A study has been made of the zinc-iron alloy electrodeposition system, using chloride solutions, to establish the composition dependence upon the deposition parameters of current density and agitation achieved by rotation of cylindrical cathodes. It is shown that a deposit composition of approximately 10 to 80 percent iron in zinc can be consistently obtained, thereby enabling two layer deposits to be obtained from a single solution by varying these two parameters. Additions of ammonium chloride act not only as conductivity salts, but as deposit grain refiners.

Zn-Fe alloy plating has been studied as a corrosion-resistant coating since 1911, when Cowper-Coles applied for the first patent. Salt applied for a second patent for electrodeposition of zinc-iron alloys in 1953 and in 1955, Jepson, Salt and their colleagues described an electroplating process for a Zn-Fe alloy in both chloride and sulfate baths. They also assessed the corrosion resistance of the Zn-Fe alloy coatings with different zinc contents. Later, Tripathi and Udupa studied the electrodeposition of zinc-iron alloy with rotating cathodes and explored the relationship of composition with current density and rotational agitation in a sulfate bath.

In more recent years, research on Zn-Fe alloy electrodeposition became more substantial. Fajardo and his colleagues reported much work on fundamental aspects of Zn-Fe alloy electrodeposition, including the influence of process parameters on alloy composition, current efficiency and micro-structure of the coatings. Sagiymama and his colleagues explored the effects of plating variables relating to mass transfer on the composition of electrodeposited Zn-Fe alloys in continuous strip plating. Further, Faucheu studied the electrodeposition of Zn-Fe alloy by pulsed current. Other factors that influence the electrodeposited coatings of Zn-Fe alloy have also been investigated. To date, some zinc-iron alloy plating processes have been used industrially.

More recent research has shown that multilayer coatings of Zn-Fe alloys with different composition may perform much better as corrosion-resistant coatings than equivalent single layers. Adaniya and his colleagues studied zinc-iron alloy electroplating on strip steel and obtained the result that a zinc alloy containing 15 to 25 percent iron has good weldability, workability and corrosion resistance, and zinc alloy deposits containing 50 percent or more iron provide better paintability after phosphating; therefore, a coating with a thin layer of iron-rich zinc over a thicker layer of zinc-rich iron alloy was recommended. Kojima et al. concluded that no single layer of Zn-Fe alloy coating can meet the requirements for automotive use, and that steel sheets with a two-layer Zn-Fe alloy electrodeposit that consists of a thin upper layer with a 75 to 85 percent Fe content and a lower layer with a 10 to 20 percent Fe content are the preferred choices. The development of multilayered coatings of composition-modulated alloys may well be a possible means of enhancing performance, as pointed out by Gabe among others. To produce such layers in a single solution by varying non-chemical process parameters would be ideal and cost-effective, and Kalantary et al. have reported research in this field with Zn-Ni alloy coatings.

In Zn-Fe alloy electroplating, there are several parameters that influence the composition of coatings, including: zinc/iron ratio, temperature, current density, agitation, pH and the concentration of other additives. Here, current density, agitation and temperature are non-chemical process parameters,

![Fig. 1—Coating thickness distribution on the Rotating Cylinder Electrode (RCE). Theoretical values calculated from Eq. (1).](image1)

![Fig. 2—Iron content (wt pct) in Zn-Fe alloys vs. current density at various RCE rotation speeds for a bath without ammonium chloride.](image2)
temperature changes being less feasible in practice. Current density and agitation, therefore, have been adopted as the two main parameters for controlling multilayer coatings of composition-modulated alloys.

The object of the current study is to establish the relationship between composition with current density and agitation speed in a chloride bath system using a Rotating Cylinder Hull Cell in a single, two-metal-ion bath. The reasons for using these arrangements are as follows: There are generally three types of bath for Zn-Fe alloy electroplating—alkaline zincate, sulfate, and chloride. An alkaline bath is used to obtain Zn-Fe coatings with a low iron content of about 0.3 to 1.0 percent, which possesses high corrosion resistance after passivation.15 Many commercial Zn-Fe electroplating baths are based on the alkaline system at present and sulfate systems have been widely investigated. The Fe content in the Zn-Fe alloy coating from these solutions can be varied over a large range, but the main problem is that it is only when the ratio of $[\text{Fe}^{2+}]/([\text{Fe}^{2+}]+[\text{Zn}^{2+}])$ in the electrolyte is greater than 0.4 that a Zn-Fe alloy coating can be effectively electrodeposited, so the concentration of Fe$^{2+}$ in solution must be controlled at a high level.16 Moreover, the Fe content of Zn-Fe alloy deposits is related to cathode current density for this bath. It changes sharply in a narrow current density range. The current efficiency for this bath is also low. The chloride system has an advantage in this change of Fe content of Zn-Fe alloy coating with current density and in the cathode current efficiency value, resulting from higher salt solubility. The Fe content of Zn-Fe coating for a chloride system is sensitive to agitation. Accordingly, the chloride system is more suitable for multilayer composition-modulated electrodeposits in a single bath process, as current density and agitation can be more fully utilized as the two convenient controlling parameters.

