

Influence of Tensile Strain on the Corrosion Behavior of Tinplate in 0.1 mol/L NaCl Solution

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The corrosion behavior of tinplate with different tensile strain in 0.1 mol/L NaCl solution was investigated by using polarization curve, electrochemical impedance spectroscopy (EIS) and immersion tests. The surface morphology of tinplate before and after immersion was observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM), and the content of iron ions dissolved in NaCl solution was determined by inductively coupled plasma mass spectrometer (ICP-MS). The experimental results showed that with the increasing of tensile strain the deformed tinplate has a lower thickness and a higher surface roughness, meanwhile the density of slip bands and defects on the tinplate is also increased. In NaCl solution, the deformed tinplate has a positive corrosion potential and a lower polarization resistance, and the corrosion current density and concentration of iron ions dissolved in solution are both raised with the increasing of tensile strain. Based on these results, the relationship between the corrosion rate and tensile strain of tinplate was built and discussed.

Keywords: tinplate, tensile strain, corrosion behavior, EIS, NaCl solution

1. INTRODUCTION

Tinplate is a cold-rolled low carbon steel sheet with pure tin plated on both sides, and is widely applied as an important raw material for sealing canned foods and beverages. Because of the good

ductility, high strength and non-toxic properties tinplate still occupies a dominant position in food packaging despite the rapid rise of two-piece can made of aluminum [1-4]. However, such problems corrosion failure, loss of seal integrity, discoloration, and food safety should be effectively addressed in order to maintain the widespread application of tinplate as a food packaging material [4-6]. Hence, it is of immense importance to explore the corrosion behavior and mechanism of tinplate so as to provide theoretical and experimental basis during production process and food storage.

The corrosion behavior of tinplate in the food packaging containers is greatly influenced by such factors as the (composition, grain size, and surface state) [2-4] of the can materials, kinds of contents (juice, pickled food, milk, beer) [2-4, 7] and storage conditions (temperature, humidity, air permeability, duration) [5, 8-10]. In addition to the above factors, the forming processes, such as punching, bending, drawing and deep drawing, necking and curing, which were used to shape the tinplate sheet into the final desired output could also have tremendous impact on the corrosion behavior of tinplate. Thus, this corrosion degradation of tinplate is principally associated with its deformation, which can result in the variation of microstructure, strain force or defects and reduction of adhesion between tin layer and steel, leading to lowering of its corrosion resistance. To this day, there is a few reports about the effect of uniaxial strain on the corrosion behavior of tinplate.

As for the influence of deformation on the corrosion properties of coating, the corrosion resistance of coil-coatings on galvanized steel was investigated under different uniaxial strain in 5wt% NaCl solution, and the obtained results showed that the protection properties of coil-coating were decreased obviously with the increasing of strain from 9%, 11%, 16%, 19% to 23% owing to the strain created defects in the coating [11, 12]. The corrosion performance of electrolytic chromium-coated steel (ECCS) in the both presence and absence of a polymer coating (a glycol-modified amorphous PET) was studied under the uniaxial deformation of 5%, 10% and 25% in 3.5% NaCl solution. With the increasing of strain deformation, the corrosion resistance of ECCS was decreased, which is attributed to the introduction of local defects in the coating leading to the increasing exposure of more active underlying steel with deformation [13]. The electrochemical behavior of epoxy coating on buried high pressure steel pipeline was measured under the tensile strain of 1%, 2.5%, 3.5% and 4% in 0.6 g/L NaCl solution [14]. The experimental results presented that the coating resistance of pipeline steel was decreased and the coating capacitance was increased with increasing strain value, and the electrolytic paths in the coating to the corrosive environment were formed by the accumulation of void space under the applied mechanical strain. The corrosion behavior of galvanized steel with silicon polyester coating was determined under the uniaxial elongation of 1%-10%, and it was noted that the corrosion resistance of steel was decreased with the increasing of strain and immersion time [15]. Meanwhile the influence of uniaxial deformation on the corrosion resistance of steel was compared with that by bending deformation.

In this present work, the corrosion behavior of tinplate with different strain deformation was investigated in 0.1 mol/L NaCl solution by utilizing polarization curve, electrochemical impedance spectroscopy (EIS) and immersion test. The surface morphology of the tinplate before and after immersion test was observed by scanning electron microscopy (SEM) and atomic force microscope (AFM). The dissolution content of Fe ions in NaCl solution was monitored by inductively coupled plasma mass spectrometer (ICP-MS). On the basis of the observed experimental results, the relationship

between the uniaxial strain and the corrosion resistance of the deformed tinplate has been built and discussed in detail.

2. EXPERIMENTAL

2.1 Materials

The tinplate sheets applied in this work were provided by the ORG Canmaking Company, which is consisted of a low carbon steel with the thickness of 0.1 mm as substrate and tin coating with the thickness of 6 μm on both sides.

The tensile test of tinplate sheet was carried out by electronic universal testing machine, and the obtained stress-strain curve was obtained in Fig. 1. As there is no strain-hardening effect in the stress-strain curve, four typical tensile strains of 0% (no deformation), 7.0%, 11.0% (middle plastic deformation) and 21.0% (near the necking zone) were selected as the deformed tinplate to conduct the corrosion experiments under different strains. All the samples in the experiment were degreased with ethanol and dried before being exposed to testing solution.

2.2 Characterization

The surface morphology of deformed tinplate was observed by Hitachi S-4800 field emission scanning electron microscopy (FESEM) operated at an applied voltage of 5.0 kV, meanwhile the surface morphology and surface roughness were also observed and calculated by Agilent AFM-5500 atomic force microscopy. Furthermore, the section morphology of deformed tinplate was observed and then the thickness of tin layer was measured by S-4800 field emission scanning electron microscopy,

2.3 Immersion tests

The deformed tinplate sheet with the dimension of 60 mm $\times$ 60 mm was immersed in 0.1 mol/L NaCl solution at room temperature for 20 days. After different immersion times, the surface morphology of corroded tinplate before and after the removal of corrosion product with the solution of 500 ml/L HCl and 3.5 g/L hexamethylenetetramine was observed by Hitachi S-4800 field emission scanning electron microscopy. Meanwhile, the concentration of Fe ions dissolved in NaCl solution was determined by Agilent 7700x inductively coupled plasma mass spectrometer (ICP-MS).

2.4 Electrochemical measurements

The polarization curve and electrochemical impedance spectroscopy (EIS) of the deformed tinplate were carried out at room temperature in 0.1 mol/L NaCl solution by using Autolab 302N electrochemical workstation at open circuit potential (OCP). A three-electrode system was employed in which the deformed tinplate with an exposed area of 1 cm^2 for polarization curve and 5.52 cm^2 for

electrochemical impedance spectroscopy as work electrode, a saturated calomel electrode (SCE) as reference electrode and a ruthenium-titanium electrode as counter electrode.

The polarization curve experiments were performed at scan rate of 1.667 mV/s from -0.5 V to 0.5 V versus open circuit potential. And EIS measurements were measured at the open-circuit potential with an amplitude signal of 10 mV and the scanning frequency ranged from 100 kHz to 0.01 Hz. After experiments, the electrochemical parameters for EIS spectrum were calculated by applying Zsimpwin software under the given equivalent circuits.

