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Nucleation and growth of tin on low carbon steel

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Abstract

The nucleation and growth of tin from stannous sulfate and sulfuric acid with an organic additive of gelatin was studied on low carbon steel. Investigations were conducted by linear sweep voltammetry and current step methods. The agitation effect on the morphology of tin deposits was also studied. From the results, a mechanism of tin deposition on a steel substrate is suggested. Initially, 3D tin crystallites are formed preferentially on step edges, and this is followed by fast covering of neighboring sites with much smaller and densely packed crystallites of about 150–180 nm in size. Without gelatin, the coverage was poor and tri-modal structures were dominating. It is discovered that the synergy between hydrogen co-evolution and gelatin contributes to fast and complete coverage of the steel substrate and the bi-modal grain size distribution is observed. The diffusion coefficient of tin ion was determined according to the Sand equation. © 2004 Elsevier Ltd. All rights reserved.

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1. Introduction

Nucleation and growth of metal deposits depend on the nature of plating bath, hydrodynamic conditions and the substrate onto which the electrochemical reduction takes place. The nucleation process is closely related to the active sites existing on the substrate [1]. Defects on a substrate surface, such as edges, corners, boundaries, and kink sites, can act as active sites for nucleation. However, the number of actual nucleation sites is small at low overpotentials when compared to the available active sites, instant nucleation on all active sites takes place at high potentials. Cathodic hydrogen evolution, either on the substrate and/or on the deposit, is also an important factor which needs to be considered. Hydrogen evolution is of scientific and technological importance. The technological importance stems from the fact that electrodeposition of some metals, such as nickel and chromium, is accompanied by simultaneous hydrogen evolution [2]. Hydrogen co-deposition is also responsible for texture variation in the deposits due to its influences on the surface-energy

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anisotropy [3]. On the other hand, hydrogen co-evolution in deposits decreases the current efficiency of the plating operation and may result in hydrogen embrittlement.

One can carry out electrodeposition by applying either potential or current. For kinetic studies, the potential step method is frequently used; while for industrial coatings preparation, the current step method (galvanostatic electrolysis) is mostly applied. The most important benefit of using the galvanostatic method is that the thickness or weight of deposits can be readily controlled according to Faraday's law of electrolysis. There is little research, however, on the nucleation and growth of electrodeposits using potential-time method (chronopotentiometry) at constant currents. No such studies on tin electrodeposition have been reported although tin has been extensively used as a coating for a wide range of metals. Tin coatings on steel (known as tinplates) are extensively used in the fabrication of containers for the food processing industry. Some researchers [4-6] have reported the nucleation and growth of tin on glassy carbon, however, there is no published work on the initial stage of tin nucleation and growth on steel. In a previous study [4], the nucleation and growth mechanism of tin, and the transformation in the morphology of initial deposits on glassy carbon

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were investigated. It has found that the nucleation and growth mechanism of tin depends on the applied cathodic potential. A transition in the deposition mechanism from 3D progressive to instantaneous nucleation and growth was observed with increasing cathodic potential. The morphology of tin nuclei also varies with applied potentials. At more positive potentials, tetragonal nuclei and crystallites are dominant, and as the potential become more negative, the fraction of clusters of tin needles increases.

The current study focuses on the nucleation and growth of tin on low carbon steel substrates. The potential–time behaviors at constant current densities were presented along with the morphology of tin deposits. The diffusion coefficient of tin ions was also determined.

