Corrosion Behavior of Electrodeposited Tin-Zinc Alloy Coatings on Steel

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This research examines the corrosion behavior of tinzinc alloy electrodeposits on a steel substrate. These coatings were prepared using a proprietary tin-zinc plating solution. Previous research has shown that during electroplating tin and zinc deposit as separate crystalline phases of nearly pure tin and zinc in accord with the phase diagram. When potentiodynamic scans were run in a slightly acidic (pH 3.6) solution from the open circuit potential (OCP) to more positive values, zinc was seen to dissolve preferentially from the Sn-Zn coating. Polarization tests were performed on the Sn-Zn coating in order to follow the changes in structure that occur as a function of the extent of zinc dissolution. Scanning electron microscopy (SEM), in conjunction with qualitative image analysis software, was used to obtain data that could be used to evaluate the role of the IR voltage in the corrosion mechanism associated with the selective dissolution of the zinc from the coating.

Protection of the environment and the safety of employees are obvious topics of concern for all industry. In an effort to eliminate these concerns, some materials and manufacturing processes have been under great scrutiny. One such material is cadmium, which has been widely used as a protective coating in the plating industry due to its corrosion resistance, lubricity and low electrical resistivity.^{1,2} However, cadmium and its compounds have been found to be highly toxic and carcinogenic. This fact causes ecological, toxic and even economic concerns for not only the plating industry, but for all parts of the manufacturing sector that rely on cadmium.

Nuts & Bolts: What This Paper Means to You

This paper deals with work in the past year on AESF Research Project #109. Tin-zinc alloy coatings show promise as a substitute for cadmium in many applications. This work deals with the unique way in which the tin-zinc alloy corrodes. The network of pores left behind by the preferentially corroded zinc offers some possibilities for further study.

The effort to replace cadmium coatings with safer materials has stimulated research to find comparable, if not superior, substitutes. One such substitute for cadmium deposits is a tin-zinc alloy electrodeposit. Tin-zinc alloy electrodeposits provide an increased corrosion resistance when compared to cadmium deposits, no visible corrosion products, a bright matte finish and they have excellent solderability.³ Although some research has been done to identify the corrosion-related properties of tin-zinc electrodeposits,^{2,4,5} the mechanisms associated with the selective dissolution of zinc and its nature as a sacrificial coating have not been fully explored or understood. The objective of this research is to understand better the corrosion mechanisms associated with tin-zinc alloy electrodeposits and to study how plating additives affect the plating process and resultant deposit properties.

In order to optimize the properties of the tin-zinc electrodeposit, one must have a full understanding of its morphology. It has been stated that tin-zinc alloy electrodeposits consist of fine zinc grains in a matrix of tin.² However, in order to determine the impact of the IR voltage drop⁶ associated with preferential zinc dissolution and the formation of pores in the deposit, one needs a better understanding of the morphology and size of tin and zinc deposits and how this morphology changes with increasing corrosion time.

Experimental

Materials

Substrates used in this study consisted mainly of 0.07-cm (27.5 mil) thick coupons of carbon steel that had been cold rolled and subsequently annealed at an unknown time and temperature. A copper wire was soldered to the back of the steel coupon. The front face of the steel coupon was then polished with 800 grit SiC polishing paper to produce a uniform starting surface for the plating process.

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Dr. Howard Pickering The Pennsylvania State University Department of Materials Science and Engineering 326 Steidle Building University Park, PA 16802 Phone: 1 (814) 863-2640 Fax: 1 (814) 865-2917 Email: pick@ems.psu.edu Immediately after polishing, the coupons were degreased with acetone and rinsed with double distilled water. An insulating lacquer was applied to all exposed areas other than a 1×1 cm (0.39 \times 0.39 in.) area, which was the area of interest for plating and subsequent corrosion tests. This step was important in order to control the current density during electroplating, which in turn, controlled the final Sn/Zn ratio in the electrodeposit.^{24,5}

