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# Corrosion failure analysis of Lightweight Tinplate in Protein Beverage

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**Abstract.**Electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and X-ray photoelectron spectroscopy (XPS) have been used to investigate the corrosion mechanism of lightweight tinplate in protein beverage. It is found that proteins in beverages can decomposed into hydrogen sulfide (H<sub>2</sub>S) and then hydrolyzed to H<sup>+</sup> and S<sup>2-</sup>. Hydrogen evolution reaction between H<sup>+</sup> and carbon steel could produce a large amount of H<sub>2</sub>, the gas assembled at the interface result in the exfoliation of corrosion product layer and accelerate the tinplate's corrosion ultimately. S<sup>2-</sup> is oxidized in the medium and generated a small fraction of S which lead to the sulfur blackening phenomenon in beverage cans.

**Key words:** Corrosion mechanism; Tinplate; hydrogen sulfide; Protein beverage

## 1.Introduction

Tinplate is a kind of non-homogeneous material with a stratified structure, basically consisting of a thin sheet of low carbon steel and two layers of commercial pure tin on both sides. Combining the formability, strength and corrosion resistance of carbon steel with great appearance of tin, tinplate is widely used as containers for kinds of products in the food processing industry[1-3]. However, tinplate cans may have some significant problems such as corrosion failure, sulfur blackening which depends on the acidity, food matrix, temperature of storage and duration, those problems can affected the nutritional value of the canned food[4]. Foodstuff can be polluted by this process. Though tin is not considered as a poisonous metal, the pollution problems may also cause the rejection of the consumers[5-6]. Many industries involving in tinplate cans for example tinplate producers, food canners and quality testing institution are concerned with the corrosion mechanism of tinplate greatly [7].

Compared with the pure tin, tinplate's corrosion process is complex due to its heterogeneity and stratified structure. Now, most studies about tinplate corrosion focus on three aspects: the films applied on, the corrosion mechanism of coating/alloy systems and the corrosion behavior in specific solution. Several hybrid sol-gel formulations applied on tinplate and indicated that sol-gel with high inorganic precursor ratios are able to form a continuous film, which is necessary to provides good



barriers properties [8]. Through the analysis of the corrosion of chromium based coating for packing steel and found that the Cr(VI) derived coatings were fully resistant to corrosion driven disbondment [9]. The amount of alloy layer increased with the reflowing temperature and time and then the corrosion potential of detinned tinplate shifted positively and the corrosion rate decreased [10]. The corrosion behavior of tinplate in NaCl solution indicated that the tinplate in 0.5mol/L NaCl solution was mainly the dissolution of carbon steel substrate because of the defects in the tin layer, and the corrosion product was mainly  $\gamma$ -FeOOH [11]. In addition, the corrosion resistance was strongly depended on the electrolyte after considered tinplate in different aggressive mediums [6]. But, few studies of tinplate corrosion behaviors in beverage solution have been reported and the corrosion mechanism in protein beverage is still unclear. Protein beverage is a popular packaged beverage whose market share increases quickly by the development of the economy. Therefore, it is significant to explore the tinplate corrosion mechanism in protein beverage.

Recently, the in-situ measurement electrochemical impedance spectroscopy (EIS) has become one of the main methods to study the corrosion mechanism of metal or coating/metal systems, besides, it was used to evaluate the corrosion resistance of tinplate quantitatively [12-15]. X-ray photoelectron spectroscopy (XPS) combined with the low energy Ar<sup>+</sup> sputtering technique has been used to investigate the chemical states of elements on the tinplate surface [16].

The aim of this work is to analyze the corrosion process of the lightweight tinplate in protein beverage by a simulation solution (PH=6): sodium sulfide and acetic acid (6.3mol/L). At last, the corrosion mechanism of tinplate in protein beverage was proposed.

