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Metal Recovery from Spent Electroless Plating Solutions By Oxalate Precipitation

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By O. Gylienė and M. Šalkauskas

It is possible to recover metals from spent electroless plating solutions by an unusual process that results in a very high percentage of recovery. Oxalate precipitation was studied to determine conditions for recovery without waste or destruction of the complexing agents.

Electroless plating solutions contain chelated metal components. Such complexes hinder metal recovery as insoluble compounds, particularly as hydroxides, to the extent that the complexing ability of most complexing agents increases with increasing pH.

Clyde S. Brooks proposed oxalate precipitation for Ni, Cu, and Co recovery from spent electroless plating solutions.[1] After destruction of the organic complexing agents by aeration, oxalic acid, in an amount from 1.5 to 2 times the stoichiometric requirement, was added at pH 5 to 6. Insoluble metal oxalates were separated by filtration.

The objective of this study was to find optimal conditions for metal (Cu, Ni, Co) removal from spent electroless plating solutions, by means of oxalate precipitation, without destruction of the complexing agents.

Experimental Procedure

All experiments were carried out at room temperature by addition of oxalic acid to metal-containing solutions. The pH of the solutions was adjusted with H_2SO_4 or NaOH. Experiments were carried out with KOH, also, because of the low solubility of sodium oxalate, compared with potassium oxalate. The results indicate that the low solubility of sodium oxalate does not affect the metal oxalate precipitation process.

Oxalate precipitates were separated by filtration after two to five days. Metals in the filtrate were determined by titration with EDTA, in small quantities, photometrically.

Table 1
Removal of Some Metals from Acidic Solutions
(Beginning metal conc., 0.1 mol/L)

Acid	Concentration mol/L	Percent metal removal Cu(II)	Ni(II)	Co(II)
H_2SO_4	1.8	99.8	53	30
	3.5	99.7	10	0
	7.0	99.5	0	0
HNO_3	3.5	99.9	20	5
	7.0	99.9	17	0
	13.0	99.9	98	47
HCl	3.0	90	75	3
	6.0	25	12	0
	12.0	0	0	0
H_3PO_4	1.7	99.9	100	99.2
	3.3	99.9	99.8	99.4
	5.0	99.9	99.8	99.4

Results and Discussion

The results obtained for removal of Cu(II), Ni(II), and Co(II) from strongly acidic solutions are listed in Table 1. As shown, the largest amounts of metals are removed from phosphoric acid solutions. The concentration of this acid does not affect the extent of metal removal, which approaches 100 percent. The concentration of hydrochloric acid, however, which is the most important and widely used acidifier, hindered the removal of metals from its solutions. The effect of the concentration of nitric and sulfuric acids on removal of Ni(II) and Co(II) is noticeably greater than on Cu(II) removal.

To investigate the forming of insoluble metal oxalates with rise in pH, oxalic acid was added to metal-containing solutions. The results are shown in Table 2. The dependence of the solubility of metal oxalates on pH is complicated. By any consideration, the solubility of metal oxalates at low pH is much less than in neutral solutions. In basic solutions, the solubility of copper oxalate is high, while the solubility product of copper hydroxide is low. This is possible because of the complexing ability of oxalate.

The most important factor for residual metal concentration is the starting metal concentration (Table 3). With increasing starting concentrations of metal ion, the residual metal concentrations decrease (*i.e.*, the extent of recovered metal increases).

In this study for electroless plating, Ni-glycine (aminoacetic acid), Ni-citrate, Co-glycine, Co-citrate, Cu-tartrate, and

Table 2
Influence of pH on Residual Metal Concentration After Oxalate Precipitation
(Beginning metal conc., 0.1 mol/L)

$H_2C_2O_4$ mol/L	pH	Residual Metal Conc., mg/L Cu(II)	Ni(II)	Co(II)
0.1	0	110	100	90
	1	125	220	120
	2	70	740	300
	3	62	300	290
	4	90	270	270
	5	210	300	280
	6	180	20	45
	7	320	27	12
	8	450	3	3
	9	640	3	2
0.3	0	13	1	7
	1	27	7	5
	2	640	23	50
	3	770	440	400
	4	730	460	400
	5	700	660	800
	6	570	140	90
	7	700	30	15
	8	700	2	3
	9	640	1	2

