Characteristics of Electroplated Zinc Nickel Deposits from Alkaline and Acid Electrolytes

ABSTRACT

Zinc nickel alloys are plated commercially from both acidic and alkaline electrolytes. For rack and barrel operations, alkaline electrolytes have been widely used. Acid zinc nickel electrolytes provide faster plating rates due to high plating efficiencies and utilize soluble nickel anodes allowing a significantly lower operating cost of ownership to the plater. This paper will compare physical properties of zinc nickel deposits obtained from ammonium chloride, potassium chloride, and alkaline electrolytes. Alloy distribution will be compared with a focus on practical applications of the electrolytes.

INTRODUCTION

Zinc nickel deposits can be plated from both alkaline and acid electrolytes. Both systems are commercially viable options for obtaining a 13-15% high alloy corrosion resistant coating. Running the systems in the field at several applications provides information that could be related to many theoretical studies to provide more insight into the complex electrochemical behavior of these electrolytes

Alkaline zinc nickel electroplating processes can be generally described as having uniform brightness, excellent alloy distribution versus current density, and excellent plated thickness distribution versus current density. These attributes make alkaline zinc processes robust and relatively simple to control with a limited set of additives. Cathode efficiencies of alkaline processes typically range from about 40-60% for new solutions and will decrease as the solution is utilized due to accumulation of organic breakdown products as well as the build-up of sodium carbonate. Nickel is typically introduced to the bath and replenished by use of proprietary nickel salt-complexor additives. The low plating efficiency coupled with nickel replenishment from proprietary additives results in a relatively high operating cost for the process. Recently, proprietary insoluble anodes have been used to eliminate the excess breakdown products – with a direct consequence for lowering chemical consumption and limiting the drop in efficiency of alkaline systems. [1]

Acid zinc nickel systems come in several forms. The full ammonium chloride-based electrolyte has been very popular for a decade. The difficulty of removing the nickel-ammonia complexes from wastewater has limited the use of these systems to full closed loop manufacturing. A relatively new type ammonia-free system has entered the market giving a third option to plate the desired deposit. The mild acid systems have cathode efficiencies of about 95%. Nickel for solution make-up comes from commodity nickel salts. Replenishment of nickel can be done with either soluble nickel anodes or commodity nickel salts. The result is a zinc nickel process that is much less expensive than alkaline zinc nickel from a chemical consumption standpoint and allows greater throughput due to the higher cathode efficiency. In addition, acid zinc nickel electrolytes are useful for the direct plating of cast iron, as in the plating of brake calipers. Zinc anodes will chemically dissolve in acid chloride electrolytes causing the zinc to nickel metal ratio to change in time. Dual rectification with separate connections to nickel and zinc anodes has been used to allow use of soluble nickel anodes. The dual rectifier system uses a common cathode (the parts to be plated).

Alloy distribution versus current density in acid zinc nickel processes is dependent on the type of conducting salts used and the presence of a mild complexor. Due to the amphoteric nature of zinc, the zinc will stay in solution at pH>10 as zincate. The hydroxyl anions can be considered as the actual complexor ligands for zinc ions in alkaline solutions. In order to obtain alloy composition required by the automotive industry for optimum corrosion resistance, 12-15% nickel content needs to be uniformly obtained on plated articles. Baldwin, et al [2] have reported that zinc nickel alloys containing greater than 21% nickel no longer provide cathodic protection to steel. From a cosmetic perspective, zinc nickel alloys greater than 21% also produce black deposits from the electrolytes described in this paper.

EXPERIMENTAL and DISCUSSION

Three different acid zinc nickel electrolytes as outlined in Table 1 were studied. All three are used in commercial applications. Electrolyte 1 is based on ammonium chloride. Electrolyte 2 is based on potassium chloride and does not contain ammonia for complexing the nickel. Electrolyte 3 is a compact alkaline system containing amine-based complexors for the nickel.

	Electrolyte 1	Electrolyte 2	Electrolyte 3
	Ammonium Chloride based	Potassium Chloride based	Sodium Hydroxide based
Zn, g/l	32	36	11 g/l
Ni, g/l	25	30	1.2 g/l
NH_4Cl, g/l	253	-	-
KCl, g/l	-	232	-
Ammonium hydroxide, ml/l	60	-	-
Sodium Hydroxide, g/l	-	-	125 g/l
Boric acid, g/l	-	20	-
pH	5.7	5.5	-
Proprietary Additives	60 ml/l	25 ml/l	1.5 ml/l
Proprietary Complexor	-	200-350 ml/l	45 ml/l
Nickel replenishment solution	-	-	16 ml/l

Table 1

Mild steel cathodes, 20 cm x 8 cm, were plated in a 500-ml Tosei plating cell [also called long Hull Cell] with magnetic spin bar agitation for 10 minutes at 2 ampères. Alloy content was measured by x-ray fluorescence on a Seiko Instruments Model SEA 5120 spectrometer. Data was collected at 2 cm intervals from the high current density edge of the panel.

Results from Electrolyte 1, ammonium chloride based electrolyte, are shown in Figure 1.

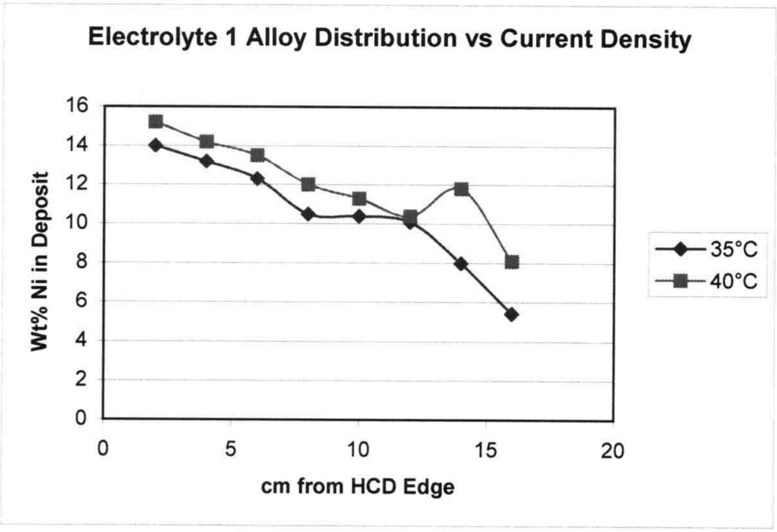

Figure 1

Figure 1 shows anomalous deposition behavior of zinc with iron group elements. Anomalous deposition as defined by Brenner: A deposition where the more electronegative alloying element (in this case Zinc) is favored to the more noble component (Nickel) [3]. As current density decreases, the amount of co-deposited nickel decreases. Increasing solution temperature increases the amount of co-deposited nickel, but does not change the anomalous deposition behavior. From a practical perspective, the areas of the cathode from the high current density edge to about 10 cm from the edge represent current densities on most production plated articles. This allows alloy ranges from 10-15% to be plated that provide desired levels of corrosion protection and are sacrificial to steel.

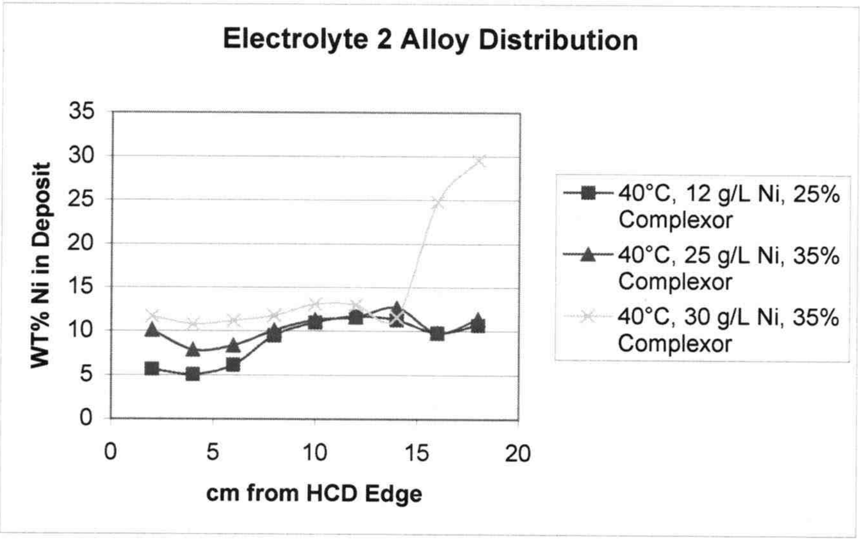

Figure 2

Results from Electrolyte 2 are shown in Figure 2. Electrolyte 2 shows alloy distribution data similar to Electrolyte 1, provided correct (mild) complexor concentration and temperature are maintained. There is a trend to normal deposition (high Ni%) that can be suppressed by increasing complexor. Also increasing Ni can lead to reversion to normal / high Ni% deposition. This effect is made very visible in the graph at 30 g/l Ni.

The concentration of nickel and the concentration of complexor must be controlled at a given temperature to produce alloys with compositions defined for automotive applications without the black, non-sacrificial alloys in the extreme low current density areas. In practice it has been demonstrated that Electrolyte 2 is capable of producing alloys in the 12-14% nickel range in rack plating applications. The ability to produce alloys in the 12-14% nickel range without the black high alloy in low current densities in barrel applications is dependent on article configuration, available current, and agitation.

