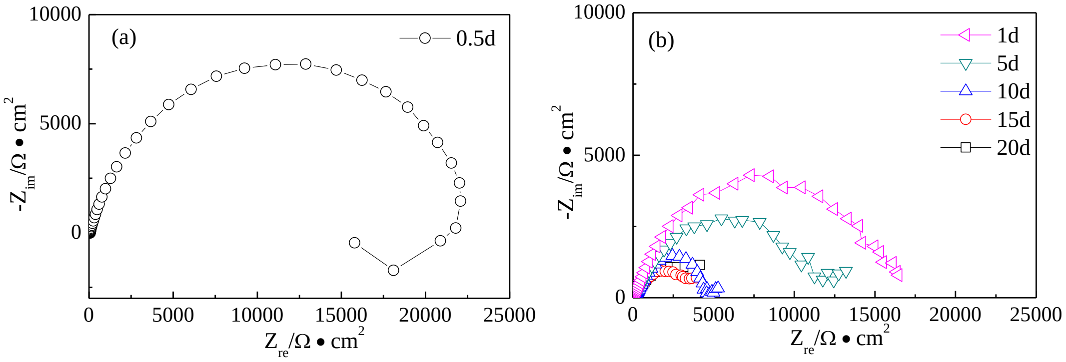


Figure 1. Polarization curve of tinplate in aerated and deaerated 0.1 mol/L NaCl solution

3.2 EIS analysis

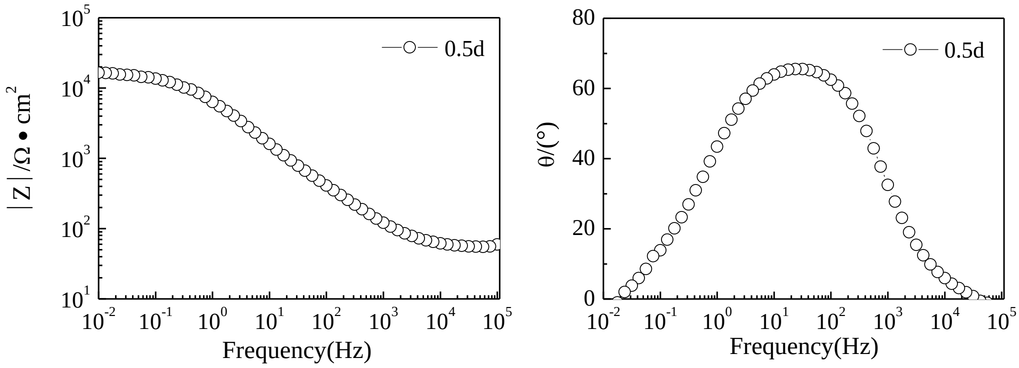
Figure 2 and Figure 3 are the Nyquist and Bode plots of tinplate in aerated 0.1 mol/L NaCl solution. At the initial immersion of 0.5d, there are a capacitance arc at higher frequency and a inductive arc at lower frequency in the EIS spectrum of tinplate (Fig.2a), which indicating that tinplate has a higher polarization resistance (2.2×10^{4}Ω*cm^2) and the surface of tinplate in NaCl solution is in a unsteady state. With the immersion time longer than 1 day, two capacitance arcs are characterized in the EIS spectrum, and the radius of capacitance arc is decreased with the increasing of immersion time (Fig.2b and Fig.3b). The capacitance arc at higher frequency is a result of tin coating interface capacitance Q_{ct} and surface pore resistance of tin coating R_{ct}, and the capacitance arc at lower frequency is a result of double layer capacitance Q_{dl} and charge transfer resistance R'_{ct} of steel substrate. This result implies that the electrolyte had permeated the defects of the tin coating and double layer capacitance was formed on the interface of steel substrate [15], and the corrosion resistance of tinplate is decreased with the prolonging of immersion time.

