

Electrodeposited cerium film as chromate replacement for tinplate

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Abstract

The cerium film was prepared on tinplate by electrodeposition method. Sulfide-stain resistance of the Ce-passivated, unpassivated and Cr-passivated tinplates was evaluated using a cysteine tarnish test. Corrosion behavior of these tinplates in contact with 3.5% NaCl solution and 0.1 M citric–citrate buffer solution was investigated using Tafel measurement and electrochemical impedance spectroscopy measurement, respectively. The adhesion of epoxyphenolic lacquer to the Ce-passivated tinplate was checked using a cross hatch cutter. The morphology, composition and thickness of the cerium film were studied by atomic force microscopy, X-ray photoelectron spectroscopy and X-ray fluorescence spectrometry. According to the results, the Ce-passivated tinplate shows the best sulfide-stain resistance and the best corrosion protection property compared with the unpassivated and Cr-passivated tinplates. The adhesion of epoxyphenolic lacquer to the Ce-passivated tinplate is good. The cerium film is composed of the closely packed particles of about 50–200 nm in diameter. The film mainly consists of cerium and oxygen, which mainly exist as CeO_2 , Ce_2O_3 and their hydrates such as $\text{Ce}(\text{OH})_4$, $\text{Ce}(\text{OH})_3$. The total cerium amount of the film is about 0.110 g/m^2 .
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1. Introduction

Tinplate is cold-rolled, low-carbon thin steel plate or steel strip, plated with pure tin on each side, which is mainly used to make food can [1–3]. Some special performances of tinplate are required because of the unique circumstance in the food can. Firstly, protein and amino acid in the canned food usually contain sulfur which can be named as organic sulfur. After the procedure of high temperature sterilization, the organic sulfur would be converted into inorganic sulfur such as H_2S , HS^- and S^{2-} . Due to the existence of the inorganic sulfur, purple SnS and black FeS as the main components of sulfide-stain can be easily formed on tinplate, resulting in serious attack of food can wall and food pollution. So sulfide-stain resistance of tinplate must be excellent [4,5]. Secondly, the circumstance in the food can is corrosive, and it is required that tinplate can't seriously corrode during food can's storage life (about one year). So tinplate should present good corrosion resistance. Thirdly, in order to improve the performance of the food can, tinplate need lacquering sometimes, so the adhesion of lacquer to tinplate must be good [6,7]. In order

to satisfy these requirements, it is important to apply a passivation treatment for tinplate during its manufacturing. At present, chromate passivation is widely used in tinplate industry, and chromate-passivated tinplate provides excellent sulfide-stain resistance, corrosion resistance and lacquer adhesion. However, chromate is both highly toxic and carcinogenic, whose use can cause environmental pollution, also bring potential danger to food security, so it is imperative to develop a chromate-free passivation technology with excellent performance [8,9].

During the last two decades, the metal passivation treatments with lanthanides have been widely investigated. Recently, lanthanides have been proposed as a good alternative for hexavalent chromium, especially in the case of cerium [10–17]. In this paper, the Ce-passivation film was prepared on tinplate through the electrodeposition method, and it is excellent as well as the Cr-passivation film.

2. Experimental details

2.1. Sample preparation

Tinplates after reflowing, of sizes $70 \times 40 \times 0.19 \text{ mm}$ and with a tin coating weight of 11.2 g/m^2 , were named as unpassivated

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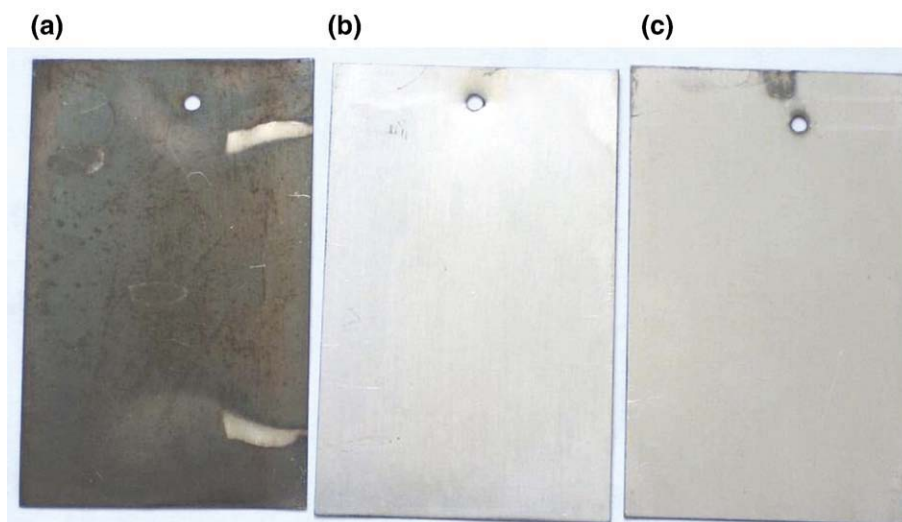


