Electrochimica Acta 131 (2014) 137–147

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

The anticorrosive properties of sol-gel films doped with hydrotalcite nanoparticles applied on tinplate

D. Álvarez, A. Collazo, X.R. Nóvoa, C. Pérez*

Corrosion Engineering and Materials (ENCOMAT) Group, E.E.I., University of Vigo, Campus Universitario As Lagoas-Marcosende, 36310, Vigo, (Spain)

ARTICLE INFO

Article history:
Received 30 September 2013
Received in revised form 3 February 2014
Accepted 5 February 2014
Available online 22 February 2014

Keywords:
Tinplate
sol-gel film
hydrotalcite
zeta potential
electrochemical impedance spectroscopy

ABSTRACT

The use of two-layer system based on the sol-gel technology is proposed as the inner lacquer for tinplate food cans. The primer was a hybrid film based on tetra-n-propoxyzirconium (TPOZ) and 3-Glycydoxypropyltrimethoxysilane (GPTMS) precursors. The topcoat was also a hybrid film based on tetraethyl orthosilicate (TEOS) and vinyltrimethilsiloxane (VTMS) precursors. The topcoat is intended to be in contact with foodstuff, thus, hydrotalcite nanoparticles were incorporated as dopants to increase the film barrier properties. The types of hydrotalcite nanoparticles studied were as-synthesized (HT) and thermally activated (CHT). The zeta potential measurements performed on the hydrotalcite suspensions indicated that they were stable in the acidic conditions used to synthesize the sol-gel solution; therefore, the particles disperse well into the sol-gel.

The electrochemical behaviour was evaluated by means of Electrochemical Impedance Spectroscopy (EIS). The results showed better performance of tinplate samples coated with doped sol-gel film than undoped films. However, there were not significant differences between the hydrotalcite types, indicating that the mechanism of inhibition has to be the same in both cases. The zeta potential evolution of HT and CHT suspensions with the NaCl concentration revealed the adsorption of Cl^- anion on the particles surface, removing the chloride ions from the surrounding environment.

1. Introduction

Tinplate consists in a thin sheet of low carbon steel coated on both faces with tin. The food packaging industry uses tinplate extensively because it combines in one material the strength and formability of steel and the corrosion resistance and good appearance of tin. However, there are significant problems related to the use of tinplate cans in contact with food medium, such as corrosion failure that will result in certain tin dissolution into the foodstuff [1,2]. The tinplate can manufacturing process comprises a passivation treatment to increase the corrosion resistance and the lacquer adhesion to the metal substrate. Additional protection is afforded by organic coatings or sanitary lacquers that also avoid the black stains produced by sulphide and decrease the bleaching action of certain fruit pigments [3]. In order to lower production costs, the percentage of Sn used in the tinplate manufacturing has declined. This makes that the role of the lacquers is gaining importance as the ultimately responsible of the foodstuff integrity. Lacquers should be chemically inert, resistant to mechanical or thermal stress and must firmly adhere to tinplate.

The lacquers based on epoxy resins are the most widely employed, due to the good barrier properties afforded [3–7]. One constituent used in the manufacture of epoxy resins is the monomer BADGE (Bisphenol A diglycidyl ether). Since the 1990s onward concerns have been raised on the possible carcinogenicity of BADGE, which is listed as an IARC (International Agency for Research on Cancer) Group 3 carcinogen, meaning it is “not classifiable as to its carcinogenicity to humans” [8]. The new legislations bounded on the use of BADGE as precursor of epoxy-phenolic resins, since some studies revealed the presence of BADGE in some canned foods at levels above 1 $mg.kg^{-1}$, which is the maximum allowed by the European Regulations No. 1895/2005 and 1935/2004 [9]. Therefore, the food can manufactures have been forced to search new formulations that avoid these compounds. Some authors are investigating natural corrosion inhibitors [10] instead of using lacquers, although the effectiveness is limited.

