Corrosion behavior of tinplate in NaCl solution under different temperature

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The corrosion behavior of tinplate in 0.1 mol/L NaCl solution under different temperature was investigated by using polarization curve, electrochemical impedance spectroscopy (EIS) and immersion tests, and the morphology of corroded tinplate was observed by stereoscopic digital microscopy and scanning electron microscopy. The dissolution content of Fe and Sn elements in NaCl solution was determined by inductively coupled plasma mass spectrometry. The results showed that the corrosion of tinplate in NaCl solution is characterized with two time constant in EIS spectrum, and the radius of capacitance arc is firstly decreased and then slightly raised with the extension of immersion time. With the increasing of temperature from 5 °C to 37 °C, tinplate has a higher corrosion current density, lower radius of capacitance arc and higher dissolution rate in NaCl solution. The activation energy of tin coating is less than that of steel substrate at the initial immersion, but afterward increased to a higher value and larger than that of steel. The corrosion process of tinplate in NaCl solution is divided into four stages, and the corrosion mechanism of every stage is proposed.

Keywords: tinplate, corrosion behavior, NaCl solution, temperature, degradation process

1. INTRODUCTION

Tinplate is extensively applied in canning industry as the most common packaging material because of its excellent formability, solderability and corrosion resistance with good appearance of tin [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 [3-6]. So it's

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 of tinplate depends 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 (aqueous, fatty foodstuffs), composition of the contained product (acid foods, sulfur and/or salt containing foods, etc.) and storage conditions (vacuum degree, duration, temperature)[3, 7]. The corrosion properties of tinplate cans in brine and pickled sauce with seafood were investigated at room temperature by using polarization curve and EIS experiments, and the degradation behavior was evaluated by the variation of electrochemical parameters in the storage duration [4, 6]. The corrosion behaviors of tinplate in the sodium chloride solution [8-10], industrial water [11], citric acid solution [7, 9], functional beverage [12] and coffee drinks [13] were also studied at room temperature, and the corrosion mechanism was proposed and discussed.

Storage conditions, particularly temperature, also have some influence on the corrosion of tinplate by affecting the rate of dissolution of tin into canned food, which may give rise to a risk to human health. In a study of canned US military rations, the tin content of five types of fruit in unlacquered cans at 37 °C after 20 months was 12 times higher than that at 1 °C (420 and 34mg/kg, respectively). For seven types of mixed dishes in unlacquered cans the tin content at 37 °C was 6 times higher than that at 1 °C (190 and 32 mg/kg, respectively) [3, 14]. However, until now there are few reports done about the tinplate corrosion under different storage temperature.

In this work, the corrosion behaviors of tinplate in 0.1 mol/L NaCl solution under different storage temperature were investigated by using polarization curve, electrochemical impedance spectroscopy (EIS) and immersion tests. The morphology of corroded tinplate was observed by stereoscopic digital microscopy and scanning electron microscopy, and the dissolution content of Fe and Sn elements in NaCl solution was determined. Based on these experimental results, the effect of temperature on the corrosion process of tinplate could be proposed.

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 is 0.4 mm and 3 μ m separately. The samples with the dimension of 60mm×60mm 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 at the temperature of 5 $^{\circ}$ C, 20 $^{\circ}$ C and 37 $^{\circ}$ C were carried out in an

electrolytic cell by using Autolab 302N electrochemical workstation. A three-electrode system with the tinplate by a exposed area of 19.6 cm² as working electrode (WE), a saturated calomel electrode as reference electrode (RE) and a ruthenium-titanium electrode as counter electrode (CE) was used. The testing temperatures of 5 °C, 20 °C and 37 °C were obtained by using biochemical incubator in order to simulate the different storage temperatures during the transportation and storage process of canned food.

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 60 mm×60 mm were immersed in 0.1 mol/L NaCl solution at the temperature of 5 °C, 20 °C and 37 °C for 30 days. After different immersion times, the corroded samples were taken out from the solution and then cleaned with distilled water and ethanol, and the corroded surface and cross section morphology of tinplate were observed by Keyence VHX-2000 stereoscopic digital microscopy and scanning electron microscopy separately. The corrosion products on the tinplate surface were removed by using 500 ml/L HCl + 3.5 g/L methylamine solution, the surface morphology was observed by Hitachi FE-SEM S4800 field-emission scanning electron microscopy, and the composition and element distribution were analyzed by EDS Genesis XM2 energy dispersion spectroscopy.