Fig. 1. Appearances of the samples after a cysteine tarnish test. (a) unpassivated tinplate; (b) Ce-passivated tinplate; and (c) Cr-passivated tinplate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

tinplate. The unpassivated tinplate was polarized in 25 g/L NaCr_2O_7 solution using a cathodic current density of 4 A/dm^2 for 1 s at 40°C – 45°C and pH 4.2. After being rinsed in distilled water and dried with compressed air, the Cr-passivated tinplate was obtained. The total chromium amount of the Cr-passivation film is about 8.1 mg/m^2 .

A solution consisting of 10 g/L $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 10 g/L NH_4NO_3 was prepared, and pH value was adjusted to 4.0 using diluted nitric acid. The unpassivated tinplate was cathodically polarized in the resultant solution at 20°C – 25°C using a current density of 4 A/dm^2 for 1 s, rinsed in distilled water and dried with compressed air, then the Ce-passivated tinplate was obtained.

2.2. Cysteine tarnish test

In order to determine sulfide-stain resistance of the three tinplates mentioned above, a cysteine tarnish test was conducted. A 4 g/L L-cysteine hydrochloride solution was prepared and pH value was adjusted to 7.00 using sodium phosphate. After being purged with purified nitrogen for 1 h, the solution was activated in water bath at 98°C – 100°C for 2 h. The prepared solution (about 100°C) was poured into a 1 liter glass jar, and the samples were suspended in the jar. Then the jar was lidded. After natural cooling for 1 h, the samples were taken out, rinsed in distilled water and dried with compressed air [18].

2.3. Electrochemical tests

In order to study corrosion behavior of the three tinplates, electrochemical tests were carried out using a Gamry Potentiostat PC4-750 system. All the measurements were conducted with a three-electrode arrangement placed in a faraday cage at room temperature ($25 \pm 1^\circ\text{C}$). The working electrode was the studied tinplate with the exposed area of 0.78 cm^2 . A commercial Saturated Calomel Electrode (SCE) and a platinum mesh were used as the reference and counter electrodes, respectively.

Tafel measurement was performed in a naturally aerated 3.5% NaCl solution at pH 6.85, which is usually used as the working solution in metal corrosion studies. The polarization scan was from -250 mV vs. E_{OC} (open circuit potential) to $+250 \text{ mV}$ vs. E_{OC} at a rate of 1 mV/s . Data were recorded after 30 min immersion in working solution.

Electrochemical impedance spectroscopy (EIS) measurement was performed in a 0.1 M citric acid/sodium citrate buffer solution at pH 4.3, commonly used as the working solution in tinplate food packing studies. In order to simulate the actual conditions found inside cans, the working solution is purged with purified nitrogen for 2 h prior to the experiments and throughout their duration. The measurements were carried out at open circuit potential in the 10 kHz to 1.7 mHz frequency range with 8 frequency points per logarithmic decade. The amplitude of the sinusoidal voltage was 5 mV rms. Data were recorded after 1 h of immersion in the working solution. The software of ZsimDemo version 3.11d written by Bruno Yeum Ph.D was used for the EIS data analysis.

2.4. Lacquer adhesion tests

An organic solvent-based epoxyphenolic lacquer (golden pigmented) was applied on the passivated tinplates by means of a bar coater to a coating mass of $15\text{--}20 \text{ g/m}^2$, followed by curing at 200°C for 10 min. The lacquer adhesion was checked by using a cross cut adhesion test based on ASTM D3359-02 [19]. In this test, a multi-blade Eichen Multi-cross Hatch Cutter model 295 was employed to form eleven cut lines in each of longitudinal and transverse directions to define 100 lattices and the results were classified according to the standard descriptions.

2.5. Characterization of the cerium film

The surface morphology of the cerium film on tinplate was observed by PicoPlusTM atomic force microscope (AFM) from

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