For EIS spectrum in Fig.2 and Fig.3, the equivalent circuit in Figure 4 was applied to analyze the experimental data, in which R_s is the electrolyte resistance, Q_{ct} is the capacitance of tin coating, R_{ct} is the resistance of tin coating, Q_{dl} is the double layer capacitance of substrate steel, and R'_{ct} is the charge transfer resistance of steel substrate. After analysis, the variation of R_{ct} and R'_{ct} with immersion time is shown in Figure 5. The resistance of R'_{ct} from steel substrate is always larger than that of R_{ct} from tin coating, and both R_{ct} and R'_{ct} values are decreased with the increasing of immersion time, i.e., the corrosion resistance of tinplate is decreased with the increasing of immersion time.

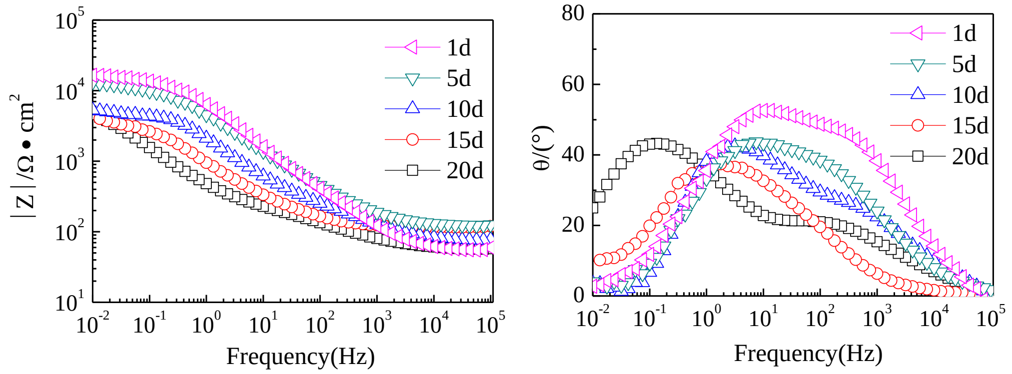


(a) 0.5 d (b) 1-20 d

Figure 2. Nyquist plots of tinplate in aerated 0.1 mol/L NaCl solution



(a) 0.5 d



(b) 1-20d

Figure 3. Bode plots of tinplate in aerated 0.1 mol/L NaCl solution

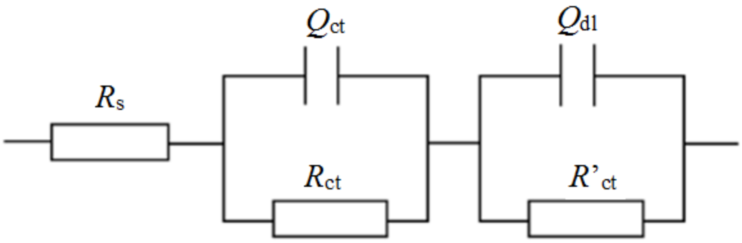


Figure 4. Electrochemical equivalent circuit for tinplate in aerated 0.1 mol/L NaCl solution

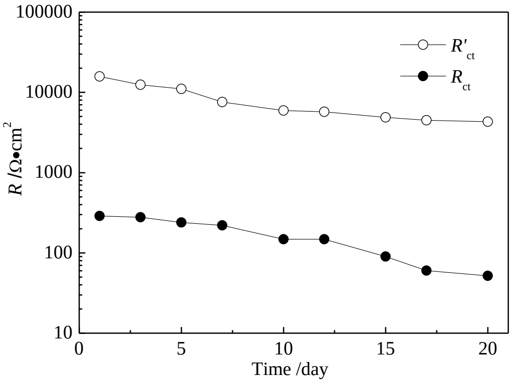
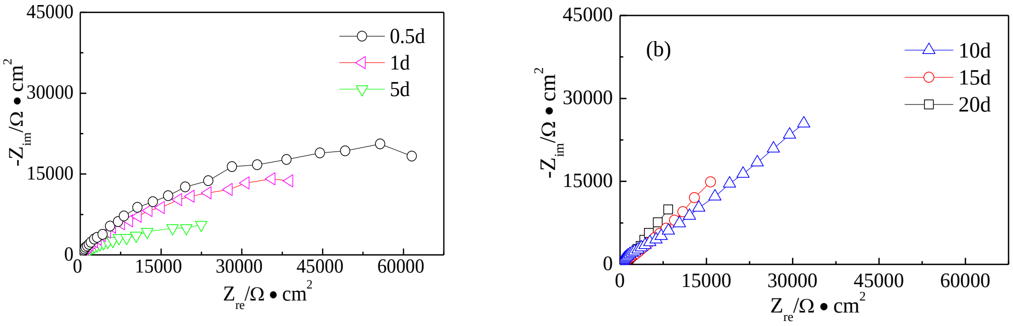


