Microstructural Morphology of Zn-Fe Alloy Electrodeposited Coatings

By Y. Liao, D.R. Gabe & G.D. Wilcox

The morphologies of zinc-iron alloy electrodeposits, produced from a chloride solution, have been studied over a wide composition range, using current density and electrode rotational agitation as the main process parameters. Change of current density was the greatest influence on morphology and can be correlated with changes of deposit composition. Rotational agitation should be high for compositions of less than 10 wt percent Fe and low for compositions of greater than 10 wt percent Fe. Additions of ammonium chloride act as a grain refiner.

Zinc-iron alloy coatings electrodeposited on steel sheet and strip possess the advantages of excellent corrosion resistance, excellent paintability, good weldability and good formability, which are the reasons that zinc-iron electrodeposited on steel sheet has been widely used for building and automobile body applications.^{1,2}. Research has shown that these properties can vary greatly with the microstructure of the coating.^{3,4} In studies of the fundamental aspects of zinc-iron alloy electrodeposition, Fajardo *et al.*⁵ have explored both the effect of composition of the coating and the current density on the microstructure. They showed that zinc-rich deposits had a uniform surface appearance, while for deposits richer in iron, the surface was quite irregular, and that four different types of deposit growth morphology were apparent: nodular (N), rhythmic lamellar (RL), field-oriented (FT) and unoriented-dispersed (UD), which evolved from type to type as current density and deposit composition were changed. Adaniya *et al.*⁶ also showed how surface morphology changes with increasing iron content; they explained that good or poor workability of zinc-iron alloy coatings corresponds to the presence of γ and η phases, respectively, in the coating structure.

For improving the quality of zinc-iron alloy coatings, some research on phase transformation and morphology has been reported. Gu *et al.*⁷ found that the phases present in electro-



Magnification for all micrographs 40 µm

Fig. 1—SEM micrographs of electrodeposited Zn-Fe alloys from chloride solution.



Fig. 2—Crystal morphology changes of electrodeposited Zn-Fe alloys.





Fig. 4-Effect of current density on electrodeposited Zn-Fe alloys containing 9% Fe.



Fig. 5—Effect of current density on electrodeposited Zn-Fe alloys containing 12% Fe.



Fig. 6—Effect of rotation speed on electrodeposited Zn-Fe alloys containing 1% Fe.

plated zinc-iron alloy coatings were η and δ phase in a nonequilibrium or metastable condition; these can be nudged toward equilibrium by heating. Kondo *et al.*⁸ utilized copper additives to accelerate morphological evolution of zinc-iron alloy electrodeposits in order to refine or define the alloy coatings.

The microstructure may be very important in multi-layered coatings of composition-modulated alloys when they are used as a means of enhancing performance.⁹ Current density and agitation are the two main process parameters for producing multi-layer coatings of composition-modulated alloys from a single bath.¹⁰ It is necessary, therefore, to know the effect of current density, accompanied by agitation, on the deposit microstructure.

In earlier work,¹¹ the variability of deposit composition with process parameters was explored and defined as the basis for later investigations. The object of the current study was to examine the microstructure changes with composition of such coatings, exploring the influence of current density and agitation on classical morphology in a chloride electrolyte system.

Experimental Procedure

Copper foil 0.034 mm thick and 99.95 percent pure was used as the substrate material. It covered a rotating cathode as a cylindrical sleeve with an effective electrode area of 28.3 cm². After being washed with water and dried with acetone, it was pickled in 10percent v/v sulfuric acid for two min. Subsequently, electrodeposition trials were performed galvanostatically on the cylinder at 50 °C in a solution containing 0.8 mol/L iron as ferrous chloride, 0.8 mol/L zinc as zinc chloride. The pH of the solution was 3. Electroplating was carried out at 0, 50, 100, 500, 1000, and 1500 rpm and current density was varied between 0.168 and 60 A/dm². A large concentric cylindrical zinc foil was used as the anode. Solutions with and without additions of ammonium chloride (100 g/ L) as a "conductivity salt" were compared during the investigation. The surface morphology and compositional analysis of the zinc-iron alloy coating were carried out by using a scanning electron microscope (SEM) and an energy dispersive X-ray microanalyzer (EDX), respectively. Deposit composition is expressed as wt percent and is realistically not better than ±0.5 percent; better accuracy is suggested in the text when a number of values is averaged. Compositional variation on the rotating cylinder surfaces was very small, except, of course, at the edges, which could be acceptably neglected.

