

Effects of reflowing temperature and time on alloy layer of tinplate and its electrochemical behavior in 3.5% NaCl solution

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Abstract: Effects of reflowing temperature and time on the alloy layer of tinplate and its electrochemical behavior in 3.5% NaCl solution were investigated by electrochemical measurements and surface characterization. It is found that the amount of alloy layer increases with the increase of reflowing temperature and time. Then the corrosion potential of detinned tinplate shifts positively and the corrosion rate decreases. After being coupled with tin, the detinned tinplate acts as cathode and tin acts as anode initially. However, after being exposed for some time, the potential shifts of both detinned tinplate and tin reverse the polarity of the coupling system. The galvanic current density decreases with the increase of reflowing temperature and time.

Key words: tinplate; alloy layer; reflowing process; galvanic corrosion

1 Introduction

Tinplate is the cold rolling low carbon steel sheet with electrolytic tin on both sides and has many excellent properties, such as high corrosion resistance, easy solderability, nontoxicity. Therefore, tinplate is widely used as containers for a wide variety of products in the food processing industry [1–8]. Although new alternative materials, such as aluminum and chromated steel sheet are increasingly used in the canning industry, the amount of tinplate used in the canning industry continues to account for more than 80% [9]. In order to keep up with competition with these new alternative materials, tinplate becomes thinner and thinner, which increases the probability of corrosion [10,11]. At the same time, the corrosion resistance of tinplate is always a primary concern for users. Therefore, study of the corrosion resistance of electrolytic tinplate becomes more and more critical [12–15].

It is acknowledged that for tinplate, electroplating of tin will produce a matte and non-reflective appearance. However, a smooth appearance of tinplate is usually required for certain applications. To improve the

brightness and reflectivity of the surface, the tin-plated coating needs to be re-melted by being placed into furnace at certain temperature for some time, which is known as reflowing treatment. During the reflowing process, an alloy layer of tinplate (an intermetallic compound FeSn_2) will be formed through thermal diffusion between Fe and Sn, and the thickness, microstructure and compactness of the alloy layer directly affect the lifetime of tinplate [16,17]. The corrosion resistance of electrolytic tinplate is mainly affected by its alloy layer. There are some literatures which studied the alloy layer of tinplate in order to improve the corrosion resistance of tinplate [18–21]. However, the property of alloy layer is primary dependent on the reflowing process after electrolytic tin is on steel sheet. The effects of reflowing process, such as the reflowing temperature and the reflowing time, on the protective property of alloy layer for substrate are still unclear.

The alloy tin couple test, in which the corrosion current density between the tin anode and the detinned tinplate is measured, has been applied to the corrosion resistance assessment for the tinplate used as the acid food container without oxygen [22–24]. However, there

are very few reports about the corrosion resistance of the alloy layer in the salt electrolyte with oxygen and the effect of reflowing process on the corrosion resistance. With the increase of coastal users and export products by means of ocean shipping, the tinplate needs to have good corrosion resistance in the salt electrolyte with oxygen. At the same time, with the increase of demands for cost reduction, the mass of tin coating is often no more than 2.8 g/m^2 and oil film thickness is $2\text{--}8 \text{ mg/m}^2$ on each side, and the content of chromium in passivation film is very low. Therefore, it is important to study and understand the corrosion resistance of the alloy layer in a wide range of environments, especially in the salt electrolyte with oxygen.

In this work, the electrochemical behavior and mechanism of the alloy layer of tinplate in 3.5% NaCl solution were investigated by the measurement of corrosion potential, potentiodynamic polarization curve, and electrochemical impedance spectroscopy (EIS). The galvanic corrosion behavior between detinned tinplate and tin was also studied by couple test. The morphologies and composition of alloy layer were characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

2 Experimental

The size of tinplate before reflowing was $150 \text{ mm} \times 10 \text{ mm} \times 0.15 \text{ mm}$, with tin coating mass of 2.8 g/m^2 on each side. The tinplate was reflowed in a temperature control equipment with different reflowing time at different reflowing temperatures. After reflowing treatment, the tinplate was degreased in acetone and dried with compressed air. In order to remove oxides and impurities, the tinplate after degreasing was electrochemically cleaned in 0.5% Na_2CO_3 solution at room temperature ($25 \pm 1 \text{ }^\circ\text{C}$) with a cathodic current density of 25 mA/cm^2 using alloy tin couple equipment (Kyushu Technology Research Inc., Japan). Then, the tinplate was detinned in 5% NaOH solution at room temperature ($25 \pm 1 \text{ }^\circ\text{C}$) with the constant 0.4 V using alloy tin couple equipment, and then rinsed in tap water, distilled water, acetone, respectively, and dried in compressed air.

For electrochemical measurements, a three-electrode system was used, which consists of the detinned tinplate with a surface area of 0.20 cm^2 as the working electrode, a platinum mesh as the counter electrode and a saturated calomel electrode (SCE) as a reference electrode, respectively. All the potentials were referred to SCE. The test solution was 3.5% NaCl solution, which was prepared with analytical grade reagent and deionized water. All the measurements were performed in a quiescent solution at room temperature.

The polarization curve measurement was performed at scan rate of 1 mV/s from -100 mV to $+100 \text{ mV}$ versus open circuit potential (OCP). EIS measurement was performed at OCP with an amplitude of sinusoidal voltage of 5 mV . All the electrochemical measurements were carried out using a commercial model 273A electrochemical analyzer/workstation (Princeton Instruments Inc., US). The galvanic current between the detinned tinplate and tin and their coupled potential were measured using zero-resistance ammeter (ZRA) model.

After detinning treatment, atomic force microscope (AFM, SEIKO SPA400, Japan), scanning electron microscope (SEM, FEI Quanta400, Holand) and electron probe micro analysis (EPMA, JXA-8800R, Japan) were used to observe the morphologies of alloy layer and analyze the composition of alloy layer.

