Electroless Deposition of Palladium-Nickel-Phosphorous Alloy

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Electroless deposition of Pd-Ni-P alloy [8-17 percent Ni, 6-12 percent P] from alkaline ammonia-ammonium chloride solutions [pH 8.5-11.5] was studied. Ethylenediamine or EDTA was added to the solutions, and sodium hypophosphite was used as reducing agent. Deposition rate varied from 2 to 6 micrometers per hour and was increasing at higher temperatures, lower pH values and lower concentrations of ethylenediamine or EDTA. Stability of plating solutions was better under conditions corresponding to lower deposition rate. Kinetics of cathodic and anodic reactions studied by polarization measurements has revealed strong mutual acceleration of both reactions. Solderability tests and measurements of microhardness and contact resistance have given good results.

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Phone: +7-095-280-0281 Fax: +7-095-200-4204 Introduction

Palladium-based alloys have received considerable attention in recent years as promising coatings in electronic devices. Another possible area of interest is production of catalysts for numerous chemical reactions. Electroless plating process is of particular importance for such type of alloys, since it allows to obtain uniformly distributed coatings on any surface irrespectively of its conductive or nonconductive nature and geometric characteristics, e.g. on fibrous materials, powders, etc. Electroless deposition of palladium-nickel-phosphorous alloy containing 6 percent Ni and 2.7 percent P was reported by Pearlstein and Weightman. They used a hypophosphite-based batrh with ammonia as a complexing agent. However, according to the results of our experiments with this solution its stability was insufficient due to spontaneous decomposition in the course of plating process. Since a major objective of the present work was Pd-Ni-P bath with sufficient stability, other complexing agents have been tested as stabilizers. Ethytlenediamine (EDA) and EDTA have been proposed by Sergienko as stabilizers for palladium-hypophosphite bath. Both of them have been tested in the present work. Stabilizing action of EDTA was found to be sufficient only, if carbon fibers or carbon-fiber cloth were used as a substrate material. For steel substrate stability was not sufficient, and EDA was used in this case.

Experimental

Two basic formulations were used:

Component	Form. #1	Form. #2
PdCl ₂ -2H ₂ O	2 g/l	2 g/l
HCl (1N)	16 mL/l	16 mL/l
NH ₄ Cl	27 g/l	27 g/l
NH ₄ OH (25% NH ₃)	160 mL/l	160 mL/l
EDA	30 g/l	-
NiCl ₂ -6H ₂ O	5 g/l	-
NaH ₂ PO ₂ -H ₂ O	11 g/l	-
Na ₂ EDTA	-	40 g/l
рН	9.5 - 10.5	8.5 - 10.5
Temp (C)	45 - 55	35 - 55

Steel specimens were cleaned in trisodium phosphate solution (50C) and then activated in 20% (w/w) HCl. Carbon-fiber cloth was pre-activated in PdCl-HCl solution. The load in each plating experiment was 1 dm/l. Cathodic and anodic polarization measurements were made using silver-silver chloride reference electrode and platinum anode preplated with Pd-Ni-P alloy. Cathodic curves were taken on steel or carbon-fiber electrodes.

Results and Discussion

Ethylenediamine Bath

Fig. 1 shows that higher temperatures facilitate plating process and simultaneously accelerate decomposition of the bath. Operation at temperatures above 55C is impracticable due to very short lifetime (about 1 hr at 65C). Increasing pH reduces the decomposition rate and improves the stability of the solution (Fig. 2). Composition of the alloy is also influenced by pH: at higher pH the contents of nickel and phosphorous are increasing (See Fig. 3). Accelerating effect of lower pH values on the deposition rate agrees with the results of polarization measurements. Cathodic and anodic polarization curves, as well as stationary (i.e. socalled "rest" potentials) are shifting towards more positive values at lower pH (See Figs. 4, 5 and 6). It should be also noted that actual deposition rate expressed in terms of current density, is considerably higher than values predicted by polarization curves. Such behavior points to a mutual acceleration of both oxidation-reduction processes. Other variables such

as the concentration of EDA (Fig. 7) and molar ratio of overall concentrations of metal ions to the concentration of hypophosphite (Fig. 8) also play important role. Here again any change in the deposition rate is accompanied by a change in the stability of the bath in the opposite direction.

Properties of Deposits

Data on the hardness are given in the following Table:

Alloy Composition %		Microhardness kg/mm ²		
Pd	Ni	Р	As plated	After 500C
				treatment
85	8	7	470	520
75	16	9	480	520
70	18	12	500	570

Hardness is close to that of electrodeposited Palladium-nickel alloy. Contact electrical resistance was determined on specimens having palladiumnickel-phosphorous coating 3 micrometers thick. Resistance of plated contacts increased 1.5 times after 20,000 on/off cycles. Solderability tests of coatings 3 micrometers thick have shown results close to those for electrodeposited gold coatings.

EDTA Bath

This solution was used only for plating on carbon-fibers and carbon-fiber cloth. Major properties of this solution do not differ considerably from those of EDA-bath.

Summary

Electroless deposition of palladium-nickelphosphorous (70 to 85 percent pallaium) may be a substitute for gold in some applications, especially if the price of palladium increases. Another prospective area might be the manufacture of catalytic devices.

References

- 1. F. Pearlstein and R.F. Weightman, *Plating*, **56**, 10, 1158 (1969).
- 2. A. Sergienko, US Pat. 3,418,143 (1968).

Figure Captions

Figure 1. Deposition rate (1) and solution stability (2) vs. temperature (C) for solution No. 1 (pH 10).

Figure 2. Deposition rate (1) and solution stability (2) vs. pH (temp. 50C).

Figure 3. Effect of solution pH on the composition of the deposit (temp. 50C)

Figure 4. Cathodic polarization curves obtained in the absence of hypophosphite.

Figure 5. Anodic polarization curves obtained in the absence of metal ions (temp. 50C)

Figure 6. Stationary potential vs. pH of the solution.

Figure 7. Deposition rate (1) and solution stability (2) vs. molar concentration of ethylenediamine (pH 10, temp. 50C).

Figure 8. Deposition rate (1) and solution stability (2) vs. molar ratio: metal ions/hypophosphite (pH 10, temp. 50C).







Figure 2







Figure 4



Figure 5



Figure 6







Figure 8