## 2. Experimental

The tinplate samples (15mm×15mm) were provided by the ShougangJingtangIron&Steel Company, China. Tin content on both side of the carbon steel is 1.1 g/m<sup>2</sup>. Samples were cleared using ultrasonic bath in acetone. After, they were divided into thirteen parts and immersion for 10min, 30min, 45min, 1h, 2h, 4h, 6h, 1d, 3d, 5d, 6d, 7d, 9d, respectively. Experiment were conducted at 25°C in incubator.

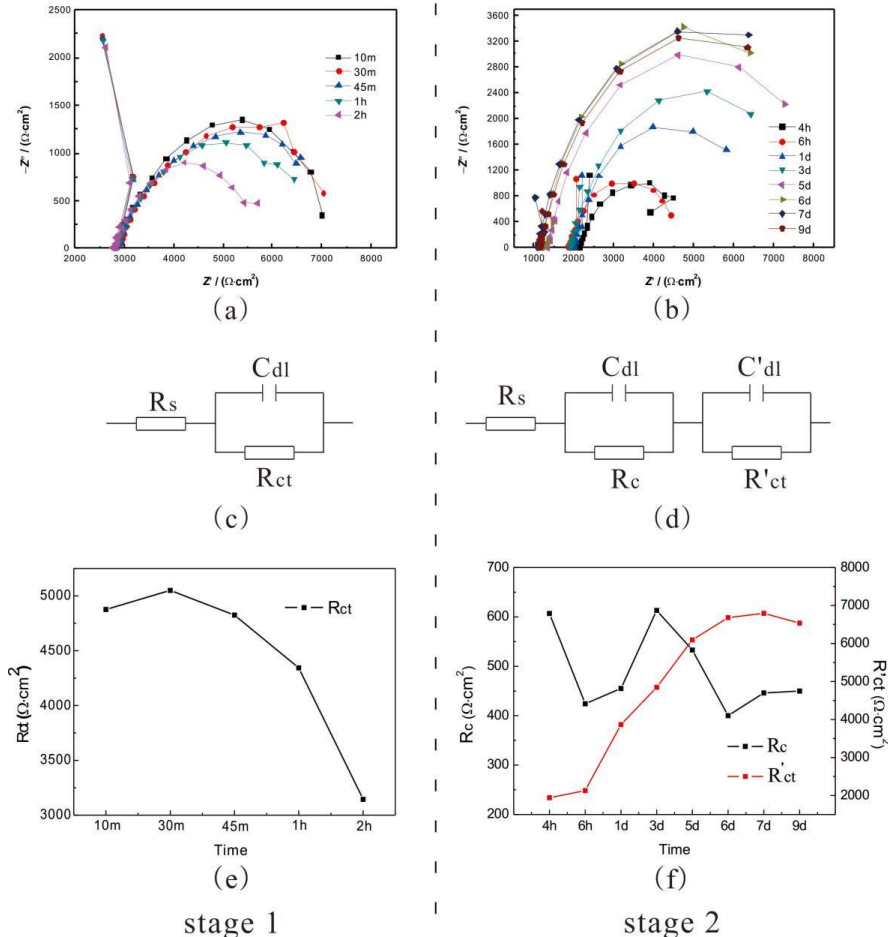
EIS measurements were carried out by PARSTAT 4000+ electrochemical workstation using the tinplate sample as the working electrode (WE), calomel electrode as the counter electrode (CE) and high-purity platinum electrode for the reference electrode (RE). The EIS measurements were performed under the open circuit potential. A 10mV alternating-current signal was imposed with frequencies stepped from 0.01 Hz to 100 kHz. The working area of the tinplate is 1cm<sup>2</sup>. ZSimpWin Software has been used to fitting the results. The electrolyte solution used nitrogen to remove oxygen before using and sealed the electrolytic cell during electrochemical measurement. SEM images were obtained by using Zeiss Ultra 55 with an InLens detector to observe the morphology of the samples on surface and cross-section, EDS has been used to analysis the composition of the rust point semi-quantitatively (Acceleration voltage 12KV). XPS measurements were conducted by ESCALAB 250Xi system with monochromatic Al K $\alpha$  (1486.71eV) radiation. XPS depth profiling was carried out by argon ion bombardment (AIB). Standard sample of C 1s (284.8eV) has been used to calibrate the instrumental binding energy scales according to ISO 15472 [17]. An ion accelerating voltage of 2KV was used to analyze the corrosion products on the surface and the sputtering rate was 0.036nm/s.