3 Results

3.1 Corrosion potential measurements of detinned tinplate

The time dependence of corrosion potentials of detinned tinplate after reflowing at different temperatures for different time is shown in Fig. 1. It is seen that the corrosion potential of the detinned tinplate without reflowing treatment shifts negatively from -0.37 V to a relative stable value of -0.62 V after being immersed in the solution for 1 h. The corrosion potentials of the detinned tinplate after reflowing at $270 \text{ }^\circ\text{C}$ for various times also shift negatively, but are more positive than those of the detinned tinplate without reflowing treatment. The corrosion potentials of the detinned tinplate after reflowing at $270 \text{ }^\circ\text{C}$ for 5, 10, 20, and 30 min reach the steady-state values of about -0.59 , -0.58 , -0.58 and -0.55 V , respectively. It is clear that the stable corrosion potentials of the detinned tinplate after reflowing shift positively with the increase of the reflowing time. The corrosion potentials of detinned tinplate after reflowing also shift negatively at various temperatures for 30 min. The corrosion potentials of detinned tinplate after reflowing at 210, 230, 250, and $270 \text{ }^\circ\text{C}$ reach the steady-state values of about -0.62 , -0.60 , -0.59 and -0.55 V , respectively, which are also more positive than those of detinned tinplate without reflowing process. Furthermore, the corrosion potentials of the detinned tinplate after reflowing at various temperatures also shift positively with the increase of reflowing temperature. Therefore, it is found that both the increases of reflowing time and reflowing temperature result in positive shifts of the corrosion potentials, which indicates that the increases of reflowing time and reflowing temperature would improve the protective property of alloy layer, and then enhance the corrosion resistance of detinned tinplate.

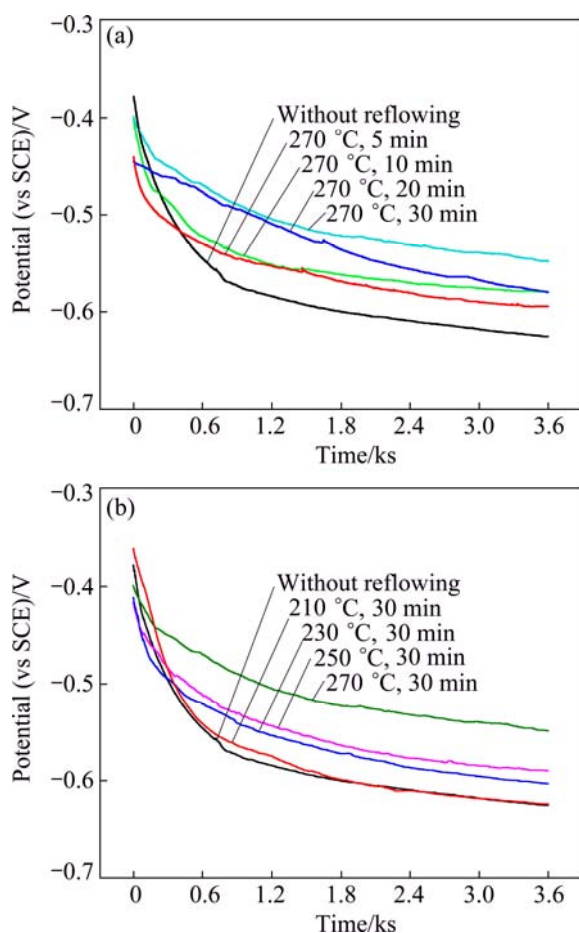


Fig. 1 Time dependence of corrosion potential of detinned tinplate in 3.5% NaCl solution after reflowing for different reflowing time (a) and at different reflowing temperatures (b)

3.2 Potentiodynamic polarization curve measurement

The polarization curves of the detinned tinplate after reflowing at different temperatures for different time are shown in Fig. 2. It is seen that the corrosion current density of detinned tinplate decreases in the reflowing process. Furthermore, with the increase of reflowing time and reflowing temperature, there is an insignificant change in the cathodic current density, while the anodic current density decreases obviously, which results in the decrease of corrosion current density and the positive shift of corrosion potential.

The electrochemical parameters, corrosion potential (ϕ_{corr}) and corrosion current density (J_{corr}), were obtained by performing a least square fit of the measured data in weak polarization region, and are listed in Tables 1 and 2. It is apparent that, with the increase of reflowing time and reflowing temperature, the corrosion current density of the detinned tinplate decreases and the corrosion potential shifts to positive direction. Therefore, the increases of reflowing time and reflowing temperature have an improvement on the corrosion resistance of tinplate in 3.5% NaCl solution with oxygen.

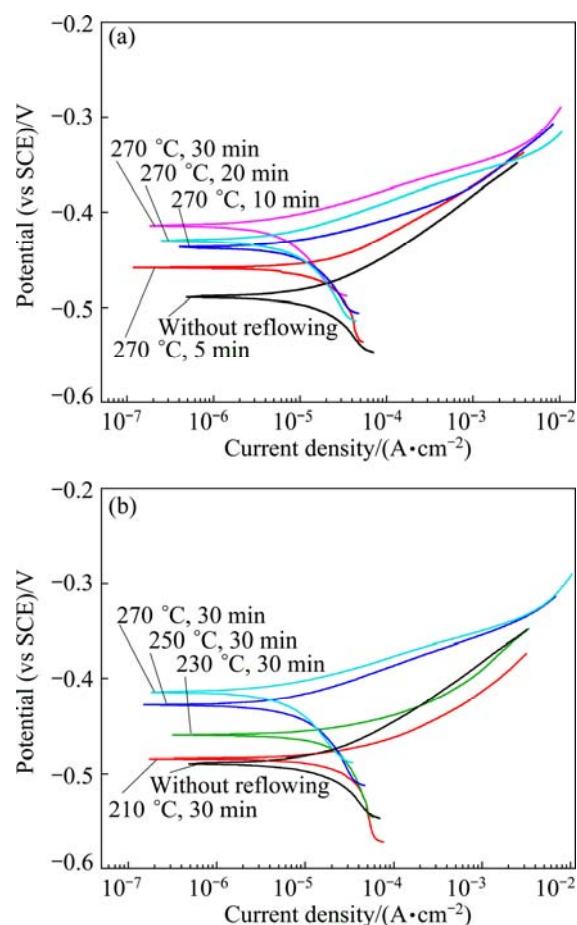


Fig. 2 Polarization curves of detinned tinplate in 3.5% NaCl solution after reflowing for different reflowing time (a) and at different reflowing temperatures (b)