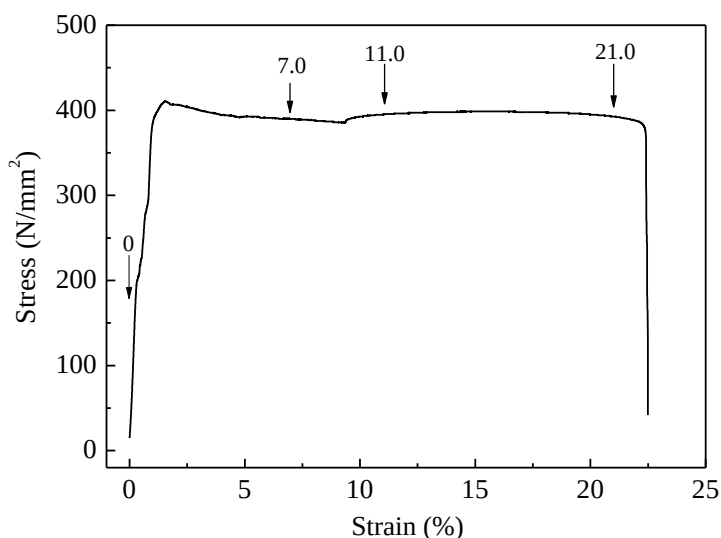


Figure 1. Stress-strain curve of tinplate sheets

3. RESULTS

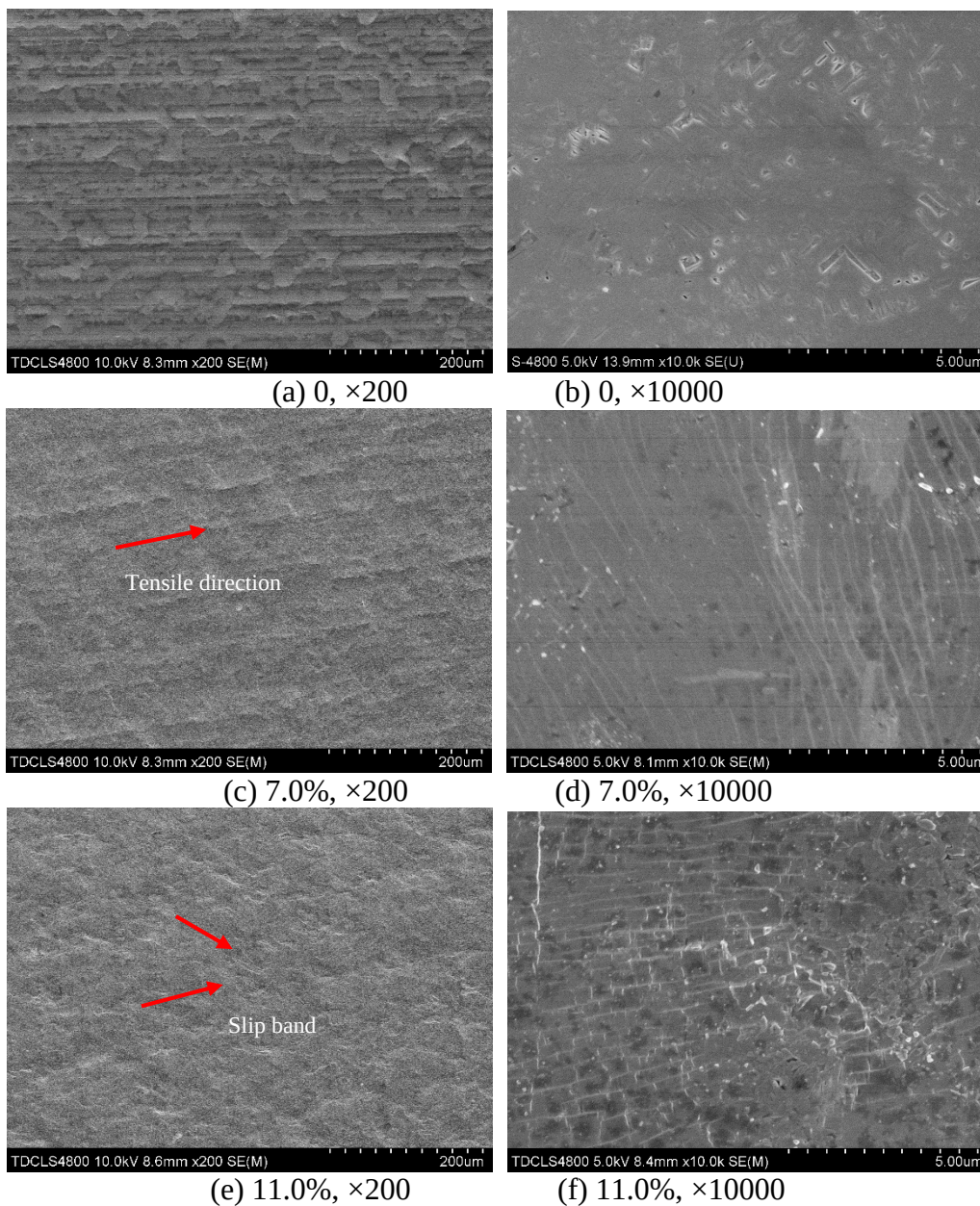
3.1 Surface morphology

The surface morphology of the tinplate with different strain deformations is shown in Fig. 2. It can be seen that the original tinplate with no deformation is in a relative smooth surface with several defects as well as reflowing and processing shallow marks (Fig. 2a and Fig. 2b). Under the strain deformation of 7.0%, the tinplate has been deformed along the tensile direction (Fig. 2c), and there are parallel slip bands emerged on the surface (Fig. 2d). With the tensile strain increased to 11.0%, there are not only parallel slip bands but also perpendicular slip bands observed as clearly depicted in Fig. 2f. Meanwhile, more defects (holes and cracks) are begun to form. Under the strain of 21.0%, lots of defects (holes and cracks) are caused besides the slip bands (Fig. 2h)

3.2 Surface roughness and thickness

The AFM morphology of the tinplate under different tensile strain values is shown in Fig. 3. The original undeformed tinplate exhibits a smooth surface with a reduced level of unevenness, Fig. 3a,

appreciable valleys or steps can be perceived on the surface of the deformed plates at different percentage of elongations. The calculated values of the surface roughness of the tinplate at different deformation percentages is illustrated in Fig. 4. It can be noted from the figure that the values consistently and gradually increased from $0.03\text{ }\mu\text{m}$ for the initial undeformed plate to 0.11 , 0.17 , and $0.19\text{ }\mu\text{m}$ for the 7.0, 11.0, and 21.0% deformations, respectively. These values accorded with the surface observations in Fig. 2 and Fig. 3.