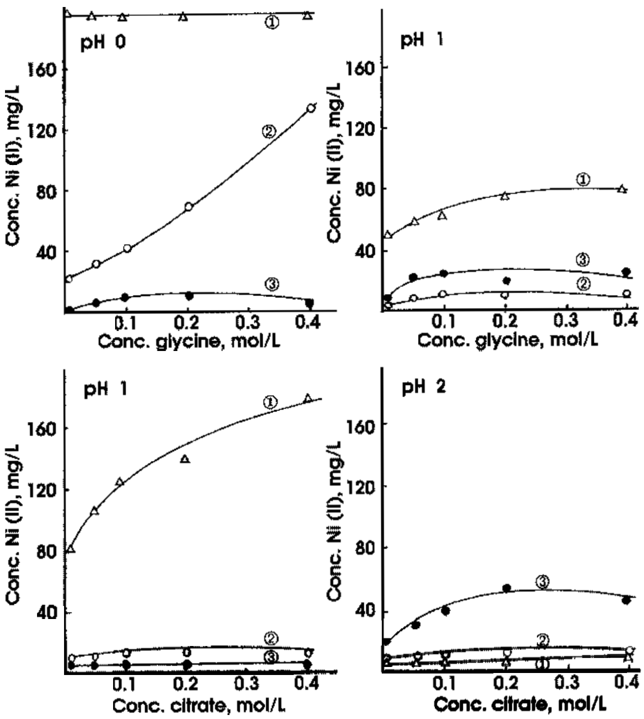

Fig. 1—Dependence of residual nickel concentration on concentration of complexing agents (glycine and ammonium citrate) after oxalate precipitation. Ni(II) conc. (mol/L): 1 - 0.01, 2 - 0.05, 3 - 0.1.

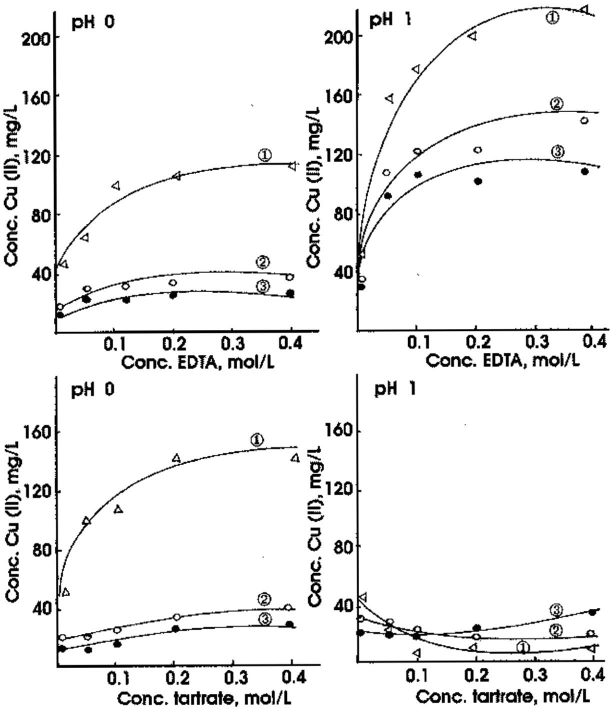

Fig. 2—Dependence of residual copper concentration on concentration of complexing agents (EDTA and tartrate) after oxalate precipitation. Cu(II) conc. (mol/L): 1 - 0.01, 2 - 0.05, 3 - 0.1.

Cu-EDTA complexes were used to examine the influence of complexing agents on precipitation of metal oxalates. Molar oxalic acid concentration in all cases was three times higher than the metal ion concentration.