Meanwhile, 1ml solution was collected from the immersion electrolyte at different immersion times, and the concentration of Fe and Sn 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 at different temperature is shown in Fig. 1. With the increasing of temperature, the corrosion potential of tinplate is firstly decreased from -0.460 mV to -0.551 mV and then increased slightly to -0.484mV, whereas the corrosion current density of tinplate is increased continuously from 0.121μ A/cm² (5 °C), 0.208 μ A/cm² (20 °C) to 1.472 μ A/cm² (37 °C). This result meant that the upgrade of testing temperature will promote the corrosion of tinplate in NaCl solution.



Figure 1. Polarization curve of tinplate in 0.1 mol/L NaCl solution at different temperature

3.2 EIS analysis

Figure 2 is the EIS spectrum of tinplate in 0.1 mol/L NaCl solution at the temperature of 5 °C. It can be seen from Fig.2 that there are two time constants during the whole immersion process, which indicating that the electrolyte had permeated the defects of the tin coating and double layer capacitance was formed on the interface of steel substrate [8,15]. The time constant at higher frequency is a result of tin coating interface capacitance Q_c and surface pore resistance of tin coating R_c , and the time constant at low frequency is a result of double layer capacitance Q_{dl} and charge transfer resistance R_{ct} . At the immersion time of 1 hour to 10 days, the radius of the capacitance arc is decreased continually from 272.4 k $\Omega \cdot cm^2$ to 3.87 k $\Omega \cdot cm^2$. But when the immersion time is prolonged to 20 and 30 days, the radius of capacitance arc is slightly increased to 4.07 k $\Omega \cdot cm^2$ and 5.75 k $\Omega \cdot cm^2$.

The EIS spectrum of tinplate in 0.1 mol/L NaCl solution at the temperature of 20 °C is shown in Figure 3. In the EIS spectrum of Fig.3, two time constants are also observed during the immersion time. At the initial immersion of 1 hour to 10 days, the radius of the capacitance arc is decreased from 96.0 k $\Omega \cdot cm^2$ to 3.28 k $\Omega \cdot cm^2$. With the immersion time prolonging to 20 and 30 days, the radius of the capacitance arc is firstly increased to 5.75 k $\Omega \cdot cm^2$ and then decreased to 4.51 k $\Omega \cdot cm^2$.



(a) Nyquist plots within 24 hours



(b) Nyquist plots from 1d to 30d



(c) Bode plot Figure 2. EIS spectrum of tinplate in 0.1 mol/L NaCl solution at temperature of 5°C





Figure 3. EIS spectrum of tinplate in 0.1 mol/L NaCl solution at 20°C



(a) Nyquist plots within 24 hours (b) Nyquist plots from 1d to 30d



(c) Bode plot Figure 4. EIS spectrum of tinplate in 0.1 mol/L NaCl solution at 37°C

Figure 4 is the EIS spectrum of tinplate in 0.1 mol/L NaCl solution at the temperature of 37 °C. It can be observed from Fig.4 that the characteristic of two time constant and radius of capacitance arc with immersion time are the same as that of 20 °C. But the radius of capacitance arc at 37 °C is lower than that of 5 °C and 20 °C under the same immersion time, i.e. the corrosion resistance of tinplate in NaCl solution is reduced with the increasing of testing temperature.



(a) Immersion time less than 24 hours (b) Immersion time longer than 24 hours

Figure 5. Electrochemical equivalent circuits used for tinplate in 0.1 mol/L NaCl solution at the immersion time less and longer than 24 hours, in which R_e is the electrolyte resistance, Q_c is the capacitance of tin coating, R_c 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