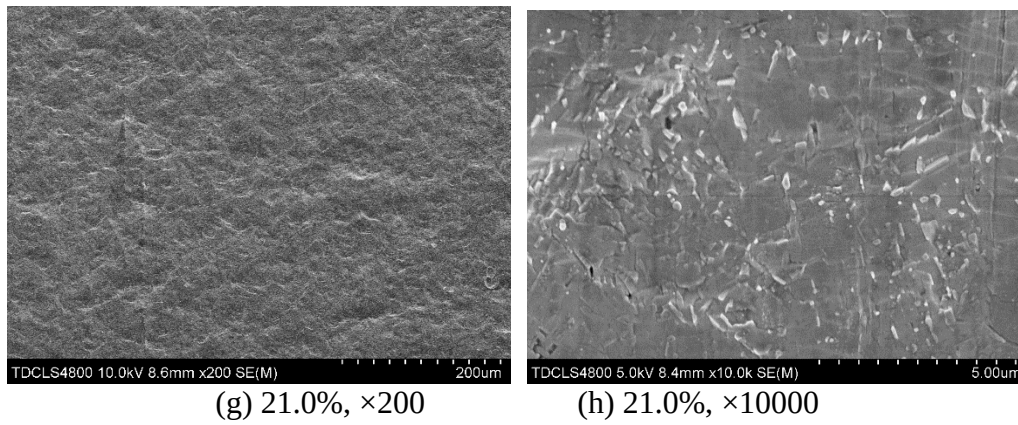


Figure 2. Surface morphology of tinplate with different tensile strain

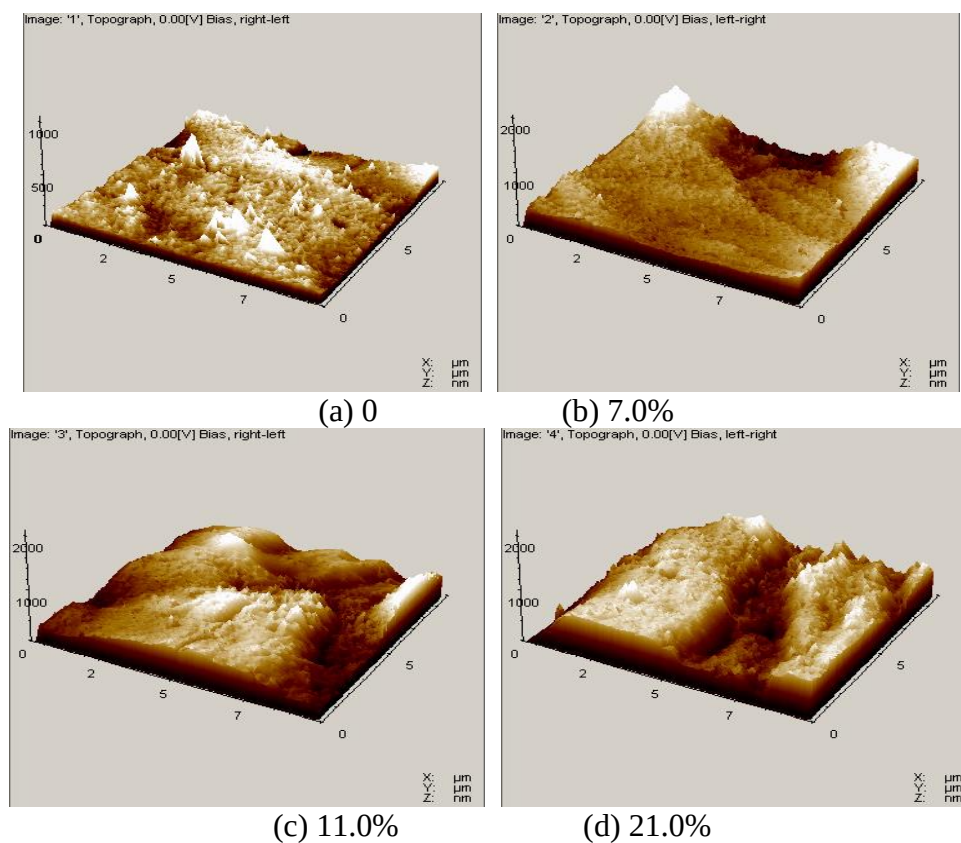


Figure 3. AFM morphology of tinplate with different tensile strain

In contrast, the measured values of tinplate thickness from the section morphological analysis study revealed a decreasing trend with rise in strain deformation, Fig. 4. The thickness of the original tinplate with no deformation was about 6.00 μm . This value declined to 4.80 μm under the strain deformation of 7.0% and yet the tinplate was still tightly adhered on the steel substrate. When the tensile strain was elevated to 11.0 and 21.0%, the thickness of the tinplate was lowered to 3.60 and 3.30 μm , respectively, and more defects began to develop, as it can be observed in the section morphology, especially in the tinplate with 21.0% strain deformation. All these results indicate that with increasing strain deformation, tinplate thickness is reduced, meanwhile, surface roughness is increased.

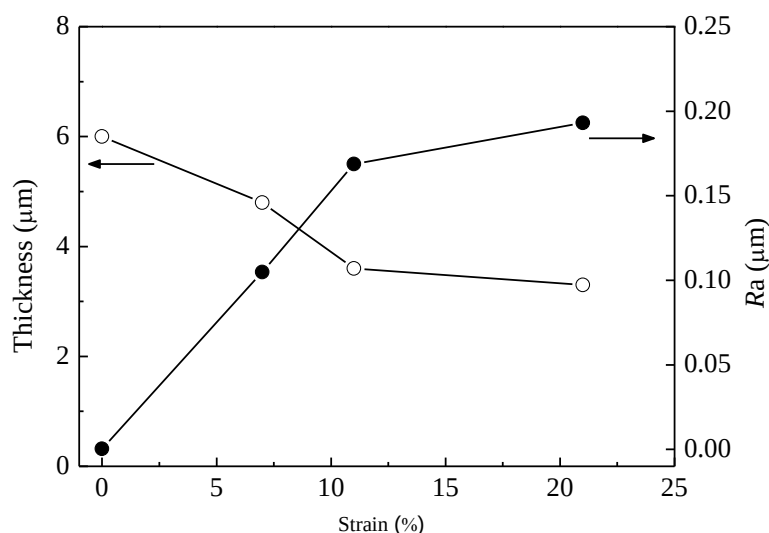


Figure 4. Surface roughness and thickness of tinplate with different tensile strain

3.3 Polarization curve

The polarization curve of the deformed tinplate in 0.1 mol/L NaCl solution is shown in Fig. 5, and the resulting calculated corrosion potential and corrosion current density of tinplate are tabulated in Table.1. In the polarization curve of the original tinplate with no deformation, a clear passivation zone can be observed in the potential range of -0.400 V to -0.280 V, which is caused by the tin oxide/hydroxide formed on the surface of tinplate when immersed in NaCl solution [16-19]. The corrosion potential and corrosion current density were -0.463 V and 0.025 $\mu\text{A}/\text{cm}^2$ respectively. Under the tensile strain of 7.0%, there is still a passivation zone exist in the potential range of -0.360 V to -0.240 V, but the maintaining passivity current density is larger than that of original tinplate. At this percent of strain deformation the corrosion current density is increased 0.044 $\mu\text{A}/\text{cm}^2$, and the corrosion potential was positively shifted to -0.411 V, which is probably attributed to the coupling effect between tin layer and low potential alloy layer of FeSn_2 partly exposed after deformation [20]. Never the less, the passivation zone in the polarization curve was hardly observed upon increasing the tensile strain to 11.0 and 21.0%, but the corrosion potential was positively shifted again to the corresponding values of -0.385 and -0.388 V while the corrosion current density was increased to 0.090 and 0.226 $\mu\text{A}/\text{cm}^2$, respectively. These results suggest that the corrosion resistance of the tinplate gradually decreases with rise in tensile strain.

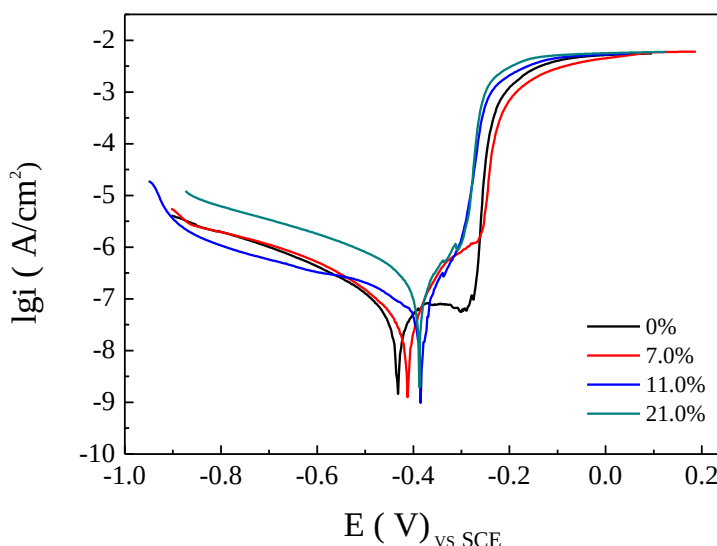


Figure 5. Polarization curve of tinplate under different tensile strain in 0.1 mol/L NaCl solution

Table 1. Corrosion potential and corrosion current density of tinplate under different tensile strain in 0.1 mol/L NaCl solution

Strain (%)	$I_{\text{corr}} (\mu\text{A}\cdot\text{cm}^{-2})$	$E_{\text{corr}} (\text{V}_{\text{SCE}})$
0	0.020	-0.463
7.0	0.044	-0.411
11.0	0.090	-0.385
21.0	0.226	-0.388

3.4 EIS spectrum

Fig. 6 is the EIS spectrum of tinplate with no deformation in 0.1 mol/L NaCl solution. In the immersion time of 3 and 6 hours (0.125 and 0.25 days), there is one time capacitance arc in the EIS spectrum (Fig. 6a and Fig. 6c) with the respective modulus resistance at 0.01 Hz of 9.4×10^4 and $4.3\times 10^4 \Omega\cdot\text{cm}^2$ (Fig. 6b). With the prolonging of immersion time, there are two capacitance arcs observed in the EIS spectrum (Fig. 6a and Fig. 6c), and the modulus resistance at 0.01 Hz of tinplate is firstly reduced from $1.7\times 10^4 \Omega\cdot\text{cm}^2$ in the immersion time of 12 (0.5 days) hours to $6.2\times 10^3 \Omega\cdot\text{cm}^2$ in the immersion of 5 days and then slightly increased to $6.5\times 10^3 \Omega\cdot\text{cm}^2$ in the immersion time of 10 days. While with the time increasing to 20 days, the modulus resistance at 0.01 Hz declines to $5.8\times 10^3 \Omega\cdot\text{cm}^2$ (Fig. 6b). From these results, it can be noted that after the immersion time longer than 6 hours, the electrolyte penetrated through the defects of the tinplate and the double layer capacitance is formed in the interface between the tin coating and steel substrate. The capacitance arc at higher frequency is. The capacitance arc at higher frequency is resulting from the capacitance (Q_c) and surface pore resistance (R_c) of tin coating, and the capacitance arc at lower frequency is resulting from the double layer capacitance (Q_{dl}) and charge transfer resistance (R_{ct}) of steel substrate [2, 7].

The EIS spectra of tinplate with the tensile strain of 7.0%, 11.0% and 21.0% in 0.1 mol/L NaCl solution Fig. 7, Fig. 8 and Fig. 9 are. It can be seen that there are two capacitance arcs found in the spectrum of deformed tinplate (Fig. 7c, Fig. 8c and Fig. 9c), and the modulus resistance of deformed tinplate at 0.01 Hz is lower than that of original tinplate with no deformation under the same immersion time, and decreased generally with the increasing of immersion time (Fig. 7b, Fig. 8b and Fig. 9b). Meanwhile the modulus resistance at 0.01 Hz of deformed tinplate is obviously reduced with the increasing of tensile strain under the same immersion time (Fig. 7b, Fig. 8b and Fig. 9b). From these experimental results it can be deduced that the corrosion resistance of tinplate is deteriorated with the increasing of immersion time and tensile strain.