Electroplating

A proprietary neutral tin-zinc plating solution^{**} was used in all plating processes. This was done to insure the consistency and quality of the electrodeposit. Unfortunately, the exact composition of the plating bath was unknown to us because of its proprietary nature. A 70%/30% tin/zinc composition ratio was achieved by applying a current density of 0.5 A/dm² (4.6 A/ft²) when plating the steel samples.^{2.5} Electroplating was performed at room temperature (25°C; 77°F) under a non-static condition by the bubbling of prepurified nitrogen. For purification, reagent-grade nitrogen was passed through a purification train to remove oxygen and moisture. The nitrogen addition was done to remove oxygen, agitate the solution and be consistent with previous tests.^{2.5} Typically, the plating time was 50 min, which resulted in an electrodeposit thickness of approximately 10 μ m (394 μ -in.).

Corrosion tests

A three-electrode glass cell was used for all plating and corrosion tests in which the steel was used as the substrate. All potentiostat driven corrosion experiments were performed at room temperature in a corrosive solution of $0.1M \text{ Na}_2\text{SO}_4$ with the pH adjusted to 3.6 by adding sulfuric acid. The $0.1M \text{ Na}_2\text{SO}_4$ solution was prepared by the addition of $14.2 \text{ g Na}_2\text{SO}_4$ in 1 L of double distilled water. Deaeration of the solution to remove oxygen was performed by bubbling pre-purified nitrogen through the solution for 30 min prior to sample testing. Pre-purified nitrogen was also bubbled through the solution during tests for agitation of the solution. The pH 3.6 value, which was within the range of acid rain, was selected so data could be compared to earlier research and because solid film formation was unlikely during the corrosion process at this pH value.

A carbon rod was used as the counter electrode, and was located in the cell facing the 1.0 cm^2 (0.16 in².) test area of the sample. A saturated calomel electrode (SCE) was used as the reference electrode. The SCE was placed in a glass holder with the tip of the Luggin capillary positioned 5.0 mm (0.2 in.) from the sample (a distance approximately equivalent to twice the outside diameter of the Luggin capillary tip). An ionically conducting frit was placed at the tip of the Luggin capillary to prevent chloride ions, present in the reference electrode, from contaminating the solution near the specimen. The potentiostat^{***} used in all potentiodynamic scans was controlled by a personal computer.

After the corrosive solution was poured into the cell, the specimen was left at open circuit potential (OCP) for 10 min to arrive at a stable and reproducible starting OCP. Progressive stages of preferential zinc dissolution were then performed by a potentiodynamic scan from the open circuit potential to more positive potentials. The scan was done to monitor the selective dissolution of zinc from the alloy electrodeposit. Each sample was scanned to a different potential, and then taken out of solution, rinsed with double distilled water and dried in air. Each scan to a particular potential was repeated three times using a fresh sample each time.

Characterization

The surfaces of the as-plated and corroded samples were observed by scanning electron microscopy (SEM) and by backscatter electron microscopy (BSE). Some of these samples were later analyzed by energy dispersive x-ray spectroscopy (EDX).

Optical microscopy and scanning electron microscopy (SEM) images were taken of the electrodeposit surface after each potentiodynamic scan. The surface of the electrodeposit was observed to determine the morphology produced by the corrosive attack. Backscatter imaging was used in an attempt to view the regions of tin and zinc in the as-plated and partially corroded samples. The SEM images were then imported into a computer software program.**** This software, often used in metallurgical analysis, can determine the relative amount of surface porosity of each corroded sample. For a more accurate measurement, several areas on each sample were taken into consideration during the calculations of surface porosity.

For a better understanding of the morphology of the tin-zinc alloy electrodeposits, cross-sections were prepared of the as-plated and partially corroded samples. SEM and energy dispersive spectroscopy (EDS) mapping were performed on the cross-sections for characterization. Elemental dot maps were then performed in an attempt to visualize the regions of tin and zinc throughout the cross-section of the electrodeposit.