## 3. Results and Discussion

### 3.1 Electrochemical behavior

The impedance spectra measured for tinplate in simulation solution with various immersion time are plotted in Fig.1(a) and (b), electrochemical equivalent circuit in Fig.1(c) and (d) were applied to explain the behavior of the tinplate-electrolyte system, the resistance value obtained from the electrochemical equivalent circuit are shown in Fig.1(e) and (f).  $Z'$  and  $Z''$  were the real part and the imaginary part of the impedance, respectively.  $R_s$  is the solution resistance,  $R_{ct}$  is charge transfer resistance of tin layer,  $R_c$  is the micro resistance of tin layer,  $R'_{ct}$  is charge transfer resistance of carbon steel,  $C_{dl}$  is the interfacial capacitance of tinplate and  $C'_{dl}$  is the double layer capacitance of carbon steel.

According to the EIS results, the corrosion behavior of the tinplate in simulated solution can be divided into two main stages with the immersion time being prolonged: stage one is the corrosion of the tin layer and the stage two is the corrosion of the carbon steel.



**Figure 1.** There are two stage of tinplate EIS results in protein beverage simulated solution: (a) (b) Nyquist plots; (c) (d) Electrochemical equivalent circuit; (e) (f) Evolution resistance of electrochemical equivalent circuit

As shown in Fig.1 (a) and (b), a characteristic arc could be seen on each EIS plots at the high frequency (100 kHz ~ 30 kHz). This is due to the poor conductivity of the solution at the beginning and the arc decrease gradually with the immersion time prolonging.

### Stage1: Corrosion of the tin layer

At the initial stage of immersion time between 10min and 2hour, the EIS plots containing one time-constant are observed (Fig.2 (a)), indicating that the layer has a good protective performance and there is no electrolyte permeation through the tin layer. Protein beverage could decomposition out gas like  $\text{H}_2\text{S}$  when heated at the sterilization temperature, so the primary type of corrosion is electrochemical corrosion between  $\text{H}_2\text{S}$  and tin layer at this stage. At this period of time, the capacitive arc radius decreases gradually and means the resistance of the tin layer become smaller.  $R_{ct}$  in Fig 1 (e) and  $R_c$  in Fig 1 (f) are the fitting result of tin layer resistance at different immersion time. An order of magnitude gap means the tin layer has been destroyed by the beverage.