Table 1 Corrosion potential and corrosion current density of detinned tinplate in 3.5% NaCl solution after reflowing at 270 °C for different reflowing time

Reflowing time/min	Corrosion potential (vs SCE)/V	Corrosion current density/(A·cm ⁻²)
0	-0.489	5.707×10^{-5}
5	-0.458	2.983×10^{-5}
10	-0.436	1.221×10^{-5}
20	-0.430	8.12×10^{-6}
30	-0.414	5.773×10^{-6}

Table 2 Corrosion potential and corrosion current density of detinned tinplate in 3.5% NaCl solution after reflowing at different temperatures for 30 min

Reflowing temperature/°C	Corrosion potential (vs SCE)/V	Corrosion current density/(A·cm ⁻²)
210	-0.484	4.769×10^{-5}
230	-0.459	3.549×10^{-5}
250	-0.430	8.624×10^{-6}
270	-0.414	5.773×10^{-6}

3.3 Electrochemical impedance spectroscopy measurements

Figure 3 shows the Nyquist plots of the detinned tinplate after reflowing at different temperatures for different time. It is seen that all the Nyquist plots are featured with a depressed capacitive semicircle at whole frequencies, which can be attributed to charge transfer process. Moreover, with the increase of reflowing temperature and reflowing time, the diameter of the capacitive semicircle increases, which indicates the improvement of corrosion resistance of the detinned tinplate.

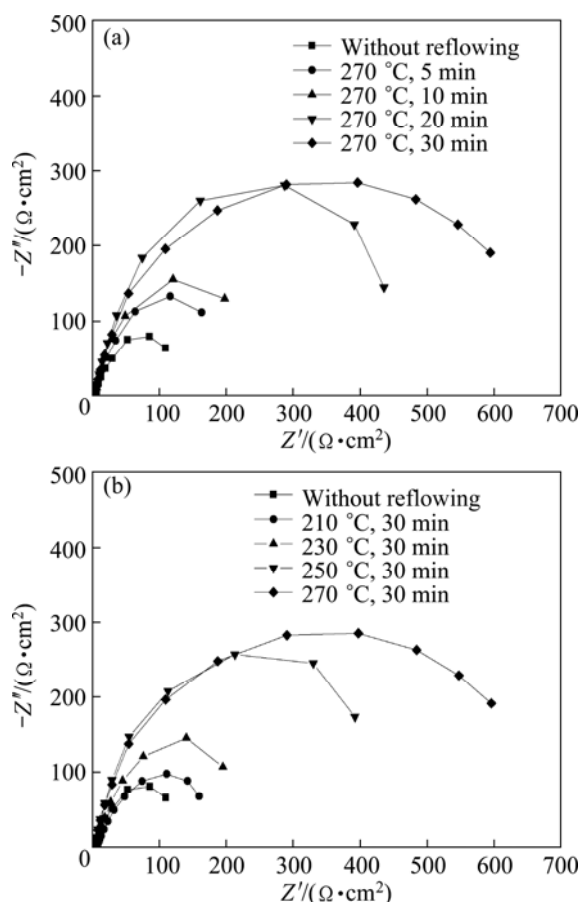


Fig. 3 EIS plots of detinned tinplate in 3.5% NaCl solution after reflowing for different reflowing time (a) and at different reflowing temperatures (b)

To quantify the EIS electrochemical parameters, an equivalent circuit ($R_s(Q_{dl}R_{ct})$) is used for fitting the EIS data, where R_s is the solution resistance, R_{ct} is the charge transfer resistance, Q_{dl} is the constant phase element (CPE). The CPE, which has non-integer power dependence on the frequency, is used to represent the capacitance of double layer accounting for the deviation from the ideal capacitive behaviour due to surface inhomogeneity, roughness and adsorption effects. The impedance of CPE is described by the expression as follows:

$$Z_{CPE} = \frac{1}{Y_0} (j\omega)^{-n} \quad (1)$$

where Y_0 is admittance adjustable parameter independent of the frequency; $j = \sqrt{-1}$; $\omega = 2\pi f$; n is the dispersion coefficient related to surface inhomogeneity. When $n=0$, CPE represents a resistance with $R = Y_0^{-1}$; when $n=1$, CPE represents a capacitance with $C = Y_0$. Table 3 lists the corresponding fitted electrochemical parameters. It is seen that the charge transfer resistance (R_{ct}) increases obviously after reflowing treatment. Furthermore, the R_{ct} increases with the increase of reflowing temperature and reflowing time. This indicates that the increase of reflowing temperature and reflowing time reduce the corrosion rate of detinned tinplate, which is consistent with the polarization curve measurements.

Table 3 Electrochemical impedance data of detinned tinplate in 3.5% NaCl solution after reflowing at different temperatures for different time

Reflowing temperature/°C	Reflowing time/min	$R_s/(\Omega \cdot \text{cm}^2)$	$Y_0/(\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^{-n})$	n	$R_{ct}/(\Omega \cdot \text{cm}^2)$
Without reflowing	Without reflowing	3.93	0.0126	0.98	142.2
210	30	3.91	0.0029	0.92	181.3
230	30	3.97	0.0026	0.94	249.7
250	30	3.76	0.0038	0.93	417.8
270	30	3.96	0.0017	0.91	578.9
270	5	3.71	0.014	0.93	236.2
270	10	3.94	0.0071	0.92	253.3
270	20	3.95	0.0045	0.95	578.9

3.4 Morphology and composition of alloy layer

The morphology and coverage of alloy layer are directly related to the corrosion resistance of tinplate. Therefore, it is important to determine its topography, distribution and composition. In this work, SEM was used to study the surface morphology and composition and EPMA was used to study the cross section morphology and element distribution of the detinned tinplate.