Results and discussion

Tin-zinc alloy electroplating

Figure 1 is a SEM image showing that the as-plated electrodeposit had a surface microstructure on the order of a few micrometers in grain size. At the boundaries of this microstructure, some very small depressions or pores appeared to exist rather uniformly in a network pattern around the micrometer-scale deposits. When viewed under higher magnification, the depressions appeared to be shallow, indicating a surface roughness rather than a porosity that penetrated deeply into the tin-zinc deposit thickness. Figure 2 is an image of the metallographically polished cross-section of the as-plated tin-zinc alloy electrodeposit. It reveals a micrometerscale surface roughness with minor imperfections existing below the surface, which could be pores in an otherwise dense $10-\mu m$ (394- μ -in.) thick tin-zinc deposit.

These observations (Figs. 1 and 2) and the knowledge that tin is the majority phase (70%) help to reveal the microstructural evolution during electroplating as follows. During the early stages of electroplating, deposits of tin formed on the steel substrate resulting in recesses between the deposits where zinc then plated out, either on individual tin deposits or as a network phase between the tin deposits. As the deposit thickened, this surface roughness, where the thickness of the tin deposits slightly exceeded that of the zinc deposits, may have persisted throughout the duration of plating, thereby yielding the roughness noted in Figs. 1 and 2. Therefore, even in the as-plated condition, very small recesses existed between the tin deposits with zinc residing at the base of the recesses.

^{**} Dipsol SZ-242 Plating Solution, Dipsol of America, Inc., Newark, NJ; Livonia, MI.

^{***} EG&G PAR Model 273A, Princeton Applied Research–Ametek, Oak Ridge, TN

^{*****}Image-Pro Plus v 4.5, Media Cybernetics, Silver Spring, MD.



Figure 1–SEM image of the surface of an as-plated tin-zinc alloy electrodeposit.

Potentiodynamic scans

Figure 3 shows a potentiodynamic scan of the 70/30 tin-zinc alloy electrodeposit. An anodic current of approximately 10 μ A existed to approximately -600 mV_{SCE} when an increase in the current occurred. The low current plateau was likely due solely to zinc dissolution, whereas the rising current at E > -600 mV_{SCE} could be either the onset of tin dissolution or, if the extent of zinc dissolution had exposed the steel substrate, the onset of iron dissolution. The drop-off of current at potentials more positive than -500 mV_{SCE} can be attributed to film formation on the tin or steel surface. The increasing current at the end of the scan was due to tin dissolution. This interpretation of the *I vs. E* curve in Fig. 3 is largely based on the earlier *I vs. E* plots of the component metals shown in Fig. 4.

From the SEM micrographs in Figs. 5 thru 7, it appears that the microstructure that developed during the potential scan in the pH 3.6 solution was qualitatively the same as that of the electrodeposited surface shown in Fig. 1. However, the morphology of the tin deposits appeared more enhanced, as if the zinc phase between them dissolved to form a void and a somewhat "sponge-like" structure. The tin-zinc alloy electrodeposit consisted of fine-grained mixtures of nearly pure tin and zinc phases. When corrosion of the electrodeposit occurred, the tin regions remained as the zinc regions dissolved into solution. Thus, the tin phase was what is mainly, if not entirely, seen in Figs. 5 thru 7 with voids formed between the tin deposits where the zinc phase existed prior to its dissolution during the scan. Therefore, it can be concluded that the



Figure 2–SEM image of the cross section of an as-plated tin-zinc alloy electrodeposit.

as-plated zinc resided in the areas that, after dissolution, became pores or trenches, and that the zinc and tin deposits existed as separate networks in the as-plated condition. The tin deposits are seen to be no larger than 5 μ m (197 μ -in.) in dimension and the width of the zinc network is noticeably smaller.

Figures 5 thru 7 show images of the surface of the tin-zinc electrodeposit as a function of the final potential of the scan. These scans were in the region of selective zinc dissolution. Figure 7 shows the surface of the electrodeposit whose final potential was closest to the potentials of steel and tin dissolution, which are shown in Fig. 4 to occur at -623 and -500 mV_{SCE}, respectively. Visually, there appeared to be little to no variation in surface porosity.