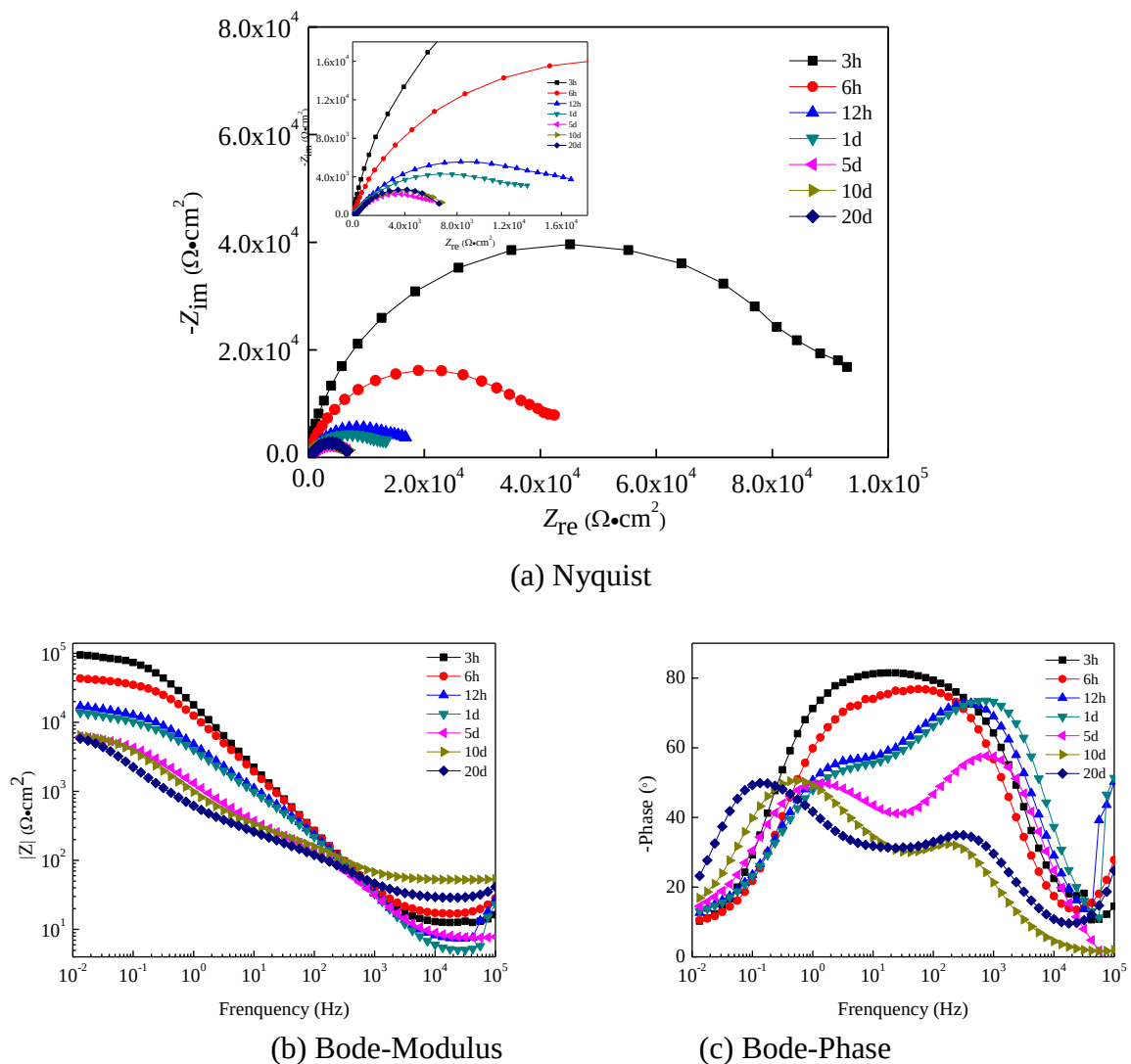


Figure 6. EIS spectrum of tinplate with no tensile strain in 0.1 mol/L NaCl solution

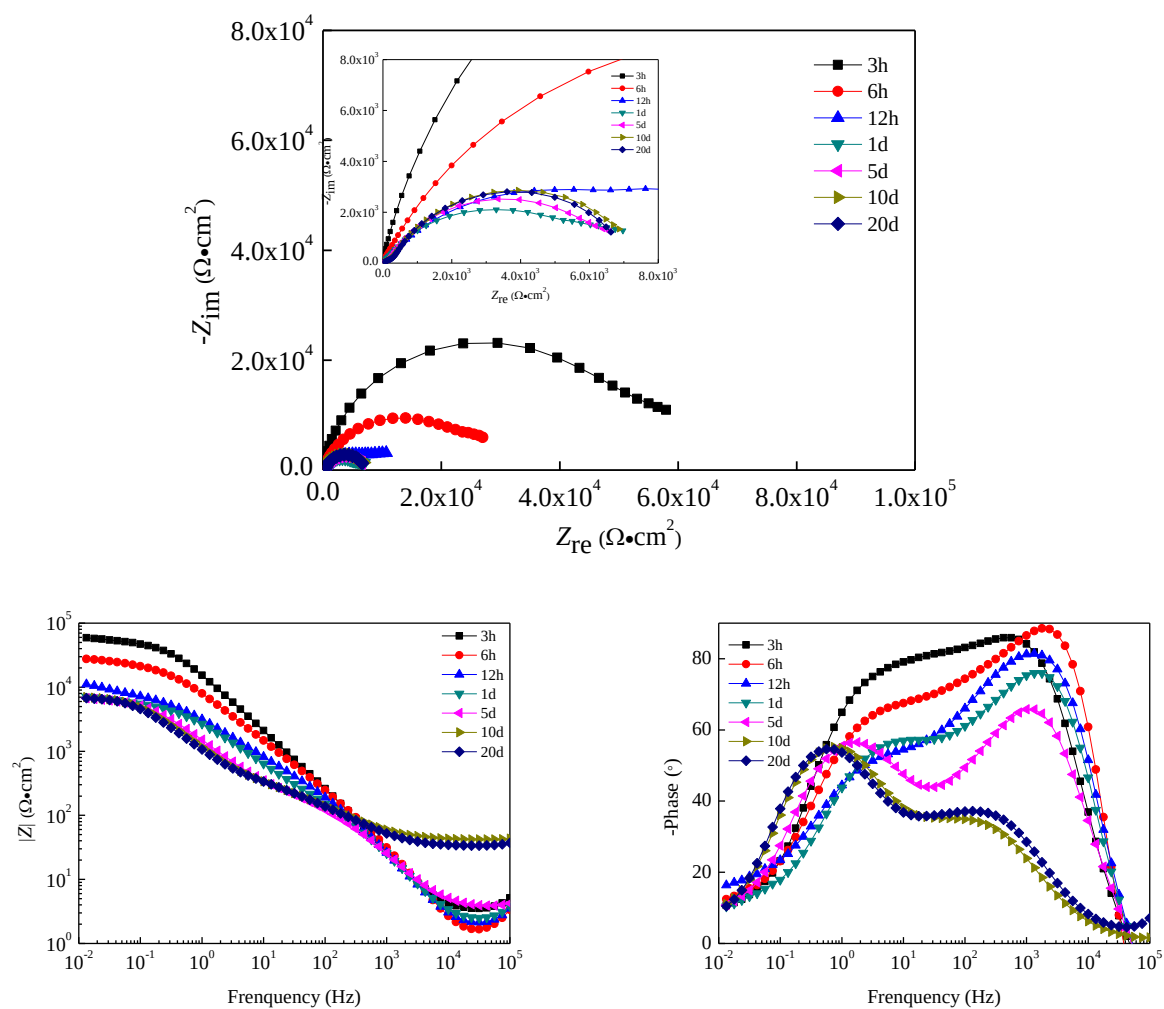
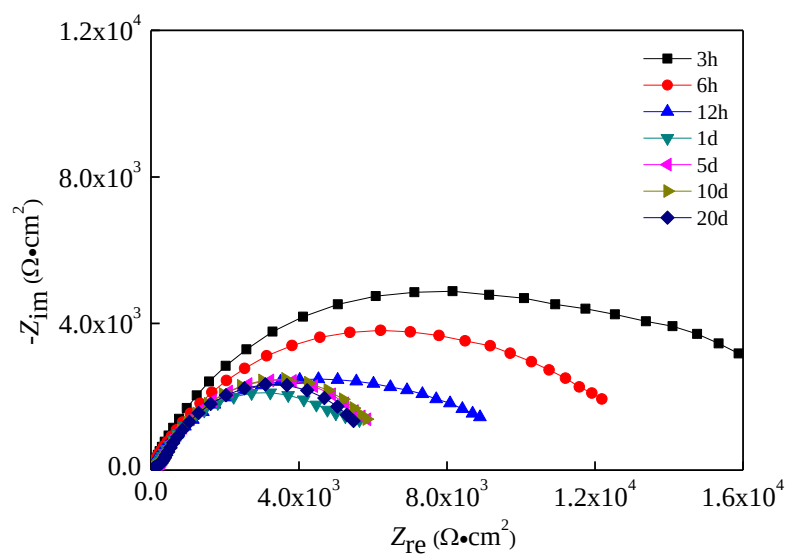


Figure 7. EIS spectrum of tinplate with the tensile strain of 7.0% in 0.1 mol/L NaCl solution



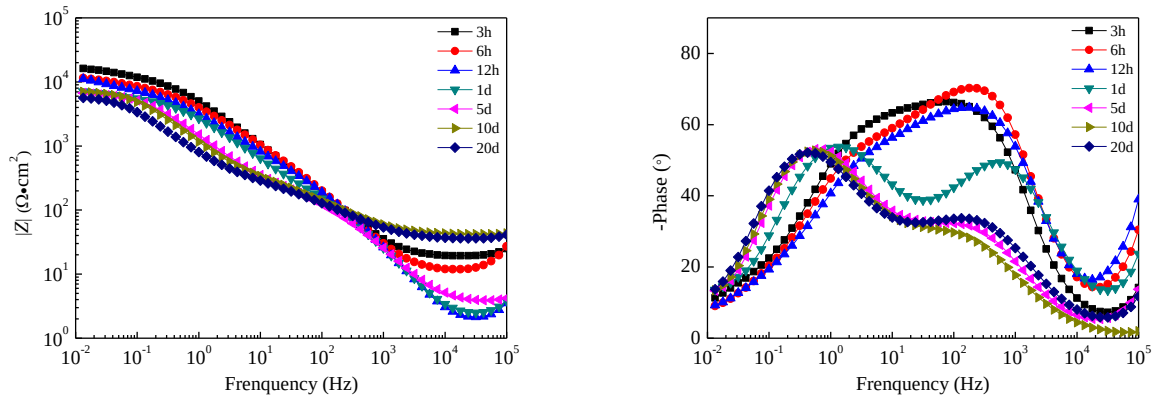


Figure 8. EIS spectrum of tinplate with the tensile strain of 11.0% in 0.1 mol/L NaCl solution

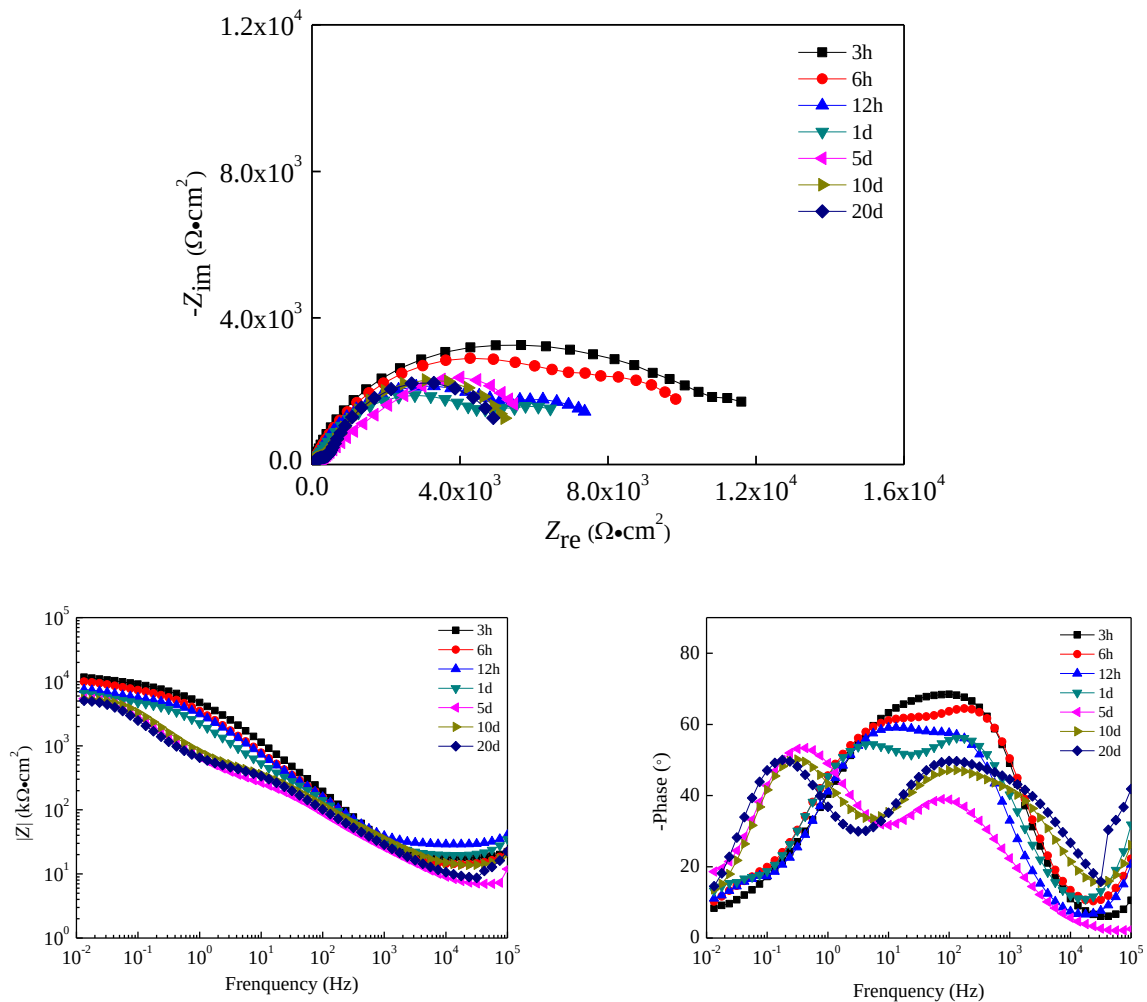


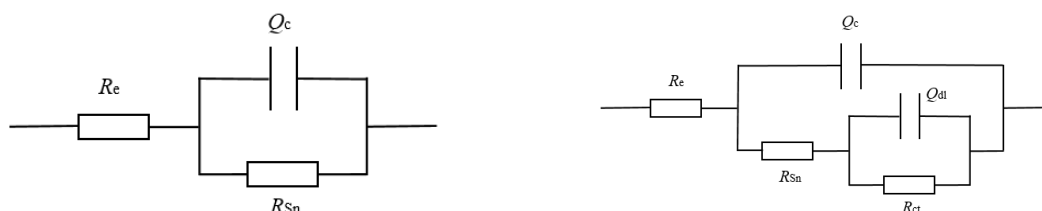
Figure 9. EIS spectrum of tinplate with the tensile strain of 21.0% in 0.1 mol/L NaCl solution

According to the above characteristics, the equivalent circuits in Fig. 10 were applied to fit the EIS results in Fig. 6, Fig. 7, Fig. 8 and Fig. 9, in which R_e is the electrolyte resistance, Q_c and R_{Sn} are the capacitance and resistance of tin coating, Q_{dl} and R_{ct} are the double layer capacitance and charge transfer resistance of steel substrate. For the undeformed tinplate in 0.1 mol/L NaCl solution under the immersion

time of 3 hours and 6 hours, the equivalent circuit $R_e(Q_cR_c)$ with one time constant in Fig. 10a was selected. Whereas for other immersion time and deformed tinplate the equivalent circuit $R_e(Q_c(R_c(Q_{dl}R_{ct})))$ with two time constants in Fig. 10b was chosen.

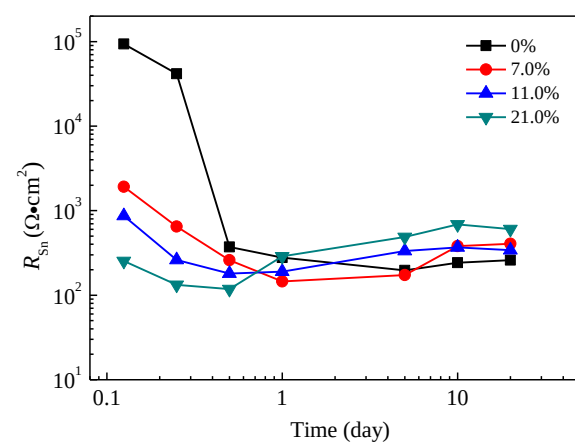
The fitting electrochemical parameters for tinplate with different stain deformation 0.1 mol/L NaCl solution under different immersion time are obtained, and the variation of tinplate resistance R_{Sn} and polarization resistance R_p ($R_{Sn} + R_{ct}$) with the immersion time and strain deformation are shown in Fig. 11. In the initial immersion time of 3 and 6 hours, the original undeformed tinplate has a higher tinplate resistance and polarization resistance of 9.34×10^4 and $4.16 \times 10^4 \Omega \cdot \text{cm}^2$. With the prolonging of immersion time, the tinplate resistance and polarization resistance are both decreased obviously, and finally reduced to 259.40 and $7.18 \times 10^3 \Omega \cdot \text{cm}^2$ respectively in the immersion time of 20 days. Under the strain deformation of 7.0%, the tinplate resistance R_{Sn} and polarization resistance R_p at the immersion time of 3 hours are only 1.92×10^3 and $6.00 \times 10^3 \Omega \cdot \text{cm}^2$ respectively, which are much less than that of tinplate with no deformation, and also decreased gradually with the prolonging of immersion time. With the increasing of tensile strain to 11.0% and 21.0%, the tinplate resistance R_{Sn} and polarization resistance R_p of tinplate at the immersion time of 3 hours are decreased again to 0.87×10^3 and $1.83 \times 10^3 \Omega \cdot \text{cm}^2$ respectively, and also decreased with the immersion time. All above results imply that the corrosion resistance of deformed tinplate is deteriorated with increasing immersion time and tensile strain.

The variation of tin coating capacitance Q_c with the immersion time and tensile strain is presented in Fig. 12. At the immersion time of 3 hours, with the increasing of tensile strain the capacitance of tin coating Q_c is raised from $5.72 \times 10^{-6} \text{ F} \cdot \text{cm}^{-2}$ (no strain deformation) to $5.91 \times 10^{-6} \text{ F} \cdot \text{cm}^{-2}$ (7.0% strain), $10.70 \times 10^{-6} \text{ F} \cdot \text{cm}^{-2}$ (11.0% strain) and $12.70 \times 10^{-6} \text{ F} \cdot \text{cm}^{-2}$ (21.0% strain). With the increasing of immersion time, the capacitance of tin coating Q_c is gradually enhanced under the same tensile strain. The promotion of tin coating capacitance Q_c is probably related to the increasing surface roughness under the higher strain deformation in Fig. 3 and Fig. 4, and the water absorption of tinplate is attributed to the holes and cracks emerged on the surface of deformed tinplate in Fig. 2 and Fig. 3. This increasing tin coating capacitance is also a characteristic of the deterioration of tinplate [21].

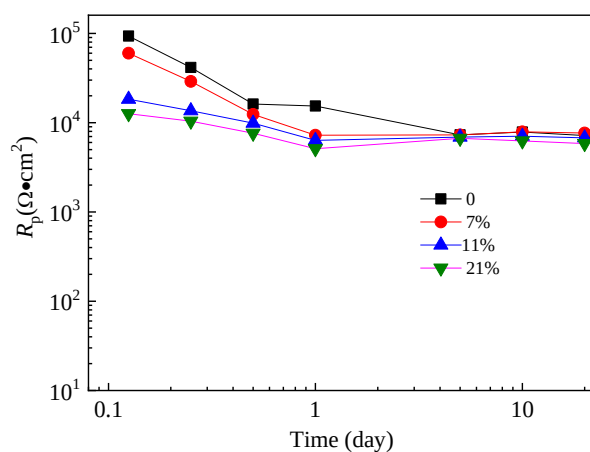


(a) no tensile strain, immersion time of 3, 6 hours (b) other immersion time and deformed tinplate

Figure 10. Equivalent circuits for EIS spectrum of deformed tinplate in 0.1 mol/L NaCl solution



(a) R_{Sn}



(b) R_p

Figure 11. Variation of R_{Sn} and R_p for the deformed tinplate with immersion time

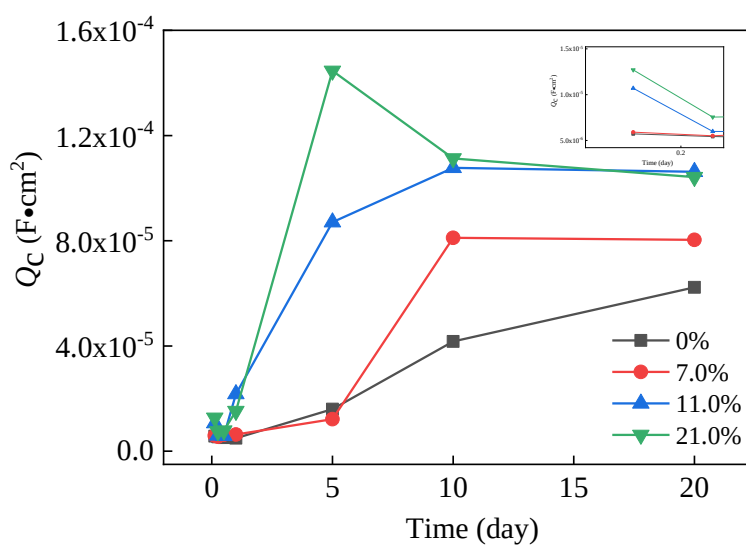


Figure 12. Variation of Q_c for the deformed tinplate with immersion time

3.5 Corroded surface morphology

The corroded surface morphologies of tinplate with the tensile strain of 0 and 21.0% after immersion in 0.1 mol/L NaCl solution are shown in Fig. 13 and Fig. 14. For the original tinplate with no tensile strain, a relatively smooth surface was observed before immersion test (Fig. 13a). After one day's immersion, the corrosion products began to form on the surface of tinplate (Fig. 13b). With the prolonging of immersion time, more and more corrosion products were formed on tinplate (Fig. 13c), and the corrosion products were started to crack (Fig. 13d). For the tinplate with the strain of 21.0%, many slip bands and holes are found on the surface before immersion test (Fig. 14a). After one day's immersion, the orange corrosion products were formed on the whole surface of tinplate (Fig. 14b). With the prolonging of immersion time, the corrosion products were accumulated and started to crack (Fig. 14c), and finally parts of the corrosion products were fall off (Fig. 14d). From above phenomenon it also can be concluded that with the increasing of tensile strain the corrosion of tinplate is easily and early occurred because of the slip bands and defects originated from the tensile strain.

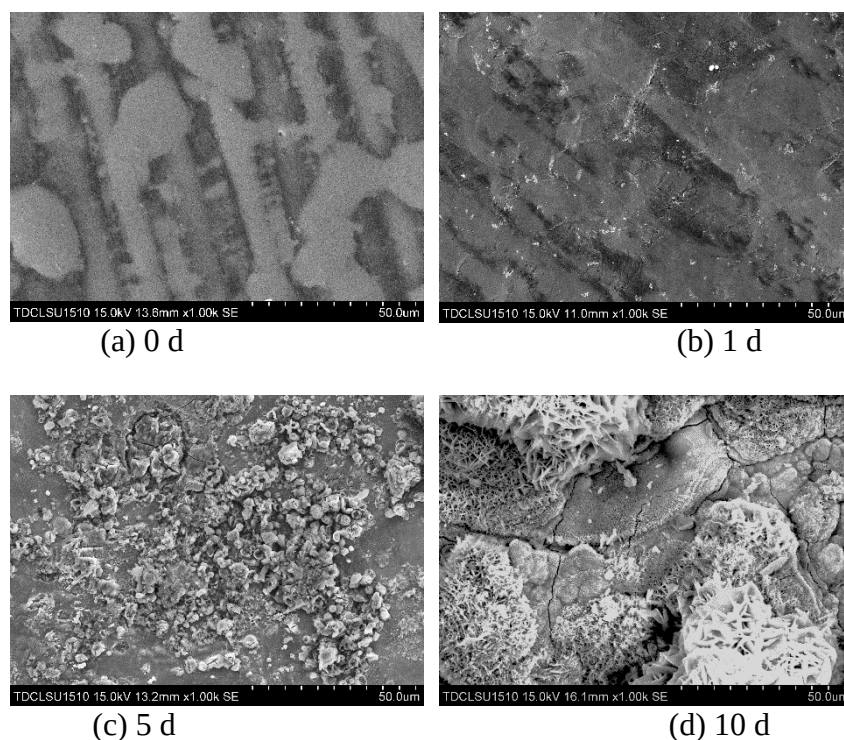
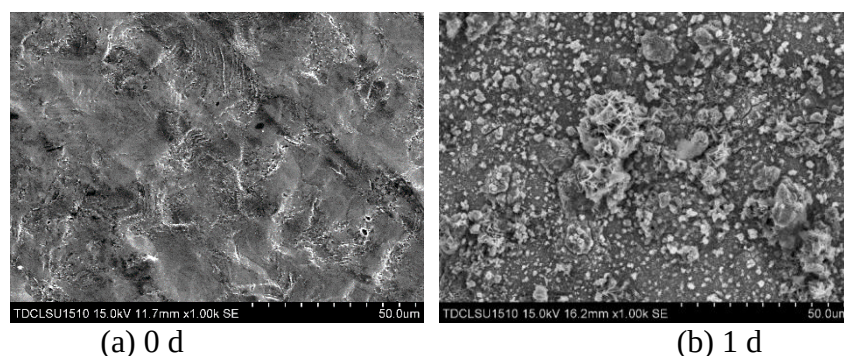