The dependence of residual nickel concentrations on complexing agent concentrations is shown in Fig. 1. The low residual nickel concentrations are obtained at pH 1–2 and starting nickel concentration at 0.01 mol/L. The effect of complexing agent concentration in most cases is negligible. Only at small (0.01 mol/L) nickel ion concentrations, when the concentration of the complexing agent is very large compared with nickel concentration, do the residual nickel concentrations increase with the increase in concentration of the complexing agent. Similar results were obtained for Co(II)-glycine and Co(II)-citrate complexes.

The insignificant influence of complexing agents on oxalate precipitation in acidic solutions enables use of this precipitation for metal recovery from spent electroless nickel solutions. It is suitable only for solutions containing small amounts of phosphite (about 0.2 mol/L), however. Spent commercial electroless nickel plating solutions contain much more phosphite. For example, for solutions containing (mol/L): Ni(II) - 0.1, glycine - 0.4, phosphite - 2.2. After acidifying with sulfuric acid to pH 1.0 and oxalate precipitation, the extent of recovered metal was about 70 percent (*i.e.*, the residual metal concentration in the solution was 1.5 g/L). Much better results were obtained when phosphoric acid was used as acidifier. In this case, residual nickel concentration was 50 mg/L.

Table 3
Influence of Beginning Concentration of Metal Ion on Metal Recovery by Oxalate Precipitation

Beginning Metal Conc., mol/L		Residual Metal Conc., mg/L pH 0	pH 1	pH 2
	0.01	46	50	560
Cu(II)	0.05	18	23	1200
	0.1	13	27	640
	0.01	590	50	8
Ni(II)	0.05	26	20	46
	0.1	1	7	23
	0.01	630	50	6
Co(II)	0.05	47	20	33
	0.1	7	5	50

In solutions containing copper complexes of tartrate and EDTA at low pH, precipitation of insoluble EDTA[2] and tartrate[3] compounds takes place. Figure 2 shows a much more complicated process than oxalate precipitation. In acidic solutions, the extent of removal of tartrate and EDTA depends on their concentrations and pH and is 30 to 60 percent for tartrate and 85 to 98 percent for EDTA.

The by-products of spent electroless copper solutions containing EDTA have much less influence on oxalate precipitation than in spent electroless nickel solutions. Oxalate precipitation has the same characteristics in fresh solutions as in spent electroless copper solutions. It enables use of oxalate precipitation for recovery of both copper and EDTA for reuse in fresh plating solutions.

Oxalic acid (0.3 M) and sulfuric acid to pH 0 were added to 1-L spent electroless copper solutions containing (mol/L): Cu(II) - 0.1, EDTA - 0.15, glycine - 0.1. Copper oxalate and H_4EDTA-acid precipitates were formed:

$$\mathrm{CuEDTA^{-2} + H_2C_2O_4 \ + \ 2H^+ \rightarrow CuC_2C_4\downarrow + \ H_4EDTA\downarrow}$$

The precipitates were dissolved in sodium hydroxide:

$$\mathrm{CuC_2O_4 + H_4EDTA + 2NaOH \rightarrow CuEDTA^{-2} + Na_2C_2O_4\downarrow + 2H_2O.}$$

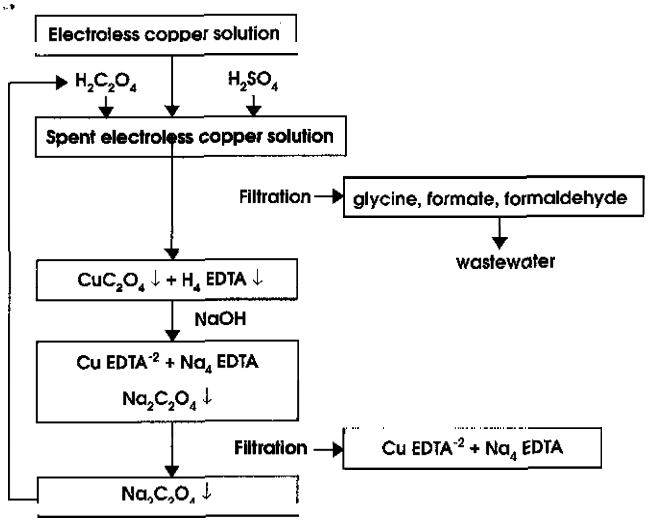

Fig. 3—Flow chart of regeneration of spent electroless copper solution

After filtering of insoluble sodium oxalate, the solution was used for preparing a plating bath (Fig. 3). Such procedure enables recovery of 95 percent of the EDTA and 99.5 percent of the Cu(II). The presence of oxalate in electroless copper solutions does not affect the plating process.