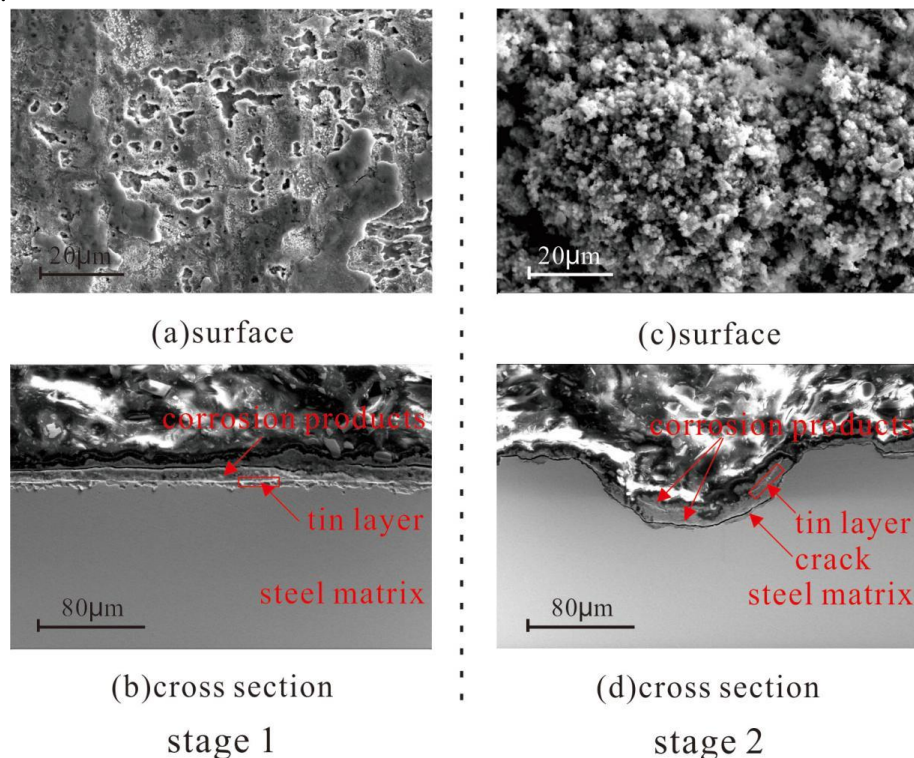
### Stage2: Corrosion of the carbon steel

After 4 hours, the EIS plots with two time-constant are presented on Fig.2 (b). The time-constant at the high frequency is caused by the resistance of the tin layer. Fig.1 (f) showed the tin layer resistance  $R_c$  maintained at 400 - 600  $\Omega \cdot \text{cm}^2$  and indicated the poor protective effect of tin layer beyond the carbon steel. The time-constant at the low frequency is a result of interfacial capacitance of tin layer and

charge transfer resistance of tinplate which reflecting the corrosion of carbon steel. At this stage, the electrolyte has permeated through the tin layer and formed interfacial capacitance at the carbon steel/tin layer interface. Fig.2 (b) shows that the capacitive arc radius increases gradually when the immersion time is more than 4 hours, besides, the resistance of carbon steel  $R'_{ct}$  increases gradually with the prolong time. This phenomenon mainly related to the formation and coverage of the corrosion product. The corrosion products formed by the reaction between carbon steel and corrosive medium assembled at the surface of the substrate, which can inhibit the penetration of the corrosive medium effectively and reduce the corrosion rate. Because of the poor adhesion between the corrosion product layer and the carbon steel, the longer the immersion time the greater the risk of peel off.

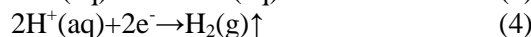
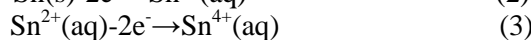
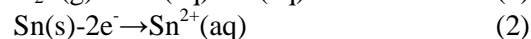
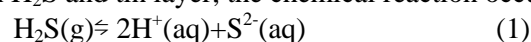
### 3.2 Surface and Cross-section characterization

Fig.2 is the SEM results of Lightweight tinplate during the corrosion process at 2 hours and 9 days. Fig.2(a) and (c), Fig.2(b) and (d) are the surface and cross-section morphologies of the samples, respectively.

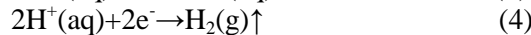
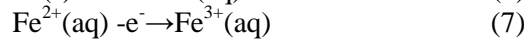
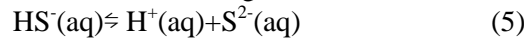