Figure 5. Evolution of R_{ct} and R'_{ct} of tinplate in aerated 0.1 mol/L NaCl solution as a function of immersion time

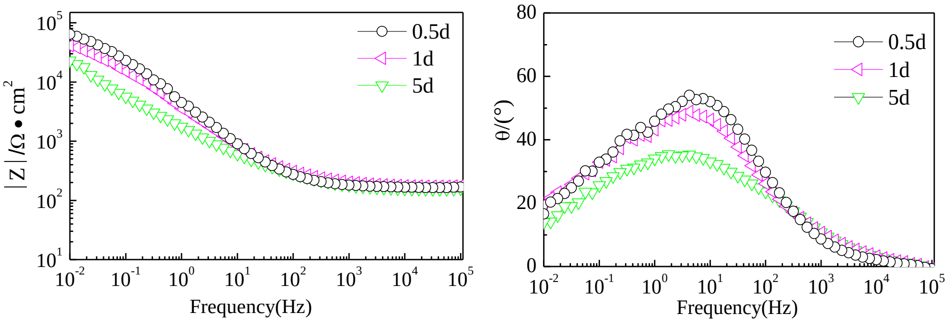
Nyquist and Bode plots of tinplate in deaerated 0.1 mol/L NaCl solution are shown in Figure 6 and Figure 7. At the immersion time less than 5 days, EIS spectrum of tinplate is characterized by a single capacitance arc, and the radius of capacitance arc is decreased with immersion time (Fig.6a and Fig.7a). This result means that the corrosion of tinplate is by the dissolution of tin coating and can be depicted by the equivalent circuit $R_e(Q_{ct}R_{ct})$ in Figure 8a. With the immersion time prolonging to 10 and 20 days, the radius of capacitance arc at higher frequency is continuously reduced, and a Warburg diffusion impedance is appeared at lower frequency (Fig.6b and Fig.7b), which indicating that the corrosion of tinplate is begun to dominate by the diffusion process owing to the formation of corrosion products. So the equivalent circuit $R_e(Q_{ct}(R_{ct}Z_w))$ in Figure 8b can be applied to analyze the corrosion process of tinplate at the immersion time of 10 to 20 days, in which Z_w is the Warburg diffusion impedance.

After data analysis by the above equivalent circuits, the polarization resistance of tinplate R_{ct} in deaerated solution with immersion time is shown in Figure 9. With the increasing of immersion time, the resistance of tinplate R_{ct} is decreased from 64000 Ω•cm^2 at the initial immersion to 8800 Ω•cm^2 at the immersion time of 20 days. By comparing the result of Fig.9 with Fig.5, It's can be observed that the corrosion resistance of tinplate in deaerated solution is always larger than that in aerated solution under the same immersion time, i.e., The presence of oxygen does promote the corrosion of tinplate in NaCl solution.