2. Experimental details

The electrochemical experiments were done in a conventional three-electrode cell, where a low carbon steel substrate embedded in epoxy resin was used as the working electrode with a surface area of 1 cm^2 exposed to the tin electrolyte, a tin rod (99.98%) with 12.7 mm in diameter was used as the anode, and a saturated calomel electrode (SCE) as a reference electrode to which all potentials in this paper are referred. The electrolyte used was composed of 0.3 M H₂SO₄ and 0.2 M SnSO₄, in some experiments, gelatin was added as an organic additive. All solutions were prepared with distilled water treated with a Millipore system. The experiments were done in an oxygen-free electrolyte, which was obtained by purging the electrolyte with nitrogen gas for at least halfan-hour. After oxygen was removed from the solution, the nitrogen bubbler was pulled above the electrolyte surface, and the inert atmosphere was maintained by saturating the chamber above the electrolyte with nitrogen. Hence, all the electrochemical measurements were done in a quiescent solution except for the agitation investigation. Before each measurement, the working electrode (the substrate) was mechanically polished using 600-grit sandpaper, and was then thoroughly rinsed with distilled water. All the electrochemical measurements were done using a computer-controlled Autolab PGSTAT30 potentiostat. For the imaging of samples, a field-emission-gun scanning electron microscope (Philips XL30 FEG-SEM) was used.

3. Results and discussion

3.1. Linear sweep voltammetry

Fig. 1 shows the voltammetric response of hydrogen evolution on a low carbon steel substrate in the supporting electrolyte (i.e., $0.3 \text{ M} \text{ H}_2\text{SO}_4$ solution). Since there were no tin ions in the solution, only hydrogen evolution was observed. When there was no gelatin (Fig. 1b), hydrogen evolution took place around -0.62 V versus SCE; with gelatin



Fig. 1. Voltammetric response of hydrogen evolution on Fe in sulfuric acid solution. Scan rate: 50 mV/s; (a) 0.3 M H₂SO₄ + 2 g/l gelatin; (b) 0.3 M H₂SO₄.

added, hydrogen evolution occurred at a more negative potential (\sim -0.82 V). This increase in hydrogen overpotential was due to the inhibitory effect of gelatin on hydrogen evolution. Fig. 2 presents the voltammetric response of hydrogen evolution on a tin coating in the supporting electrolyte. Comparing to steel, hydrogen evolution started at more negative potentials on tin, -0.8 V, for the sulfuric acid solution without gelatin and -0.95 V while gelatin added. The voltammetric response for tin reduction in the $0.3 \text{ M H}_2\text{SO}_4$ and 0.2 M SnSO₄ electrolyte is shown in Fig. 3. As can be seen, in the absence of gelatin, the abrupt increase of current density in magnitude was observed at the negative potential of -0.44 V, which was due to the deposition of tin (II) ions. At around $-0.50 \,\mathrm{mV}$, the current peaks were observed in both situations, indicating that there is a nucleation and growth mechanism controlled by diffusion [4,5]. As potentials became more negative, limiting current density regions were evident. The magnitude of the limiting current density for the tin electrolyte without gelatin was 236 A/m². The limit-



Fig. 2. Voltammetric response of hydrogen evolution on tin in sulfuric acid solution. Scan rate: 50 mV/s; (a) $0.3 \text{ M} \text{ H}_2\text{SO}_4 + 2 \text{ g/l}$ gelatin; (b) $0.3 \text{ M} \text{ H}_2\text{SO}_4$.



Fig. 3. Voltammetric responses from tin sulfate solutions on low carbon steel at a scan rate of 10 mV/s. (a) $0.3 \text{ M } H_2 \text{SO}_4 + 0.2 \text{ M } \text{SnSO}_4 + 2 \text{ g/l gelatin;}$ (b) $0.3 \text{ M } H_2 \text{SO}_4 + 0.2 \text{ M } \text{SnSO}_4$.

ing current was reduced to 185 A/m^2 when gelatin was added, indicating an inhibitory effect of gelatin on the reduction of tin ions.

3.2. Current step method

The galvanostatic experiments, also known as chronopotentiometry, were used to study the potential behaviors with time. Fig. 4 shows E-t transients on a steel substrate for acid stannous sulfate electrolytes without gelatin at different current densities. At different current densities, the potential–time curves were different. At a low current density of 100 A/m², the potential remained constant with time. At an increased current density of 200 A/m² (Fig. 4b), there was a fairly slow decrease in potential up to 35 s and then a gradual increase in potential. The initial decrease in potential is determined by the Nernst equation; the gradual increase resulted from a dendrite tin growth, which increased the surface area with time and the real current density decreased. Curve (c) for 400 A/m² shows an abrupt potential drop at



Fig. 4. Potential-time transients for the tin sulfate electrolyte $(0.3 \text{ M} \text{ H}_2\text{SO}_4 + 0.2 \text{ M} \text{ SnSO}_4)$ on steel at different current densities. (a) 100 A/m^2 ; (b) 200 A/m^2 ; (c) 400 A/m^2 ; A: 3 s; B: 6 s; C: 8 s; D: 15 s; E: 30 s.