Figure 4 shows the cross section morphology and element distribution of the detinned tinplate after reflowing at 270 °C for 30 min. It is seen that there is Sn element distribution layer on the detinned tinplate surface and the corresponding decrease in Fe element content. This indicates that there is a Fe–Sn alloy layer with an approximate thickness of 1 μm on the detinned tinplate surface. This alloy layer is formed by the mutual diffusion of Fe and Sn elements during the reflowing process.

Figure 5 shows the surface morphologies of the detinned tinplate after reflowing at 270 °C for different

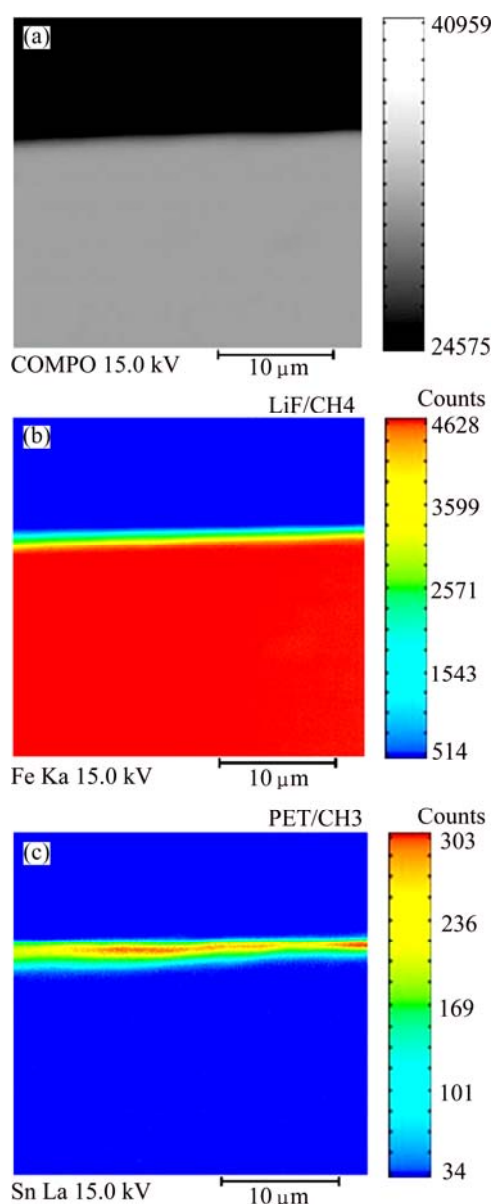


Fig. 4 Cross section morphology and element distribution of detinned tinplate after reflowing at 270 °C for 30 min: (a) Cross section morphology; (b) Cross section distribution of Fe element; (c) Cross section distribution of Sn element

time. It is seen that the formed alloy layer (bright sites in Fig. 5) is few after reflowing for 3 min, while with the increase of reflowing time, the content of alloy layer increases obviously. The alloy layer disperses on the detinned tinplate surface, and there are some regions not covered by alloy layer.

Figure 6 shows the surface morphologies for the detinned tinplate after reflowing at different temperatures for 30 min. It is seen that there is an alloy layer on the tinplate surface at all the reflowing temperatures of 230, 250 and 270 °C, and the content of the alloy layer increases with the increase of reflowing temperature.

Figure 7 shows the energy dispersive spectrum of

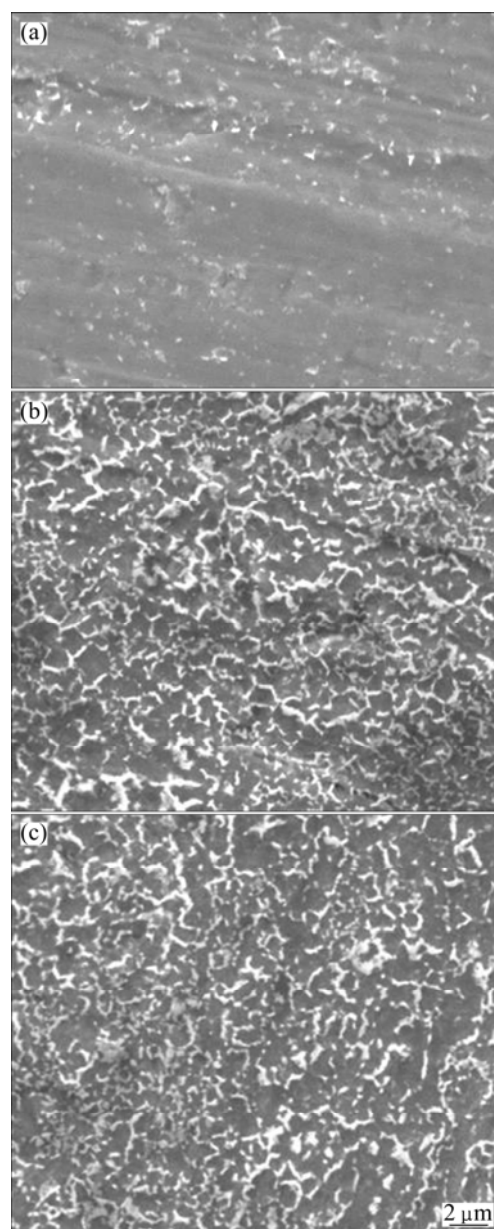


Fig. 5 SEM images of surface morphology of detinned tinplate after reflowing at 270 °C for different reflowing time: (a) 3 min; (b) 5 min; (c) 10 min

the detinned tinplate after reflowing at 270 °C for 30 min. It is seen that Fe and Sn elements are detected on the detinned tinplate surface, which indicates that the alloy layer is composed of Fe and Sn elements.

Tables 4 and 5 list the Sn content of the detinned tinplate after reflowing at different temperatures for different time. It is seen that with the increase of reflowing time from 3 to 20 min, the content of Sn increases from 0.68% to 10.21% (mass fraction). Furthermore, the Sn content is very low after reflowing for 3 min, while after reflowing for 5 min, Sn content increases quickly and then increases slowly from 5 to 20 min. From Table 5, it is seen that at reflowing

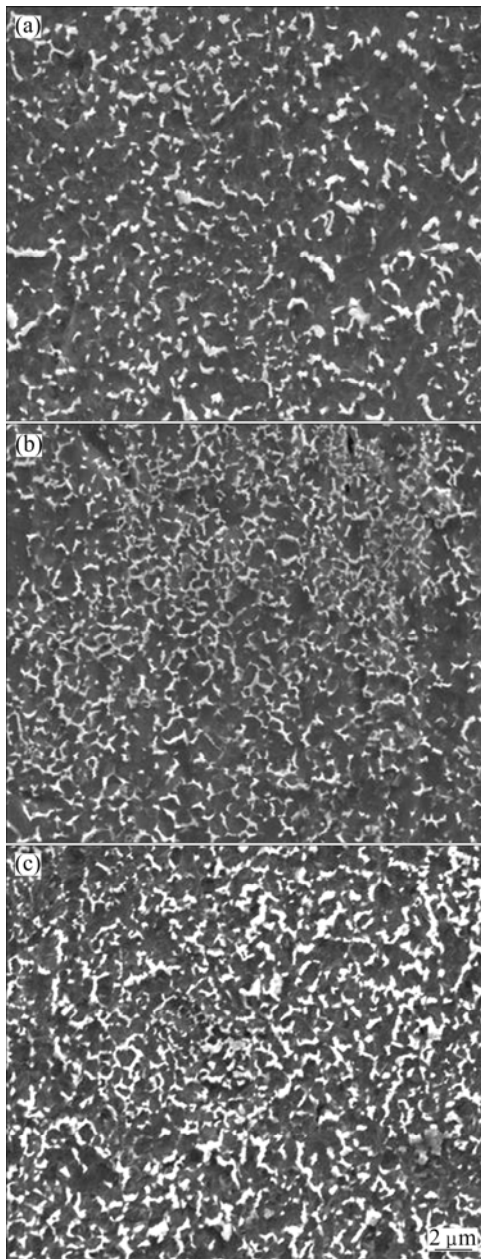


Fig. 6 SEM images of surface morphology of detinned tinplate after reflowing at different reflowing temperatures for 30 min: (a) 230 °C; (b) 250 °C; (c) 270 °C

temperature of 210 °C, the Sn content is only 2.79%. When the reflowing temperature increases from 210 to 230 °C, the Sn content increases quickly from 2.79% to 8.31%. With the further increase of the reflowing temperature, the increase of Sn content slows down. Therefore, it seems that there are critical reflowing time and reflowing temperature to activate the diffusion of Sn.

Both the surface morphology observation and composition analysis of the detinned tinplate indicate that the increase of reflowing time and reflowing temperature improve the protective property of Fe–Sn alloy layer for steel substrate.

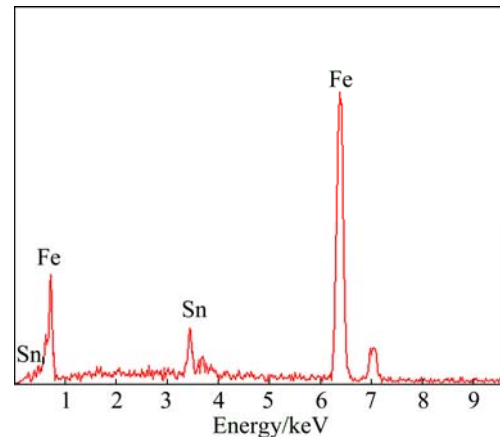


Fig. 7 EDS spectrum of detinned tinplate after reflowing at 270 °C for 30 min

Table 4 Sn content of detinned tinplate surface after reflowing at 270 °C for different reflowing time

Reflowing time/min	Mass fraction/%	Mole fraction/%
3	0.68	0.32
5	8.07	3.97
10	9.84	4.89
20	10.21	5.08

Table 5 Sn content of detinned tinplate surface after reflowing at different reflowing temperatures for 30 min

Reflowing temperature/°C	Mass fraction/%	Mole fraction/%
210	2.79	1.33
230	8.31	4.09
250	9.29	4.60
270	10.66	5.32

3.5 AFM measurement of detinned tinplate after corrosion

Conventional electrochemical methods, such as the measurements of corrosion potential, potentiodynamic polarization curve and electrochemical impedance spectroscopy (EIS), provide very important information about the general property of the alloy layer/solution interface. However, the corrosion of the detinned tinplate exposed to 3.5% NaCl solution with oxygen will occur heterogeneously. In particular, corrosion is initiated at very small surface area (i.e. microscopic pits or pores) without any obvious surface sign of deterioration. Thus AFM technique is often applied to analyzing corrosion process [12,25].

Figure 8 shows the AFM surface images of detinned tinplate (after reflowing at 270 °C for 30 min) before and after corrosion in 3.5% NaCl solution. It is found that before corrosion, Fe–Sn alloy layer is observed on the detinned tinplate surface. After the tinplate is exposed to

3.5% NaCl solution, corrosion of tinplate occurs in the area without alloy layer covered, especially in the regions adjacent to alloy layer. It seems that the corrosion preferentially occurs in the steel substrate region close to alloy layer. This indicates that the adjacent area between naked substrate and alloy layer is more susceptible to corrosion. The preferential attack in the adjacent area is the internal factor causing localized corrosion in the oxygen environment when tinplate is used as food processing material. Then, improving the density of alloy layer is advantageous to resist the localized corrosion.

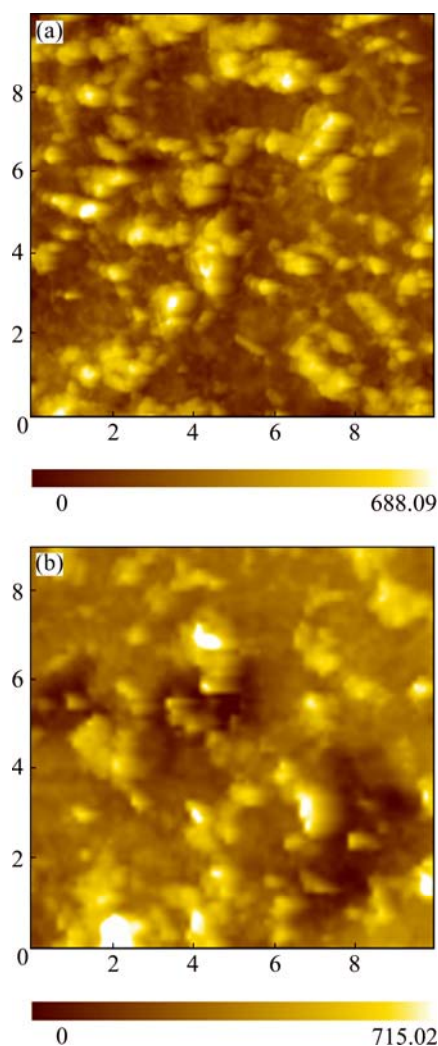


Fig. 8 AFM images of detinned tinplate after reflowing at 270 °C for 30 min: (a) Before corrosion in 3.5% NaCl solution; (b) After corrosion in 3.5% NaCl solution

3.6 Coupled potential and galvanic current density between detinned tinplate and tin

To determine the galvanic effect between the detinned tinplate and tin, the corrosion potential of tin in 3.5% NaCl solution was also measured, and the potential versus time curve is shown in Fig. 9. The corrosion potential of tin shifts positively from -0.52 V to a relative stable value of -0.45 V after being immersed in

the solution for 1 h. Compared to the corrosion potentials of the detinned tinplate after reflowing at different conditions (Fig. 1), the corrosion potentials of the detinned tinplate are more positive than those of tin in the initial stage. However, after the detinned tinplate is immersed in the solution for some time, the corrosion potentials of the detinned tinplate become more negative than those of tin. This suggests that when the detinned tinplate is coupled with tin, the detinned tinplate acts as cathode while tin acts as anode in the initial stage. But after coupled with tin for some time, the detinned tinplate becomes the anode while tin becomes the cathode. This is different from the case in deaerated solution, in which tin acts as the anode.

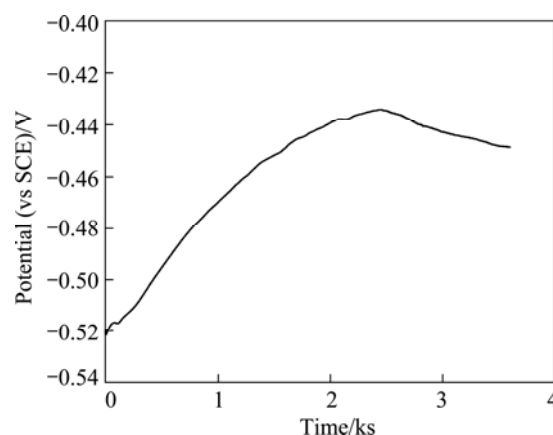


Fig. 9 Time dependence of corrosion potential of tin in 3.5% NaCl solution

Figure 10 shows the coupled potentials and galvanic current densities between the detinned tinplate and tin in 3.5% NaCl solution after reflowing at 270 °C for different time. It is seen that the coupled potentials shift to negative direction during the immersion, which is attributed to negative shifts of the corrosion potentials of the detinned tinplate after reflowing, as shown in Fig. 1. Furthermore, the coupled potential is more positive with the increase of reflowing time, which is associated with the corrosion potentials of the detinned tinplate after reflowing at 270 °C for different time. For the galvanic current densities, there are negative galvanic current densities in the initial stage, suggesting that the detinned tinplate is the cathode in the initial stage. After the two electrodes are coupled for some time, the galvanic current densities change from negative to positive, i.e., the detinned tinplate changes from cathode to anode. Furthermore, the galvanic current densities decrease with the increase of reflowing time due to the decrease of potential difference between the detinned tinplate and tin.

Figure 11 shows the coupled potentials and galvanic current densities between the detinned tinplate and tin in 3.5% NaCl solution after reflowing at different

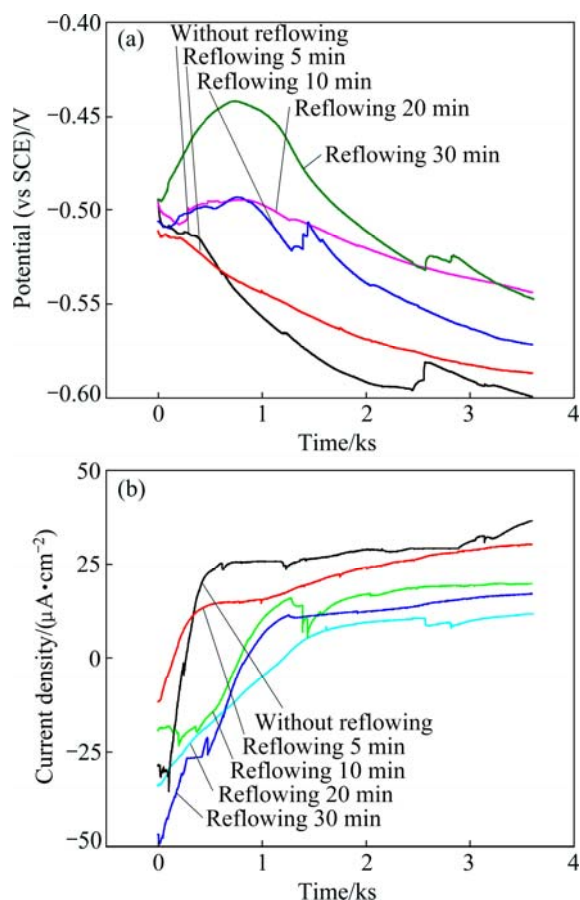


Fig. 10 Couple potential (a) and galvanic current density (b) between detinned tinplates and tin electrode in 3.5% NaCl solution after reflowing at 270 °C for different time

temperatures for 30 min. It is seen that the coupled potentials also shift to the negative direction due to the negative shift of corrosion potentials of the detinned tinplate after reflowing. The coupled potentials are more positive with the increase of reflowing temperature, which is associated with the corrosion potentials of detinned tinplate after reflowing at different temperatures for 30 min, as shown in Fig. 1. The galvanic current densities are negative in initial stage, but become positive after being coupled for some time, suggesting that the detinned tinplate changes from cathode to anode during the coupled process. Furthermore, the galvanic current densities decrease with the increase of reflowing temperature.

