### Characterization of Zn-Ni Alloy Deposits

By V. Ravindran, R.M. Krishnan and V.S. Muralidharan

Zinc-nickel alloys of varying zinc content were deposited from a sulfamate bath. The deposits were characterized by microhardness, surface morphology and surface structure. The predominant phase found in the deposit was Ni<sub>3</sub>Zn<sub>22</sub>, plus Zn(OH)<sub>2</sub>. The inclusion of Zn(OH)<sub>2</sub> caused an enormous increase in microhardness.

Scarcity and cost of cadmium at the close of World War II led to the development of alloy coatings. The growth of the other commercially used zinc alloys (*i.e.*, nickel-zinc, iron-zinc, and cobalt-zinc) are a result of one factor: the enhancement of the corrosion resistance of the deposit. There has been considerable study of sulfate baths, with and without sulfamate. Sulfate baths with pH 4 have been used at 50 °C.<sup>1</sup> Gamma-phase Ni-Zn deposits were obtained when the Zn/Ni mole ratio in the bath was kept between 2 and 3 in a sulfate bath at pH 1.5 to 2.5.<sup>2</sup> Also known are an ammoniacal sulfate bath,<sup>3</sup> a boric acid sulfate bath,<sup>4</sup> an alkaline sulfate bath,<sup>5</sup> and a mixed sulfate/sulfamate bath.<sup>6</sup> A sulfamate bath has been developed, and the characteristics of the Zn-Ni alloy electrodeposits obtained using the bath have been studied, with the results presented here.

#### **Experimental Procedure**

Cold-rolled steel plates (10 x 7.5 x 0.1 cm) were degreased with trichloroethylene and electrocleaned cathodically for 2 min in an alkaline solution composed of 35 g/L NaOH and 25 g/L Na<sub>2</sub>CO<sub>3</sub>, at 80 °C. The plates were washed in running water, followed by a dip for 10 sec in 5-percent  $H_2SO_4$  solution, with subsequent thorough washing and drying.

The plates were electrodeposited with Zn-Ni alloy from a sulfamate bath. The deposits were removed chemically by immersion in 1:1 HNO<sub>3</sub>, and the resulting solutions containing zinc and nickel were analyzed. The zinc content was analyzed both volumetrically and by atomic absorption spectra (AAS).

A modified procedure was followed for the analysis of zinc. In the solution containing the alloy deposits, 25-percent KCN was added to mask Ni<sup>+2</sup> ions; then, addition of HCHO

Table 1 XRD Parameters for Electrodeposit without $NH_4Cl$					
No	<b>2</b> 0	d	I	$\mathbf{I}/\mathbf{I}_0$	
1.	36.700	2.447	201	13	
2.	38.500	2.336	420	28	
3.	43.000	2.102	1495	10	
4.	54.700	1.172	170	11	
5.	69.000	1.345	235	16	
6.	82.200	1.172	242	15	

aided in release of zinc ions. The solution was titrated against EDTA for zinc ions, using Eriochrome Black T as the indicator. The pH of the solution was adjusted to 10 with  $NH_4OH$  and  $NH_4Cl$ . A change in the color of the solution from pink to blue was taken as the end point.

Microhardness of the deposits was measured using a microhardness meter, with a diamond pyramid of square base, and with an angle of  $136^{\circ}$  at the vertex between the two opposite faces, yielding the microhardness of the deposit in kg/mm<sup>2</sup>. The surface structure of the deposits was followed using an X-ray diffractometer (Cu-K $\alpha$  radiation). The surface morphology was investigated at 5000X magnification with a scanning electron microscope.

#### Bath Composition

Zinc sulfamate, 0.1 to 0.9 M + nickel sulfamate, 0.9 M to 0.1 M (5 compositions) and boric acid, 0.84 M.

#### Additives

Beta-naphthol, 3 x  $10^{-3}$  M; sodium lauryl sulfate, 3 x  $10^{-3}$  M, and NH<sub>4</sub>Cl, 1.12 M.



Fig. 1-XRD pattern for Zn-Ni deposit without NH<sub>4</sub>Cl.



Fig. 2—XRD pattern for Zn-Ni deposit with NH<sub>4</sub>Cl.



Fig. 3—SEM photo for Zn-Ni alloy deposit at 1 A/dm<sup>2</sup>, without additives. 5000X.



Fig. 4—SEM photo for Zn-Ni alloy deposit at 1 A/dm<sup>2</sup>, with additives. 5000X.



Fig. 5—SEM photo for Zn-Ni alloy deposit with 80 percent zinc. 5000X.



Fig. 6—SEM Micrograph for Zn-Ni alloy deposit with 85 percent zinc. 5000X.



Fig. 7—SEM Micrograph for Zn-Ni alloy deposit with 90 percent zinc. 5000X.

#### Results

Adhesion of the Zn-Ni deposits obtained from the sulfamate bath was tested by subjecting the plated specimens to standard bend tests; the coating neither cracked nor peeled. A ferroxyl test to show the presence or absence of pores in the deposits did not reveal any blue spots on deposits above 6  $\mu$ m thickness, thereby indicating that above that thickness, the deposits were non-porous.

Zn-Ni electrodeposits obtained under varying conditions were examined for their structure using an X-ray diffractometer. Tables 1 and 2 list the XRD parameters of different Zn-Ni deposits. Figures 1 and 2 show the XRD patterns obtained for the various Zn-Ni deposits. The predominance of delta-Ni<sub>3</sub>Zn<sub>22</sub> phases, and the inclusion of Zn(OH)<sub>2</sub> are observed. The deposits obtained from plating baths containing NH<sub>4</sub>Cl indicated inclusions of ZnCl<sub>2</sub>· 3NH<sub>4</sub>Cl along with Zn(OH)<sub>2</sub>.

Table 3 shows the influence of 60 g/L  $NH_4Cl$  on the microhardness of Zn-Ni deposits. Addition of  $NH_4Cl$  to the sulfamate bath resulted in increased hardness, and increased zinc content of the alloy.

When viewed at 5000X magnification in the scanning electron microscope, the deposit obtained at 1 A/dm<sup>2</sup> current density from a bath composed of 0.5 M zinc sulfamate (128.6 g/L) + 0.5 M nickel sulfamate (125.5 g/L) and 0.84 M boric acid (50 g/L), the surface exhibited sparse coverage of polycrystallites displaying voids (Fig. 3). The introduction of  $\beta$ -naphthol and sodium lauryl sulfate helped in the leveling and complete coverage of the surface; the growth of spherical

crystallites covered the entire surface, thereby giving it a uniform appearance (Fig. 4).

Introduction of  $NH_4Cl$  in the sulfamate bath resulted in interesting features in the nature of the deposits. When viewed at 5000X magnification, the surface exhibited spherically shaped crystallites separated from one another, with zinc-nickel nucleation at the peripheries (Fig. 5).

An increase of zinc content in the deposit showed that the surface, already covered, was further enriched with more such crystallites (Fig. 6). Finally, an electrodeposit with high zinc content exhibited massive agglomeration of the zincrich alloy, covering almost the entire surface (Fig. 7).

#### Discussion

Electron probe microanalyses on the Zn-Ni electrodeposits obtained from the sulfate bath<sup>7</sup> showed that nickel and zinc were homogeneously distributed, without evidence of any segregation. Of the five alloy compositions identified,<sup>8</sup> it was found that the beta phase was not deposited. The delta phase was suspected in some deposits that also contained either the gamma or the beta phase, but was not observed alone. The reason for non-deposition of the beta phase is that the energy of formation of the beta lattice is greater than that for the gamma lattice, resulting in a more negative deposition potential for the beta phase. Earlier, the delta phase was not observed. In this study, the deposits obtained from sulfamate baths, with and without NH<sub>4</sub>Cl, exhibited the presence of delta-Ni<sub>3</sub>Zn<sub>22</sub> and Zn(OH)<sub>2</sub>, along with ZnCl<sub>2</sub>· 3NH<sub>4</sub>Cl.

XRD	Param	neters for	Electro	deposit	: with NH <sub>4</sub> Cl
	No.	20	d	I	I/I <sub>0</sub>
	1.	36.700	2.447	666	36
	2.	39.300	2.291	457	25
	3.	43.500	2.079	1845	100
	4.	54.700	1.677	293	16
	5.	70.700	1.331	392	21
	6.	82.500	1.168	263	14

Table 2

## Table 3Microhardness & Zinc Content (%)Of Various Zn-Ni Electrodeposits

Effect of addition of NH <sub>4</sub> Cl (60 g/L)					
Sulfamate Bath	e Bath   Zinc in the Alloy		Microhardness		
Composition	%	%		(kg/mm <sup>2</sup> ) ±0.5	
	without	with	without	with	
	NH₄Cl	NH₄Cl	NH <sub>4</sub> Cl	NH₄Cl	
0.1 M Ni + 0.9 M Zn	71.0	81.0	64.7	74.0	
0.25 M Ni + 0.75 M Zn	77.0	88.0	66.0	75.0	
0.50 M Ni + 0.50 M Zn	65.0	82.0	67.9	76.7	
0.75 M Ni + 0.25 M Zn 78.0		90.0	69.4	86.4	
0.90 M Ni + 0.10 M Ni	68.0	80.0	80.5	125.7	
Other bath components:					
Boric acid		0.84M	pH 5.5		
Beta-naphthol		3 x 10 <sup>-3</sup> N	1		
Sodium lauryl sulfate		3 x 10 <sup>-3</sup> M			
Current density		1 A/dm <sup>2</sup> , stirring			
Temp		30 °C			
0.1 M Ni + 0.9 M Zn 0.25 M Ni + 0.75 M Zn 0.50 M Ni + 0.50 M Zn 0.75 M Ni + 0.25 M Zn 0.90 M Ni + 0.10 M Ni Other bath components Boric acid Beta-napht Sodium lau Current de Temp	NH4Cl 71.0 77.0 65.0 78.0 68.0 : hol uryl sulfate nsity	NH <sub>4</sub> Cl 81.0 88.0 82.0 90.0 80.0 0.84M 3 x 10 <sup>-3</sup> N 3 x 10 <sup>-3</sup> N 1 A/dm <sup>2</sup> , 30 °C	NH 4Cl 64.7 66.0 67.9 69.4 80.5 pH 5.5 4 4 stirring	NH Cl 74.0 75.0 76.7 86.4 125.7	

In the deposition of Ni-Zn alloy, the predominant presence of zinc is a result of anomalous codeposition. The suppression of Ni<sup>+2</sup> ion discharge began when the hydrogen evolution rate exceeded the diffusion-limited current caused by proton discharge, so that metal hydroxides were formed at the cathode surface. The suppression of nickel discharge results from preferential adsorption of Zn(OH)<sub>2</sub>, as can be seen from the XRD data.

The deposits obtained from the baths containing  $NH_4Cl$  exhibited not only the presence of  $Zn(OH)_2$ , but  $Zn(NH_4)_3Cl_5$  as well;  $Zn(OH)_2$  would have reacted with  $NH_4Cl$ , resulting in the formation of mixed chlorides.

The higher current density and zinc content in the plating bath caused enhanced inclusions of  $Zn(OH)_2$ . These inclusions in the delta  $Ni_3Zn_{22}$  caused an increase in microhardness. The formation of  $ZnCl_2 \cdot 3NH_4Cl$  compounds in the deposits resulted in higher microhardness of the deposits, as compared with those obtained from baths without  $NH_4Cl$  additions.

The hardness values of the deposits obtained are comparable to those obtained earlier. For coatings greater than 8  $\mu$ m thick, the value was not influenced by the substrate. Alloys containing greater than 70 percent nickel had an essentially constant Vickers hardness value of 600. Below 70 percent, with decreasing nickel content, the hardness decreased to about 65 percent for zinc.<sup>4</sup> Somewhat harder deposits (*i.e.*, 150 to 180 Vickers for 5 to 10 percent alloys) were also reported.<sup>9</sup>

#### Conclusions

The zinc-nickel alloy electrodeposits were smooth and welladherent. Increased zinc content caused uniform surface coverage. The alloy was found to include the delta–Ni<sub>3</sub>Zn<sub>22</sub> phase, along with Zn(OH)<sub>2</sub> and ZnCl<sub>2</sub>· 3NH<sub>4</sub>Cl. Inclusions of the zinc compounds caused enhanced microhardness.

To obtain better results, the bath should be operated at 50 °C, with stirring, and should have the following composition:

Zinc sulfamate	0.5 M
Nickel sulfamate	0.5 M
Boric acid	0.84 M
β-naphthol	3 x 10 <sup>-3</sup> M
Sodium lauryl sulfate	3 x 10 <sup>-3</sup> M
NH <sub>4</sub> Cl	1.12 M (60 g/L)

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