4.8 s, which was due to the concentration depletion of tin ions on the surface of the electrode. The time taken from the bulk concentration of tin to zero at the electrode surface is defined as the transition time τ or the Sand time, which is given by the Sand equation (Eq. (1)) [7]

$$|I\tau^{1/2}| = \frac{nF(\pi D)^{1/2}c^0}{2} \tag{1}$$

where *I* is the current density, *n* the number of electrons, here equals 2, *F* the Faraday's constant, *D* the diffusion coefficient and c^0 the tin ion concentration.

The diffusion of tin ions to the substrate by natural convection was then no longer sufficient to maintain the applied current density, and the potential dropped rapidly to -0.88 V until hydrogen evolution took place. Through visional observation, lots of small bubbles approximately 1 mm in diameter were seen emerging from the sample. It is interesting to have observed the peaks of the potential in Fig. 4c and the bubbling on the substrate decreased progressively, and finally the potential increased slowly and the bubbling halted. Fig. 4 also shows the potential-time transients obtained from sulfuric acid solution without tin ions on steel, and on steel completely coated with tin. The potential arrest at -0.88 V was related to hydrogen evolution on steel rather that tin, which indicated the steel sample was poorly covered by tin, as seen further through morphological examination. The potential perturbation between 4 and 11 s (Fig. 4c) can be explained as follows: the first sharp and biggest peak was due to depletion of tin ions on the sample and hydrogen evolution on steel. The generation of hydrogen bubbles at the electrode surface stirred the solution in the immediate vicinity of the growing tin particles. As the depletion layer around growing tin particles was eliminated, tin deposition occurred more favorably and potential restored to a higher value of -0.57 V determined by the Nernst equation. It is obvious that the restored concentration of tin ions on the electrode surface is still smaller than that of the bulk concentration. As deposition progressed, the potential increased due to the growth of tin dendrites (as can



Fig. 5. Potential-time transients for tin sulfate on steel with gelatin at different current densities. (a) 100 A/m^2 ; (b) 200 A/m^2 ; (c) 400 A/m^2 .



Fig. 6. Potential–time transient for tin sulfate on steel with gelatin at different current densities. (a)200 A/m² with agitation; (b) 400 A/m² without agitation; (c) 400 A/m² with agitation.

be seen in the SEM images of Fig. 7e and f). This process increased the actual electrode surface area, and therefore decreased the actual current density below its limiting value; thus no more hydrogen evolved.

Table 1

Product of $I \times \tau^{1/2}$ and calculated diffusion coefficient in the electrolyte composed of 0.3 M H₂SO₄ + 0.2 M SnSO₄ + 2 g/l gelatin on steel

I/Am ⁻²	τ/s	$I \times \tau^{1/2}$	Calculated $D/cm^2 s^{-1}$
200	12.063	69.46	$4.1 imes 10^{-6}$
270	6.783	70.31	4.2×10^{-6}
300	5.322	69.20	4.1×10^{-6}
400	2.739	66.20	$3.7 imes 10^{-6}$
810	0.636	64.60	$3.6 imes 10^{-6}$

Without organic additives, smooth deposits cannot be obtained and tin dendrites form. In order to get smooth coatings, a variety of organic additives can be used. Fig. 5 shows the potential–time curves for the tin electrolyte with gelatin $(0.3 \text{ M H}_2\text{SO}_4 + 0.2 \text{ M SnSO}_4 + 2 \text{ g/l gelatin})$. At 100 A/m^2 , the potential remained stable with time. The potential oscillated at 200 A/m^2 for the recording time of 3 min, here presented for only 2 min. The frequency of oscillation remained constant after the second potential drop. Such oscillations have also been observed by other authors [8]. This oscillating feature is due to repeated tin ions depletion and restoration by hydrogen evolution. At an even higher current density of