Results & Discussion

Microstructure of Coatings with Different Composition The microstructure of zinc-iron alloy coatings changes greatly as the composition of the coatings and the rotation speeds are varied. The surface morphologies of coatings with different composition are shown in Fig. 1. It is clear from this figure that deposit grain structure is fine and appears hexagonal when the iron content is below one wt percent. When the iron content is between one and five wt percent, the crystal structure is nodular. When the iron content is between 5 and 20 wt percent, the grains have a splintered appearance. Above 20 wt percent iron content, the deposit grains tend to be fine and compact, and keep the same appearance until the iron content is more than 75 wt percent. The surfaces of highiron-content coatings are rough, so the coatings are better in quality when iron content is below one wt percent or in the range of 15 to 75 wt percent. For these various microstructural changes, more details can be seen in Fig. 2 (i.e., that the crystals appear triangular when the iron content is 18 wt percent, and begin to change further when the iron content reaches 19 wt percent. The crystals appear as hexagonal when the iron content reaches 25 wt percent. At 21 wt percent, the crystal structure is a mixture of triangular and hexagonal shapes. If structural consistency of coatings is required, therefore, it is better to deposit the coatings with a composition range not embracing the structure change point.

Effect of Current Density on the Microstructure of Coatings Generally, high current density leads to large grain size and the structure of coatings becomes less compact, but in a different composition range, the effect of current density can be revealed in a different way. From Fig. 3, it can be

seen that the current density has a great effect on the structure of coatings with low iron content (< 2 wt pct), which may mean that obtaining low iron content coatings with low current density is a valuable strategy. When the iron content is larger (about 9 wt pct), the current density has little effect on the structure of the coatings, as shown in Fig. 4. A larger current density makes the grain size smaller and the structure



Fig. 11-Effect of ammonium chloride on electrodeposited Zn-Fe alloys containing 7% Fe.

of the coatings more compact when the iron content is between 10 and 15 wt percent (*e.g.*, the structures in Fig. 5). When the iron content is greater than 15 wt percent, which normally requires high current density electrodeposition, the current density influences the structure of coatings relatively little. High current density is recommended, therefore, to deposit high-iron-content coatings from a chloride solution.



Fig. 12—Effect of ammonium chloride on electrodeposited Zn-Fe alloys containing 3.5% Fe.

Effect of Rotation Speed on the Microstructure of Coatings

Rotation speed does not influence coating morphology so markedly as current density, but its effect is more complex. If the iron content is lower than one wt percent, the deposit grains appear hexagonal, but tend to grow at such points preferentially when there is no agitation. When the rotation speed is 500 rpm, the grains become fine and the coating is compact; when the rotation speed reaches 1500 rpm, some grains have a splinter appearance, as shown in Fig. 6. If the iron content is about four wt percent, the surface structure of the coating is nodular, but tends to grow preferentially at some points when no agitation is employed. The degree of agitation at 500 rpm makes the grains splintery in appearance and, finally, the surface structure becomes nodular but finer, and the coating is compact when the rotation speed reaches 1500 rpm, as shown in Fig. 7. In the deposits of Fig. 8, the iron content is about nine wt percent, and the effect of rotation speed on coating structure is nearly the same as in Fig. 7, but in this situation, no level of agitation (e.g., up to 1500 rpm) makes the deposit grain structure finer. Another situation can be seen in Fig. 9, where the iron content being about 12 wt percent, the crystal structure appears splintery and is finest when the rotation speed is 50 rpm. It can be concluded, therefore, that high rotation speeds lead to better coating crystal morphologies if the iron content is below 10 wt percent, and low rotation speed is better for coatings with iron content greater than 11 wt percent.