One type of Rotating Cylinder Hull Cell (RCHC) has been designed by Madore and Landolt.17 Its advantage is that the primary current distribution closely resembles that of the classical Hull Cell, and the rotation speed (i.e., degree of agitation) is under full control. It is thought, therefore, that it is convenient for the study of electroplating with current density and agitation as the main influencing factors.

The simulated primary current distribution for the RCHC is described by the following expression:17

$$i(z) = \frac{(0.535 - 0.458 z)}{(0.0233 + z^2)^{1/2}} + 8.52 \times 10^{-3} \exp(7.17z)$$

(1)

where $z$ is the dimensionless distance along the cathode from the lowest current density side, $i(z)$ is the current density along the cylinder cathode at point $z$ and $i_{avg}$ is the applied current density. Because this current distribution is fundamental for this investigation, it was first checked by the method of Holmbom.18 The results are shown in Fig. 1, which confirms that the Rotating Hull Cell gives a deposition thickness distribution (Ni electrodeposition) that agrees well with that predicted by the primary distribution formula. Note that Eq. (1) presumes that the cathode current efficiency (CCE) is always 100 percent. From Fig. 1, it can be seen that when the current efficiency is considered (the greater the current density, the lower the current efficiency), the agreement is better. (The method devised by Holmbom is based on a modified Watts nickel solution designed to operate approaching 100 percent current efficiency. The operating conditions included temperature of 61 °C; 2, 2.6, and 3.0 A plating current; one and five min time; and 500 and 1000 rpm rotation speed.)

### Experimental Procedure

Copper foil of thickness 0.034 mm and purity 99.95 percent was used as the substrate material. It covered the cathode of the RCHC as a cylindrical sleeve with an effective area of 28.3 cm$^2$. After being pickled in 10-percent v/v sulfuric acid for two min, it was washed with water and dried in acetone. Subsequently, electrodeposition trials were performed galvanostatically on the cylinder at 50 °C in a solution containing 0.8 mol/L iron as ferrous chloride, and 0.8 mol/L zinc as zinc chloride, with pH 3. Electroplating was carried out at 0, 50, 100, 500, 1000, and 1500 rev/min (rpm) and at average current densities of 1 A/dm$^2$ and 9 A/dm$^2$. The current densities of each point mea-
sured were calculated by Eq. (1). A cylindrical zinc foil was used as the anode. Solutions with and without ammonium chloride at 100 g/L concentration 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. The calibration employed standards, and the resulting accuracy is probably ±0.2 percent at best. The analytical data have been used to identify trends rather than establish definitive compositional values.

The current efficiency data were obtained by weighing the samples before and after plating, when the samples were electroplated at a certain current density on the whole cylinder. To do this, the insulating separator in the container of the RCHC was removed.

**Results & Discussion**

**Relationship between Composition of Coating and Current Density**

The relationship between the composition of the coating and the current density (indispensable for design and control of multilayered coatings of composition-modulated alloys in a single bath), was established using a Rotating Hull Cell. The compositions of the coating were measured by EDX; the relationships between coating composition and current density at different rotation speeds and for different solutions were derived and are shown in Figs. 2-5. The large changes in composition seen at low current densities in Figs. 2 and 4 are believed real; their effect is to make practical exploitation at low current densities impractical.

From these results, it can be seen that the concentration of iron in the coatings increases with plating current density throughout almost the whole range studied. The change of composition is very wide, from about one percent Fe to about 78 percent in the solution without ammonium chloride addition, and from about two percent Fe to about 75 percent in the solution with ammonium chloride added, when the current density was altered from 0.15 A/dm² to 30 A/dm². In the solution containing ammonium chloride, however, the iron content in the coating decreases with current density when the current density is below 3.5 A/dm². It can also be seen that when rotation speed increases, the concentration of iron in the coating tends to be small and changes more slowly as the current density increases.

Normally, increase in current density will lead to a higher pH near the cathode because of hydrogen evolution and hydrogen ion depletion; zinc hydroxide precipitation becomes a possibility as well. A zinc hydroxide film on the electrode will be a barrier to the deposition of the more noble iron, whereas zinc could be readily deposited from it. (Evidence for this film, which has been observe with thicknesses in the range 0.1 to 1 µm will be presented elsewhere.¹⁹) Agitation would normally help the relatively noble iron to be deposited, because it is more likely to be mass-transfer-controlled as the more noble metal; this would make Fe⁺² concentrations near the cathode lower. The opposite effect is obtained, which requires some explanation.