Summary

The metals from spent electroless plating solutions can be recovered by means of pH change and addition of oxalate. For spent electroless copper plating solutions containing EDTA, oxalate precipitation can be used for recovery of both Cu(II) and EDTA at 99.5 and 95 percent, respectively.

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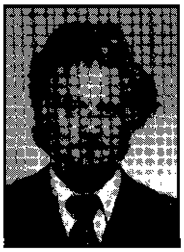
About the Authors



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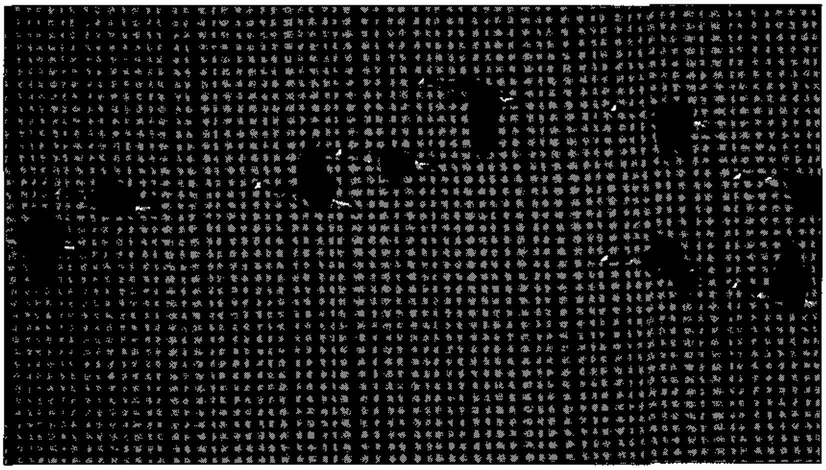

Electrodeposition of Ni-Mo-P Alloy Coatings

By Y. Zeng, S. Yao and H. Guo

Electrodeposition of Ni-Mo-P alloy coatings from ammoniacal citrate baths was studied, as well as characterization of low overpotential electrocatalysis for hydrogen evolution in alkaline solution. It was observed that the use of cathodes electrodeposited with Ni-Mo-P alloy containing 25 to 29 atomic percent molybdenum, and 0.1 to 0.8 atomic percent phosphorus, relative to Mo for water electrolysis, resulted in decreased overpotential for hydrogen evolution. Some scanning electron microscope (SEM) observations were also made.

Hydrogen has attracted considerable attention as a possible fuel for the future.[1] Although various methods have been proposed for large-scale production of hydrogen fuel from water, water electrolysis remains the simplest method; commercial electrolyzers have been available for many years.[2,3] Most commercial water electrolyzers use nickel electrodes and are operated at 70 to 90 °C in 25 to 35 percent KOH[2,4] to obtain high electrical conductivity, favorable electrode kinetics and minimal corrosion problems. At 80 °C, the specific conductivity of 35 wt percent KOH solutions reaches a maximum value of about 1.5 $\text{ohm}^{-1}\ \text{cm}^{-1}$.[4]

One of the ways of lowering electrical energy consumption in water electrolysis is to reduce the hydrogen evolution overpotential of the electrodes. Deposition of an electrocatalytic coating on the cathode surface has been investigated intensely for many years. Usable results were obtained with the use of steel, nickel or copper cathodes electrolytically covered by an alloy layer. M.H Miles *et al.* have systematically investigated hydrogen evolution of transition metals and their binary alloy electrocatalysis in alkaline[5] and acid[6] solutions. Ni-Zn alloy coatings have been used in water electrolysis processes also.[7]

Our previous experiments have indicated that the amorphous Ni-Mo alloy coatings obtained by electrodeposition have a lower overpotential.[8] Electrodeposition of the ternary Ni-Mo-P alloy coatings and their corrosion behavior were investigated.[9] Electrodeposition of Ni-Mo-P alloy coatings from ammoniacal citrate baths and the characterization of low overpotential electrocatalysis for hydrogen evolution were the primary subjects of this study.