Effect of Ammonium Chloride Additions

Some effects of ammonium chloride on the microstructure of coatings have been mentioned.11 Ammonium chloride appears to make the deposit grain size smaller and the coatings more even and compact. From Fig. 10, it can be seen that the grains in the coating deposited from an ammonium chloridecontaining solution are fine, but the coating from the solution without ammonium chloride is uneven when the iron content is high (>40 wt pct). When the iron content is between 5 and 40 wt percent, the influence of ammonium chloride is not very clear; the grains of the coatings from the ammonium chloride-containing solution are finer, but some of the crystal structure is splintery. The crystal structure of the coating from the solution without ammonium chloride is nodular, and both these situations can be seen in Fig. 11. When the iron content is lower, the ammonium chloride may be able to disrupt zinc hydroxide films on the surface, as suggested by Fig. 12. Ammonium chloride is recommended, therefore, as an addition to solutions for zinc -iron alloy electrodeposition. At the same time, it must be noted that it is difficult to obtain a very low (< 5 wt pct) or very high (> 80 wt pct) iron content



Fig. 13—Microstructure of uneven electrodeposits of Zn-Fe alloys.

zinc-iron alloy coating from the chloride solution with ammonium chloride, when the ratio of $[Fe^{+2}]/{[Fe^{+2}] + [Zn^{+2}]}$ in the solution is 0.5.

Effect of Other Process Factors

During this investigation, a potentiostat was used to supply a well-controlled, definable current. On some occasions, coatings with nodular outcrops were obtained, as shown in Fig. 13. Although the real accuracy of the compositions quoted is ± 0.5 percent, more accurate values are given as a result of averaging several measurements and to indicate differences and trends. The composition at the apex of these structures was found to be different from the composition of the whole coating. For example, the iron content was 54 wt percent on the outcrop apex of A (iron content was 57 wt percent for the rest of the deposit) and the iron content was 60 wt percent on the outcrop apex of B, while iron content was 84 wt percent for the overall deposit. This is a typical incipient dendritic growth phenomenon and can be controlled through the use of ammonium chloride, which then makes the coating smoother with, consequently, fewer incipient peaks to take the residual current.

Findings

- 1. For the coatings of Zn-Fe alloy electrodeposited from a chloride solution, the surface morphology is fine and compact when the iron content is below one wt percent, or between 15 and 75 wt percent. The structure of the coatings changed correspondingly with the composition changes.
- 2. Current density has the greatest influence on the microstructure of Zn-Fe alloy coatings. High current density makes the coatings less compact, low current density makes them more compact, especially when the iron content is low. When the iron content is higher than 10 wt percent, however, the coatings are more compact and the current density has relatively little effect.
- 3. Agitation has a less direct influence on the microstructure of Zn-Fe alloy coatings. In general, a high rotation speed is better for the coating with an iron content below 10 wt percent, while a low rotation speed is better for the coatings with an iron content higher than 11 wt percent.
- 4. Ammonium chloride additions to the solution, ostensibly as a "conductivity salt," have a great effect on the microstructure of the coatings, leading to finer grains and more level coatings.

Editor's note: This paper is the second of a series of three devoted to the study of Zn-Fe alloy deposition. The first paper appeared in P&SF in March 1998, p. 60. Manuscript received, July 1997.

RUY2KOK[™]? Are You Year 2000 [Y2K] OK?

Plating Shop Owners & Managers: Do you have complete control over your millennium computing problems? Are you absolutely positive? AESF is joint-venturing with CWE2 in a new course that will help your shop be able to identify,



evaluate and overcome its Year 2000 risks.