Fig. 7. Morphology of tin deposits at 400 A/m² for different times corresponding to arrows A (3 s); B (6 s); C (8 s); D (15 s); E (30 s) in Fig. 4. (a) 400 A/m², 3 s; (b) 400 A/m², 6 s; (c) 400 A/m², 8 s; (d) 400 A/m², 15 s; (e) 400 A/m², 15 s; (f) 400 A/m², 30 s.



Fig. 8. Morphology of tin deposits at 200 A/m² for times corresponding to arrows A (10 s), B (16.3 s), C (25 s) in Fig. 5b, and at 400 A/m² for times corresponding to arrows A (2 s), B (4.5 s), C (8 s) in Fig. 6b. (a) 200 A/m², 10 s; (b) 400 A/m², 2.5 s; (c) 200 A/m², 16.3 s; (d) 400 A/m², 4.5 s; (e) 200 A/m², 25 s; (f) 400 A/m², 8 s.

400 A/m², however, a damping oscillation was observed, and the potential increased slowly and tended to remain constant at longer time, which was attributed to hydrogen evolution on tin coatings. The Sand time can be easily determined. At different current densities, the product of $I \times \tau^{1/2}$ should be constant as expected for a mass-transfer-controlled process. Knowing the bulk concentration of tin c^0 , the diffusion coefficient can be calculated from Eq. (1). Table 1 presents the product of $I \times \tau^{1/2}$ and calculated diffusion coefficients in a tin sulfate electrolyte with gelatin. As expected, the results reflect a mass-transfer-controlled process with a diffusion coefficient of about 3.9×10^{-6} cm² s⁻¹ (averaged value).

As was mentioned earlier, at low and moderate current densities, potentials were relatively stable and the deposition of tin was sufficiently supplied by diffusion. At high current densities, however, the supply of tin ions by natural convection was not sufficient. In order to maintain the concentration of tin ions on the electrode surface, forced convection was introduced. Fig. 6 presents the potential–time curves for tin sulfate electrolyte with gelatin on steel in the presence or absence of agitation at 200 and 400 A/m². As can be seen in both

cases, the potential remained constant with time when agitation was applied, which means that at this level of agitation, tin concentration on the sample surface could be maintained. The small perturbation of potential for 400 A/m^2 indicated there was a difficulty in supplying tin ions at high current densities even with agitation. It should be noted that the agitation should not exceed a certain level where turbulent flow occurs. A detailed explanation is beyond the scope of this paper. By rule of thumb, there should have been no visible vortices in the solution.

3.3. Scanning electron microscopy

Morphological examinations of tin deposits by the SEM were carried out to better understand the electrochemical results. The morphology and coverage of tin coatings are directly related to the properties of tin coatings and are of great importance in industrial applications. Fig. 7 shows the morphology of tin deposits at 400 A/m^2 for different times corresponding to arrows A (3 s), B (6 s), C (8 s), D (15 s), E (30 s) in Fig. 4. As can be seen in the deposits obtained for



Fig. 9. Morphology of tin deposits (obtained at different current densities) on steel in tin sulfate electrolyte with gelatin $(0.3 \text{ M } H_2 \text{SO}_4 + 0.2 \text{ M } \text{SnSO}_4 + 2 \text{ g/l}$ gelatin) with and without agitation. (a) 200 A/m², 60 s, without agitation; (b) 200 A/m², 60 s, with agitation; (c) 400 A/m², 30 s, without agitation; (d) 400 A/m², 30 s, with agitation.

