Generation reason and corrosion characteristic of cavity of tinplate alloy layer

HUANG Jiangu(黄久贵) 1,2, LI Ning(李 宁) 1, ZHOU Derui(周德瑞) 1
(1. Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001, China;
2. Cold Rolling Thin Strip Mill, Baoshan Iron and Steel Company Limited, Shanghai 200431, China)

Abstract: The surface morphology of alloy layer of tinplate was studied by means of scanning electron microscopy. By using the layer on layer debounding technology of glow discharge spectrum, the contents of C and O at the boundary of layer and black plate were analyzed. And the corrosion characteristic of cavity of tinplate alloy layer was studied on line and in situ by means of electrochemical atomic force microscope. The corrosion depth of cavity of alloy layer in situ after different corrosion time was measured. The results show that the cavity of alloy layer is a critical factor causing rapid decline of corrosion resistance of tinplate, and the formation of cavity of alloy layer is due to incorrect pretreatment of black plate before electrotinning. The cavity of alloy layer is the internal factor causing pitting corrosion of tinplate when the tinplate is applied to food packaging material. And the dynamic equation of pitting corrosion generated in the cavity of alloy layer conforms to logarithm law.

Key words: tinplate alloy layer; scanning electron microscopy; glow discharge spectrum; electrochemical atomic force microscope; corrosion resistance

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1 INTRODUCTION

Tinplate is a low carbon mild steel sheet coated with tin on both sides 1,2. It is generally used for equipment and containers for a wide variety of products from food cans to cleaners in form of aerosol due to its nontoxity, appearance, easy solderability and a corrosion resistance adequate for a wide range of environments 3,4. Despite the increasing use in the canning industry of new alternative materials, such as aluminum and chromated steel sheet, tinplate continues to be used in more than 80% of cases 5. But, in order to maintain competition with these alternative materials, tinplate has a tendency to become thinner and thinner, which increases the probability of pitting corrosion 6-8. So understanding the role of the structure and composition of the tinplate and the steel substrate surface chemistry becomes critical 9.

At all times, the corrosion resistance of tinplate is a primary concern for both the manufacturer and the food packaging industry. Due to the fact that the corrosion resistance of tinplate is mainly affected by alloy layer and in order to improve the corrosion resistance of tinplate, a lot of researches were carried out for the alloy layer of tinplate and practical results were gained 10-14. Aluminum alloy layer is an intermetallic compound formed through thermal diffusion between Fe and Sn during the reflowing process after electrotinning on steel sheet. The thickness, microstructure and compactness of the intermetallic compound directly determine the lifetime of tinplate as food packaging material. For this reason, generation reason and corrosion characteristic of cavity of tinplate alloy layer were studied in this paper.

2 EXPERIMENTAL

Tinplate was provided by Baoshan Iron and Steel Company Limited. The methods of removing the free tin coating and the measurement of galvanic current density value of alloy-tin couple (JATC) were referred to Ref. [15]. The corrosion resistance of tinplate was evaluated by JATC value. And the lower the JATC value, the better the corrosion resistance of tinplate.

An S-570 type scanning electron microscope (SEM) produced in Hitachi Company of Japan was used to observe the morphology of alloy layer of tinplate. A 750A type glow discharge spectrum (GDS) produced in Leco Company of America was used to measure the component of black plate and tinplate.

An nanoscope III type electrochemical atomic force microscope (ECAFM) produced in American Digital Instrument Company was used to study the corrosion in the cavity of SrFe alloy layer on-line and in situ. The scanning range was 10 μm × 10 μm, and
a scanning graph was sampled every 1.5 min. The scanning frequency was 30 Hz, and there were 256 sampling points on each graph. Testing was carried out in the laboratory at (24 ± 1) °C. The electrolyte applied to ECAFM corrosion testing was a solution with 5% NaCl + 7% HCl + 5% C₆H₅OH, in which all reagents were analytical grades, and the solvent was ultrapure water produced with American MIL-L-Q-A type ultrapure water apparatus.

3 RESULTS AND DISCUSSION

3.1 Morphology and \( J_{ATC} \) value of tinplate alloy layer

\( J_{ATC} \) value is one of norms to evaluate corrosion resistance of tinplate. At present, the testing \( J_{ATC} \) value is widely applied by many tinplate manufacturers in the world. The \( J_{ATC} \) value is determined by its microstructure\(^{15}\). For this reason, the morphologies of alloy layer of 3 tinplates were observed by means of SEM, as shown in Fig. 1. The \( J_{ATC} \) value of alloy layer was tested according to Ref. \(^{115}\), and the results are shown in Table 1.

From Fig. 1 and Table 1, it is found that \( J_{ATC} \) value will be low if grains of tinplate alloy layer are big and orderly, and its corrosion resistance will be good. However, if there are big cavities on the surface of the alloy layer, the corrosion resistance of tinplates will rapidly decline.

3.2 Glow discharge spectrum testing of black plate and corresponding tinplate

In order to find the reason why there is a big cavity on the surface of alloy layer in Fig. 1(c), the contents of C and O of the black plate corresponding to the 3 tinplates in Fig. 1 before being electrotinned were measured by glow discharge spectrum (GDS), the results are shown in Fig. 2.

The contents of C and O of the 3 tinplates in Fig. 1 were measured by GDS, and the results are shown in Fig. 3.

