Corrosion Resistance of Electroplated Sn-Zn Alloy & Its Improvement

By K. Wang, H.W. Pickering & K.G. Weil

A 70% Sn-30% Zn alloy was deposited from a neutral non-cyanide bath. Measurements of the corrosion rate by use of an electrochemical quartz crystal microbalance (EQCM) and observation by scanning electron microscopy (SEM) of the deposit's cross section show that, without sufficient agitation in the plating bath, a film of zinc hydroxide is formed on top of the metal film. In order to obtain a uniform deposit layer without the formation of hydroxide, one has to agitate the solution during the plating process. The effects of different chromate treatment methods are tested and compared with those on pure zinc samples. 1,2,3-benzotriazole (BTA) was added to the corrosive solution and found to be an effective corrosion inhibitor that acted mainly on the anodic zinc dissolution reaction.

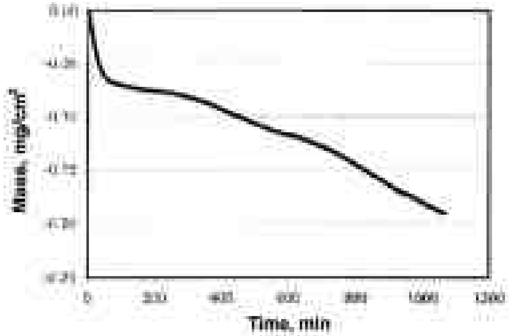

Fig. 1—Mass loss of a Sn-Zn deposit during corrosion in 0.1M Na_2SO_4 (pH=3.6) solution.

Electroplated cadmium coatings have been widely used in many areas such as cars, ships and on fasteners. Because of the toxicity of cadmium and its compounds, however, its application has been restricted.[1-3] In Japan, further use of cadmium coatings has been prohibited. As the concern for environmental protection has increased, a viable replacement for cadmium coatings has become more important. Electroplated tin-zinc alloys have been proposed to be good cadmium substitutes.[4,5] A preliminary study of their corrosion behavior was the subject of our previous work.[6,7] It was shown that a tin-zinc deposit was a fine mixture of the two pure components. The open circuit potential (OCP) of these deposits was close to the OCP of pure zinc, which meant that zinc dissolution *was* the corrosion reaction. The sacrificial property of zinc cathodically protected the steel substrate and the tin.

At the same time, comparison of the polarization curves of the tin-zinc deposit with those of the pure components and of the steel substrate showed that the anodic current of the tin-zinc deposits remained very small, as long as the potential was more negative than the potential where the tin began to dissolve. The combination of sacrificial and barrier properties of tin-zinc coatings was similar to the properties of cadmium coatings. In the current study, we electroplated a 70 wt% Sn-30wt% Zn deposit onto a steel substrate from a neutral non-cyanide bath, and examined the effects of chromate treatment and benzotriazole (BTA) as corrosion inhibitors.

Nuts & Bolts: What This Paper Means to You

Tin-zinc is one of the many alloys used in place of pure zinc, in this case for fasteners for electrical grounding applications, among others. This work, part of the AESF Research program (Project #99), takes a look at how the process works (agitation is critical) and how the coatings respond to chromates. The researchers also found that the old benzotriazole used to protect copper solderability in electronics finishing works as a corrosion inhibitor on this alloy. Who knows where this might lead?

Experimental

The substrates used in this investigation were carbon steel coupons cut from 0.07-cm (0.27-in. —> 0.027-in.) thick, cold-rolled and annealed steel sheets. A copper wire was connected to the back side of the steel plates by soldering. An insulating lacquer covered the sample surface so that only a 1 cm · 1 cm area of the front surface was exposed to the solution. The tin-zinc alloy plating bath is a newly developed commercial neutral non-cyanide solution. Prior to deposition, the steel plates were polished with #800 SiC polishing paper, degreased with acetone, and rinsed with double-distilled water. After plating, the samples were again rinsed with double-distilled water and air-dried.

Chromate treatment is a common post-plating treatment for zinc coatings to improve corrosion resistance.[8-10] In this study, several chromate treatment methods were applied on the 70% Sn-30% Zn coatings. The treatments are listed in Table 1. After treatment, the samples were rinsed and dried in air for several hours. Their properties were examined by subsequent corrosion and polarization experiments, as well as by surface observation. The results were compared with pure zinc coatings that had been produced from an alkaline bath.

Corrosion experiments were performed at room temperature in a 0.1M Na_2SO_4 solution, with the pH adjusted to 3.6 with sulfuric acid. Voltammetric curves were taken

Table 1—Chromate Treatment Methods

Solution	Treatment
0.1M H_2CrO_4 (pH=0.5)	Immersion for 60 sec
0.1M $K_2Cr_2O_7$	60 sec anodic + 15 sec cathodic treatment with 30mA/cm^2
0.1M $K_2Cr_2O_7$	30s cathodic treatment with 30mA/cm^2
0.15M $K_2Cr_2O_7$, 0.04M Na_2SO_4 (pH=1.6)	Immersion for 30 sec

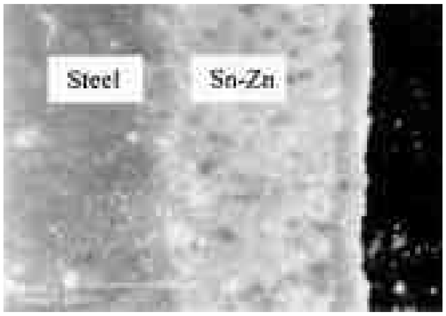

Fig. 2—Without agitation, the deposit is composed of two layers (cross section).

with a potentiostat connected to a personal computer. A saturated calomel electrode (SCE) was used as the reference, and a carbon rod as the counter electrode. All experiments were done in deaerated solutions.

An electrochemical quartz crystal microbalance (EQCM) was used to measure the mass loss rate of the coatings during the corrosion process. The EQCM is a highly sensitive device for measuring the mass change of coatings. The principle of EQCM is explained elsewhere.[11]

To observe the inhibition effect of BTA, 20 mM of BTA was added to the corrosive solution. Polarization curves of samples were measured and compared with those obtained in solutions without BTA. The EQCM was also used to measure the corrosion rate.

Results & Discussion

For the electroplated 70% Sn–30% Zn deposits, corrosion experiments were performed with an EQCM to determine the mass loss through corrosion. A typical curve of the mass loss is shown in Fig. 1.

Figure 1 shows that the dissolution process can be divided into two stages. The first stage lasts less than one hr, and here the mass loss is quite rapid. Following that stage, the mass loss rate slows down and reaches a more steady state.

A cross section of the tin-zinc deposit on a steel substrate was analyzed by scanning electron microscopy (SEM). The image is shown in Fig. 2. The coating consists of two layers: an outer layer and an inner layer. A comparison by SEM of the sample surface appearance before and after a two-hr period of corrosion at open circuit potential is shown in Fig. 3. It can be seen that notable changes occurred on the surface during corrosion. A cross section of the corroded sample was again observed with the SEM. The outer layer had disappeared. This indicates that the outer layer rapidly dissolved in the acid solution, accounting for the high rate of mass loss during the first stage. EDX analysis showed the outer layer to be mainly $Zn(OH)_2$. The formation of $Zn(OH)_2$ is understandable because, during the electroplating process, copious amounts of hydrogen bubbles evolved at the cathode. Because of this, the H^+ ion concentration at the metal surface decreased. If the transport of H^+ ions from the bulk solution to the cathode surface is less than the consumption rate, the local pH value will increase. At a certain critical pH value, zinc hydroxide will precipitate on the surface.

To prevent the formation of the hydroxide, nitrogen gas bubbling was introduced into the bath to provide sufficient agitation during plating. The cross section of a sample produced with such agitation is shown in Fig. 4. Here, the deposit is a single layer without hydroxide on the top. SEM observation also showed that, after two hr of corrosion exposure, the sample surface showed no apparent changes.

The effect of agitation was also reflected by the mass loss measurements with the EQCM. Figure 5 shows the curve of mass loss vs. time during corrosion at OCP of a sample that was produced with agitation. Compared to the previous curve (Fig. 1), the initial stage of rapid mass loss does not exist.

The polarization curves of tin-zinc deposits after different chromate treatments are shown in Figs. 6 and 7. Compared with untreated samples, there are two common features of these curves. First, the OCPs of the treated samples are tens of millivolts more positive than those of the untreated samples. Second, the anodic current densities of the treated samples are usually smaller than those of the untreated samples. Both of these features can be explained by the protective function of the chromate layers. The chromate forms a barrier layer on the surface that hinders the dissolution of zinc. As a result of the increased difficulty of the anodic reaction, the OCP increases and the anodic current density decreases.

Among the treatment methods summarized in Table 1, the first treatment, using chromic acid, resulted in a sample surface that appeared rough, and the chromate layer did not adhere well. For the second process—anodic/cathodic treatment in potassium dichromate solution—the layer was colorless, which meant that the chromate layer was very thin. It also did not improve the characteristics of the anodic polarization curve. For the third treatment—cathodic treatment only in potassium dichromate solution—the anodic current was good at lower potentials, but the layer was

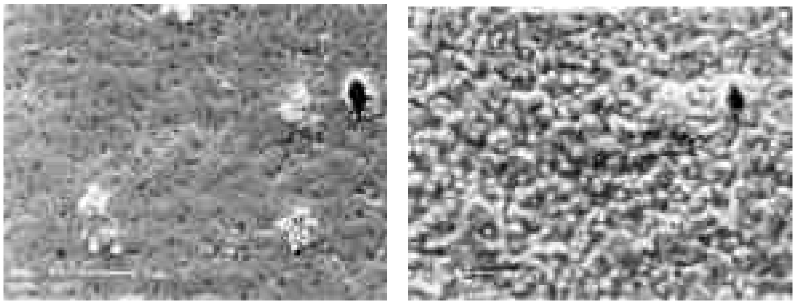
(a) (b)

Fig. 3—Sn-Zn deposit surface before and after two-hours of corrosion at OCP in 0.1M Na_2SO_4 (pH=3.6) solutions (a) before (b) after.

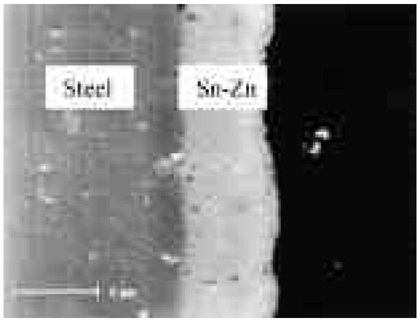

Fig. 4—Cross section of a deposit produced with N_2 gas bubble agitation.

Table 2—Polarization Resistance* of Deposits In Different Solutions

Chromate treatment	Pure Zn		Sn-Zn	
	No	Yes	No	Yes
0.1M Na_2SO_4 (pH=3.6)	167	323	676	806
5% NaCl (pH=5.5)	195	1840	2048	2406

*R_p (Ω.cm^2)

also very thin, and the current became larger at higher potentials. For the fourth treatment—immersion in the potassium dichromate/sodium sulfate solution—the surface showed an iridescent yellow color, which meant that the thickness of the chromate was moderate. The anodic current density showed an apparent decrease after treatment. It also showed good adhesion. Therefore, the forth treatment was chosen for the further experiments.

On pure zinc coatings, chromate treatment showed polarization results similar to those for the tin-zinc deposits. Figure 8 shows the polarization curves of pure zinc coatings with and without the fourth chromate treatment. With a chromate layer on the surface, the anodic branch of the curve still did not exhibit a passive region. This means that its protection is limited. It is likely that the structure of the chromate layer is not compact; therefore, it can only retard zinc dissolution to a limited extent.

The EQCM was used to measure the mass loss of pure zinc and tin-zinc coatings in 0.1M Na_2SO_4 solution (pH=3.6). Contrary to expectation, however, for both metals, the mass loss rates of the treated samples were slightly higher than those of the untreated samples. This may be because of the dissolution of the chromate layer in the slightly acid solution. The soluble ingredients in the chromate layer, such as Cr^{+6} and SO_4^{-2}, will dissolve in this solution. Furthermore, from the Pourbaix diagram, Cr_2O_3 or $Cr(OH)_3$, the dominant species in the chromate layer, is not stable in acid solutions and can also dissolve. This can lead to additional mass losses beyond zinc dissolution. It appears, therefore, that such experiments cannot show the beneficial effect that a chromate treatment may have under different environments.

Because the mass changes detected with the EQCM may not have truly reflected the rate of zinc dissolution, the polarization resistance was measured for different metals by use of the linear polarization technique. The results are shown in Table 2. Comparing the results, one can see that the protection by chromate is more effective on pure zinc than on tin-zinc alloys. For pure zinc, chromate treatment was more effective in neutral solutions than in acid solutions. For the tin-zinc alloy, there were no major differences among the various solutions. The polarization resistances increase by less than 20 percent in both cases. This is not surprising, because we know that for tin-zinc deposits, the tin provides barrier properties that are similar to the way in which chromate layers act. Therefore, it makes the chromate treatment less important.

Benzotriazole (BTA) has been widely used as a corrosion inhibitor for copper, its alloys, and for mild steels.[12,13] Inhibition data of BTA for zinc and its alloys, however, are not readily available. In this study, mass loss vs. time curves for tin-zinc deposits during corrosion in 0.1M Na_2SO_4 (pH 3.6) solutions, with and without 20mM BTA, were determined. They are shown in Fig. 9. The mass loss of tin-zinc coating in BTA solution is about one-third of that in the solution without BTA. This means that BTA has an apparent inhibition effect on the corrosion of the tin-zinc coating. Because we already know that the corrosion of the alloy is, for all practical purposes, the dissolution of zinc, polarization curves of zinc in the corrosive solutions were determined. From the polarization curves for pure zinc in the solutions with and without BTA (Fig. 10), it can be seen that the anodic polarization curve of zinc was drastically shifted to the left by BTA, while the cathodic polarization current was almost unchanged. Consequently, the open circuit potential of zinc was increased by about 100mV with BTA. This suggests that BTA mainly inhibits the anodic dissolution of zinc, rather than the cathodic reaction, the hydrogen evolution reaction in deaerated solution.

Conclusions

During electroplating of tin-zinc alloys, agitation is necessary to prevent the formation of hydroxide on the surface. In acidic Na_2SO_4

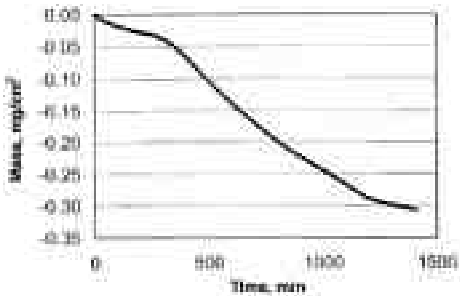

Fig. 5—Mass loss of a Sn-Zn deposit produced with agitation during corrosion.

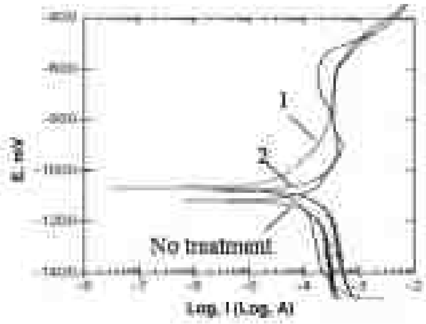

Fig. 6—Polarization curves of samples with the first two chromate treatments and without treatment.

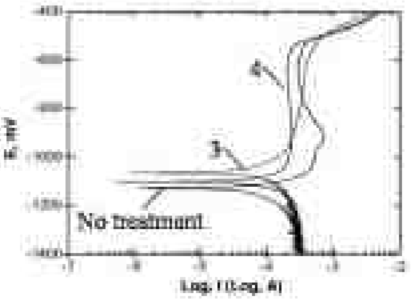

Fig. 7—Polarization curves of samples with the third and the fourth chromate treatment and without treatment.

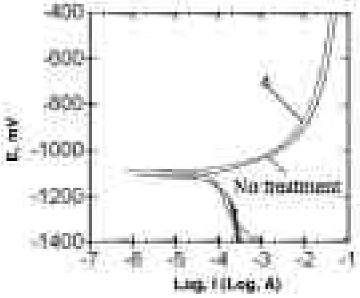

Fig. 8—Polarization curves of Zn in 0.1M Na_2SO_4 (pH=3.6) solutions with and without chromate treatment.

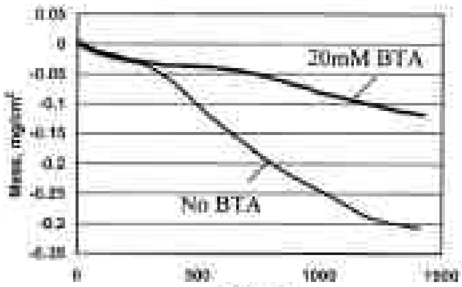

Fig. 9—Mass loss of Sn-Zn deposit in 0.1M Na_2SO_4 (pH=3.6) solutions with and without BTA.

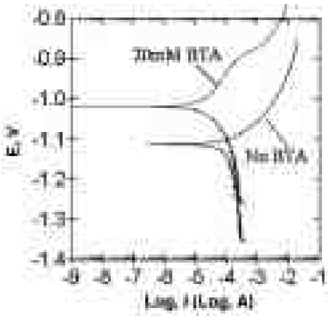

Fig. 10—Polarization curves of Zn in 0.1M Na_2SO_4 (pH=3.6) solutions with and without BTA

solutions, a chromate treatment can decrease the corrosion rate of zinc or tin-zinc alloy, but its effect is limited. Chromate treatment is more effective for pure zinc than for tin-zinc deposits, and is more effective in neutral solutions than in acid solutions. Because of the dissolution of the chromate layer, its protection could ultimately be lost. BTA is an effective inhibitor for the corrosion of zinc from tin-zinc alloy coatings. It primarily effects the anodic partial reaction of the zinc dissolution.

Acknowledgments

This work was supported by the American Electroplaters and Surface Finishers Society (AESF Research Project #99) and the National Science Foundation (NSF Grant No. DMR-9612303). Thanks are due to Bethlehem Steel Corporation and Dr. C.R. Shastry, who provided the steel samples, and Dipsol Gumm Ventures, who provided the plating solutions.

References

1. S.J. Blunden, *Adv. Mat. Proc.*, **137**, 37 (1991).
2. E. Budman & D. Stevens, *Trans IMF*, **76**, B34 (1998).
3. K.R. Baldwin & C.J.E. Smith, *Trans. Inst. Met. Fin.* **74**, 227 (1953).
4. R.M. Angles & R. Kerr, *Engineering*, **161**, 289 (1946).
5. W.H. Ailor, *Atmospheric Corrosion*, J. Wiley & Sons, New York, NY 1982; p. 520.
6. K. Wang, H.W. Pickering, K.G. Weil, *Proc. of AESF SUR/FIN 2000*, AESF, Orlando, FL, June, 2000.
7. K. Wang, H.W. Pickering & K.G. Weil, *Electrochimica Acta*, **46**, 3835 (2001).
8. N. Zaki, *Metal Fin.*, **86**, 75 (February 1988).
9. R. Sarmaitis, *Plating & Surface Finishing*, **68**, 83 (Sept. 1981).
10. L.F.G. Williams, *Surf. Technol.*, **5**, 105 (February 1977).
11. C. Eickes, J. Rosenmund, S. Wasle, K. Doblhofer, K. Wang & K.G. Weil, *Electrochim. Acta*, **45**, 3623 (2000).
12. L. Tommesani, G. Brunoro, A. Frignani, C. Monticelli & M.D. Colle, *Corr. Sci.*, **39**, 1221 (July 1997).
13. G.K. Gomma, *Mat. Chem. Phys.*, **55**, 235, (1998).

About the Authors


Wang


Pickering


Weil

Kai Wang is a PhD graduate student in the Materials Science and Engineering Department, College of Earth and Mineral Sciences at The Pennsylvania State University.

Dr. Howard W. Pickering is current Distinguished Professor in the Materials Science and Engineering Department, College of Earth and Mineral Sciences at The Pennsylvania State University, 326 Steidle Bldg., University Park, PA 16802 (pick@ems.psu.edu).

Dr. Konrad G. Weil recently retired from the Technical Hochschule, Darmstadt, Germany, and is currently a scholar in the Materials Science and Engineering Department, College of Earth and Mineral Sciences at The Pennsylvania State University.