The amount of surface porosity was then calculated and is represented as a function of scanned potential in Fig. 8. Standard deviation bars were added to the data points to reflect the variance in the data sets. Figure 8 shows only a slight upward trend in the surface porosity from approximately 5 to 12% as the time of zinc dissolution increased (represented by the more positive final scan potential). This increased trend of surface porosity persisted even for final scan potentials that were above the potentials of tin and steel dissolution. The average of the surface porosity was 8 or 9%. This consistency over a wide range of potential and dissolution time indicates that the pore depth increased more than the pore width.

A cross-section of the electrodeposit was then performed on the partially dissolved sample. Figure 9 shows the cross-section of



Figure 3—Potentiodynamic scan (negative to positive) of a 70%Sn-30%Zn alloy electrodeposit on steel in deaerated 0.1M Na₃SO₄ (pH 3.6).



Figure 4—Polarization curves (negative to positive) of 70%Sn-30%Zn alloy, Zn, Sn and steel in deaerated 0.1M Na₃SO₄ (pH 3.6).⁴



Figure 5–SEM image of the electrodeposit surface after a potentiodynamic scan from OCP to –800 mV $_{\rm SCF}$



Figure 6–SEM image of the electrodeposit surface after a potentiodynamic scan from OCP to -700 mV_{scr} .



Figure 7–SEM image of the electrodeposit surface after a potentiodynamic scan from OCP to $-600 \text{ mV}_{\text{SCF}}$.



Figure 8—Surface porosity as a function of the final potential.



Figure 9–Cross section SEM image of a tin-zinc alloy electrodeposit after a potentiodynamic scan from the OCP to -650 mV_{scr} .



Figure 10–SEM image of the surface of the remaining tin-zinc alloy electrodeposit after a potentiodynamic scan from the OCP to -650 mV_{SCE} and removal of much of the tin-zinc layer by mechanical polishing.

the electrodeposit after a potentiodynamic scan from the OCP to -650 mV_{SCE}. In this case, there was noticeable surface roughness highlighted by penetrations a few micrometers apart. Thus, these penetrations were on the same scale as what appear to be penetrations in the images of the surfaces of the scanned samples in Figs. 5 thru 7. In addition, there were what appear to be varying sizes of pores in the interior of the electrodeposit. In order to determine if pores reside in the tin-zinc layer close to the steel substrate surface, most of the thickness of a scanned sample was removed by polish-

ing with a $0.3-\mu$ m alumina suspension until small regions of steel could be seen in the microscope. Figure 10 shows the surface of the remaining electrodeposit after the polishing step. Because nonconductive materials charge when struck with an electron beam, it was concluded that the white particles in Fig. 10 were residual alumina remaining despite post-polish cleaning. These particles likely collected in low regions or recesses of the deposit during polishing. The clusters seen in Fig. 10 were thus concluded to be resident in the pores that existed deep in the scanned tin-zinc electrodeposition close to the steel/deposit interface. Therefore, it appears that the porosity formed when the zinc was dissolved out of the tin-zinc layer, and that it existed throughout the electrodeposit down to the steel substrate.

EDS mapping of the as-plated cross section, shown in Fig. 11, did not yield an accurate measure of the grain sizes for tin and zinc, likely because the resolution in backscattered imaging was limited due to beam interaction between the submicron grains. However, Fig. 11 does confirm that the distribution of zinc in the as- plated electrodeposit was fairly uniform throughout the entire plating thickness.

Conclusions

- 1. Corrosion of the tin-zinc alloy electrodeposit first begins with selective dissolution of zinc. A porous network is created as a result of the selective zinc dissolution that eventually extends all the way to the steel substrate, at which time the electrodeposit is mostly if not entirely composed of the tin phase and a network of void space.
- 2. Some indication of passivation of the steel substrate at potentials significantly more positive than the OCP is apparent in the potentiodynamic scan.
- 3. During electroplating, the reduction of zinc ions occurs at the base of crevices existing between tin deposits.
- 4. The relative area of exposed zinc remains nearly the same throughout the duration of zinc dissolution during the scan. This reaffirms that only zinc dissolves and neither steel nor tin dissolve during open circuit exposure so long as zinc is present in the tin-zinc electrodeposit.

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Figure 11–EDS map of the tin-zinc alloy electrodeposit with a thickness (indicated by the arrow) of 13 μ m (~.0.5 mil).

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