**Figure2.**SEM results: Stage 1, (a)surface and (b) cross section; Stage 2, (c)surface and (d) cross section.

Spotted corrosion products were observed on the surface after being exposed to protein beverage for 2 hours(Fig.2(a)) and cluster corrosion products formed on the surface for 9 days(Fig.2(c)). The increase of the corrosion products means the deepening of the corrosion process. Cross section could show the process of ions corrosion to the tin layer and carbon steel clearly. In Fig.2(b), a white strip in the red rectangular frame is the tin layer and above it covered by a thick corrosion product layer. There were no corrosion products between the tin layer and carbon steel have been discovered what indicated that the corrosive ions have not permeated through the tin layer. Fig.2(a) and (b) corresponding to the stage one when corrosion between  $H_2S$  and tin layer, the chemical reaction occurs as follows:



It is worth noting that there are two-layers of corrosion products clipped the tin layer as shown on Fig.2 (d). Therefore, it is proposed that the presence of two-layer corrosion product results from the corrosive ions permeated through the tin layer. Because the metal activity of iron is better than that of tin, once the tin layer is corroded, the first stage of corrosion stopped with the second stage corrosion beginning. The chemical equation would be changed below:



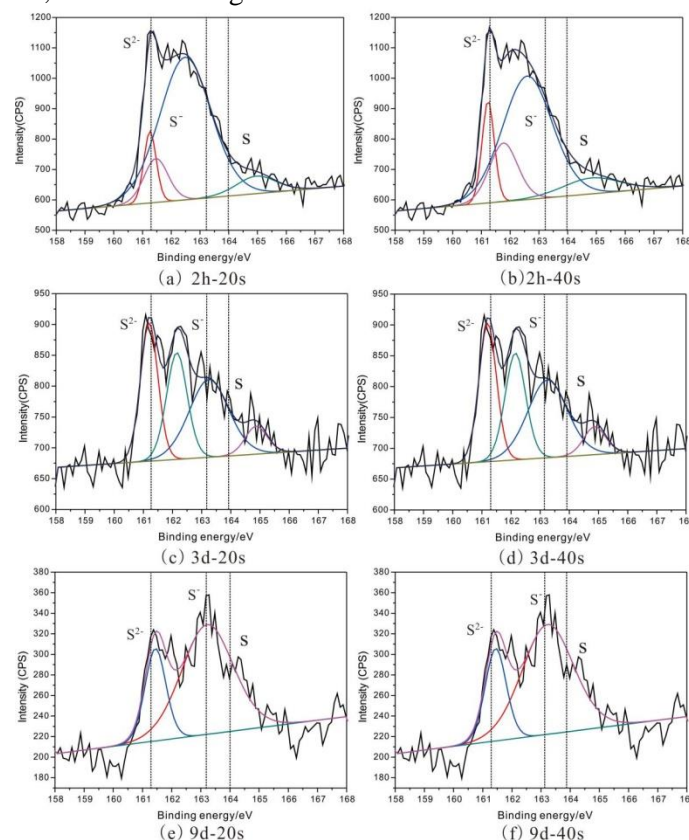
Because Fe is more abundant and active than Sn, the hydrogen produced at the second stage is abundant. Amount of hydrogen accumulated at the interface between the carbon steel and corrosion products, which lead to the separation of the corrosion products layer eventually as shown in the Fig.2 (d).

EDS has been used to investigate the component of the corrosion products. S, Sn, O, Fe were detected as the mainly elements in the corrosion products and shown in table 1.

**Table 1.** Contents of main elements in corrosion products (atomic fraction)

Element \ Time	S	Sn	O	Fe
2 hours(stage 1)	5.6	21.8	43	29.6
9 days(stage 2)	8.4	14.5	33	44.1

The corrosion products (stage 1) measured contained 29.6% Fe and 21.8% Sn, while stage 2 contained 44.1% Fe and 14.5% Sn. Due to the chemical equation (6) (7) instead of (2) and (3) took place at the second stage, the Fe and Sn content changes significantly. S element was mainly from the protein beverage and XPS has been used to analyze the valence state of sulfur in corrosion products for different immersion time, as shown in Fig.3.