3 s (Fig. 7a), 3D tin crystallites of similar size preferentially formed along polishing lines or step-edges. This phenomenon is also called step-edge decoration, which was used to prepare molybdenum nanowires [9]. At a longer deposition time of 6s (Fig. 7b), tin crystallites were still of similar size but bigger than those for 3 s, and the number of tin crystallites was roughly the same, which indicated instantaneous nucleation. In Fig. 7c, a sub-layer of small grains in the range of 100-200 nm can be seen. Those grains tended to be interconnected. At a much longer deposition time (15 s in Fig. 7d and e), those grains became densely packed. When comparing the bi-modal structure of tin deposits with the potential-time result (Fig. 4c), it is clear that the growth of a sub-layer of small grains was credited to hydrogen evolution. As hydrogen evolution starts, the depletion layer around tin crystallites was eliminated by the stirring effect of hydrogen evolution, which made tin reduction happen again. At such negative potentials (around -0.6 to -0.7 V), instant nucleation took place on the whole surface, resulting in a rapid coverage of tin on steel. When there was no additive in the electrolyte, dendritic growth above early deposits (as shown in Fig. 7e and f) occurred at certain preferred sites. Fast growth of dendrites on the sample edges was readily visible with naked eyes after 8 s at 400 A/m^2 . It is also evident that without organic additives, the coverage of steel with tin was poor, and a tri-modal structure was observed.

In order to achieve a smooth coating and well covered steel substrate, gelatin was used as an organic additive in the tin sulfate electrolyte. Fig. 8 shows the morphology of tin deposits at 200 A/m² for different deposition times corresponding to arrows A, B and C in Fig. 5b, and at 400 A/m^2 for different

deposition times corresponding to arrows A (2s), B (4.5s), C (8s) in Fig. 6b. At both current densities, tin initially nucleated at polishing lines before hydrogen evolution started. When hydrogen evolution started at very negative potentials, there were numerous small crystallites around 150–180 nm covering steel substrates completely. The thickness of the fine grain layer was estimated to be around 100 nm according to the Faraday's law of electrolysis.

The sudden growth of numerous grains can be explained as follows. As the onset of hydrogen evolution, the stirring effect of hydrogen bubbles enhances the supply of tin ions to the substrate for the deposition of tin. Such negative potentials allow tin deposition occurring on the whole substrate surface, resulting in a full coverage of tin. It must be noted, however, that the full and rapid coverage of tin is not solely due to hydrogen co-evolution. When comparing images in Fig. 8f with Fig. 7c and d, it is clear that for the same current density of 400 A/m², a full coverage of steel with numerous small tin grains could not be achieved without gelatin.

Based on the above results, there are two possible factors that can contribute to the rapid growth of grains with 150– 180 nm in diameter. In order to isolate these factors, agitation was introduced since the sufficient supply of tin ion for electrochemical reduction was feasible through forced convection (see Fig. 6b and c). Fig. 9 shows the morphology of tin deposits at different current densities with or without agitation.

In Fig. 9, the deposition time was chosen to achieve $1 \mu m$ thick tin coatings. For both processing conditions, the substrates were well covered with tin and the coatings were compact if no agitation was involved. However, when the electrolyte was stirred (and no hydrogen evolution took place),

steel could not be well covered. It was evident that with gelatin alone, fully covered tin coatings could not be obtained. It is therefore, discovered that hydrogen co-evolution and gelatin had a synergistic effect that resulted in a rapid full coverage of tin on steel. It is also clear that the grain sizes of the tin deposits obtained at 400 A/m² were smaller than those obtained at 200 A/m². The grain size of deposits decreased with an increase in current density was as expected.

4. Conclusions

For tin electrocrystallization on steel substrates, 3D tin crystallites are initially formed preferentially on step edges, followed by fast deposition of other sites with much smaller and densely packed crystallites of about 150–180 nm in diameter. It is discovered that hydrogen co-evolution and gelatin have a synergy effect contributing to the fast and complete coverage of steel substrate with tin and the bi-modal grain size distribution at very short deposition times. In order to achieve compact uniform tin deposits, the following conditions should be met: (a) the addition of an organic additive (at least); (b) hydrogen co-evolution; and (c) at relatively longer

deposition times depending on the current densities. It is also demonstrated that the chronopotentiometry is a very useful and efficient tool to study the deposition process when combined with the SEM.

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