Figure 13. Surface morphology of tinplate with no strain after immersion in 0.1 mol/L NaCl solution



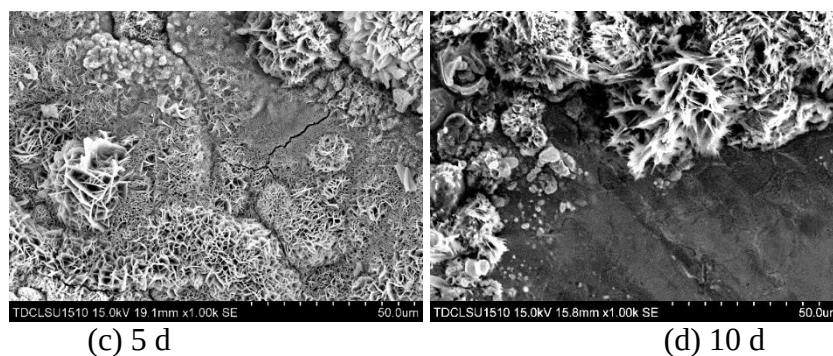


Figure 14. Surface morphology of tinplate with the tensile strain of 21% after immersion in 0.1 mol/L NaCl solution

After removing of corrosion products, the corroded surface morphology of tinplate with the tensile strain of 7.0% and 21.0% are shown in Fig. 15 and Fig. 16. For the tinplate with the tensile strain of 7.0%, several corrosion pits are observed and the rod-like FeSn_2 structure is exposed after one day's immersion (Fig. 15a), which indicates that parts of tin coating on the tinplate was dissolved [17, 22, 23].

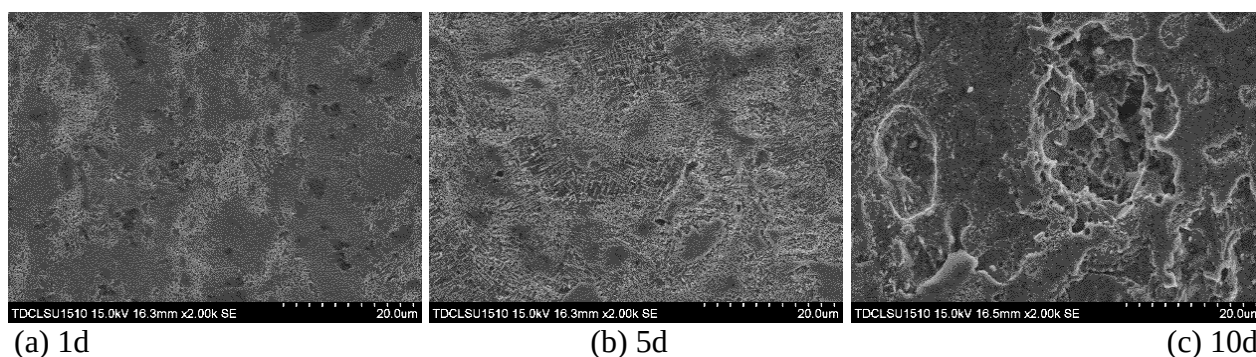


Figure 15. Surface morphology after removal of corrosion products of tinplate with the tensile strain of 7% after immersion in 0.1 mol/L NaCl solution

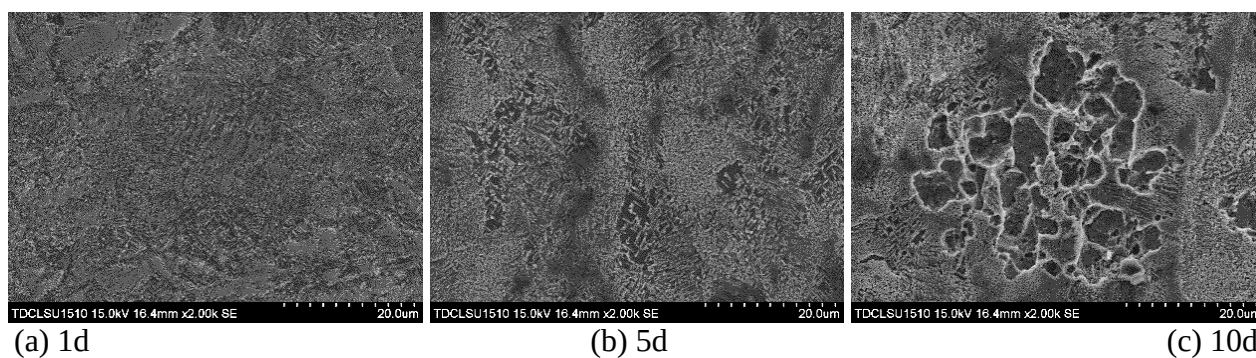


Figure 16. Surface morphology after removal of corrosion products of tinplate with the tensile strain of 21% after immersion in 0.1 mol/L NaCl solution

After the immersion time of 5 days, the tin layer on the tinplate almost disappeared and the FeSn_2 structure underneath the tin coating largely emerged (Fig. 15b). With the immersion time increasing to 10 days, severe local corrosion with deeper and bigger pits were caused on the steel substrate (Fig. 15c). For the tiplate with 21.0% strain, most parts of the tin coating fall off after one day's immersion, and a large area of FeSn_2 are exposed (Fig. 16a). As the immersion time increased to 5 days, the thin FeSn_2 layer i began to dissolve (Fig. 16b). Finally, the larger corrosion pits are caused and the heavier corrosion is occurred on the steel substrate (Fig. 16c).

3.6 Ions dissolution behavior

During the immersion test, the Fe concentration dissolved in NaCl solution detached from tinplate was detected and shown in Fig. 17. For the original undeformed tinplate, there is only a lower dissolution rate of iron ions in the initail immersion time of 3 and 6 hours (Stage I). In the immersion time of 6 to 24 hours (Stage II), Fe ions are rapidly dissolved in NaCl solution. During the immersion time from 24 hours to 10 days (Stage III), the dissolution rate of Fe ions in NaCl solution is slightly decreased. After the immersion time longer than 10 days (Stage IV), the dissolution rate of Fe ions is then increased again than that in Stage III.

For the deformed tinplate with the tensile strain of 7.0% and 11.0%, a similar dissolution behavior was observed with the original undeformed tinplate and four stages could also be divided, but the dissolution rate of tinplate with the strain of 7.0% and 11.0% is higher than that of tinplate with no deformation. For the tinplate with the strain of 21.0%, the stage I with lower dissolution rate of Fe ions is hardly observed, and other three stages with relative higher dissolution rate of Fe element are almost the same as tinplate with the strain of 7.0% and 11.0%. All these results imply that the strain deformation in the tinplate could accelarate the corrosion process and corrosion rate of tinplate.

