The Role of Mass Transport Phenomena in the Microdistribution of Electrodeposited Alloys

S.S. Kruglikov, V.I. Kharlamov, T.A. Vagramyan, S.S. Kruglikov consultants, Moscow, Russia

Non-uniform microdistribution of electrodeposited individual metals is closely related with mass transport phenomena in the cathodic diffusion layer. In the electrodeposition of alloys, both local deposit thickness' at different points of a microprofile and the composition of an alloy depend on the effects of mass transport on the partial deposition rates. A number of different types of cathodic microdistribution were found. For example, non-uniform microdistribution of an alloy is accompanied in certain cases by a uniform chemical composition of the deposit. More typical cases correspond to an appreciable variation in the alloy composition over the microprofile. Non-uniform microdistribution was shown to effect the functional characteristics of alloy coatings.

For more information contact: Prof. Valery I. Kharlamov Miusskaya Sq., 9, 125047, Moscow, Russia Phone – 7 (095) 978 6195 Fax – 7 (095) 978 5651 E-mail: <u>semm@online.ru</u>

Introduction

Properties and performances of electrodeposited layers depend on their composition and thickness. In case of individual metals any variations in the coating thickness over the surface of plated parts appear due to unsufficient throwing power and are usually undesirable. However, on the microscale non-uniform distribution of metal deposits may by on objective of the process (e.g. leveling in bright-plating or deposition of microrough coatings for better adhesion of polymers to metal surfaces). In the electrodeposition of alloys apart from uniform or non-uniform macro- and microdistribution of the coating variations in the composition of the alloy over the plated surface are also possible ^{1,2,3}. Properties of electrodeposited alloys were shown to depend not only on the average composition, but also on the character of the microdistribution of individual components ^{4,5}. However, the mechanism of microdistribution in the electrodeposition of alloys is not completely clear. A study of different types of microdistribution in the electrodeposition of alloys analysis of factors, playing major roles in the microdistribution, are described in this paper.

Experimental

Electrodeposition experiments were carried out under potentiostatic conditions. Polarization measurements were made using stationary, rotating disc and rotating cylinder electrodes. 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 deposits composition was determined by atom-absorption spectroscopy, and local one - by X-ray electron probe.Local current densities and local deposits composition were determined on selected areas, shown in Fig. 1, witch 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_i , was calculated as follows:

$$i_j = \frac{\rho \times S \times N_j}{g_j \times \Delta l \times t},$$

where \mathbf{r} is density of the deposited alloy, S is deposit cross-section area (found from microsection) on selected parts, \mathbf{D} , of the microprofile, t is duration of the electrolysis, N_j is mass fraction of an alloy component, and g_j is its electrochemical equivalent.



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

A. Classification of the types of microdistribution.

1. Uniform microdistribution of an alloy as a whole and uniform chemical composition.

Uniform microdistribution of an alloy with uniform chemical composition is a relatively rare case. It may happen in the absence of diffusion limitations for each of the components. This means that their partial current densities are far below limiting currents. Fig.2 illustrates such a case.



Fig.2 Distribution of partial current densities (c.d.) and components of Ni-Co alloy (wt.%) over the microprofile (Fig.1). Composition of the solution (M): NiSO₄ - 0,9; NiCl₂ - 0,17; CoCl₂ - 1; H3BO₃ - 0,5; pH 5,0; $t = 20^{\circ}C$; E = -1 V (she)

Partial deposition rate of cobalt is approximately ten times greater then that of nickel, but both are distributed uniformly over the microprofile because of the absence of diffusion limitations even for the discharge of cobalt ions.

2. Uniform microdistribution of an alloy with chemical composition varying over the microprofile.

Non-uniform composition of an alloy over a microprofile is more common case and it may happen, if the discharge of certain ions is at least partially controlled by the rate of their diffusion to the cathode. The above example – Ni-Co alloy – shows such type of microdistribution, if the concentration of cobalt ions is lowered from 1M down to 0,3M (Fig. 3). It is clear that simultaneously with an appreciable reduction in the average partial current for the discharge of cobalt ions, its local values are changing along the microprofile: higher at the peak and lower at other points. The average rate of the discharge of nickel ions is higher than from the solution containing 1M Co^{2+} (Fig. 2). Since certain retardation of nickel deposition produced by cobalt is not so strong, as in Fig. 1, deposition rate of nickel is somewhat higher at the peak. This leads to a practically uniform microdistribution of the alloy as a whole.