4 Discussion

4.1 Electrochemical reactions of detinned tinplate in NaCl solution

In the corrosion process of detinned tinplate in 3.5% NaCl solution with oxygen, the anodic reaction should be the dissolution of iron through several steps [26]:

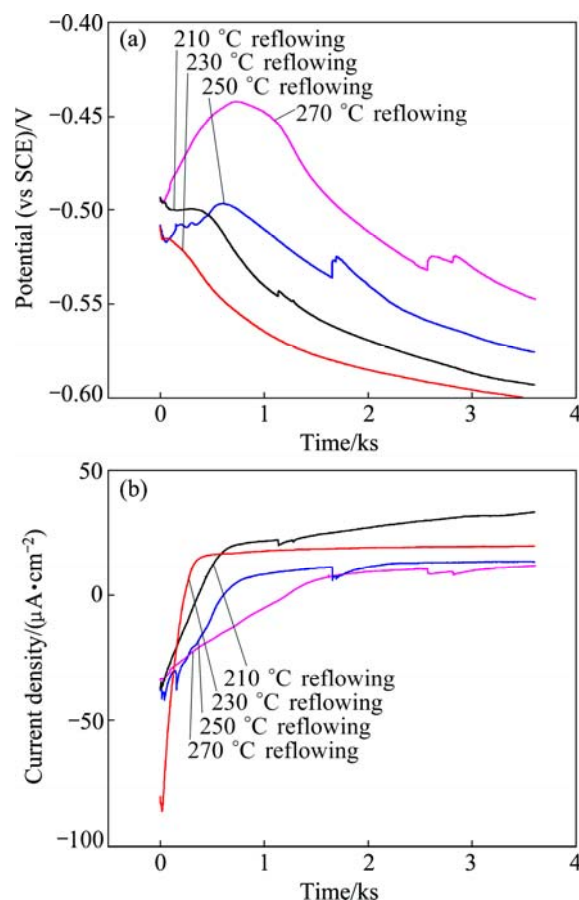
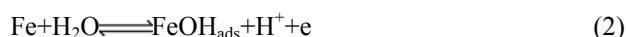


Fig. 11 Couple potential (a) and galvanic current density (b) between detinned tinplates and tin electrode in 3.5% NaCl solution after reflowing at different temperatures for 30 min



The cathodic reaction should be the reduction of oxygen as follows:



For the detinned tinplate, there is Sn-Fe alloy layer (FeSn_2) on the surface, which works usually as the cathodic phase with respect to steel substrate. Then, the reduction of oxygen mainly occurs on the Sn-Fe alloy layer. Figure 12 shows the schematic diagram of the effect of the amount of alloy layer (cathodic phase FeSn_2) on the reduction of oxygen on detinned tinplate. As shown in Fig. 12(a), when the amount of alloy layer on the detinned tinplate surface reaches to a certain value, all the diffusion paths for oxygen in diffusion layer will be occupied so that the maximum amount of oxygen diffusing to the cathodic phase is obtained. Then, further increasing the amount of cathodic phase would not increase the amount of oxygen diffusing to cathodic phase since the paths for oxygen diffusion do not increase, as shown in Fig. 12(b).

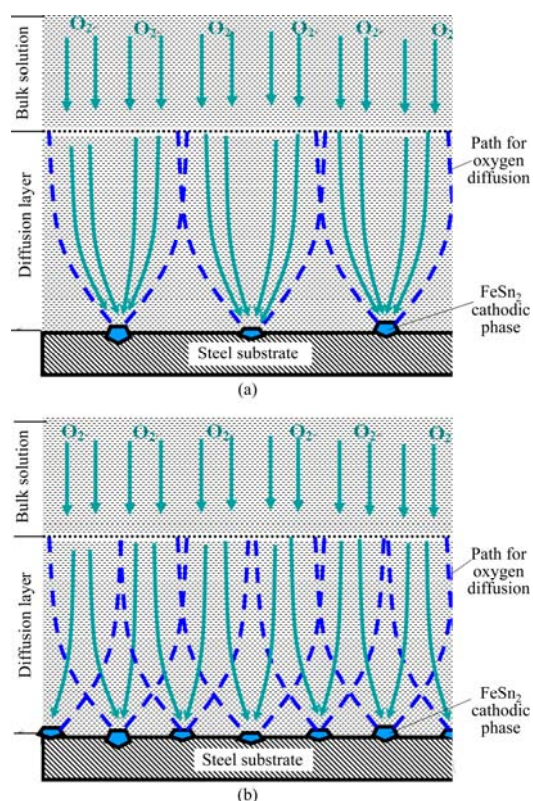


Fig. 12 Schematic diagram of effect of amount of cathodic phase (FeSn_2) on reduction of oxygen on detinned tinplate: (a) Low amount of cathodic phase; (b) High amount of cathodic phase

Therefore, in the polarization curve measurements (Fig. 2), the cathodic current densities of the detinned tinplate after reflowing treatment are higher than those without reflowing treatment. However, with the increase of reflowing temperature and reflowing time, although the amount of cathodic phase (Fe–Sn alloy layer) increases on the detinned tinplate surface, as shown in Figs. 5 and 6, the cathodic current densities do not increase significantly. For the anodic current densities, since the area of anodic region decreases with more Fe–Sn alloy layer on the surface, the anodic current densities decrease with the increase of reflowing temperature and reflowing time, which results in the decrease of corrosion current densities (Fig. 2) and positive shifts of the corrosion potentials (Fig. 1).