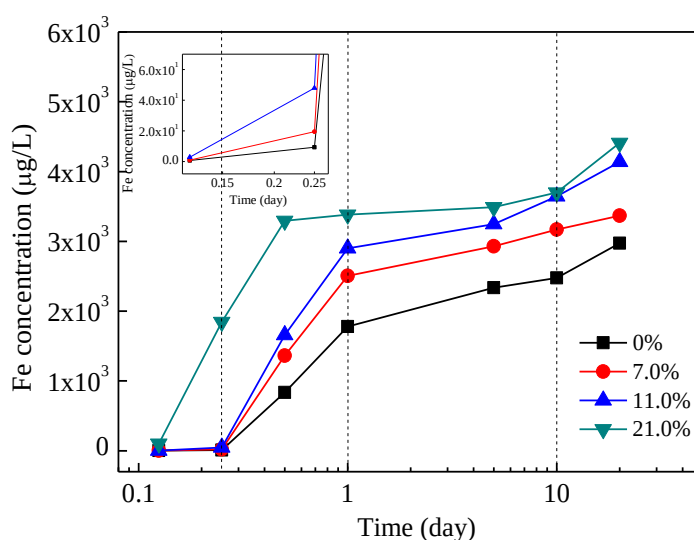


Figure 17. Fe concentration of tinplate with different tensile strain dissolved in 0.1 mol/L NaCl solution under different immersion time

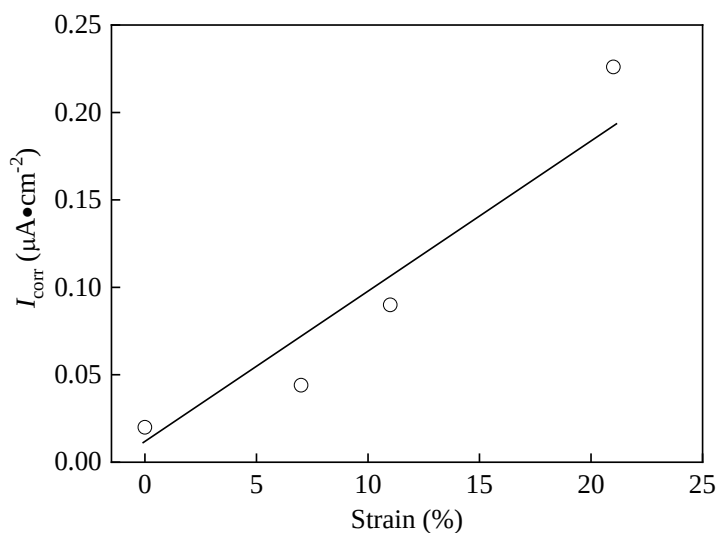
4. DISCUSSION

4.1 Influence of tensile strain

From above experimental results, it can be concluded that the deformed tinplate has a lower thickness, higher surface roughness, positive corrosion potential, larger corrosion current density and smaller polarization resistance with the increasing of tensile strain. In order to reveal the relationship between the corrosion behavior and the tensile strain, the corrosion current density in Table 1 and the polarization resistance R_p in Fig. 11 (as the polarization resistance R_p is inversely proportional to corrosion rate by Stern-Geary equation $i=B/R_p$, in which B is the Stern-Geary constant) were correlated with the tensile strain.

The dependence of I_{corr} and $1/R_p$ for tinplate in 0.1 mol/L NaCl solution on tensile strain is shown in Fig. 18. From the Figure, it can be clearly observed that there is a good linear relationship lying between the corrosion current density or $1/R_p$ and tensile strain with the linear correlation coefficients R^2 between 0.68 and 0.99. This relationship between the corrosion rate and tensile strain implies that the strain deformation in the tinplate could promote the corrosion its rate of deformed tinplate in NaCl solution [23].

Compared with the original undeformed tinplate, there are more slip bands and defects in the tinplate after plastic deformation as shown in Fig. 2. When the tinplate is exposed to the corrosive solution, more activation sites will be in contact with the solution owing to the larger surface roughness of the deformed tinplate, as illustrated in Fig. 4 and easier intrusion path of corrosive solution by the defects on the tinplate in Fig. 2 [24]. Thus, the deformed tinplate has a higher corrosion rate or lower polarization resistance in NaCl solution with increasing tensile strain as shown in Fig. 5, Fig. 11 and Table 1. Besides the above factors, the lower coating thickness of tinplate after strain deformation is the other reason to reduce the protection effect of tin coating, promoting the corrosion rate of the tinplate in NaCl solution (Fig. 4).



(a) I_{corr}

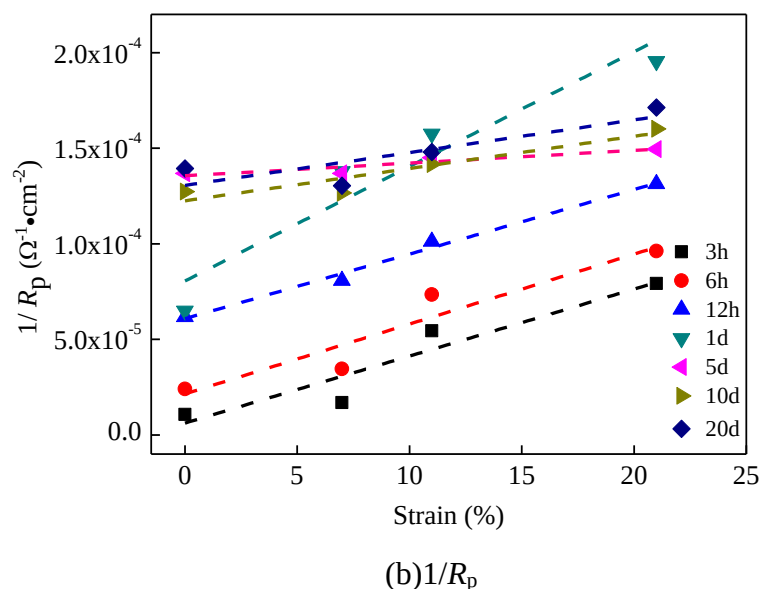


Figure 18. Dependence of I_{corr} and $1/R_p$ for tinplate in 0.1 mol/L NaCl solution on tensile strain and immersion time

4.2 Corrosion process under tensile deformation

From above analysis, the corrosion process of tinplate in NaCl solution could be divided into four stages reasonably. In the initial immersion test, only tin coating or a small parts of steel substrate are exposed to the corrosive solution (Stage I). Thus, in this stage tinplate presents a lower corrosion current density, lower content of Fe ions dissolution and a higher coating resistance or polarization resistance owing to the protection effect of tin coating (Table 1, Fig. 11 and Fig. 17). With the proceeding of corrosion process, the tin coating on the tinplate is gradually corroded and more and more steel substrate began to dissolve (Stage II). Therefore, two capacitance arcs are observed in EIS spectrum (Fig. 6, Fig. 7, Fig. 8 and Fig. 9), and the tin coating resistance and polarization resistance of tinplate are obviously decreased (Fig. 11). Meanwhile the concentration of Fe ions in NaCl solution is rapidly increased with the immersion time (Fig. 17). After this stage, appreciable corrosion products are formed on tinplate (Fig. 13b and Fig. 14b), the decreasing of tin coating resistance and polarization resistance is slightly lessened and the increasing of Fe concentration is also reduced because of the temporarily prevention effect of corrosion products (Fig. 11 and Fig. 17) (Stage III). In the final stage, the corrosion products gradually fell off and the corrosion process could be promoted again (Stage IV), in which the polarization resistance is further declined (Fig. 11) and the concentration of Fe element is raised again (Fig. 17).

For the undeformed tinplate, four stages of corrosion process of tinplate could be divided by the immersion time of 0-6 hours (Stage I), 6-24 hours (Stage II), 1-10 days (Stage III) and 10-20 days (Stage IV), as shown in Fig. 11 and Fig. 17. As for the deformed tinplate with the tensile strain of 7.0% and 11.0%, the four stages corrosion process could also be classified by the immersion time, but the deformed tinplate owns a lower polarization resistance and larger Fe concentration than that of original tinplate

under the same immersion time. When the tensile strain is increased to 21.0%, the first stage of corrosion process is disappeared because of the higher corrosion rate by the defects and lower tin coating thickness of tinplate. And the second and third stage of corrosion process shift to the earlier immersion time of 0-12 hours and 0.5-5 days. All these results also prove that the plastic deformation does promote the corrosion process of tinplate.

5. CONCLUSIONS

(1) The deformed tinplate has a lower thickness and a larger surface roughness with increasing tensile strain, and more slip bands and defects are formed on the tinplate with the increasing of tensile strain.

(2) With the increasing of tensile strain the deformed tinplate presents a positive corrosion potential and a lower polarization resistance, and but has a higher corrosion current density and larger iron dissolution rate.

(3) In NaCl solution a linear relationship between the corrosion rate and tensile strain of tinplate is found. The higher corrosion rate of tinplate under larger tensile strain is related from the more activation region generated by the plastic deformation and the easier intrusion path of corrosive solution by the lower tin coating thickness and defects in the tinplate.

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