The standard electrode potential of iron E⁰(Fe⁺²/Fe) is -0.440 V vs. SHE and that of zinc E⁰(Zn⁺²/Zn) is -0.763 V vs. SHE. Because there is a relatively large overpotential for Fe⁺² to deposit, and there is precipitation of zinc hydroxide during plating to hinder deposition of Fe, the concentration of zinc in the alloy coatings is larger than in the plating solution, this is called anomalous codeposition. It is not always this way, however. Some other factors that influence the movement of Zn⁺² and Fe⁺² in solution can change anomalous codeposition to normal codeposition. When the current density is very low, no zinc hydroxide forms on or near the surface of the cathode, but when the current density is higher, a zinc hydroxide layer is formed that can act as a barrier to the deposition of iron. In this situation, however, high speed agitation can sometimes remove or reduce the barrier film, as may certain chemicals in the bath (e.g., ammonium chloride), and the effect of these then aids the deposition of iron; this will be further discussed later.

When the current density is raised, the deposition rate of zinc becomes much higher, and the zinc hydroxide film may

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Fig. 5—Iron content (wt pct) in Zn-Fe alloys vs. current density at various RCE rotation speeds for a bath with ammonium chloride.

Fig. 6—Iron content (wt pct) in Zn-Fe alloy vs. rotation speed at various current densities for a bath without ammonium chloride.
be disrupted. In these circumstances, hydroxide ions migrate too slowly to form a new layer, whereupon iron deposits on the cathode more rapidly, because deposition of the iron ions is also accelerated by higher current density. At this step, the relative diffusion of zinc or zincate ions and iron ions is the dominating factor. Agitation, however, may also help movement of zinc ions and formation of a new zinc hydroxide layer which, when formed or reformed, slows the deposition of iron. If the agitation/rotation speed is not too high, ammonium chloride can reduce the formation of zinc hydroxide and zinc ions can move more quickly, which also helps zinc deposition. At high levels of current density and rotation speed, the system is dominated by the latter and the deposits then reach a certain composition with zinc richer than iron.

Relationship between Coating Composition and Rotation Speed

The relationship between coating composition and rotation speed must also be understood for the design of multilayered coatings of composition-modulated alloys. Using the Rotating Cylinder Hull Cell, rotation speeds of 0, 50, 100, 500, 1000, and 1500 rpm were employed and data obtained to establish the relationship of the Fe percentage to rotation speed in the Zn-Fe alloy coatings (Figs. 6-9).

From the results, it can be observed that rotation speed markedly influences the composition of the coating. Iron content falls quickly as rotation speed increases and remains almost unchanged when the rotation speed is above 500 rpm. Moreover, it is clear that when the rotation speed is high enough, the iron content in the coatings reaches a certain value dependent upon bath chemistry and other process parameters, but not current density (this has been explained above). By controlling the rotation speed, therefore, the coatings with low iron content (< 10 %) and high iron content (> 60 %) can be electroplated in the single bath with assured consistency.

Influence of Conductivity Salts

In this investigation, ammonium chloride was used as a conductive salt. It also tends to raise the iron content of the electrodeposits when the current density is low or the rotation speed is high (i.e., it disrupts films of zinc hydroxide), but not when the current density is high (reducing the formation of zinc hydroxide films, which aids both Zn$^{2+}$ and Fe$^{2+}$ diffusion and deposition, although not necessarily to the same extent). Addition of ammonium chloride changes the pattern of composition dependence on current density employed, and when the current is above 3.5 A/dm$^2$ and the rotation speed low, the dependence is linear for 6.6 to 74 percent Fe. In practical terms, ammonium chloride can raise the iron content when it is in a low range, and reduce the iron content when it is at a high level, and it narrows the composition range in which iron is obtained. It also accentuates the trend for the iron.

![Fig. 7](image1)

**Fig. 7**—Iron content (wt pct) in Zn-Fe alloy vs. rotation speed at various current densities for bath without ammonium chloride.

![Fig. 8](image2)

**Fig. 8**—Iron content (wt pct) in Zn-Fe alloy vs. rotation speed at various current densities for a bath with ammonium chloride.

![Fig. 9](image3)

**Fig. 9**—Iron content (wt pct) in Zn-Fe alloy vs. rotation speed at various current densities for a bath with ammonium chloride.
content in the coating to go in the opposite direction of current density when the current density is below 3.5 A/dm², which is unfavorable for composition control by current density. An analogous approach has recently been offered by Yan et al. for lamination deposits of Zn-Co alloys in which hydroxide formation was suggested to explain current oscillations during deposition. In this case, however, a sulfate solution was employed in which the formation of a “passive” hydroxide film is more likely. With chloride-based solutions such passivity is unlikely in most circumstances.