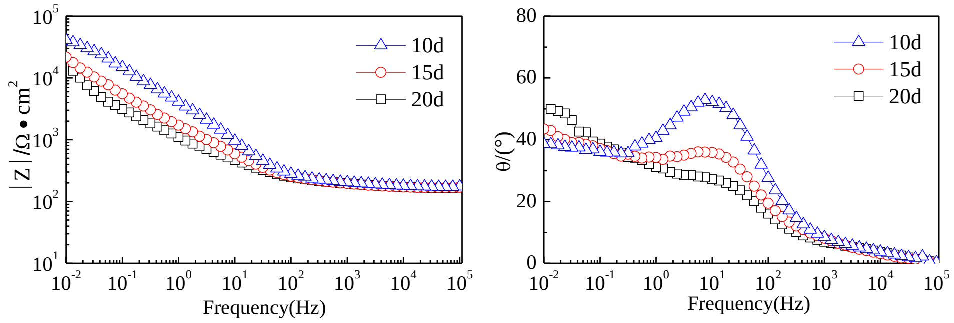


(a) 0.5-5d (b) 10-20d

Figure 6. Nyquist plots of tinplate in deaerated 0.1 mol/L NaCl solution

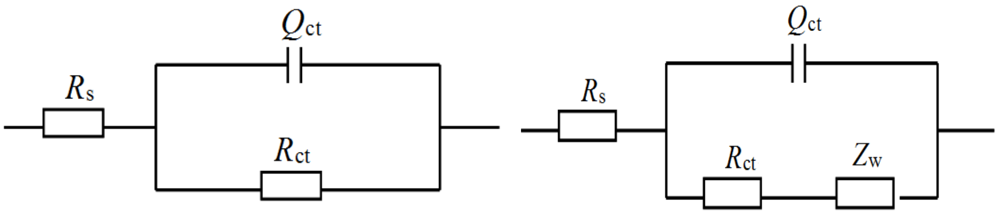


（a）0.5-5d



(b) 10-20d

Figure 7. Bode plots of tinplate in deaerated 0.1 mol/L NaCl solution



(a) 0.5-5d (b) 10-20d

Figure 8. Electrochemical equivalent circuits for tinplate in deaerated 0.1 mol/L NaCl solution

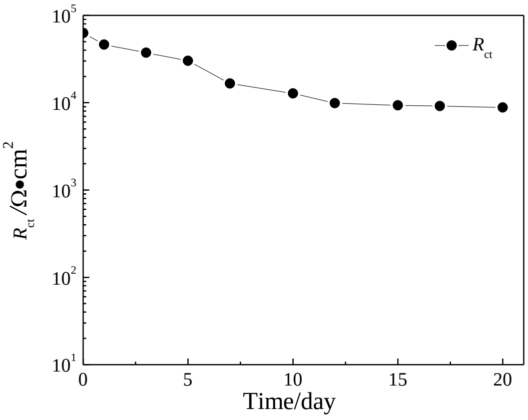
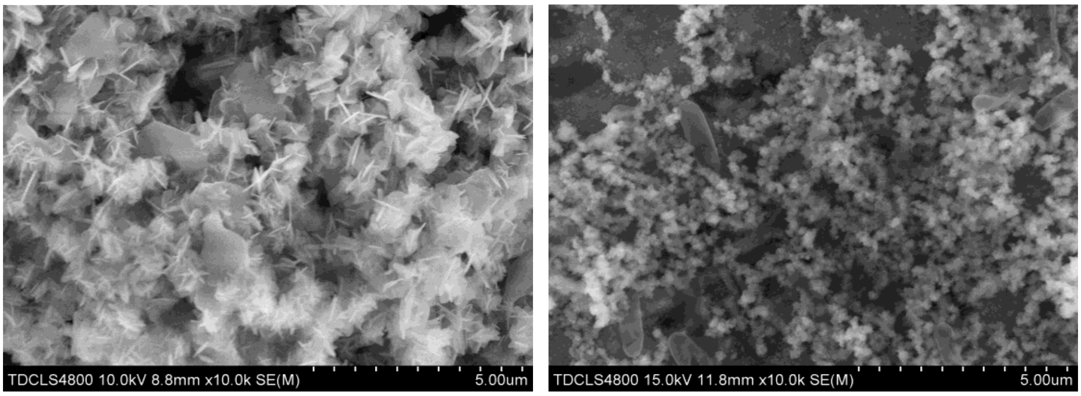


Figure 9. Dependence of R_{ct} value for tinplate in deaerate 0.1 mol/L NaCl solution on immersion time

3.3 Surface Morphology and valence analysis

The surface morphology of tinplate after 20 days' immersion in aerated and deaerated 0.1 mol/L NaCl solution is shown in Fig.10. In aerated solution, tinplate is covered by white corrosion products with the shape of needle and plate (Fig.10 a). Whereas in deaerated solution the white corrosion products are only partially formed on the surface of tinplate (Fig.10 b). This result also implies that the corrosion of tinplate in aerated solution is heavier than that in deaerated solution.



（a） in aerated 0.1 mol/L NaCl solution （b） in deaerated 0.1 mol/L NaCl solution

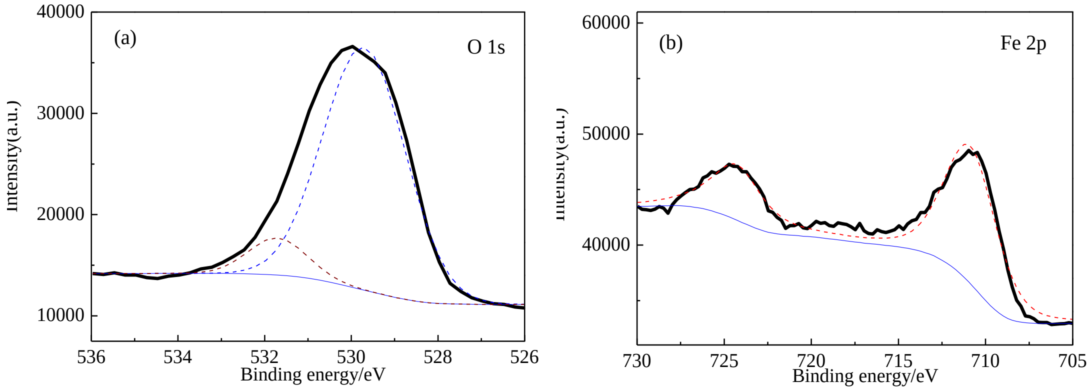
Figure 10. Surface morphology of tinplate in aerated and deaerated 0.1 mol/L NaCl solution

The chemical composition of corrosion products on tinplate was determined by X-ray photoelectron spectrometer. In aerated solution, the corrosion product is composed by 36.5 at.% O, 0.4 at.% Sn and 14.2 at.% Fe, which indicating that the corrosion of tinplate in aerated solution is mostly by the dissolution of steel substrate. But in deaerated solution, the chemical composition of corrosion product is 32.3 at.% O, 13.6 at.% Sn and 4.6 at.% Fe, which means that the corrosion of tinplate in deaerated solution is probably predominated by the dissolution of tin coating.

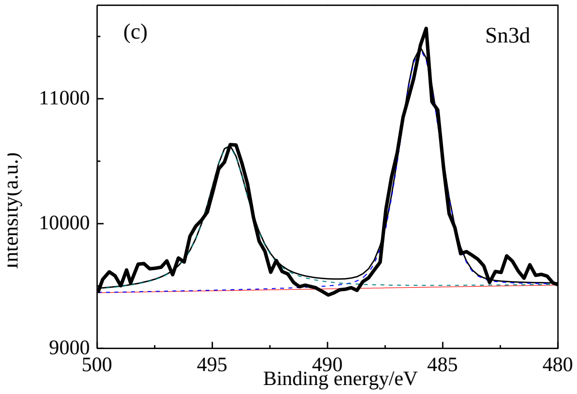
Figure 11 is the XPS spectra of corroded tinplate in aerated NaCl solution. In the XPS spectrum of O1s, one peak at the binding energy of 530.0 eV is detected (Fig.11a), which corresponded to the character of O^{2-} and OH^- ions. In the XPS spectrum of Fe2p, two peaks at the binding energy of 711.2 eV and 724.8 eV are observed (Fig.11b), which corresponded to Fe^{3+} ions in Fe 2p 3/2 and Fe 2p 1/2 states. In the XPS spectrum of Sn3d, two peaks at the binding energy of 486.0 eV and 494.0 eV are observed (Fig.11c), which corresponded to Sn^{4+} ions in Sn 3d 5/2 and Sn 3d 3/2 states. These results show that the corrosion products on tinplate in aerated NaCl solution are mainly in Fe_2O_3 and a small amount of SnO_2, which is accorded with the results in Ref. [16].