T	t	$R_{\rm e}$	$Q_{ m c}$	$n_{\rm c}$	$R_{\rm c}$	$Q_{\rm ct}$	$n_{\rm ct}$	$R_{\rm ct}$
(°C)	(d)	$(\Omega \cdot cm^2)$	$(\mu F \cdot cm^{-2})$		$(\Omega \cdot cm^2)$	$(\mu F \cdot cm^{-2})$		$(\Omega \cdot cm^2)$
5	0.125	66.71	2.799*10 ⁻⁶	1	440.7	8.408*10-6	0.7355	$2.007*10^{5}$
	0.25	42.44	3.114*10-6	1	745.7	8.325*10-6	0.7310	$1.283*10^{5}$
	0.5	14.60	4.041*10-6	1	1843	1.098*10-5	0.7010	$5.546*10^4$
	1	28.57	4.023*10-6	1	717.4	2.252*10-5	0.7077	$1.468*10^4$
	5	14.04	1.628*10-5	1	248.8	1.785*10-4	0.7279	8916
	10	7.17	9.469*10 ⁻⁵	0.9689	266.5	2.129*10-4	0.7014	3835
	20	12.96	2.632*10-4	0.9747	696.9	3.812*10-4	0.7790	3267
	30	22.88	5.655*10-4	0.9294	838.2	3.783*10-4	0.8637	5670
20	0.125	34.5	1.393*10-5	0.6907	346.5	1.873*10-5	0.7829	9.175*10 ⁴
	0.25	32.9	3.664*10-5	0.8475	8394	8.435*10-5	0.6207	$2.541*10^4$
	0.5	28.5	3.086*10-5	0.8031	641.9	1.055*10-4	0.4547	6899
	1	31.81	1.198*10 ⁻⁴	0.7959	561.1	$1.280*10^{-4}$	0.7326	5002
	5	32.96	4.743*10-5	0.9396	132.0	3.212*10-4	0.6408	3814

Table 1. Electrochemical parameters in equivalent circuit of tinplate in NaCl solution under different immersion time and temperature

	10	7.097	3.264*10-4	1	329.8	5.327*10-4	0.9490	2772
	20	16.15	9.230*10-4	0.9793	242.7	4.888*10-4	0.9314	5173
	30	11.11	3.642*10-4	0.9981	173.2	3.876*10-4	0.7612	4589
37	0.125	7.253	1.18*10-5	0.9665	240.7	3.812*10-5	0.8580	6614
	0.25	7.514	$1.006*10^{-5}$	1	341.9	3.681*10-5	0.8860	5172
	0.5	5.552	6.496*10 ⁻⁶	1	252.5	1.073*10-4	0.6541	3667
	1	6.307	1.898*10-5	1	221.3	1.481*10-4	0.8586	2575
	5	7.892	7.572*10-4	0.8429	24.86	8.095*10-4	0.7545	2552
	10	7.403	6.316*10 ⁻⁴	0.7063	8.586	1.255*10 ⁻³	0.7591	2057
	20	6.561	3.608*10-4	0.6841	22.96	1.189*10 ⁻³	0.7656	3578
	30	6.378	2.971*10-4	0.7331	29.71	1.189*10 ⁻³	0.7810	2021



Figure 6. Variation of R_c and R_{ct} of tinplate in 0.1 mol/L NaCl solution with immersion time and temperature

For EIS spectrum in Figs.2, 3 and 4, the equivalent circuits in Figure 5 were applied to analyze the experimental data [8.15]. At the initial immersion stage less than 1 day, equivalent circuit of $R_e(Q_c(R_c(Q_{dl}R_{ct})))$ was characterized owing to the corrosion of tin coating and steel substrate by the defects of tin coating (Fig.5a). But when the immersion time is longer than 1 day, the equivalent circuit was changed to $R_e(Q_cR_c)(Q_{dl}R_{ct})$ owing to the formation of corrosion pits and fall off of partial corrosion products (Fig.5b). The fitting electrochemical parameters are listed in Table 1, and the variance of R_c and R_{ct} with the immersion time and temperature is shown in Figure 6. It can be concluded from Table 1 and Fig.6 that the resistance of R_{ct} from steel substrate is always larger than that of R_c from tin coating, and both R_c and R_{ct} are decreased with the increasing of temperature, i.e., the upgrade of temperature will promote the corrosion of tinplate.