**Figure3.** Scanning spectra of XPS for S element: (a) (c) (e) sputtering 20s for immersion 2 hours, 3 days and 9 days; (b) (d) (f) sputtering 40s for immersion 2 hours, 3 days and 9 days

Since ions can be freely exchanged and diffused in solution, the valence state of S element at the two corrosion product layers are consistent. Fig.3 shows the XPS spectrum of S element acquired on the corrosion products of the tinplate surface. From S 2p XPS spectra acquired at sputtering time 20s and 40s, it is obvious to see that the content of different S valence state on the corrosion products is various. It is noticed that there are only two main peaks in the Fig.3 (a)(b)(c)(d), and beside the two main peaks has a shoulder peak in the Fig.3(e)(f). Though peak fitting, the component with the binding energy of 164.0eV is attributed to nonmetallic S, while those with the binding energy of 163.2eV and 161.3eV can be attributed to S<sup>-</sup> and S<sup>2-</sup> [18]. From Fig.3(a)(b)(c)(d), it is clear that S<sup>2-</sup> and S<sup>-</sup> component are the major parts of the sulfur valence state while S component exists on the surface with a small amount when immersion for 3 days. After immersion for 9 days, S<sup>-</sup> has become the major part of the S element, while S<sup>2-</sup> concentration reduces sharply and nonmetallic S concentration increase gradually. S<sup>2-</sup> is highly reductive, and it's easy to lose electrons in the medium into nonmetal S. The chemical reaction took place as follows:



The chemicals reaction equation (8) and (9) explain the phenomenon that S<sup>-</sup> and S contents increases gradually with the prolong immersion time.

Compared with Fig.3(a)(b), Fig.3(c)(d) and Fig.3(e)(f), it is clear to see that with the prolongation of the immersion time, the peak intensity of the sulfur element measured by the XPS is reduced from 1150 CPS at 2h to 350 CPS at 9d on the maximum peak strength. This phenomenon is the double result of the decrease of sulfur element concentration in the solution and the diffusion of sulfur element to the matrix. At each etched time, the contents of S element binding state almost have no changes.

#### 4. Conclusion

A comparison between tinplate samples immersion for different times in simulation solution: sodium sulfide and acetic acid (PH=6), with regards to their resistance to protein beverage corrosion, has been completed to show that with the immersion time being prolonged:

- EIS diagram of tinplate in the simulation solution shows the transition from single capacitance arc to double capacitance reactance arc, and the corrosion process can be divided into two stages: first stage is the corrosion of the tin layer and the second stage is the corrosion of carbon steel after the tin layer has been corroded.
- SEM images indicated that ions in the medium can permeated through the tin layer and then corroded the carbon steel. Besides, the hydrogen produced at this stage can separated the corrosion productive layer and carbon steel matrix easily.
- EDS and XPS results revealed that Fe has replaced Sn as the main metal element in the corrosion process and the peak strength of sulfur in corrosion products decreases gradually while the ratio of high valence atoms of sulfur is increasing.

The sulfur corrosion resistance mechanism of lightweight tinplate in protein beverage is proposed that: Decomposition of proteins in beverages to produce hydrogen sulfide (H<sub>2</sub>S), etc. H<sub>2</sub>S hydrolysis into H<sup>+</sup> and S<sup>2-</sup> and then hydrogen evolution reaction of H<sup>+</sup> with tin layer under the electrochemical action which product H<sub>2</sub> and leaving S<sup>2-</sup> in the medium. Once the tin layer is corroded or damaged, the second stage of hydrogen evolution occurs and accompanied by the production of a large amount of H<sub>2</sub>. The accumulation of H<sub>2</sub> at the interface between corrosion product and carbon steel matrix would result in the exfoliation of corrosion product layer and accelerate the corrosion. S<sup>2-</sup> is oxidized to produce a small amount of S which lead to the sulfur blackening phenomenon in beverage cans.

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