The XPS spectra of corroded tinplate in deaerated NaCl solution is shown in Fig.12. In the XPS spectrum of O1s, one peak at the binding energy of 530.0 eV is corresponded to the character of O^{2-} ions (Fig.12a). In the XPS spectrum of Fe2p, one peak at the binding energy of 715.2 eV is observed and corresponded to Fe^{2+} ions (Fig.12b) [17]. In the XPS spectrum of Sn3d, two peaks at the binding energy of 486.0 eV and 495.0 eV were observed and corresponded to Sn^{4+} ions in Sn 3d 5/2 and Sn 3d

3/2 states(Fig.12c). These results imply that the corrosion products on tinplate in deaerated NaCl solution are mainly in SnO_2 and FeO.

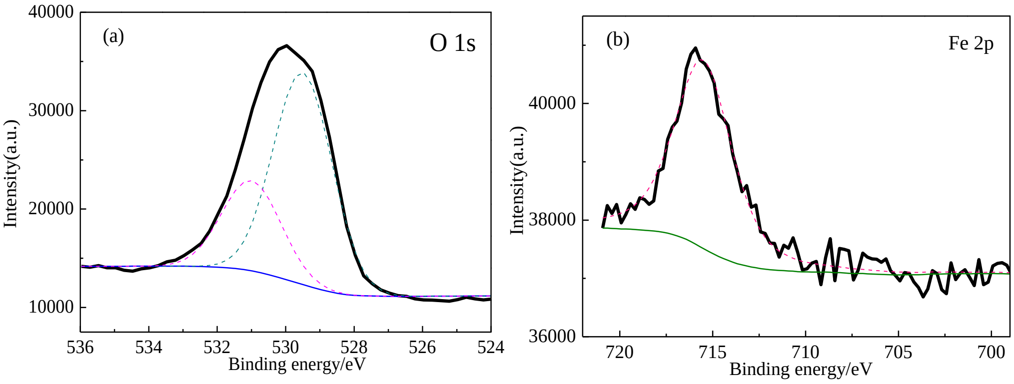


(a) O1s (b) Fe 2p

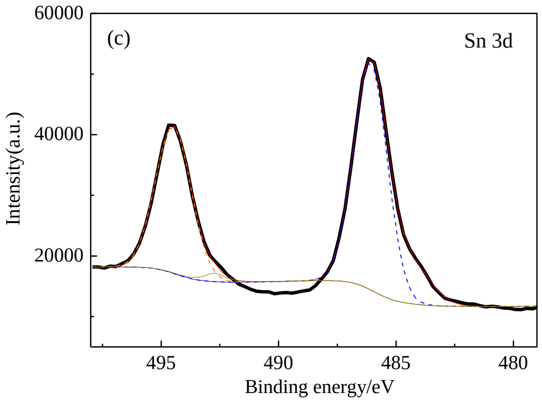


(c) Sn 3d

Figure 11. XPS spectra of corrosion product for tinplate in aerated 0.1 mol/L NaCl solution