Fig.3 Distribution of partial c.d. and components of Ni-Co alloy (wt.%) over the microprofile. Composition of the solution (\hat{I}): NiSO₄ - 0,9; NiCl₂ - 0,17; CoCl₂ - 0,3; H₃BO₃ - 0,5; pH 5,0; t = 20 °C; E = -1 V

3. Negative leveling of an alloy with uniform composition.

Uniform composition of an alloy under conditions of negative leveling is observed in the presence of diffusion control of the rate of deposition, on the one hand, and strong accelerating effect of the discharge of

one of the components by the other. Electrodeposition of Cu-Zn alloy from cyanide-type solutions is a good example (Fig. 4 & 5). A comparison of partial currents for both copper and zinc measured on stationary and rotating electrodes (curve 1, 3 and 2, 4 respectively) gives an evidence of partially diffusion controlled deposition of both components. However, the rate of deposition of copper into the alloy produced much stronger accelerating action on the rate of codeposition of zinc (in comparison with the effect of agitation). That is why the composition of the alloy deposited on the micropeak does not differ from that deposited on other areas (Fig. 5). At the same time the local deposit thickness' differ considerably, demonstrating considerable negative leveling.



Fig. 4 Partial current densities and composition of Cu-Zn alloy vs. concentration of copper in the solution (\dot{I}): ZnSO₄ - 0,075; NaCN_{free} - 0,17; pH 10,5; t = 20 °C; E = -1,4 V

Curves 1, 2 - copper; curves 3, 4 - zinc.

Curves 1, 3 – stationary cathode; curves 2, 4 – rotating cathode, N = 1100 rev/min.



Fig.5 Distribution of partial c.d. and components of Cu-Zn alloy (wt.%) over the microprofile. Composition of the solution (\hat{I}): CuCN - 0,32; ZnSO₄ - 0,075; NaCN_{free} - 0,17; pH 10,5; t = 20°C; E = -1,4 V

4. Negative leveling of an alloy with non-uniform composition.

In alloy plating solutions the concentration of the more electropositive components is usually lowered in order to avoid their excessive enrichment in the deposit. This results in the appearance of diffusion control of the deposition rate for this component and leads to non-uniform distribution of the alloy as a whole (usually to negative leveling). Typical examples of such type of alloys are Cu-Ni, Cu-Co, Cu-Cd, Ni-Pd, Zn-Sn, Zn-Ni.



Fig.6 Partial c.d. for Pd and Ni vs. square root of the cathode rotation speed (rad/sec). Composition of the solution (M): $PdCl_2 - 0,11$; $NiCl_2 - 0,19$; $NH_4Cl - 0,6$; NH_4OH to adjust pH to 9,0; $t = 20^{0}C$; E = -0,6 V

Data in Fig. 6 for the deposition of Pd-Ni alloy show that at constant potential partial deposition rate of nickel is independent on the rotation speed of the cathode, while that of palladium is increasing at greater rotation speed. Therefore, the alloy layer deposited on the micropeaks has greater thickness and contains more palladium (Fig.7).



Fig.7 Distribution of the partial c.d. and components of Pd-Ni alloy over the microprofile. Composition of the solution (M): $PdCl_2 - 0,11$; $NiCl_2 - 0,19$; $NH_4Cl - 0,6$; NH_4OH to adjust pH to 9,0; $t = 20^{\,0}C$; $E = -0,7 \, V$

5. Positive true leveling with non-uniform composition.

If the rate of deposition of a component of the alloy is controlled predominantly by diffusion and this component suppress the codeposition of the other component (or components), positive leveling takes place. Inhibiting action produced by this component is stronger at micropeaks and thus, local deposition rates of other components are decreased at such sites. On the other hand, diffusion rate and corresponding partial current of the component which acts as a leveling agent, is higher at micropeaks, where the local plate thickness is smaller than at other sites of the microprofile. The alloy deposited at micropeaks is characterized by higher concentration of the leveling component. This type of microdistribution is observed in the electrodeposition of copper, nickel, cobalt or zinc alloys with cadmium. A typical example is shown in Fig. 8 & 9.