From the aspect of immersion time, the corrosion process of tinplate in NaCl solution could be divided into four stages. Stage I is from the beginning of immersion to 1 day, in which the resistance of tin coating R_c is slightly increased or decreased but the resistance R_{ct} is obviously decreased. At stage II of 1 days, both R_c and R_{ct} are decreased distinctly. Whereas at the stage III of 10 to 20 days, both R_c and R_{ct} are increased clearly. At the final stage of 20 to 30 days, R_c and R_{ct} are not varied in a fixed rule with the immersion time.

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3.3 Surface Morphology

The surface morphology of tinplate after immersion in 0.1 mol/L NaCl solution at 20 °C is shown in Fig. 7. After 1 day's immersion, the corrosion products with yellow color is scattered on the surface of tinplate (Fig.7a). With the increasing of immersion time, there are more corrosion products formed (Fig.7b). At the immersion time of 20 days, the surface of tinplate is fully covered by the corrosion products (Fig.7c). When the immersion time is prolonged to 30 days, the corrosion products are partially peeled off (Fig.7d).



Figure 7. Surface morphology of tinplate in 0.1 mol/L NaCl solution at 20°C after different immersion time





Figure 8. Surface morphology of tinplate after the removal of corrosion products in 0.1 mol/L NaCl solution at 20°C



Figure 9. Cross section morphology and element distribution of tinplate in 0.1 mol/L NaCl solution at 20°C after different immersion time

Fig.8 is the surface morphology of tinplate after the removal of corrosion products. At the immersion time of 1 day, the surface of tinplate becomes rough and uneven (Fig.8a). With the immersion time increased to 10 days, corrosion pits are formed on the tinplate (Fig.8b). At the

immersion time of 20 days, the area of tin coating is decreased with the enlargement of corrosion pits (Fig.8c). With the immersion time further prolonged to 30 days, the depth and area of corrosion pits is promoted and tin coating is hardly observed (Fig.8d). For the corrosion of tinplate at temperature of 5 °C and 37 °C, similar results are also obtained.

3.4 Cross section

The cross section morphology and element distribution of tinplate after corrosion in NaCl solution at 20 °C is shown in Fig. 9. After one day's corrosion, Fe, Sn and O elements (in the corrosion products) are detected on the surface and there is no clear dividing line between the tin coating and steel substrate (Fig. 9a). With the increasing of immersion time to 10 days, the corrosion products with containing of Fe and O elements are formed on both sides of tin coating (Fig. 9b). At the immersion time of 20 days, the corrosion products composed by Fe, Sn and O elements are observed on the surface and corrosion pits are located underneath the corrosion products (Fig. 9c). When the immersion time is prolonged to 30 days, the corrosion products are partially peeled off and a rough and uneven substrate was left (Fig.9d). These observations are in agreement with the results of surface morphology in Fig.7 and Fig.8.

3.3 ICP analysis

After immersion test, the concentration of Fe and Sn dissolved in NaCl solution was determined and shown in Fig.10. It can be seen that the concentration of Fe element in the solution is one or two orders higher than that of Sn element under the same immersion time and temperature, i.e., the corrosion of tinplate in NaCl solution is mainly by the dissolution of steel substrate. With the increasing of testing temperature, the concentration of Fe and Sn elements in solution is raised under the same immersion time, which means that the increased temperature promotes the corrosion process of tinplate in NaCl solution.



Figure 10. Concentration of Fe and Sn elements dissolved in 0.1 mol/L NaCl solution under different immersion time and temperature

At the initial immersion time less than 24 hours, the concentration of Fe and Sn elements is increased almost linearly with the immersion time. After the immersion time longer than 1 day, the dissolution rate of Fe and Sn elements in the solution is dropped down, especially in the immersion time of 20 days and 30 days. This result is probably correlated with the formation of corrosion products on the surface of tinplate, and it is this thick layer of corrosion products at longer immersion time that hinder the dissolution of Fe and Sn elements in solution.

4. DISCUSSION

4.1 Activation energy



Figure 11. Dependence of $Log(1/R_c \text{ or } R_{ct})$ for tinplate in 0.1 mol/L NaCl solution on 1/T



Figure 12. Variance of activation energy of tin coating and steel substrate with immersion time in 0.1 mol/L NaCl solution

From the results of Figs.1 to 4, Fig.6 and Fig.10, it can be seen that tinplate under higher testing temperature has a higher corrosion current density, lower polarization resistance and higher Fe and Sn content in NaCl solution. These experimental data proved that the enhancement of testing temperature will promote the corrosion rate of tinplate in NaCl solution.

