

Short Communication

Influence of Current Density on Coating Mass Distribution and Surface Coverage during Electrodeposition of Tin on Carbon Steel

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Received: 24 April 2020 / Accepted: 11 June 2020 / Published: 10 July 2020

In this work, the influence of current density on coating mass distribution and surface coverage during electrodeposition of tin on carbon steel was investigated using optical microscopy, scanning electron microscopy, energy dispersive spectroscopy, and atomic force microscopy. Results illustrate that the amount and distribution of tin coating mass can greatly affect the surface coverage of tinplate. A lower tin coating mass 1.1 g cm^{-2} obtained at current density 0.4 A dm^{-2} after 60 seconds electrodeposition leads to tinplate with a higher surface roughness, less coverage integrity and uniformity. An increased tin coating mass by higher current density contributes to tinplate of lower surface roughness, improved surface integrity and uniformity. Besides, the surface roughness of carbon steel substrate is a key factor in determining the surface coverage integrity of tinplate, especially with a lower tin coating mass.

Keywords: Tinplate; tin coating mass; thickness; surface coverage; roughness

1. INTRODUCTION

In packaging industry, tinplate has found its main application for containers [1,2] and it usually consists of a low-carbon steel sheet, with controlled levels of Cu, P, and S elements [3–6], and a thin tin coating layer. The conventional tinplate is usually obtained by initially electrodepositing a porous layer of the pure tin onto the cathodic steel substrate [7], and the tin coating acts both as a physical barrier from the surrounding corrosive solution and as a self-sacrificial anodic protective layer during the tinplate corrosion [8]. The used steel substrate is commonly about 0.25 mm in thickness, despite a range of about 0.15–0.5 mm may be employed [9], and the development tendency is to thinner thickness. The tin coating is on the order of several microns in thickness, though it is more usually defined in terms of tin coating mass (g m^{-2}) [10]. At present, it ranges from about 2 g m^{-2} to 11 g m^{-2} on each side of the

steel substrate [11]. After electrodeposition process, the tin coating subjects to momentary fusion process by inductive or resistive heating at a temperature of 232–300 °C for less than 10 seconds followed by quenching in water, contributing to the formation of a bright and dense tin layer, and a partial or complete FeSn₂ intermetallic layer between the tin coating layer and the steel substrate [12]. Nevertheless, the recently increasing price of tin worldwide has led to a need in reducing the used tin amount in tinplate whilst preserving enough corrosion resistance [13]. One way in achieving this is to anneal the as-deposited tin coating (about 1 g m⁻²) in a reducing atmosphere with a temperature above 500 °C, and in such a way that nearly all of the free tin could be converted to FeSn₂ layer [14].

In commercial tinplate production line, the tin coating thickness is controlled by the applied line speed and current density [1–3]. Higher current density or lower line speed are usually employed to increase the deposition of tin ions on steel substrate [2]. In practice, the total current and line speed values are calculated in priority based on Faraday's law [6]. Practically, the line speed and applied current could be on-line tuned if necessary, according to the thickness measurements sampled during the process [8–10]. As to the variables that have influences on the tin coating thickness, they include [7-13]: (I) Variables related to the steel substrate such as, width and coating thickness; (II) Variables related to the electrodeposition, including length of anodes, total number of tanks, temperatures and concentrations that are difficult to control due to the time needed to change their values; (III) Parameters selected by the operator, which determine the way that the coating process should be performed, and (IV) The line speed and applied current. Among these, the line speed and current density are the basis of the control strategy. Therefore, investigations on the influence of current density are always of interest.

Although primarily used in food and beverage cans, tinplate is a traditional market for tin, which functions as a corrosion protector in the material [7]. Until recently, tin used in the sector has remained largely stable, with little change over the last decade. As stated, the need for reducing tin coating mass on tinplate is of great practical importance. However, for tinplate with a lower coating mass, the poor boundaries to steel substrate, residual porosity, micro-cracks, and rough surface are the commonly related drawbacks [15]. To date, the influence of current density on coating mass distribution and surface coverage of tin coating on tinplate has not been detailed. In our previous work [16], the electrodeposition processes, tinplate structure, and the passivated film composition and formation mechanism have been carried out. The present work mainly aims to investigate the influence of current density on coating mass distribution and surface coverage during electrodeposition of tin on carbon steel using optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and atomic force microscopy (AFM). Besides, the corrosion effect caused by lower tin coating mass has been discussed from the practical view.

2. EXPERIMENTAL

2.1 Preparation of samples

All the used tinplate samples in this investigation were prepared under the assistance of a company in Shanghai from China. Q235 low-carbon steel was employed as the substrate, and its surface roughness was in range of 0.77–1.02 µm. Details of the electrodeposition process can be found in Table

1, and the coating mass is achieved by controlling the current density at fixed deposition time. Before electrodeposition, all the steel samples were mechanically polished, and then successively subjected to processes of alkaline cleaning, electrodeposition, reflowing treatment, and passivation process [16]. Four values of 0.4, 1.0, 2.0, and 4.0 A dm⁻² were selected to investigate the influence of current density on coating mass distribution and surface coverage during electrodeposition of tin on carbon steel. The tin coating mass can be calculated by Eq. (1) as follows:

$$m = \frac{A}{z \times F} I \times t \times 0.95 \quad (1)$$

where A is Sn atomic mass; z is Sn²⁺ valence; F is Faraday constant; I is Current density; t is deposition time, and 0.95 is current density efficiency. The obtained coating masses corresponding to each applied current density are 1.1, 2.8, 5.6, and 11.2 g m⁻².

Table 1. Processes and parameters for electrodeposition tin coating on low-carbon steel substrate

Process	Operation	Process parameters		Condition
Step 1	Polishing	Abrasives paper		
Step 2	Alkaline cleaning	NaOH	50 g L ⁻¹	70 °C
		Na ₃ PO ₄ ·12H ₂ O	10 g L ⁻¹	10 min
Step 3	Electrodeposition Sn coating	SnSO ₄	35 g L ⁻¹	Temperature 25 °C
		H ₂ SO ₄	180 g L ⁻¹	
		Methyl sulfonic acid	15 g L ⁻¹	
		ENSA	3.0 g L ⁻¹	
		EN	5.0 g L ⁻¹	
		Fe ²⁺	< 7.0 g L ⁻¹	Plating time 60 s
		Sludge	< 2.0 g L ⁻¹	
		Sn ⁴⁺	< 1.0 g L ⁻¹	
		Anode	99.9 % Sn	
			0.4 A dm ⁻²	
Step 4	Reflowing treatment	Current density	1.0 A dm ⁻²	Plating time 60 s
		(Efficiency 95 %)	2.0 A dm ⁻²	
Step 5	Surface passivation treatment		4.0 A dm ⁻²	
Step 5	Surface passivation treatment	Temperature	235 °C	Temperature 42 °C
		Time	10 s	
		Na ₂ Cr ₂ O ₇	25 g L ⁻¹	
Step 5	Surface passivation treatment	pH	4.4	Moderate
		Cathodic current		

2.2 Tin coating characterizations

The OM observation of tinplates with various tin coating mass was carried out by employing Carl Zeiss Axio Observer.Z1m. The surface morphology and composition of the tinplates with various tin coating mass were characterized using SEM, (Inspect™ F, produced by FEI Company) and EDS analysis. The surface roughness of tinplates was observed using AFM (Pico Scan 2500, Agilent instrument) under a contact operating mode.

3. RESULTS AND DISCUSSION

3.1 Optical Microscopy observation

OM observation allows a relatively larger surface area morphology, and Figure 1 shows the OM observation of tinplate samples with various tin coating mass. For the sample with a tin coating mass 1.1 g m^{-2} obtained at 0.4 A dm^{-2} in Figure 1(a), the surface scratches on steel substrate by mechanical grinding are observed with depth, and the coating integrity and uniformity are poor. Figure 1(b) shows that the surface scratches are further covered by an increasing tin coating mass of 2.8 g m^{-2} obtained at 1.0 A dm^{-2} . For the sample with a tin coating mass 5.6 g m^{-2} obtained at 2.0 A dm^{-2} in Figure 1(c), the surface integrity and uniformity improve greatly despite the scratch trails that can still be found. When the tin coating mass increases to 11.2 g m^{-2} obtained at 4.0 A dm^{-2} in Figure 1(d), the sample surface is of complete integrity and uniformity without any scratch trails being found, and the observed tinny cracks may due to the brittleness of tin coating [17]. Usually, the surface pores in tin coating or scratches on the underlying steel substrate can be defects, which are of high activeness during the subsequent corrosion process of tinplate [17–19]. Therefore, the OM observation results indicate that a lower tin coating mass of 1.1 g m^{-2} obtained at 0.4 A dm^{-2} cannot cover the surface scratches on steel substrate, and increased tin coating mass can contribute to improved surface integrity and uniformity of tinplate.

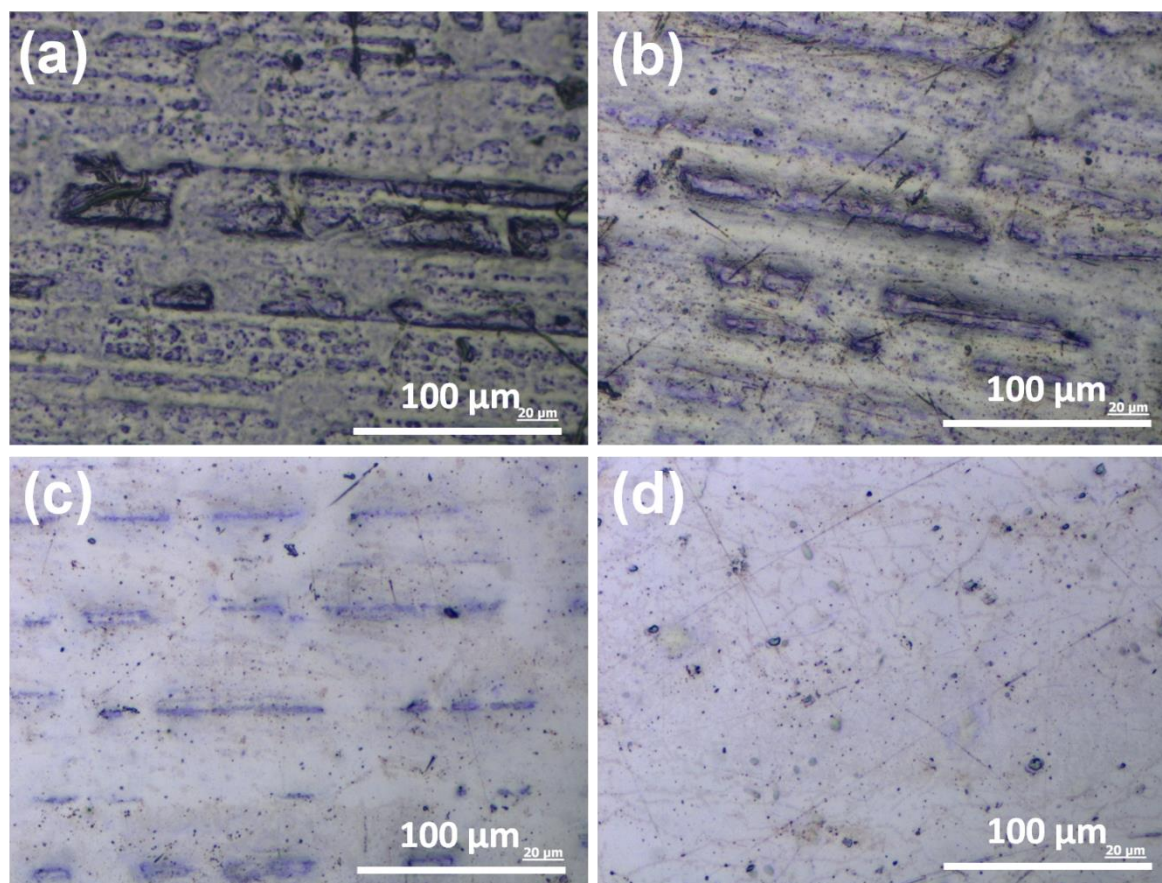


Figure 1. Optical microscopy observation of the tinplate samples obtained at different current density after 60 s deposition. (a) 0.4 A dm^{-2} ; (b) 1.0 A dm^{-2} ; (c) 2.0 A dm^{-2} ; (d) 4.0 A dm^{-2} .

3.2 Scanning electron microscopy and energy dispersive spectroscopy characterization

After the electrodeposition process, the tinplate sample usually subjects to momentary fusion by inductive or resistive heating at a temperature of 232–300 °C for less than 10 seconds followed by quenching in water, and thus a layer of FeSn₂ alloy forms between the tin coating and the steel substrate [12,14]. Therefore, the variation of an amount of Fe and Sn elements on the tinplate sample surface can illustrate the surface uniformity and integrity by various tin coating mass coverage. SEM and EDS have been employed to further characterize the surface characteristics of tinplate samples with various tin coating mass distribution. Figure 2 shows the SEM observations of the obtained tinplate samples. Figure 2(a) shows that the scratches by mechanical grinding are observed, indicating that the tinplate sample surface with 1.1 g m⁻² tin coating mass distribution is coarse. When the tin coating mass increases to 2.8 g m⁻² in Figure 2(b), the surface grinding scratches are greatly covered, indicating the deposition of a thicker tin coating layer distribution but still showing obvious scratches. For the tinplate sample with 5.6 g m⁻² tin coating mass in Figure 2(c), the scratches by mechanical grinding are almost uniformly covered by tin coating distribution with only slight scratch trails being observed, and Figure 2(d) shows that a tin coating mass 11.2 g m⁻² has contributed to the tinplate surface with high integrity and uniformity.

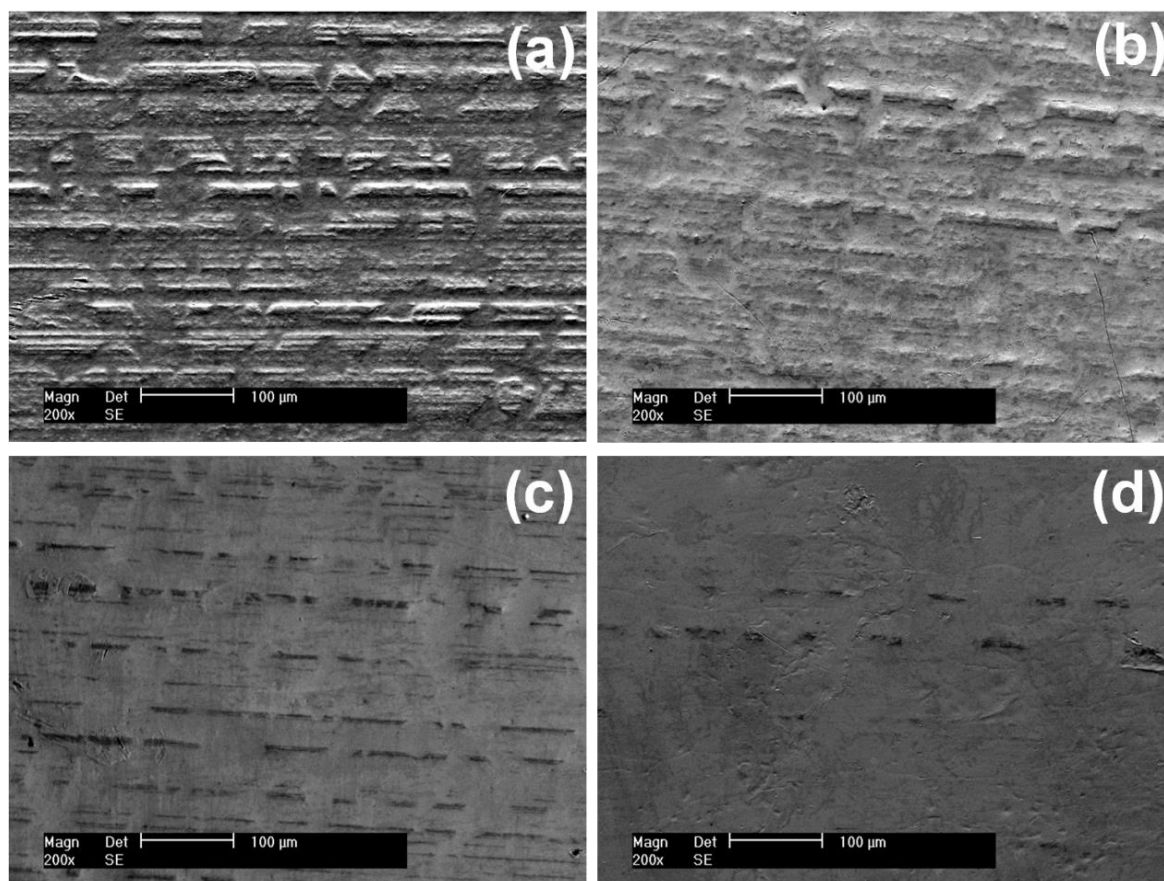


Figure 2. Scanning electron microscopy observation of the tinplate samples obtained at different current density after 60 s deposition. (a) 0.4 A dm⁻²; (b) 1.0 A dm⁻²; (c) 2.0 A dm⁻²; (d) 4.0 A dm⁻².

Figure 3 shows the EDS characterization of tinplate samples with various tin coating mass distribution to further illustrate the influence of tin coating mass distribution on the surface coverage on tinplate. The detected Fe content on the surface of tinplate samples with various tin coating mass is in order of $1.1 \text{ g m}^{-2} \text{ sample} > 2.8 \text{ g m}^{-2} \text{ sample} > 5.6 \text{ g m}^{-2} \text{ sample} > 11.2 \text{ g m}^{-2} \text{ sample}$, and the detected Sn content is in the opposite order. The highest Fe content on tinplate with a tin coating mass 1.1 g m^{-2} demonstrates the poor surface coverage on steel substrate, and the lowest Fe content on tinplate with a tin coating mass 11.2 g m^{-2} indicates the best surface integrity among the four test samples. The origin of detected Fe content is thought to lie in the exposure of the steel substrate or FeSn_2 layer. Therefore, EDS results indicate that the surface area of the exposed base steel substrate or FeSn_2 layer decreases predominantly with the tin coating mass distribution increasing, and thus the tin coating mass distribution can influence the surface coverage integrity on tinplate.

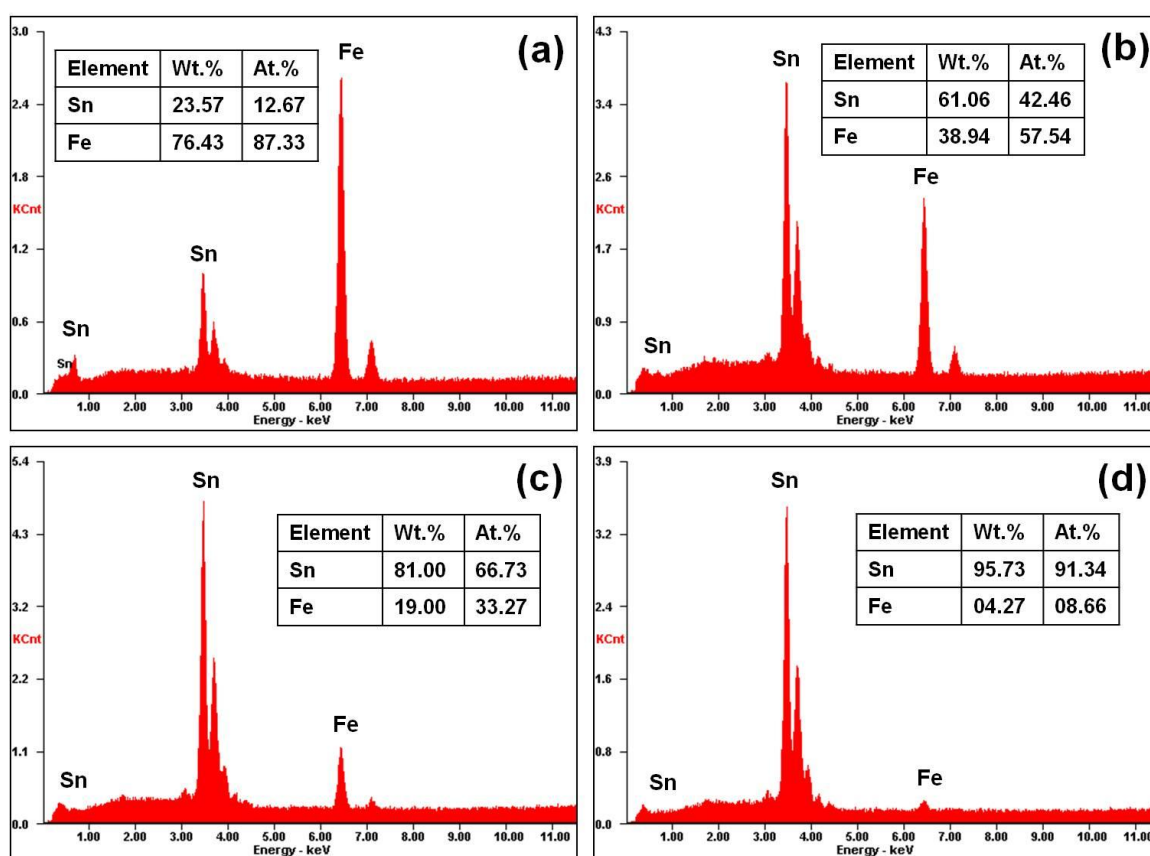


Figure 3. Energy dispersive spectroscopy detection of the tinplate samples obtained at different current density after 60 s deposition. (a) 0.4 A dm^{-2} ; (b) 1.0 A dm^{-2} ; (c) 2.0 A dm^{-2} ; (d) 4.0 A dm^{-2} .

3.3 Atomic force microscopy characterization

The variation in the roughness of the tinplate surface is usually in the submicron regime and thus beyond the detection limit of most conventional analytical techniques, such as SEM. AFM is a very powerful technique, and it is capable of providing high-resolution three-dimensional (3-D) surface topography on the submicron scale [20]. Hence, an AFM study has been undertaken to test the surface

roughness of tinplate samples with various tin coating mass. Figure 4 shows the 3-D AFM topographies of the tinplate samples with various tin coating mass. Based on the total of six AFM images randomly selected with a scanning area of $20 \times 20 \mu\text{m}^2$, the root mean square roughness, R_q , of the four samples with various tin coating mass was computed using the “Roughness” procedure of the standard software, based on Eq. (2):

$$R_q = \sqrt{\frac{\sum_{i=1}^n \sum_{j=1}^n (D_{i,j} - \bar{D})^2}{N^2}} \quad (2)$$

where N is the total number of collected image data points, D_n is the height of the point n on the image, and $\bar{D}$ is the mean height of the $\sum_{i=1}^n \sum_{j=1}^n D_{i,j}$ points on the AFM topography. The calculated data are given in Figure 5. The calculated R_q shows a decreasing tendency with the tin coating mass increasing on the tinplate sample. For the sample with tin coating mass 1.1 g cm^{-2} , it has the largest roughness value of 592 nm among the four tested tinplate samples. When the tin coating mass increases to 2.8 g cm^{-2} , the surface roughness sharply decreases to 164 nm.

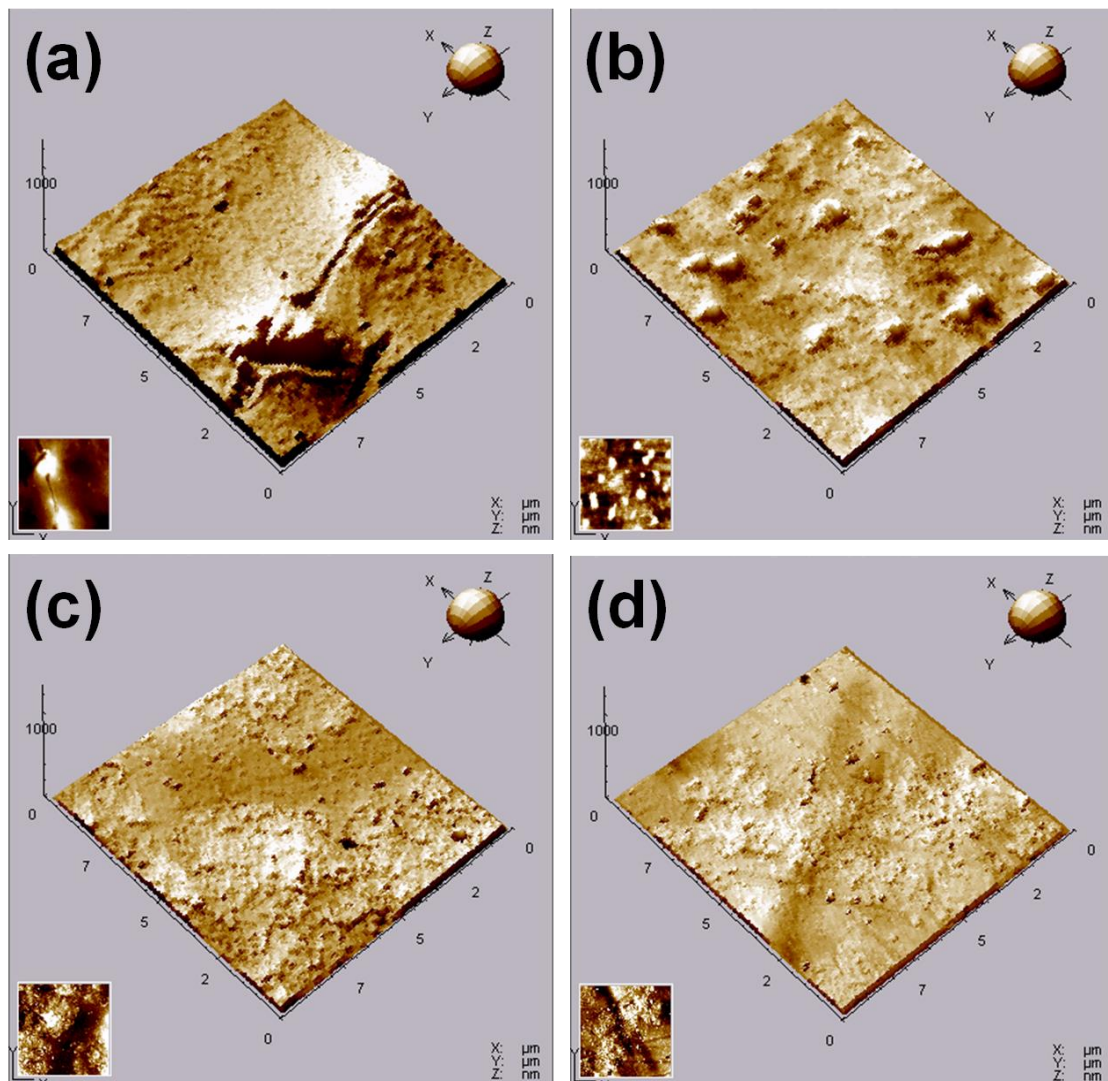


Figure 4. Atomic force microscopy characterization of the tinplate samples obtained at different current density after 60 s deposition. (a) 0.4 A dm^{-2} ; (b) 1.0 A dm^{-2} ; (c) 2.0 A dm^{-2} ; (d) 4.0 A dm^{-2} .

Further increasing the tin coating mass to 5.6 g cm^{-2} contributes a much lower surface roughness of 120 nm, and the tinplate sample with a tin coating mass 11.2 g cm^{-2} has the lowest surface roughness of 66 nm compared with other three tinplate samples having a relatively lower tin coating mass. Therefore, AFM observation also indicates that a higher tin coating mass on tinplate contributes to a smooth coating surface, but a lower tin coating mass of 1.1 g cm^{-2} cannot cover the rough surface of the base steel sheet.

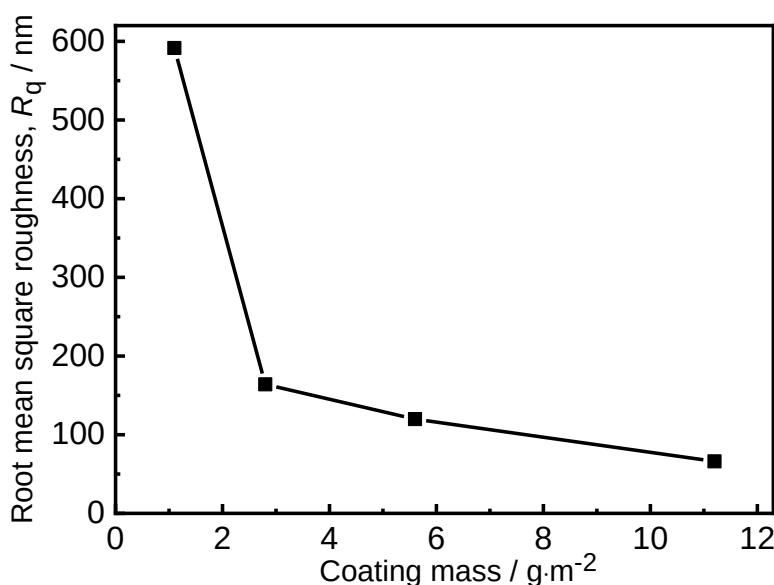


Figure 5 Surface root mean square roughness (R_q) of the tinplate samples with various tin coating mass

3.4 Discussion

As tinplate is a metallic coating system and the tin coating itself has a positive potential than steel substrate, the uniformity and integrity of tin coating are quite important for tinplate [21]. Moreover, the roughness and other surface defects on steel substrate can predominantly affect the surface coverage by tin coating [22]. At the coating defect sites, it is believed that the FeSn_2 layer is exposed to an aggressive electrolyte. But the layer is too thin that the underlying steel substrate is soon exposed to the electrolyte. Hence, the thickness of the tin coating and its integrity and uniformity, which are all related to tin coating mass distribution, play a key role in resisting the attack by an aggressive electrolyte. Besides, due to the potential difference at tin/steel substrate and the defects in the tin coating, corrosion prefers to occur at the defects on tinplate surface because of the high activity of exposed steel substrate. In addition, corrosion needs a cathodic process to consume the electrons produced in the anodic process, and it is likely to be slow in the absence of dissolved oxygen or other cathodic depolarizers [23]. Furthermore, tin has a high hydrogen evolution overpotential; the reduction of H^+ then takes place on tin only with difficulty [24–25]. Therefore, the contact of tin coating with steel having a low hydrogen overpotential will tend to accelerate the attack of tin. The involved reactions may be summarized as follow:



The first cathodic reaction Eq. (4) proceeds readily on the tin coating, while the latter reaction Eq. (5) takes place more readily on the steel of lower hydrogen overpotential. It can be concluded that in the practical corrosion environment with certain cathodic depolarizer type and content, the amount of tin coating mass and its distribution is vital in shaping the subsequent corrosion behavior of tinplate. A lower tin coating mass distribution, that cannot uniformly cover the steel substrate surface, may lead to the rapid loss of tin and the exposure of steel substrate, and thus premature failure can occur. Therefore, the choice of tinplate in good quality, free of defects, and with a higher tin coating mass distribution to lower steel substrate exposure, is beneficial for reducing the risk of H^+ discharge on steel. The tinplate manufacturing and handling practices, that reduce the risk of scratches and dents, also help to reduce the steel substrate exposure with the same beneficial effect. Nowadays, although there is a need in reducing the tin amount (tin coating mass and distribution) used in the tinplate industry, the requirement for a flat and uniform steel substrate surface with a lower roughness should also be taken into consideration for better application of tinplate, especially with lower tin coating mass.

4. CONCLUSIONS

Based on characterizations in influence of tin coating mass distribution on the surface coverage property of tinplate samples, it can be concluded: (1) A lower tin coating mass of 1.1 g cm^{-2} obtained at 0.4 A dm^{-2} leads to the tinplate surface of less coverage integrity and uniformity, and an increased tin coating mass distribution can contribute to improved surface integrity and uniformity of tinplate; (2) The coverage by tin coating mass 1.1 g cm^{-2} obtained at 0.4 A dm^{-2} cannot cover the tinplate surface with high roughness, which can be greatly lowered by an increased tin coating mass distribution; (3) The surface roughness on underlying steel substrate is an important factor in determining the characteristics of tinplate, especially under the condition of lower tin coating mass.

ACKNOWLEDGEMENTS

This work is supported by the Scientific Research Fund of Provincial Natural Science Foundation of Hunan (2020JJ4243), and the authors acknowledge the assistance.

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