Experimental Procedure

Electrochemical experiments were carried out with H-type glass cells having a single chamber volume of 150 mL. Porous glass was used as a diaphragm. A 30 wt percent KOH solution was used as the electrolyte at 80 ±2 °C. All potentiodynamic and open-circuit decay measurements were carried out on electrodes coated with the Ni-Mo-P alloy electrocatalyst. To minimize problems with oxide films, the test electrodes were first subjected to hydrogen evolution at a constant 500 mA/cm^2 for at least 30 min. The electrode was then transferred to another electrolyzer containing fresh solution. The electrode potential was measured relative to a saturated calomel electrode (SCE). Platinum gauze served as an auxiliary electrode.

The Ni-Mo-P alloy deposits were electrodeposited from ammoniacal citrate solution on copper substrates that were masked on one side. The substrates were degreased in hot alkaline solution at 70 °C and lightly etched with 5 wt percent H_2SO_4 immediately before plating. The composition of the bath is shown in Table 1. Electrodeposition was finished in a 400-mL bath under a cathode moving at 40 times/min. Before electrodeposition, the plating baths not containing NaH_2PO_2 were electrolytically aged (pre-electrolyzed) with a low current density of about 8 mA/cm^2, using titanium grid and platinum gauze as the cathode and anode, respectively. After aging and before plating, NaH_2PO_2 was added. The chemical composition of the alloys was assayed by an energy dispersion spectrometer (EDS). Some scanning electron microscope (SEM) observation was also performed.

Results and Discussion

Electrodeposition of Ni-Mo-P Alloy Coatings

If baths were not aged, the appearance of the coatings deteriorated. They peeled or became dark, especially when molybdate concentration was high. Figure 1 shows the effect

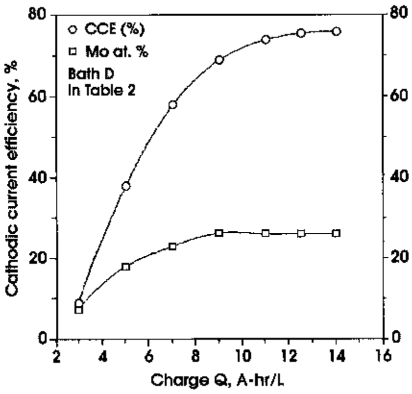

Fig. 1—Effect of current loading for electrolytic aging on Ni-Mo alloy content and current efficiency.

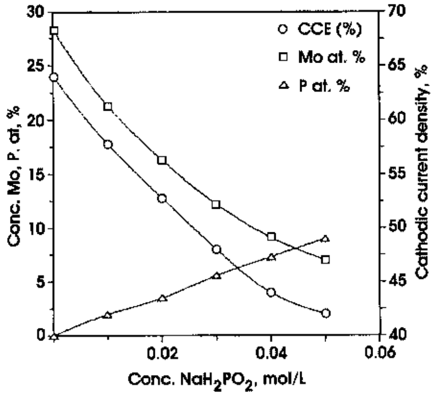

Fig. 2—Effect of NaH_2PO_2 concentration on content of Ni-Mo-P deposits and on current efficiency.

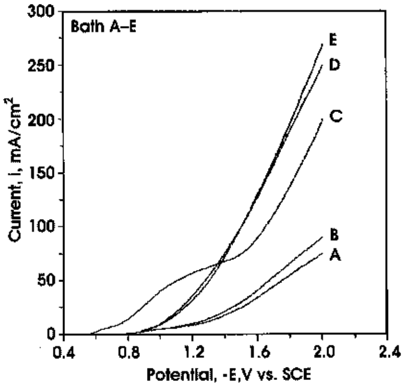

Fig. 3—Potentiodynamic polarization curves for electrolytes with composition as in Table 2. Sweep rate: 2 mV/sec.