Current Efficiency
Current efficiency is, of course, important for energy saving and a hazard when low for high tensile steels, through hydrogen embrittlement tendencies; it also affects the thickness control of each layer in multilayer plating. The current efficiency data were obtained by weighing samples before and after plating, and trends were examined with respect to composition of the coating and current used. The current efficiencies were more than 90 percent in the whole range researched. They decreased very slowly from 98 to 93 percent when current density changed from 0.15 to 30 A/dm². Rotation speed had little effect on the current efficiency, as did the ammonium chloride addition.

Surface Morphology
Morphological studies of the Zn-Fe alloy electrodeposited samples, using the two solutions both with and without ammonium chloride, are illustrated in Figs. 10 and 11. They show the structure of coatings with current density and rotation speed as variables. From Fig. 10, it can be seen that some of the precipitate film adheres to the surface of the coatings when the current density is below 1 A/dm² and the rotation speed is below 100 rpm. This supports the suggestion above that zinc hydroxide may be forming near the surface of the cathode. It can also be seen that, when the rotation speed is greater than 500 rpm, some zinc hydroxide adheres to the surface only when the current density is between 1 A/dm² and 5 A/dm², which explains the observation that rotation speed can help removal of zinc hydroxide, but that it can also destroy the formation of a zinc hydroxide layer when the current density is low.

By comparing Figs. 10 and 11, it can be seen that ammonium chloride in the solution has an effect on the structure of the coatings. First, it refines the grain size, although the visual appearance of the coatings may not show the difference. For coatings having a high iron content (plated at high current density and low rotation speed), ammonium chloride causes the structure of coatings to be more even.
coatings with a low iron content (plated at low current density in the ammonium chloride bath), the grains have a splintered appearance, but the grains of coatings from the bath without ammonium chloride are nodular. Second, there is no gross zinc hydroxide filming on the surface of the coatings in the ammonium chloride bath. This does not mean that there is no zinc hydroxide forming near the surface of the cathode during plating, but it does show that ammonium chloride reduces the formation of zinc hydroxide, which explains why the ammonium chloride causes an increase in iron content of the electrodeposits at a low level, or that ammonium chloride makes it easier to remove zinc hydroxide completely from the surface after plating. Accordingly, ammonium chloride in the solution can improve the quality of coatings.

Current density, besides strongly influencing the composition of the coating, influences the crystal structure as well. When the iron content of the coatings is low (plated at low current density or high rotation speed, or both), high current density tends to lead to some of the crystals appearing as discrete clusters and growing at these points preferentially. As a result, high current density makes the coatings less dense or adherent when the iron content is low. When the iron content is high (> 50%), through plating at a high current density and low rotation speed, the crystal structure of the coatings is compact and the visual appearance is brighter.

Findings
1. A Rotating Cylinder Hull Cell has been shown to be a valuable tool for studying alloy electrodeposition, especially for a system with two process parameters, current density and agitation, considered simultaneously.
2. A chloride solution for electrodeposition of a Zn-Fe alloy should be suitable for the production of multilayer coatings or composition-modulated alloys, because the composition of coatings produced using this system can be changed over a large range by varying the current density and agitation. The current efficiency of this system is greater than 90 percent.
3. Ammonium chloride additions (“conductivity salt”) to the solution narrow the range of coating composition, but improve the coating quality. Use of this “conductivity salt” must, therefore, be related to specific composition requirements.
4. The relationship between composition of coatings and current density has been clearly defined:
   (a) in a bath without ammonium chloride, when the rotation speed is zero, the iron content in the coatings increases, as current density increases, from 1.5 to 7.6 wt pct when the current density is between 0.18 and 10 A/dm², then more rapidly, but nearly linearly to 78.3 wt pct when the current density reaches 30 A/dm².

Fig. 11—Crystal morphology of Zn-Fe alloy electrodeposits from a solution with additions of ammonium chloride.
(b) in a bath with ammonium chloride present, the iron content in the coatings changes randomly when the current density is below 3.5 A/dm², but generally tends to decrease. When the current density is between 3.5 and 30 A/dm² and the rotation speed is zero, it increases as current density increases, almost linearly from 6.6 to 74.4 wt pct.

5. Rotation speed reduces the iron content of the coatings sharply as it increases from 0 to 500 rpm. When the rotation speed is greater than 500 rpm, the iron content of the coatings reaches a constant value related to the bath composition and parameters other than current density. This constant value is about 1.5 wt pct in a bath without ammonium chloride, and 5.0 wt pct in a bath with ammonium chloride additions.

6. Finally, it is clear that it is feasible to electroplate a coating of Zn-Fe alloy with composition changing from 1.5 to 78.3 wt pct Fe in a single bath without ammonium chloride, or from 5.0 to 74.4 wt pct Fe in a single bath with ammonium chloride additions, by controlling only the two convenient process parameters, current density and agitation. This makes production of multilayered coatings feasible.

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