The use of hybrid organic-inorganic films obtained by sol-gel technology represents a new alternative. These films have been successfully used to improve the corrosion resistance of several metallic substrates, mainly aluminium and its alloys [11]. The use of this technology in the tinplate industry was delayed,

* Corresponding author. Tel.: +34986812603; fax: +34986812201.
E-mail address: cperez@uvigo.es (C. Pérez).

http://dx.doi.org/10.1016/j.electacta.2014.02.033

maybe because the complex nature of the system: metallic substrate/coating/foodstuff. However, the possibility to design tailored films makes this technology a promising alternative [12–14].

The present study focuses on the possible use of two-layer system based on the sol-gel technique for corrosion protection of tin can surfaces. The primer employed was a hybrid film based on tetra-n-propoxyzirconium (TPOZ) and 3-Glycydoxypropyltrimethoxysilane (GPTMS) precursors. The top-coat was also a hybrid film based on tetraethyl orthosilicate (TEOS) and vinyltrimethilsiloxane (VTMS) precursors. The top coat, being in contact with foodstuff, must have good barrier properties to avoid food contamination with tin or iron. On the other hand, sulphur-containing foodstuffs can react with tin and iron causing sulphide stains that, although harmless, can provoke consumer displeasure [15]. In order to increase the barrier properties, the sol-gel in contact with food was doped with hydrotalcite (HT) nanoparticles. HT is an additive allowed to be included in the materials and articles intended to be exposed to foodstuff. Hydrotalcite belongs to the layered double hydroxides family, whose structure consists in positively charged brucite-like layers due to the substitution of divalent cation by trivalent cation. The formula of hydrotacites is $\left[Mg_{1-x}Al_x[OH]_2\right]^{x+}\left[A^{z-}_{x/z}\cdot nH_2O\right]^{x-}$ where A^{z-} is the interlayer anion (CO_3^{2-}, NO_3^-, Cl^- ⋯) that balances the positively charged layers [16]. The laminar structure of HT may increase the barrier properties of the film. Moreover, the high anionic exchange capability of HT will contributes to remove aggressive ions from the environment. The anionic exchange capability is enhanced in thermally treated hydrotalcite due to the restoration process to the original layered structure (“memory effect”) [17]. Several researchers corroborate the inhibition properties when hydrotalcite is incorporated into organic coatings [18–20] or sol-gel films [21] applied on aluminum alloys, mainly the 2000 series.

Following this line, the present work evaluates hydrotalcites, as-synthesized (HT) and thermally activated (CHT), as possible corrosion inhibitors when they are added to sol-gel films formed on tinplate cans.

2. Experimental design

2.1. Materials

Commercial tinplate specimens with 2.8 g.m^{-2} tin coating weight each face were employed. The specimens had a “stone surface finishing”, which is characterized by directional grindstone patterns and by a mild melt treatment after the tin electroplating, to generate the intermetallic $FeSn_2$ alloy. Fig. 1a depicts the ToF-SIMS (Time-of-flight secondary ion mass spectrometry) depth profiles of different ions. The outer part of the tin coating is rich in tin and chromium oxides. The former was generated during the heat treatment, while the latter is a consequence of the passivation process that usually undergo these substrates. The $FeSn_2^-$ ion profile in Fig. 1a corroborates the presence of the intermetallic alloy, and the accumulative image, Fig. 1b, indicates that it is distributed along discrete bands.

The sol-gel system consists in two different films. The primer was made from two sols: 3-glycydoxypropyltrimethoxysilane (GPTMS) as organic precursor and tetra-n-propoxyzirconium (TPOZ) as inorganic precursor. In order to prepare the inorganic sol, 2.4 mL of ethylacetate (ETac) (Aldrich 97%) and 2.4 mL of (TPOZ) (70% in 2-propanol) were mixed in a 25 mL beaker under mechanical stirring for 20 min. Afterwards, a HNO_3 solution with pH 0.5 was added under ultrasonic stirring for 90 min. Meanwhile, the organic sol was prepared by mixing 5 mL of 2-propanol and 5 mL of GPTMS with HNO_3 solution pH 0.5 under mechanical stirring for 60 min. Finally, both solutions were mixed. The topcoat was other hybrid