In order to analyze the effect of temperature on the corrosion process of tinplate, Arrhenius equation $i = Ae^{\frac{E_a}{RT}}$ [16] and Stern-Geary equation i = B/Rp [17] were applied to determine the

activation energy of tinplate in NaCl solution, in which E_a is the activation energy of the corrosion process (J/mol), *R* is the universal gas constant of 8.314J/(mol·K), *T* is the testing temperature (K), *A* and *B* are the preexponential factor and Stern-Geary constant. Based on the resistance of tin coating R_c and steel substrate R_{ct} in Fig.6, the calculation of activation energy can be simplified as the following equation [18]:

$$Log(1/Rc \text{ or } Rct) = Log(A') - \frac{E_a}{2.303RT}$$

Where $A' = A/B$.

The dependence of $\text{Log}(1/R_c \text{ or } R_{ct})$ for tinplate in NaCl solution on 1/T is shown in Fig.11, and the activation energy of tin coating and steel substrate at different immersion time is calculated and plotted in Fig.12. At the immersion time within 24 hours, the activation energy of tin coating is less than that of steel substrate, which indicating that the tin coating is predominantly exposed in the solution and the steel substrate is only dissolved by the defects of tin coating. But after 1 day's immersion, the activation energy of tin coating is increased to a higher value, and larger than that of steel substrate, which means that the corrosion of tinplate is changed into the dissolution of steel substrate. These results are consistent with the concentration data of Fe and Sn elements in Fig.10.

4.2 Corrosion process

From the surface and cross section morphology in Figs. 7-9, and experimental results in Fig. 6, Fig.10 and Fig.12, the corrosion process of tinplate in 0.1 mol/L NaCl solution could be divided into four stages, which is illustrated schematically in Fig.13.

At the initial immersion less than 24 hours (Stage I), the tin coating on tinplate is predominantly exposed in the solution, and the steel substrate is only dissolved by the defects of tin coating. So the corrosion of tinplate is composed by the dissolution of tin and steel substrate (Fig.10) [8, 13], and small amount of yellow corrosion products is formed on the surface (Fig. 7a and Fig.13a). As the immersion time is increased from 1 day to 10 days (Stage II), the activation energy of tin coating is larger than that of steel substrate (Fig.12), the dissolution of steel substrate gradually becomes the main corrosion process. So more and more corrosion products are emerged on the surface and corrosion pits are formed underneath the tin coating (Fig.13b). With the further immersion to 20 days (Stage III), the corrosion products are covered the whole surface (Fig.7c) and the thick layer of corrosion products has the tendency to fall off. At the final immersion stage (Stage IV, longer than 20 days), the corrosion products around the tin coating are partially peeled off and larger corrosion pits are left (Fig.8d). Meanwhile the corrosion products on the surface are formed again, and then the corrosion of tinplate is mainly changed into the dissolution of steel substrate (Fig.13d) [8, 13].





Figure 13. Schematic diagram of corrosion process of tinplate in 0.1 mol/L NaCl solution

5. CONCLUSIONS

1. The corrosion of tinplate in NaCl solution is characterized with two time constant in EIS spectrum, the radius of capacitance arc is firstly decreased and then slightly raised with the extension of immersion time.

2. With the increasing of temperature from 5 °C to 37 °C, tinplate has a higher corrosion current density, lower radius of capacitance arc and higher dissolution rate in NaCl solution. At the first stage of immersion, the activation energy of tin coating is less than that of steel substrate. After that the activation energy of tin coating is increased to a higher value and larger than that of steel substrate.

3. The corrosion process of tinplate in NaCl solution is divided into four stages. The first stage is the corrosion of tin coating and the dissolution of steel substrate through the defect of tin coating, and Stage II is the corrosion of steel substrate and the formation of corrosion pits. Stage III is the thickening of corrosion products, and the final stage is the fall off of corrosion products and the continual dissolution of steel substrate.

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