Technical Article

Corrosion Behavior Of Electroplated Tin-Zinc Coatings

by K. Wang, H.W. Pickering^{*}, & K.G. Weil

The corrosion behavior of electroplated tin-zinc coatings in an acidic sodium sulfate solution was studied. The open circuit potentials (OCP) of the coatings increased with corrosion time. The less zinc content in the deposit, the more rapidly its OCP increased. An IR drop mechanism might have been responsible for the OCP increase. As zinc dissolved into the solution, cavities appeared on the deposit surface. Further zinc dissolution only occurred at the bottom of these pores, while the hydrogen evolution reaction mainly occurred on the outer surface. The separation of the anodic and cathodic sites caused an IR drop in the pore electrolyte. An equivalent circuit representing this situation is proposed. The values of its elements were determined by electrochemical impedance spectroscopy. Their development with time was in accordance with the IR drop mechanism.



Fig. 2–SEM image of the electroplated 70Sn-30Zn deposit after 24 hours of corrosion at OCP in 0.1M Na₂SO₄ (pH 3.6) solution.

Electroplated tin-zinc deposits are attracting more and more industrial attention because of their good corrosion resistance, mechanical properties and electrical conductivity.



Fig. 1-OCP changes of tin-zinc coatings with different zinc contents in 0.1 M Na₂SO₄ (pH 3.6) solution.

Nuts & Bolts: What This Paper Means to You

The corrosion performance of zinc alloys is specified in terms of performance tests – salt spray, field tests, etc. Yet studies into **how** the alloys corrode are rather rare. This work, part of AESF Research Project #99, looks into the corrosion behavior plated tin-zinc in acidic sodium sulfate solution. The development of pores which penetrate into the surface, along with the preference for dissolving zinc over tin, makes for interesting behavior. These results can lead to the design of better performing alloys, by manipulating the structure.



They are regarded as good replacements of toxic cadmium coatings.¹⁻⁵ Several researchers⁶⁻⁹ have studied the corrosion resistance of tin-zinc coatings of various compositions since the 1940s, and concluded that the corrosion resistance of tin-zinc films is comparable to that of cadmium or zinc. It is also commonly accepted that a deposit containing 20 to 30 wt% zinc shows the best corrosion resistance and comprehensive properties. Therefore, commercial tin-zinc plating baths have mainly been developed to produce coatings within this composition range. However, research on the corrosion resistance of tin-zinc coatings has mainly been carried out from the industrial perspective, *i.e.*, by standard

*Corresponding Author: Dr. Howard W. Pickering Distinguished Professor of Metallurgy Department of Materials Science and Engineering 326 Steidle Building The Pennsylvania State University University Park, PA 16802 E-mail: pick@ems.psu.edu test methods such as salt spray, humidity and prolonged environmental exposure. Little is known about the corrosion mechanism of tin-zinc coatings. In our previous work,¹⁰ it was shown that tin-zinc electrodeposits consisted of tiny tin and zinc phases, which were physically mixed, because of their extremely low mutual solubilities. The open circuit potential (OCP) of a tin-zinc electrodeposit in weak acid solution is close to that of pure zinc, suggesting that the zinc dissolution reaction is the dominant anodic reaction and thus the coating provides cathodic protection to the steel substrate. In this paper we further studied the microscopic corrosion phenomena of tin-zinc coatings. A mechanism describing their corrosion behavior is also proposed.

Experimental

Tin-zinc coatings of various compositions and an exposed area of 1.0 cm² (0.155 in.²) were electroplated onto mild steel coupons from a commercial neutral non-cyanide plating bath. The compositions of the coatings were determined by dissolving the plated samples in nitric acid followed by analysis of the acid solution by inductively coupled plasma (ICP) techniques. As reported previously,¹⁰ the composition of the tin-zinc electrodeposit depended on the plating current density,

so the content of zinc could be controlled by varying the plating current density. Four tin-zinc coatings, with 18, 30, 35 and 38 wt% of zinc, respectively, were produced from the plating bath. The specimens then were immersed into a deaerated $0.1M \text{ Na}_2\text{SO}_4$ solution with its pH adjusted to 3.6 with sulfuric acid. Their open circuit potentials were measured over time with a potentiostat.^{**} A saturated calomel electrode (SCE) was used as the reference electrode and a carbon rod was used as the counter electrode. After a corrosion period of 20 hr, the sample surface was observed by SEM to see any changes in surface morphology.

Electrochemical impedance spectroscopy (EIS) measurements were carried out with a second potentiostat^{***} at different corrosion times. The EIS data were obtained in the AC frequency range of 5000-0.05 Hz with 4 points per decade. An equivalent circuit for the tin-zinc coated electrodes was devised and the equivalent circuit elements were determined with the potentiostat analysis software.

Results & discussion

The open circuit potentials (OCP) of different tin-zinc deposits as a function of time are plotted in Fig. 1. As can be seen, the open circuit potentials of the coatings all shifted in a positive direction

with exposure time. The less zinc content the coating had, the more rapidly the OCP increased. A micrograph of the surface of a 70 wt% tin coating after 20 hr of corrosion at the OCP is shown in Fig. 2. A porous surface was observed. We know that, since tin is a rather inert metal, the corrosion process is mainly the dissolution of zinc. Energy dispersive X-ray spectroscopy (EDX) elemental analysis confirmed that after corrosion the composition of the outer surface was almost pure tin. This suggests that the formation of the porous structure was due to the dissolution of zinc in the corrosive solution.





RE

The OCP increase may be explained by an IR drop mechanism. As can be seen in Fig. 2, after corrosion has proceeded for a time, the surface appears porous because of the dissolution of the zinc in the deposit. Based on these observations, a schematic diagram of the IR drop mechanism is shown in Fig. 3. As zinc dissolves, cavities form from the removal of zinc particles and the outer surface becomes dominated by pure tin. As corrosion proceeds, zinc will only be available at the bottom of the pits, where the anodic reaction will occur. On the other hand, the cathodic reaction, which in the deaerated solution is hydrogen evolution, is mainly occurring on the outer surface where the hydrogen ions are readily available.

This separation of the anodic and cathodic sites leads to a potential difference between the anode and cathode. This potential difference, arising from the IR drop, is the product of the ionic (corrosion) current flowing between these sites and the resistance of the solution trapped in the pores of the coating. The pore resistance is

$$R_{pore} = \rho L/A,$$
 (1)

where ρ is the resistivity of the solution, L the depth of the pores, and A the cross sectional area of the pore electrolyte, which is taken as the cross sectional area of the pore in the absence of gaseous or

Table 1Fitted Values for the Impedance Elements of Fig. 5For Various Corrosion Times (Resistance Values in ohms,Capacitance Values in farad·sec^{$\alpha-1$}).

Time (hr)	\mathbf{R}_{s}	R _{pore}	R _{zn}	C _{sn}	α (Sn)	C _{zn}	α (Zn)
2	19.41	157.2	145.6	2.041E-5	0.911	8.21E-3	0.577
4	19.16	170.9	199.2	1.940E-5	0.919	6.56E-3	0.519
7	19.15	239.2	344	1.853E-5	0.927	2.97E-3	0.387
10	18.83	460.1	229	1.922E-5	0.922	1.337E-3	0.595
20	18.68	1858	5606	2.333E-5	0.901	7.222E-5	0.192
24	18.31	20679	9657	2.825E-5	0.879	4.176E-4	0.795
28	18.00	335959	12645	3.053E-5	0.872	3.828E-4	0.935

WE

^{**} EG&G PAR 273 Potentiostat, Princeton Applied Research, Division of AMETEK, Paoli, PA 19301.

^{***} GAMRY PC3 Potentiostat, Gamry Instruments, Warminster, PA 18974.



Fig. 5—Nyquist plots of the experimental and the fitted impedance spectra at corrosion times of: (a) 2 hr; (b) 7 hr and (c) 20 hr.



Fig. 6–Anodic and cathodic partial currents in a corroding system (schematic).

solid corrosion products within the pore. Since the cross section of the pores is very small, the pore resistance R_{pope} may reach signifi-

cant values. The IR drop mechanism has been proven to be responsible for the initiation of crevice corrosion for several metal/solution systems.¹¹⁻¹⁵ As shown in Fig. 3, the cathodic potential shifts from the OCP in the positive direction as the IR drop increases, while the anodic potential shifts in the negative direction. Since the potential measured by the reference electrode is actually the potential of the outer surface, *i.e.*, the cathodic potential, it increases as the IR drop becomes more and more significant.

In order to substantiate the IR drop model we measured electrochemical impedance spectra at varying corrosion times. An equivalent circuit, shown in Fig. 4, was designed that takes the separation of anodic and cathodic sites into account. R_s is the solution resistance between tip of the Luggin capillary and the working electrode. R_{pore} is the resistance of the solution trapped in the pores that were formed from the dissolution of zinc. R_{zn} is the charge transfer resistance of the zinc dissolution reaction at the bottom of the pores. For the circuit fitting procedure C_{dl} and C_{zn} are replaced by constant phase elements (CPE) that represent the capacitive part of the tin/electrolyte interface and of the zinc/electrolyte interface at the bottom of the pores. A CPE has an impedance (Av^α) where v is the frequency and α is the phase of the CPE. If α is near unity, the CPE represents a condenser and A approaches its capacitance.

The equivalent circuit elements of a 70%Sn-30%Zn coating for different corrosion times at OCP are shown in Table 1. The Nyquist plots from which the circuit values were derived are shown in Fig. 5, for three of the corrosion times. The CPE's are characterized by their value and phase. The value of the CPE of the outer, tin surface remains nearly constant and its phase is close to unity at all times, indicating that the outer surface behaves similarly to an ideal condenser. For an ideal metal/electrolyte double layer of 1 cm^2 (0.155 in.²), one would expect C_{sn} values around 20×10⁻⁶ farad, close to the values reported in the table. Further, the solution resistance remains constant during corrosion, as would be expected for our model. The CPE related to the zinc surface at the bottom of the pores has phases well below unity, as would be expected for a rough reactive surface. The pore resistance R_{pore} and the charge transfer resistance R_{7n} increase dramatically with corrosion time. This is also in agreement with the IR drop mechanism. As the dissolution of zinc proceeds, the depth of the pores becomes deeper and deeper, so that the resistance of the solution trapped in the pores increases with time. When the IR drop increases, the potential at the zinc/electrolyte surface shifts in the cathodic direction, as seen in Fig. 6. This leads to a decrease of the slope of the anodic partial current. Because R_{7n} , the charge transfer resistance of the zinc oxidation reaction, is the reciprocal of this slope it is evident that the IR drop should lead to an increase of R_{Zn} with increasing corrosion time.

Conclusions

In this paper the corrosion behavior of electrodeposited Sn-Zn coatings in a 0.1M Na₂SO₄ (pH 3.6) solution is reported and the corrosion mechanism discussed. For Sn-Zn deposits with different zinc contents, the rates of increase of the open circuit potential (OCP) vary. The lower the zinc content in the coating, the more rapid the increase in the OCP. The increase probably occurs through an IRdrop mechanism. As zinc dissolves into the solution, cavities appear on the deposit surface, and further zinc dissolution will only occur at the bottom of the pores, while the hydrogen evolution reaction mainly occurs on the outer surface. The separation of the anodic and cathodic sites causes an IR drop in the corrosion cell circuit. The more zinc dissolves, the deeper the cavities, the larger the IR drop and the more positive the measured OCP. An equivalent circuit was devised according to the IR drop mechanism. The values of the circuit elements were calculated. The resultant behavior of the circuit with time was in accordance with the IR drop mechanism.

Acknowledgments

This work was supported by the American Electroplaters and Surface Finishers Society (AESF Research Project #99) and the National Science Foundation (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

- O.A. Ashiru & J. Shirokoff, *Applied Surface Science*, **103**, 159 (1996).
- 2. E. Budman & D. Stevens, Trans. IMF, 76, B34 (1998).
- A. Brenner, *Electrodeposition of Alloys, Volume II*, Elsevier Inc. Science & Technology/Academic Press, San Diego, CA, 1963.
- 4. A.E. Davis, R.M. Angles & J.W. Cuthbertson, *Trans. IMF*, **29**, 227 (1953).
- 5. Technical Bulletin, Dipsol Gumm Ventures Co., Kearny, NJ, 1996.
- 6. R.M. Angles, J. Electrodepositor's Tech. Soc., 21, 45 (1946).
- 7. J.W. Cuthbertson & R.M. Angles, J. Electrochem. Soc., 94, 73 (1948).
- 8. F.M. Lowenheim, U.S. patent 2,675,347 (1954).
- 9. M.E. Warwick & P.E. Davis, *Plating and Surface Finishing*, **74**, 77 (December 1987).
- K. Wang, H.W. Pickering & K.G. Weil, *Electrochimica Acta*, 46, 3835 (2001).
- 11. C.M. Chen, F.H. Beck & M.G. Fontana, *Corrosion*, **27**, 234 (1971).

- 12. K. Cho & H.W. Pickering, J. Electrochem. Soc., 138, L56 (1991).
- E.A. Nystrom, J.B. Lee, A.A. Sagues & H.W. Pickering, J. Electrochem. Soc., 141, 358 (1994).
- 14. Y. Xu & H.W. Pickering, J. Electrochem. Soc., 140, 658 (1995).
- 15. H.W. Pickering, J. Electrochem. Soc., 150, K1 (2003).

About the Authors



K. Wang

H.W. Pickering

K.G. Weil

Kai Wang earned his Ph.D. in the Materials Science and Engineering Department, College of Earth and Mineral Sciences at The Pennsylvania State University.

Dr. Howard W. Pickering is distinguished professor in the Materials Science and Engineering Department, College of Earth and Mineral Sciences at The Pennsylvania State University.

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.