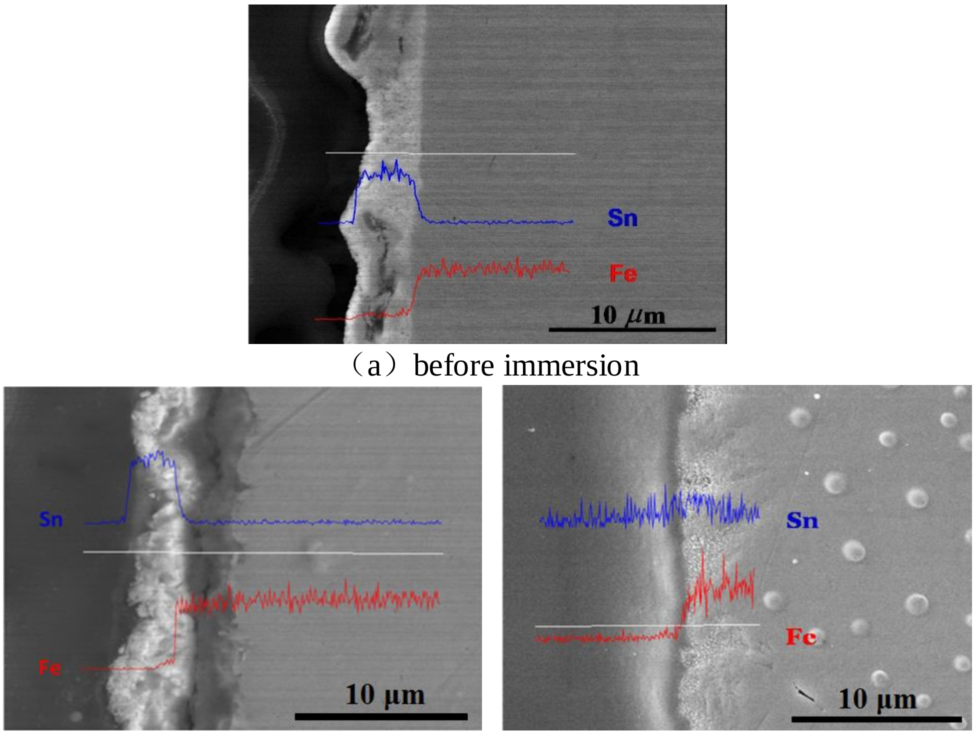
(a) O1s (b) Fe 2p



(c) Sn 3d

Figure 12. XPS spectra of corrosion product for tinplate in deaerated 0.1 mol/L NaCl solution

3.4 Cross section analysis



（a）before immersion

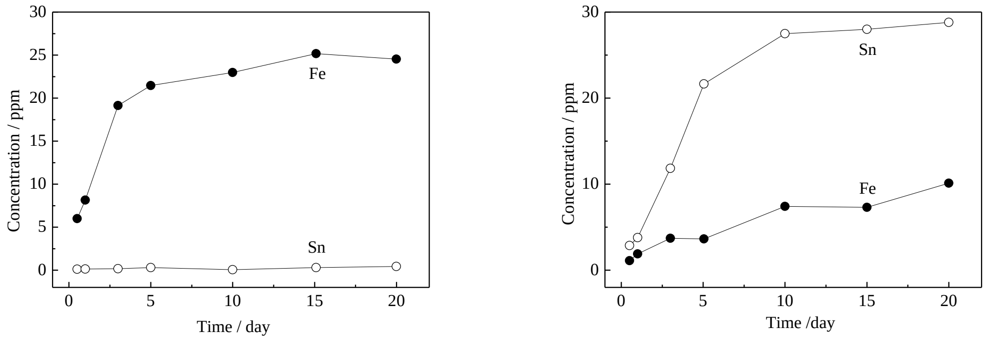
（b）after immersion in aerated solution （c）after immersion in deaerated solution

Figure 13. Cross section and element distribution of tinplate before and after immersion in aerated and deaerated 0.1 mol/L NaCl solution

Figure 13 is the cross section morphology and element distribution of tinplate before and after immersion in aerated and deaerated NaCl solution. Before immersion, tin coating is clearly located outside the steel substrate with the thickness of 3 μm, and there are some pores and defects existed in the tin coating (Fig.13a). After 20 days' immersion in aerated solution, tin coating is still existed on the steel substrate, but there are corrosion products appeared between the tin coating and steel substrate (Fig.13b), which indicating that corrosion is occurred by the dissolution of steel substrate underneath the tin coating. After immersion in deaerated solution, tin coating is almost corroded away and hardly observed (Fig.13c). Meanwhile, the steel substrate is started to react with NaCl solution.