Fig.8 Partial c.d. for Ni and Cd vs. concentration of Cd in the solution (M): NiSO₄ – 0,1; $K_4P_2O_7 - 0,75$; NH₄Cl – 0,75; pH 9,0; t = 20⁰C; E = -0,95 V



Fig. 9 Distribution of partial c.d. and components of Ni-Cd alloy over the microprofile. Composition of the solution (M): NiSO₄ – 0,32; CdSO₄ – 0,028; NH₄Cl – 0,75; K₄P₂O₇ – 0,75; pH 9,0; $t = 20^{0}$ \tilde{N} ; E = -0,95 V

6. Positive true leveling with uniform composition.

If leveling action is produced by one of the components of the alloy, the compositions of the deposit will inevitably differ over the microprofile. Leveled deposits with uniform composition can be obtained principally in the presence of an organic leveler which will produce equal inhibiting action on every component of the deposited alloy. Unfortunately, the authors are still unfamiliar with any examples of such alloy plating baths.

B. Classification of types of mutual interaction.

Analysis of different types of microdistribution of an alloy as a whole and its components leads to a conclusion that chemical composition of deposits and their distribution over a microprofile depend strongly on mutual interaction between the components of alloys. If one of the components inhibits or accelerates the deposition of other components, the kinetics of its deposition determines not only its own microdistribution but also the microdistribution of other components and of the alloy as a whole.

1. Inhibition by one of the components for the alloy

Codeposition of cadmium with other metals produces inhibiting action, which does not depend on the type of a particular plating solution and kinetic characteristics of the process. For example, deposition of copper, zinc, nickel (Fig. 8), nickel-cobalt and copper-zinc (Fig. 10) are inhibited by adding cadmium ions to sulfate, pyrophosphate or acetate plating solutions.



Fig. 10. Partial c.d. for Ni, Co and Cd vs. concentration of Cd in the solution (M): NiSO₄ - 0,55; CoSO₄ - 0,06; NaCH₃COO - 1,5; CH₃COOH to adjust pH to 3,0; $t = 20^{0}C$; E = -1 V

Since codeposition of cadmium in all these cases is controlled by the diffusion stage, the deposition of cadmium on micropeaks proceeds with greater rate and its inhibiting action is more pronounced at these sites (Fig. 9 & 11). As a result percent of cadmium is higher in the alloy deposited at micropeaks.



Fig.11 Distribution of partial c.d. and components of Ni-Co-Cd alloy over the microprofile. Composition of the solution (M): NiSO₄ - 0,55; CoSO₄ - 0,06; CdSO₄ - 0,028; NaCH₃COO - 1,5; CH₃COOH adjusted to pH to 3,0; $t = 20^{\circ}C$; E = -1 V

2. Acceleration by one of the components of the alloys

Many examples of accelerating effects give codeposition of copper and cadmium, zinc and nickel from sulfate, pyrophosphate, tripolyphosphate, tartrate and ammonia-pyrophosphate solutions. Since deposition of copper in all these cases is controlled (at least partially) by the diffusion, accelerating effect is more pronounced at micropeaks and apart from that copper itself is deposited at these sites with greater rate. Sometimes depolarizing action of copper allows to achieve more uniform composition of the deposited alloy due to acceleration of the deposition of the second component at micropeaks in cases, when its deposition rate is not controlled (even partially) by diffusion. An example of such behavior is given above (Cu-Zn in Fig. 4 & 5).

Summary

Diffusion control for the discharge of ions and mutual effects of codepositing metals are major factors determining the type of microdistribution of an alloy as a whole as well as of any variations in its composition over a microprofile. Two types of mutual effects – inhibition and acceleration – lead to positive or negative leveling respectively, provided there is at least partial diffusion control.

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