Background

Since the days when programmers had to fit all their data on tiny little 80-character punchcards, they've used dates in the format of 10/12/96 or MM/DD/YY. Using two extra valuable characters for the "19" didn't make sense. Everyone—including machines—just asumed a "19" in front of the two-digit year, and we knew what it meant. But now, on the eve of the 21st century, we have a problem. All those computer records, computers and programs aren't set up to handle "20" instead of "19."

The problem isn't limited to your mainframes. Most PCs shipped through the last quarter of 1997 do not understand 2000 and will have to be reconfigured. Embedded systems (HVAC systems, process control systems, alarm systems and other date-sensitive, purpose-built systems) may only have been programmed to understand "19."

Two examples: (1) If your credit card has an expiration date of 06/02, we humans know that doesn't mean it expired in 1902. But it you run it through an older credit card system (a machine), that is precisely what may happen. The machine will think your card has been expired for 98 years. (2) Your accounts receivable system might get very confused about the aging of your receivables. Your accounts payable system might pay your bills way too early.

What's the Answer?

There are no "silver bullets," and the solutions aren't going to be easy. The only solution is planning, and the thorough review and repair of your systems.

Course Outline

Day 1—Focus on the problem generically (the technical nature of the problem and the operational, legal and financial risks if your company doesn't address the issue); day 2—focus on problems specific to the surface finishing industry.

Ready for Action

At the completion of the course, you'll be armed with a plan template, an inventory of potential risks, suggested letters for suppliers, and plenty of knowledge to get your company ready to take action. You'll walk out the door with an action plan to implement as soon as you get back to your company.

For more information call the AESF Educational Services at 407/281-6441

Acknowledgments

The first-named author thanks the British Council for the award of a post-doctoral visiting fellowship at Loughborough University. This study was undertaken as part of the EC-funded Brite-Euram program (BRE2-CT94-0608).

References

- T. Adaniya, M. Saiyama & T. Honma, *Nippon Kokan Giho*, **82**, 105 (1984).
- 2. K. Kondo, Kagaku Kogaku, 10, 773 (1994).
- 3. N. Miura et al., Trans. Iron Steel Inst. Jpn., 23, 913 (1983).
- 4. T. Hara et al., ibid., 23, 954, (1983).
- 5. A.R. Fajardo, R. Winand, A. Weymeersch & L. Renard, Fundamental Aspects of Zn-Fe Alloy Electrodeposition, unpublished report.
- 6. T. Adaniya, T. Hara, M. Sagiyama, T. Homa & T. Watanabe, Plat. and Surf. Fin., **72**, 52 (Aug. 1985).
- 7. M. Gu, M.R. Notis & A.R. Marder, *Metallurgical Trans. A*, **22**, 1737 (1991).
- 8. K. Kondo, T. Murakami & K. Shinohara, *J. Electrochem. Soc.*, **143**, 75 (1996).
- 9. D.R. Gabe, Electrochim. Acta, 39, 1115 (1994).
- 10. M.R. Kalantary, G.D. Wilcox & D.R. Gabe, *ibid.*, **40**, 1609 (1995).
- 11. Y. Liao, D.R. Gabe & G.D. Wilcox, *Plat. and Surf. Fin.* (to be published) 1998.

About the Authors



Dr. Owen Yongzhong Liao was educated in China and was a lecturer in electrochemistry at the South China University of Technology, Guangzhou. After a sabbatical year at Loughborough University with Dr. Gabe, he has moved to Canada to work in surface finishing.



Dr. D.R. Gabe* is director of the Institute of Polymer and Materials Engineering at Loughborough (England) University of Technology, where he directs a substantial and diversified effort in metal finishing. He is a graduate of the University of Wales (Cardiff) and received a PhD from the University of Sheffield, England.



Dr. Geoffrey. D. Wilcox is a lecturer in Materials Engineering at Loughborough University. His research interests center on surface modification of materials, including electrodeposition processes, conversion coating treatments and corrosion processes. He holds a BSc from Nottingham University and a PhD from Loughborough University.

* To whom correspondence should be addressed.