3.5 Ions release analysis

After immersion test, the concentration of iron and tin ions dissolved in aerated and deaerated NaCl solution was determined and shown in Fig.14. In aerated solution, the concentration of iron ions is obviously increased with immersion time, especially at the initial immersion of 3 days, but only a small amount of tin ions (0.1-0.4 ppm) is dissolved and hardly varied with the immersion time (Fig.14a). In deaerated solution, the concentration of iron and tin ions is increased with the prolonging of immersion time, and the concentration of tin ions in the solution is larger than that of iron ions under the same immersion time (Fig.14b). These results show that the corrosion of tinplate in aerated NaCl solution is mainly by the dissolution of steel substrate, whereas the corrosion of tin coating is predominated in the corrosion of tinplate in deaerated NaCl solution, which is the same with the corrosion process of tinplate in aerated and deaerated citric acid solution [14].



（a） in aerated solution （b） in deaerated solution

Figure 14. Concentration of iron and tin ions in aerated and deaerated 0.1 mol/L NaCl solution

4. DISCUSSION

From the above results, it can be deduced that the presence of oxygen not only has an influence on the corrosion rate of tinplate in NaCl solution but also has an impact on the characteristics and process of corrosion. So tinplate has a different corrosion behavior in aerated and dearated NaCl solution.

In deaerated NaCl solution, tinplate has a characteristic of one time constant (single capacitance arc) in EIS spectrum (Fig.6 and Fig.7) and a higher concentration of tin ions in the solution (Fig.14b). These results indicate that the dissolution of tin coating is the main corrosion process of tinplate in deaetaed solution. Once the tin coating is consumed, the steel substrate under the tin coating will begin to react with the solution (Fig.13c). So under deaerated solution tin is anodic to iron, and displays a real electrochemical protective effect on the steel substrate [18, 19]. This is the reason why canning procedures are geared to reduce the presence of oxygen to a minimum so as to protect the steel base of container by sacrificing tin coating on the steel.

In aerated NaCl solution, tinplate has a characteristic of two time constants (two capacitance arcs) in EIS spectrum (Fig.2 and Fig.3) and a higher concentration of iron ions in the solution (Fig.14a), which implying that the electrolyte had permeated the defects of tin coating and double layer capacitance was formed on the interface of steel substrate. As the activation energy of steel substrate in aerated 0.1 mol/L NaCl solution (23.47 kJ/mol) is lower than that of tin coating (77.05 kJ/mol), the corrosion process of tinplate in aerated solution is predominated by the dissolution of steel substrate [15]. Under this condition, steel is anodic to tin coating, and tin coating is only as a simple coating layer physically protecting the steel [18, 19]. These corrosion mechanism could be proved by the fact that the tin coating is still existed on the steel substrate after corrosion (Fig.13b) and a lower concentration of tin ions is appeared in the solution (Fig.14a).

5. CONCLUSIONS

(1) In aerated NaCl solution, tinplate has a higher corrosion current density and a characteristic of two time constants in EIS spectrum. But there is a lower corrosion current density and one time constant in EIS spectrum for tinplate in deaerated solution.

(2) In aerated NaCl solution, the electrolyte could permeate the pores and defects of tin coating, and the corrosion of tinplate is predominated by the dissolution of steel substrate. Under this condition, steel is anodic to tin coating, and tin coating is only as a simple coating layer physically protecting the steel.

(3) In deaerated NaCl solution, the dissolution of tin coating is the main corrosion process of tinplate. Under this situation, tin coating is anodic to steel and displays a real electrochemical protective effect on the steel substrate.

ACKNOWLEDGEMENT

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