Comparing Fig. 2 with Fig. 3, it is found that the contents of C and O of tinplates in Fig. 1(c) appear to abnormally rise at the interface between

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>( J_{ATC} ) (μA·cm(^{-2}))</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>0.04</td>
</tr>
<tr>
<td>2</td>
<td>0.06</td>
</tr>
<tr>
<td>3</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Fig. 1 Morphologies of alloy layer of tinplate
(a) —Sample 1; (b) —Sample 2; (c) —Sample 3

Fig. 2 GDS curves of contents of C and O of black plate
(a) —Content of C; (b) —Content of O
alloy layer and black plate. The explanation can be excluded that it is resulted from the enrichment of C from black plate to the boundary of alloy layer. One reason is that the coating blocks oxygen diffusing from the outside to the boundary between alloy layer and black plate, which can restrain the abnormal rise of content of O at the boundary. The other reason is that if the tinplate of Fig. 1(c) appears to be the enrichment of C from black plate to the boundary of alloy layer, there should be abnormal rise of C for other 2 tinplates.

So, it can be inferred that the adhered organics to the steel sheet during the pretreatment process result in an abnormal rise of the contents of C and O at the boundary of alloy layer and black plate in Fig. 1.

### 3.3 Effects of rolling oil of black plate on morphologies of alloy layer of tinplate

In order to examine whether the adherence of organics during the pretreatment process causes the abnormal rise of the contents of C and O and cavities in alloy layer, the effects of rolling oil of black plate on the morphologies of alloy layer were studied. Firstly, different regions of the same black plate were polluted to different degrees by rolling oil. Then, the black plate was electrotinmed and reflowed. After removing the free tin coating, the morphologies of alloy layer were observed by means of SEM, as shown in Fig. 4.

From Fig. 4 it can be concluded that oil does bring about cavities in alloy layer of tinplate. Comparing Fig. 1(c) with Fig. 4(b), it is found that the cavity of alloy layer of tinplate gained from oil experiment in laboratory is similar to that provided by manufacturer, which further proves that the cavity of alloy layer of tinplate in Fig. 1(c) is caused by incorrect pretreatment, resulting in the adherence of organics to the surface of black plate.

### 3.4 Corrosion characteristic of tinplate cavity of alloy layer

From Fig. 1 and Table 1, it is found that there are big cavities on the surface of alloy layer of tinplate which has high $J_{ATC}$ value and poor corrosion resistance. Aiming at these cavities of alloy layer of tinplate, in the corrosion electrolyte which is composed of 5% NaCl, 7% HCl and 5% CaH$_2$O$_7$, their corrosion morphologies after different corrosion time were observed every 1.5 min by electrochemical atomic force microscope (EC-AFM) on-line and in-situ, and the results are shown in Fig. 5.

**Fig. 3** GDS curves of contents of C and O of tinplate  
(a) — Content of C; (b) — Content of O

**Fig. 4** SEM images of alloy layer of tinplate  
(a) — Not contaminated by rolling oil; (b) — Lightly contaminated by rolling oil;  
(c) — Seriously contaminated by rolling oil
Fig. 5 ECAFM images of cavities of alloy layer with different corrosion time

$t$/min: (a) $-0$; (b) $-62$; (c) $-120$; (d) $-169$; (e) $-227$; (f) $-296$; (g) $-350$; (h) $-411$

In order to observe the corrosion morphologies of cavities of alloy layer more directly, 3-dimensional ECAFM image at $t = 0$ was compared with that at $t = 411$ min, the results are shown in Fig. 6, indicating that the marked dissolution occurs in the cavities of alloy layer. Furthermore, the corrosion section images of the locked part in Fig. 5 were superimposed according to time sequence, and a profile curve cluster is shown in Fig. 7, showing that the bottom of cavity of alloy layer (point $A$ in Fig. 7) is gradually dissolved with the increase of corrosion time, while other region is hardly dissolved.

Fig. 6 3-dimensional ECAFM images of cavities of alloy layer with different corrosion time

$t$/min: (a) $-0$; (b) $-411$

Fig. 7 In-situ ECAFM section curves of cavities of alloy layer

The relationship between corrosion depth of point $A$ and logarithm of time is shown in Fig. 8. From Fig. 8, it can be seen that the bottom of cavity of alloy layer is dissolved about 140 nm after being corroded for 7 h. In addition, it is found that the corrosion rate equation conforms to logarithm law, which can be expressed as

$$y = 226.031 + 65.057 \log t$$

Eqn. (1) is a corrosion dynamic equation in the cavity of alloy layer under the thin liquid film of corrosion. The corrosion rate equation conforming to logarithm law reflects the following 2 cases:
1) corrosion process controlled by the migration of electrons or ions;
2) corrosion occurring in the cavity when chemical adsorption layer or corrosion resistant film appearing cavity.

From the above results, a conclusion can be drawn that the cavity of alloy layer is the internal factor causing pitting corrosion of tinplate when the tinplate is applied to food packing material.

Fig. 8 Relationship between corrosion depth and logarithm of time

4 CONCLUSIONS

1) Cavity on the surface of alloy layer is a critical factor causing rapid decline of corrosion resistance of tinplate.

2) By means of GDS testing and simulation experiment in the laboratory, it is proved that the cavities of alloy layer are caused by incorrect pretreatment of black plate before electroplating.

3) The cavity of alloy layer is the internal factor causing pitting corrosion of tinplate when the tinplate is applied to food packaging material. Through measuring the corrosion depth of cavity of alloy layer in-situ after different corrosion time, it is found that dynamic equation of pitting corrosion generated in the cavity of alloy layer conforms to logarithm law.

REFERENCES


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