4.2 Effect of reflowing time on corrosion behavior of detinned tinplate

All the electrochemical measurements, including polarization curve and EIS measurements, indicate that the corrosion rate of the detinned tinplate decreases with the increase of reflowing time. It is obvious that the corrosion resistance of the detinned tinplate is dependent on the protective property of Fe–Sn alloy layer formed during the reflowing process, while the reflowing time

affects the protective property of the Fe–Sn alloy layer. The Fe–Sn alloy layer is formed by the mutual diffusion of Fe and Sn, as demonstrated by the element cross-section distribution of the detinned tinplate after reflowing treatment (Fig. 4). During the reflowing process, both the Fe from substrate and the Sn from coating will diffuse to substrate/coating interface and form Fe–Sn alloy layer. With the increase of reflowing time, the mutual diffusion of Fe and Sn is sufficient. Then, the amount of Fe–Sn alloy layer formed in Fe/Sn interface will increase. The SEM morphologies of the detinned tinplate after reflowing demonstrate that there is more Fe–Sn alloy layer formed in Fe/Sn interface with the increase of reflowing time, as shown in Fig. 5. Fe–Sn alloy layer provides protective property for steel substrate by obstructing the contact of solution with steel substrate. Therefore, with the increase of reflowing time, more Fe–Sn alloy layer is formed in Fe/Sn interface. Then, less area of steel substrate is exposed to solution, which results in the decrease of corrosion rate and positive shift of corrosion potential of detinned tinplate with the increase of reflowing time.

4.3 Effect of reflowing temperature on corrosion behavior of detinned tinplate

Both polarization curves and EIS measurements indicate that the corrosion rate of the detinned tinplate decreases with the increase of reflowing temperature. The corresponding corrosion potential shifts to positive direction. This suggests that the protective property of Fe–Sn alloy layer for substrate is improved by the increase of reflowing temperature. Furthermore, when the reflowing temperature is $210\text{ }^{\circ}\text{C}$, the improvement of corrosion resistance of detinned tinplate is not prominent. But when the temperature is more than $230\text{ }^{\circ}\text{C}$, the corrosion resistance of the detinned tinplate is improved prominently. It is well known that the melting point of tin is $232\text{ }^{\circ}\text{C}$. At $210\text{ }^{\circ}\text{C}$, the tin coating is in the solid state and the diffusion of tin is relatively slow, which results in less Fe–Sn alloy layer formed on the detinned tinplate surface after reflowing treatment. While once the temperature is more than $230\text{ }^{\circ}\text{C}$, the tin coating is in melting state. Then, the diffusion of tin will be enhanced prominently and the amount of the formed Fe–Sn alloy layer increases obviously, as shown in Fig. 6. The corresponding content of Sn on the detinned tinplate surface is low after reflowing at $210\text{ }^{\circ}\text{C}$, while the Sn content on the detinned tinplate surface increases prominently when the reflowing temperature is more than $230\text{ }^{\circ}\text{C}$.

4.4 Galvanic corrosion behavior between detinned tinplate and tin

The corrosion potential measurements show that the

corrosion potential of the detinned tinplate is more positive than that of tin in 3.5% NaCl solution in the initial exposure stage, which means that the detinned tinplate is the cathode and tin is the anode in the beginning of coupling. However, the corrosion potential of tin shifts positively during the exposure, which should be attributed to the formation of oxide film on tin surface, while the corrosion potentials of the detinned tinplate shift to negative direction, which is related to the dissolution of Fe–Sn alloy layer after being exposed to solution and the decrease of protective property. The shift of potentials of both detinned tinplate and tin results in the change of coupling system, namely, the detinned tinplate becomes anode and tin becomes cathode. This means that the tin coating on steel will become cathodic one after 1 h exposure in 3.5% NaCl solution without removing oxygen. Therefore, the porosity or damage of tin coating has an important effect on the corrosion resistance of steel substrate. If the porosity of tin coating is large or some damage is present in the tin coating, then it would create a large cathode-small anode effect, resulting in fast corrosion of the underlying substrate.

The corrosion potentials of the detinned tinplate are more positive with the increase of reflowing temperature and reflowing time since more Fe–Sn alloy layer are formed on steel/tin interface. Then, the potential difference between detinned tinplate and tin, which is the driving force for galvanic corrosion, decreases with the increase of reflowing temperature and reflowing time. Therefore, the galvanic current density also decreases with the increase of reflowing temperature and reflowing time.

5 Conclusions

1) Fe–Sn alloy layer is formed on the electrolytic tinplate after reflowing treatment. The amount of alloy layer increases with the increase of reflowing temperature and reflowing time, which should be attributed to the more sufficient mutual diffusion of Fe and Sn during the reflowing process.

2) The corrosion potential of the detinned tinplate after reflowing treatment in 3.5% NaCl solution with oxygen shifts positively and the corresponding corrosion rate decreases with the increase of reflowing temperature and reflowing time since more Fe–Sn alloy layer is formed on the detinned tinplate surface.

3) After being coupled with tin, the detinned tinplate acts as cathode in the beginning of coupling. However, after the detinned tinplate is exposed for some time, the potential shifts of both the detinned tinplate and tin reverse the polarity of the coupling system, i.e., the detinned tinplate becomes anode. The potential difference between the detinned tinplate and tin, which is

the driving force for galvanic corrosion, decreases with the increase of reflowing temperature and reflowing time. Therefore, the galvanic current density also decreases with the increase of reflowing temperature and reflowing time.

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软熔处理温度和时间对镀锡钢板中合金层及其在 3.5% NaCl 溶液中腐蚀电化学行为的影响

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摘 要: 利用电化学测试和表面分析方法研究软熔处理温度和时间对镀锡钢板中合金层及其在 3.5% NaCl 溶液中腐蚀电化学行为的影响。结果表明: 随着软熔处理温度 and 时间的增加, 镀锡钢板的合金层数量增多。且腐蚀电位正移, 对应腐蚀速率下降。与锡偶接后, 在初始阶段, 脱锡处理后的镀锡钢板为阴极而锡为阳极。然而经过一段时间后, 电偶对的极性反转。随着软熔处理温度 and 时间的增加, 电偶电流下降。

关键词: 镀锡钢板; 合金层; 软熔处理; 电偶腐蚀

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