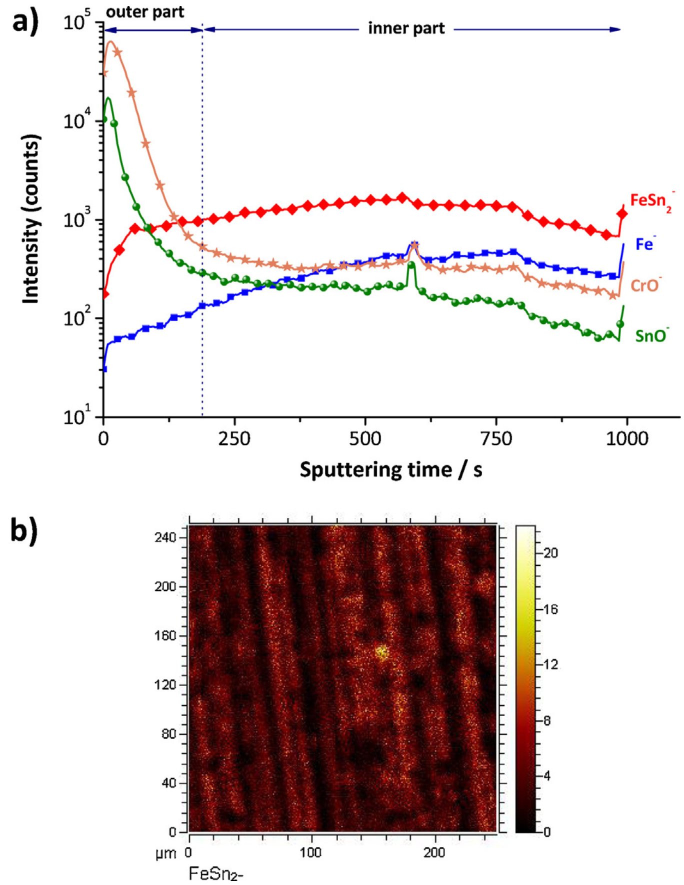

Fig. 1. ToF-SIMS depth profiles of $FeSn_2^-$, Fe^-, CrO^- and SnO^- obtained from commercial tinplate samples (a). Accumulative image (x-y) of $FeSn_2^-$ fragment (b).

sol-gel prepared from tetraethyl-orthosilane (TEOS) as the inorganic precursor and vinyltrimethoxysilane (VTMS) as the organic one. The procedure followed for preparing both sols was that used for GPTMS sol. The doped sol-gels were obtained by addition of 1% (w/w) of as-synthesized hidrotalcite (HT) or calcined hydrotalcite (CHT) to the topcoat.

Hydrotalcite was synthesised by the co-precipitation method. Two aqueous solutions were prepared, one containing 32.5 g of $Mg(NO_3)_2{\cdot}6H_2O$ with 18.75 g of $Al(NO_3)_2{\cdot}9H_2O$ dissolved in bi-distilled water and a second solution containing 6.36 g of Na_2CO_3 and 5.6 g of NaOH in a 120 mL of bi-distilled water. Then, both solutions were mixed in a glass reactor at 70 °C for 18 h. Afterwards, the precipitate was washed in hot water, filtered several times and dried at 70 °C overnight. The calcined CHT was obtained by heat treatment at 450 °C for 24 hours [21].

The commercial tinplate samples (3 cm x 5 cm x 0.2 cm) were cleaned before the deposition using an ultrasonic bath in acetone. After the ultrasonic treatment, the samples were rinsed with soapy water and finally with distilled water. The hybrid sol-gel films were obtained by a dip-coating procedure at 180 mm/min withdrawal speed with a holding time of 120 seconds. The same curing process, 155 °C during 20 minutes, was conducted for both films. Fig. 2 shows a schematic cross section of the studied system. The total sol-gel film thickness was about 3 µm (as measured by a mechanical profilometer).

2.2. Experimental Techniques

The coated tinplate samples were characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX)