Non-uniform Microdistribution of Zinc-Nickel Alloy Electrodeposits & Its Effect on the Protective Properties of the Coatings

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The composition of Zn-Ni coatings may be non-uniform on a microscale. With the average Ni content of 12 to 14 %, its total value may vary in the alloy deposited on a microrough surface from 4% on micropeaks up to more than 20% in microrecesses. These variations result in appreciably decreased protective action of the coating. Bath composition and plating conditions are recommended that minimize local variations in the composition of the coatings and allow the improvement of their protective values.

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Introduction

Non-uniform distribution of electrodeposited individual metals and alloys both on macro- and microscales may play an important role in various plating processes. Appreciable local variations in the coating thickness usually produce negative effect on the protective properties of the coatings.

In case of an alloy a nonuniformity in its composition apart from variations in the thickness may also be of importance [1,2,3,4,5].

Variations in the plate thickness and in the composition of an alloy over the surface of shaped parts are usually related with insufficient throwing power.

On the other hand nonuniform distribution of local thickness' and alloys composition on a microscale is related with the decisive role of mass-transport processes in the kinetics of the cathodic reactions [6].

Codeposition of zinc with iron-group metals is an example of an "abnormal" electrodeposition process.

Zinc content in the alloy is much higher than relative concentration of zinc ions in the solution due to preferential discharge of more electronegative zinc ions.

Preferential discharge of zinc ions in a combination with mass-transport limitations may be the cause for higher codeposition rate of zinc on micropeaks.

In the present paper the microdistribution of Zn-Ni alloy and its components over a microprofile was studied as well as its effect on the protective properties of Zn-Ni coatings.

Experimental

Electrodeposition experiments were carried out under potentiostatic and galvanostatic conditions. Polarization measurements were made using stationary, rotating disc and rotating cylinder electrodes. Platinum was used as an anode and silver chloride electrode as a reference one. All potentials are given with respect to standard hydrogen electrode. Partial current densities for zinc and nickel were calculated from the results of the analysis of the alloy deposited under potentiostatic conditions:

where i_j is partial current density for j-component (Zn or Ni), m_j is its amount in the deposit,

$$i_j = \frac{m_j}{g_j.S.\hat{o}}$$

g_j is its electrochemical equivalent, S is the cathode surface area, and τ is the duration of the electrolysis.

Partial current density for hydrogen evolution, i_{H2}, was found from the equation:

$$i_{H_2} = i - \left(i_{Zn} + i_{Ni}\right)$$

where i is overall current density.

Microdistribution measurements were made using microsections of deposits obtained on microprofiled cathodes having a series of parallel ridges triangular in cross-section, 25±2 μm high and approximately 100 μm distance between peaks. The average deposit thickness was measured gravimetrically. Local thickness was measured on microsections microscopically. Average deposit composition was determined by atom-absorption spectroscopy, and local one – by X-ray electron probe.

Local current densities and local deposit composition were determined on selected areas, shown in Fig. 1, which corresponded to micropeaks (Mp), microrecesses (Mr) and smooth (Sm) sites of surface. When calculating local partial current densities, initial surface area values were used and any changes in the surface area in the course of electrodeposition were not taken into account.

Local partial current density, i_j, was calculated as follows:

$$i_j = \frac{\tilde{n} \cdot S \cdot N_j}{g_j \cdot \ddot{A}l \cdot t},$$

where ***r*** is density of the deposited alloy, *S* is deposit cross-section area (found from microsection) on selected parts, ***Dl***, of the microprofile, N_j is mass fraction of an alloy component.

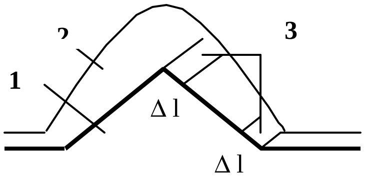

Fig.1 Measurements of local thickness' for calculations of partial current densities: 1- substrate (electroformed Ni plate); 2 – deposited alloy; 3 – selected areas for thickness measurements.

Results and Discussion

Partial current densities for Zn and Ni deposition at constant potential of –0,8V are shown in Fig.2.

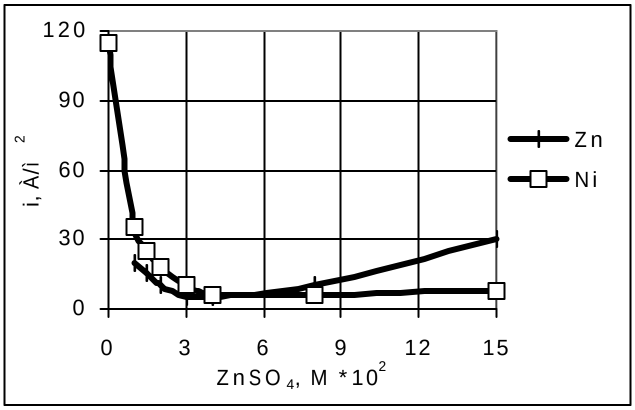

Fig.2. The effect of $ZnSO_4$ concentration in the plating bath on partial current densities for the deposition of Zn and Ni into the alloy: $NiSO_4$-0.9 M; $NiCl_2$-0.16 M; H_3BO_3-0.5 M; pH 5.0; 20^0C; no agitation; potentiostatic deposition at E=-0.8 V.

Strong inhibiting action of zinc for the deposition of Ni is evident: at Zn^{2+} concentration 0,03M partial current density for Ni is about 100 times lower than in the absence of Zn^{2+} in the solution. On the other hand, the rate of Zn^{2+} ions discharge from this solution is also smaller than at lower concentration of zinc salt, e.g. 0,01 M. The presence of diffusion limitations for zinc discharge results in appreciably higher zinc content in the alloy deposited at micropeaks (Fig.3).

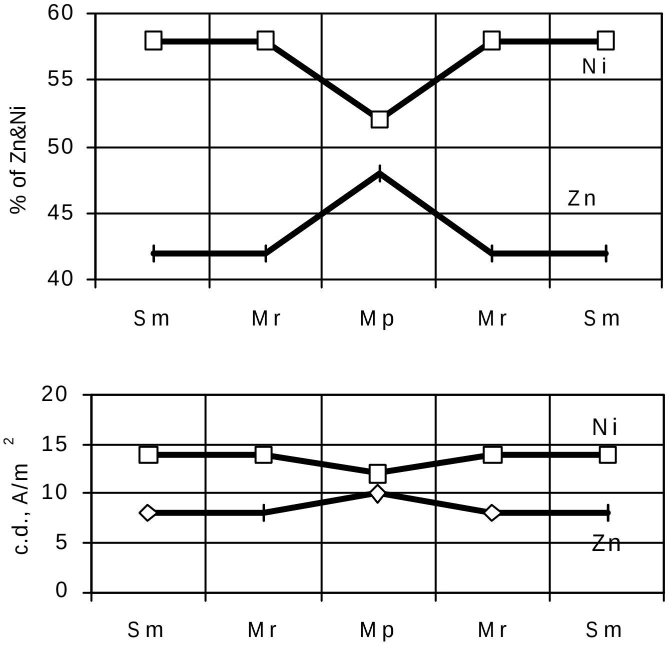

Fig.3 Distribution of partial current densities (c.d.) and components of Zn-Ni alloy (wt.%) over the microprofile (Fig.1). Composition of the solution (M):$ZnSO_4$ - 0,03; $NiSO_4$ - 0,9; $NiCl_2$ - 0,16; H_3BO_3 - 0,5; pH 5,0; 20 ^oC; no agitation; potentiostatic deposition at E = - 0.8 V

Higher local zinc codeposition rate at micropeaks leads to still lower local nickel codeposition rate and correspondingly lower Ni content in the deposit. This effect is in good agreement with the character of the curve for i_{Ni} in Fig.2, where maximum inhibiting action produced by zinc on the nickel deposition rate is observed at concentrations of zinc salt close to 0,03M. The rate of diffusion of Zn^{2+} to micropeaks in 0,03M solution is obviously higher than that to flat surface, represented in the data in Fig.1. Somewhat higher codeposition rate for zinc and lower codeposition rate for nickel at micropeaks result in practically uniform microdistribution of the alloy as a whole.

At high concentration of Zn^{2+} (0,15M) its inhibiting action on nickel is not increased appreciably. On the other hand, zinc codeposition rate becomes several times greater, which results in much higher zinc content in the alloy.

High partial current density for zinc reduction explains the existence of diffusion limitations and rather strong negative leveling. Nevertheless the composition of the alloy is practically the same both on micropeaks and flat areas. Obviously, over the concentration range for Zn^{2+} from 0,05 to 0,15 M partial current density for nickel is increasing along with increasing concentration of zinc ions and results in a uniform composition of the alloy at all sites of the surface (Fig.4). Similar effect was found for a number of other alloys [6].

Cathode process at more negative potentials (-1,1V) proceeds at much higher current densities (~ 140 A/m^2). Diffusion limitations are mach stronger in this case and therefore the differences between local partial current densities for zinc are still greater (Fig.5).

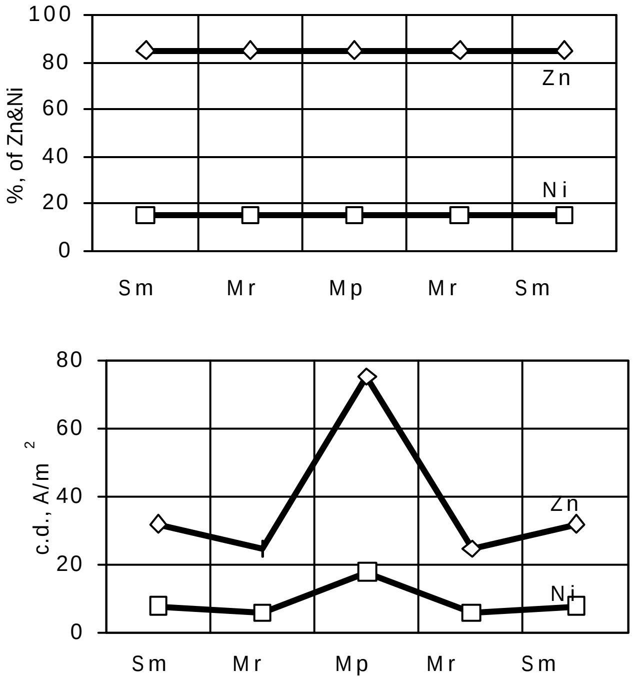

Fig.4 Distribution of partial current densities (c.d.) and components of Zn-Ni alloy (wt.%) over the microprofile (Fig.1). Composition of the solution (M):$ZnSO_4$ - 0,15; $NiSO_4$ - 0,9; $NiCl_2$ - 0,16; H_3BO_3 - 0,5; pH 5,0; 20 ^oC; no agitation; potentiostatic deposition at
E = - 0.8 V

As in previous case (Fig.4) nickel partial current density is higher at micropeaks. However the composition of the alloy varies now over the microprofile: zinc content in the deposit at micropeaks is greater than on other areas while nickel content is much lower (Fig.5).

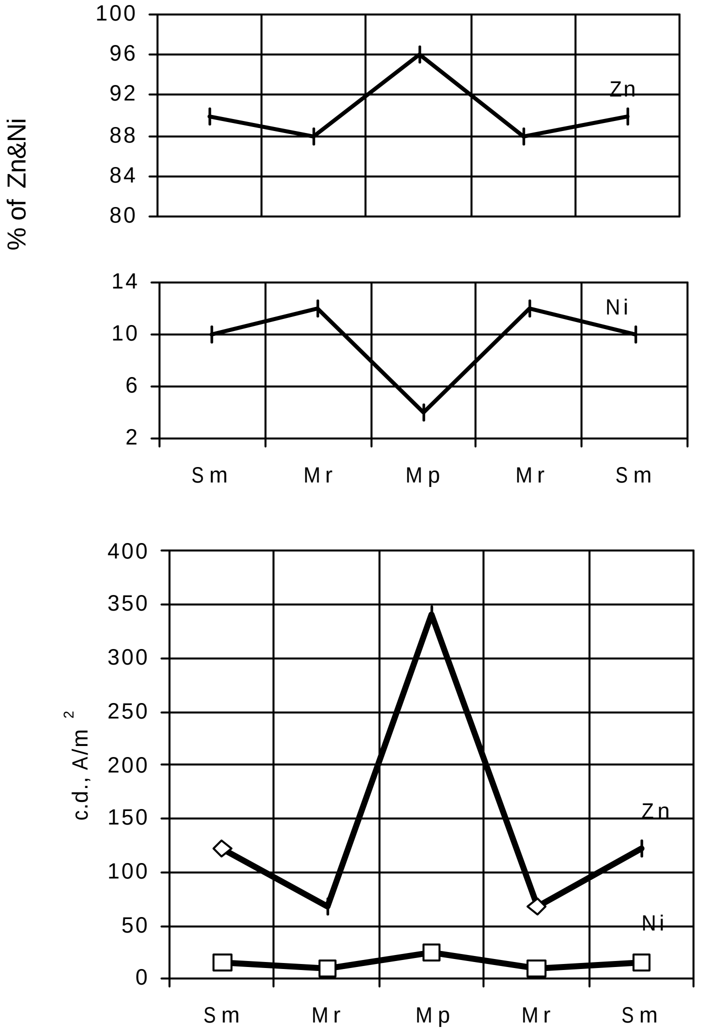

Fig.5 Distribution of partial current densities (c.d.) and components of Zn-Ni alloy (wt.%) over the microprofile (Fig.1). Composition of the solution (M):$ZnSO_4$ *- 0,15;* $NiSO_4$ *- 0,9;* $NiCl_2$ *- 0,16;* H_3BO_3 *- 0,5; pH 5,0; 20* ^oC*; no agitation; potentiostatic deposition at*
E = - 1.1 V

Since major contribution to the total thickness of the deposit is that of zinc, strong antileveling is observed.

Similar results were obtained under galvanostatic conditions in agitated solutions, however, at higher current densities. For example, conditions, represented in Figs.4 and 5 (potentiostatic deposition, no agitation) are realized at current density of 100 A/m^2 and 400 A/m^2 respectively.

Average composition of the alloy in galvanostatic experiments is close to 12-14% Ni. At lower current densities (100 A/m^2) these values represent also actual composition at different points of a microprofile. At higher current densities (400 A/m^2) much lower nickel content is observed in the alloy, deposited at micropeaks and much higher content in microrecesses. Such differences in the composition produce appreciable effect on the corrosion properties of Zn-Ni coatings (Table 1).

Table 1.Corrosion tests for Zn (composition of the solution is given in Fig.5) and Zn-Ni coating (not passivated) in 5% NaCl solution

Composition of the coating	**Cathode current density, A/m^2**	**Appearance of corrosion products, hrs**	
		White rust	**Red rust**
Zn	200	0,2–1	180–200
Zn-Ni (12-14%)	100	4–6	350–420
Zn-Ni (12-14%)	400	0,2–1	120–180

Areas on the surface with lower nickel content have reduced corrosion resistance and are responsible for rapid corrosion of the coating. It should be expected that the corrosion behavior will also depend on cathode surface microgeometry. Since on polished surfaces the composition of the alloy will be much more uniform than on microrough ones, the coatings on polished surfaces may afford better protection against corrosion.

The presence of areas with higher nickel content (microrecesses) may play negative role in the passivation treatment of Zn-Ni coatings. These areas may form local microcathodes facilitating initially the corrosion of the coating and later that of steel base.

Summary

Zn-Ni coatings may be obtained over a wide range of conditions including concentrations of metal salts, current densities, etc. Since uniform distribution of the composition of the alloy is desirable, plating should be carried out under conditions, which minimize negative effects of diffusion limitations of metal ions discharge: possibly higher concentrations and temperatures, moderate current densities and effective agitation of the solution.

References

1. S.S. Kruglikov, V.I. Kharlamov, T.A. Vagramyan, *Transac. of the Inst. of Metal Finish.*-Birmingam, 74, 6, 189 (1996).
2. Ya.V. Mumladze, V.I. Kharlamov, S.S. Kruglikov, T.A. Vagramyan, *Zashchita metallov*, 24, No 3, 502 (1988).

3. V.I. Kharlamov, S.A. Matuhin, S.S. Kruglikov, A.V. Shatunova, T.A. Vagramyan, *Elektrokhimia*, 25, No 8, 1137 (1989).
4. V.I. Kharlamov, T.A. Vagramyan, T.L. Azarchenko, M.V. Khloptseva, *Elektrokhimia*, 27, 2, 282 (1991).
5. V.I. Kharlamov, T.A. Vagramyan, T.L. Azarchenko, A.B. Vakka, *Elektrokhimia*, 27, 1, 107 (1991).
6. V.I. Kharlamov, T.A. Vagramyan, S.S. Kruglikov, Proc. AESF SUR/FIN 2002, p.648-655.