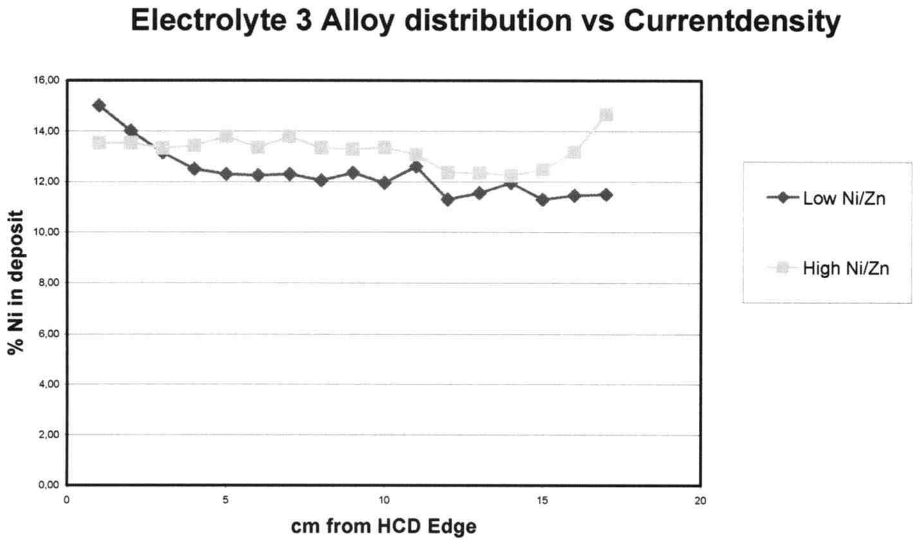

Figure 3

Results from Electrolyte 3, the alkaline Zn/Ni system, are shown in Figure 3. Low Ni/Zn is 1.2-g/l: 8-g/l =0.15; High Ni/Zn is 1.6-g/l : 8-g/l = 0.20.

The relationship with temperature is governed by efficiency and metal distribution. In practical applications temperatures are kept constant at 25°C. The factor determining alloy distribution is mainly the ratio of Nickel to Zinc concentration. Although the alloy distribution is very uniform for alkaline systems – it seems to be very difficult to obtain high nickel %. The anomalous deposition of zinc seems to be very strong. Zinc discharge to metal ions is believed to be kinetically favoured from hydroxyl complexes. Raising the nickel concentration will give a very uniform distribution of 14% without burning effects (sometimes seen with low Ni ratios) – but in the low current density the deposit reverts to normal deposits with high Ni %. For practical use the operating parameters will be adjusted for the current density operating window used in the application (such as barrel versus rack).

If the anomalous deposition is caused by the fast kinetics of the zinc discharge from the hydroxide ligands, the reversion to normal deposition seems to be controlled by a catalytic action of hydrogen. Additive free zinc systems (alkaline and acid) have a typical cup shape in alloy distribution: normal (high Ni%) in the low current densities and high current densities (hydrogen evolution in the HCD) and anomalous (high zinc) in the mid section of current densities.

Measurements made by Muller [4] show that alkaline zinc nickel can contain η -phase zinc nickel (with 6% Ni) a solid solution of nickel in zinc next to the expected γ-phase. The γ-phase in alkaline zinc is highly textured with (330) and (600) reflections. For analyzing the acid electrolytes X-ray diffraction was used to identify the main orientations of the Ni_5Zn_{21}- γ-phase phase. For X-ray diffraction studies, mild steel panels were plated in a conventional hull cell with spin bar agitation at 2 amperes for 10 minutes. Alloy content obtained versus current density is summarized in Table 2. Alloy content and thickness were determined by XRF. XRD data was obtained on a D8 Discover diffractometer with GADDS detector from Bruker Analytical X-Ray Systems, Inc.

		4.0 ASD	**2.0 ASD**	**1.0 ASD**	**0.2 ASD**
Electrolyte 1	**% Ni**	**12.0**	**12.3**	**4.3**	**1.2**
(Ammonium Chloride)	**Thickness, µm**	**13.8**	**7.0**	**4.3**	**1.2**
Electrolyte 2	**% Ni**	**12.1**	**12.2**	**13.4**	**15.5**
(Potassium Chloride & mild complexor)	**Thickness, µm**	**14.3**	**8.2**	**3.8**	**1.1**

Table 2

Figure 4 is a 2Θ scan of zinc nickel alloy obtained from Electrolyte 1. Only γ-phase Ni_5Zn_{21} is present at all current densities. The phase does appear to change with current density, while the texture varies slightly with the current density. Qualitative analysis of the scan indicates the (330) orientation is the only orientation seen at 4 ASD; also (600) orientations start to appear in mid to low current density range.

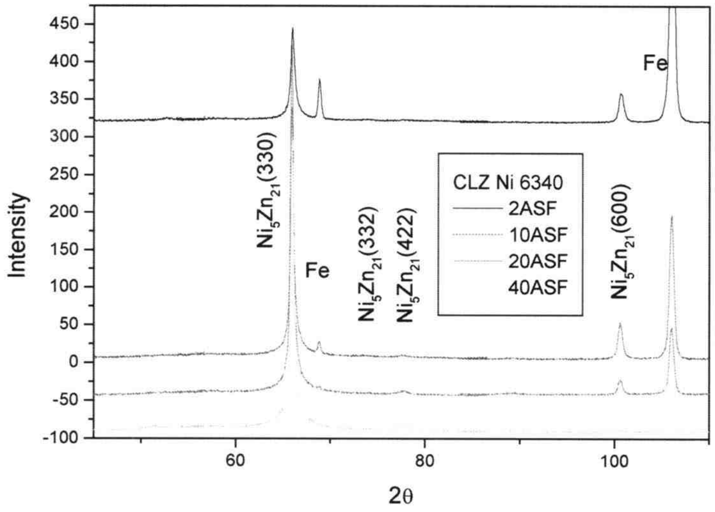

Figure 4

Figure 5 is the 2Θ scan of zinc nickel alloy obtained from Electrolyte 2. Only γ- phase Ni_5Zn_{21} is present at all current densities. However, the texture changes significantly with current density. Qualitative analysis of the scan indicates the (600) orientation is the only orientation seen at 4 ASD. As current density increases (330) orientations start to appear and increase as current density decreases. At 0.2 ASD, the (330) orientation appears to be more dominant than the (600). Deposits from the potassium electrolyte appear to have opposite texture characteristics of deposits obtained from the ammonium chloride electrolyte. The (330) orientation tends to correlate with bendability while the (600) orientation tends to correlate with luster [5], this observation confirms the practical usage of ammonia-free acid Zn/Ni deposits with postforming.

The dark low current density deposits obtained from unbalanced electrolytes and "burned "deposits in high current densities show traces of α-phase deposits (solution of zinc in very rich nickel phase) The presence of this phase is believed to deteriorate the cathodic protection of the coating due to high nobility towards the substrate (mild steel in this case). Avoiding α-phase deposits seems to be the main reason to limit Ni% to 15% average.

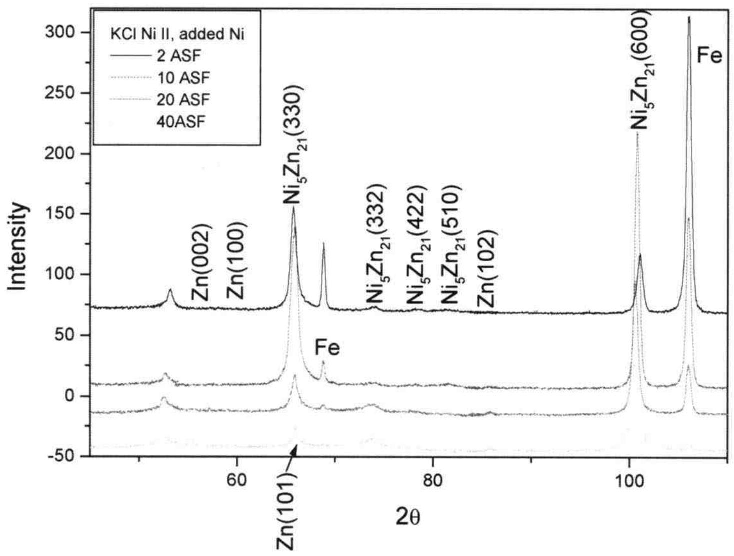

Figure 5

CONCLUSIONS

Zinc nickel deposits produced from acid chloride electrolytes contain γ phase Ni_5Zn_{21} when nickel content is 12-15% by weight. Ammonium chloride electrolytes produce deposits with crystal orientations versus current density that are opposite of that seen with a potassium chloride electrolyte. Ammonium chloride electrolytes will produce alloys with nickel content versus current density distribution that are more favorable for commercial applications. In fact, ammonium chloride zinc nickel baths are in commercial operation in both rack and barrel applications.

However, where there are restrictions on the use of ammonium chloride, commercially viable potassium chloride based electrolytes are available. In order to control the alloy content in extreme low current density areas, a mild complexor is preferred to control the alloy deposition. While mild-complexed potassium chloride processes have been made commercially available, the high nickel content alloy obtained in extreme low current density areas and the narrow temperature operating range require close monitoring. But both processes are fast and can deposit Zn/Ni on difficult substrates such as cast iron.

All three types of electrolytes provide practical solutions for obtaining zinc nickel deposits with the desired properties. With the automotive industry's demand for cost control, a high efficiency zinc nickel electrolyte provides clear advantages. Overall, the final selection must be based on the end user's performance requirements, application, and substrate type.

REFERENCES

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