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Electroless Ni-Co-Cu-P Alloy Deposition in Alkaline Hypophosphite Based Bath

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Abstract. The use of electroless deposition method to deposit nickel alloy attracts attention due to its uniformity, corrosion resistance in neutral media and low friction. Quaternary nickel alloy deposit can be achieved by adding metal ion additive into the plating bath. Furthermore, the use of alkaline bath can accelerate the deposition rate, and provide sufficient thickness for corrosion protection. In this study, an electroless quaternary nickel alloy is deposited on iron coupons by adding cobalt and copper ions in hypophosphite based Ni-P alkaline bath. The nickel alloy deposit surface morphology is studied using scanning electron microscope (SEM) and x-ray fluorescence (XRF). Corrosion behavior of the nickel alloy is investigated using polarization curve measurement in 3.5wt% NaCl aqueous solution. From the results, the elecroless Ni-Co-Cu-P alloy coating produced at higher plating bah pH is harder than the lower bath pH. Higher Co, Cu and P content in the Ni alloy exhibit broader passive area in the polarization curve measurement results.

Introduction

Electroless nickel deposition provide a good uniform coatings on any type and shape of substrate due to its redox reaction that does not requires external current density as electrodeposition. Usually, a binary nickel alloy is produced by reducing agent that provides secondary element co-deposited along with nickel. Thus, a binary nickel alloy such as Ni-P, exhibits superior corrosion resistance, low friction, and higher hardness compare to nickel itself. Such alloy can be used in various applications such as corrosion resistant material, memory hard disc, circuit board and even in automobile finishes [1].

Quaternary nickel alloy can be developed by adding another metal ion additive, mainly from the transition metal element such as Zn, Cu, W, and Co, depending on the alloy's purpose [2,3]. The addition of Cu improves the corrosion resistance in neutral media by providing barrier protection [3]. While Zn addition decreases the corrosion potential, can be used as sacrificial anodic material [2]. Co or Fe addition changes the Ni-P magnetic properties from paramagnetic to ferromagnetic. Metal ion additives also will decrease the deposition rate due to its inhibitor properties in electroless nickel deposition reaction [4]. The electroless nickel deposition reaction can be improved by increasing the plating bath pH up to pH 11 [1].

The addition of Cu and W improves the hardness as well as corrosion resistance in NaCl aqueous solution significantly [3]. Cu and Zn addition in the Ni-P alloy exhibit barrier protection at less noble corrosion potential [5]. However, both Co and Cu metal ions effect on the nickel alloy deposit is less known. Furthermore, Co and Cu ions act differently in various plating bath pH due to its' complex ion stability.

In this study, the quaternary nickel alloy deposition is done on Fe substrate in various alkaline pH plating bath using Co and Cu as metal ion additives. The effect plating bath pH on the nickel alloy's composition, hardness, and corrosion behavior in NaCl aqueous solution is investigated.

Experimental

Pure Fe (99.5%, Nilaco) substrate was used as substrate. The substrate was cleaned and degreased using distilled water and ethanol, respectively. Etching was conducted on the substrate using diluted hydrochloric acid for 60 s and then rinsed heavily using distilled water. The surface treated substrate was then immersed in electroless quaternary nickel alloy plating bath solution at plating bath pH 8.50, 9.00 and 9.50, adjusted using NaOH. The deposition was done at 358±2K for 3600 s. The plating bath solution comprised of nickel sulfate (0.10 M), sodium hypophosphite (0.28 M), trisodium citrate (0.20 M) and ammonium sulfate (0.50 M). The metal ion additives were copper sulfate (0.001 M) and cobalt sulfate (0.01 M).

The surface morphology of the quaternary nickel alloy coating was observed using SEM. The composition of the coating was measured using XRF analysis. Micro Vickers Hardness tester was used to determine the coated substrate hardness.

Polarization curve measurements were conducted to investigate the coatings corrosion behavior in 3.5wt% NaCl aqueous solution. The electrochemical measurement was done using classical three electrode system. The coated substrate, graphite and Ag/AgCl/KCl(saturated) were used as working electrode, counter electrode and reference electrode, respectively. Scanning rate is set to 1 mV/s from -1.00 V to 1.00 V in the 3.5wt% NaCl aqueous test solution.

Results and discussion

The deposition rates of the electroless quaternary nickel alloy calculated based on its composition, density and weight difference after deposition are shown in Table 1. The increase of deposition rate at higher plating bath pH is due to hypophosphite ion oxidize better in high OH^- ion concentration. Thus, at higher plating bath pH, Ni content (wt%) increases steadily while Cu and Co content decrease (Table 1). At plating bath pH 8.50, the coating produced shows the highest Cu and Co content compared to other pH, at 2.68 wt% and 7.54 wt% respectively. P content also descends gradually at higher pH because of the P co-deposit easily with H^+ ion. The reduction of Cu and Co content at higher plating bath pH is due to their ability to form more stable metal complex at high pH than at lower pH. The Cu content is significantly lower than Ni and Co due to lower Cu(II) ion concentration in the bath and also due to reaction inhibitor property of Cu(II) itself [6].

Table 1 Deposition rate of electroless Ni-Co-Cu-P alloy coating.

Plating bath pH	Deposition rate, R [μm/hr]	Ni [wt%]	Co [wt%]	Cu [wt%]	P [wt%]
8.50	26.1436	83.53	11.60	3.43	1.44
9.00	36.7261	88.73	7.54	2.68	2.13
9.50	45.0155	91.09	5.79	2.13	1.00

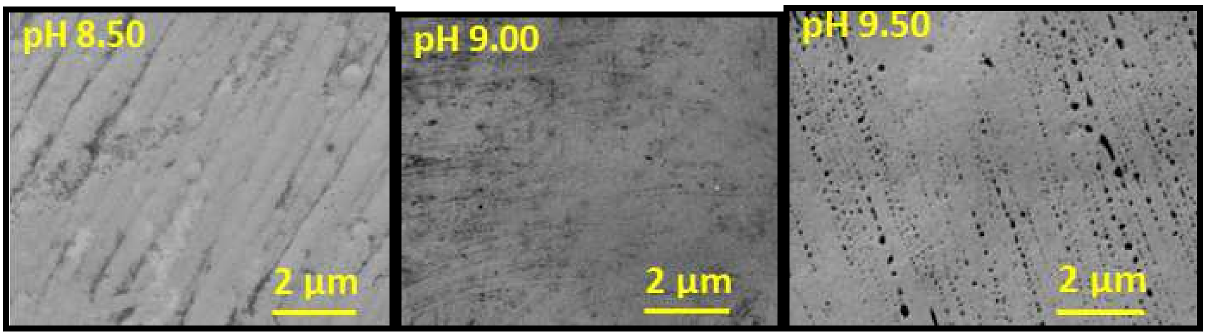

Fig. 1 SEM images of electroless Ni-Co-Cu-P alloy coating surfaces.

The quaternary Ni-Co-Cu-P alloy exhibits a very smooth and compact surface when deposited at plating bath pH of 9.50 compared to less alkaline bath (Fig. 1). This is caused by the higher deposition rate which promotes fine grain and dense deposition of the Ni alloy at more alkaline plating bath. Consequently, the hardness of the Ni alloy coating is hardest when it is produced at pH 9.50 as shown in Table 2.

Table 2 Microhardness of electroless Ni-Co-Cu-P alloy coatings.

Plating bath pH	Uncoated Fe hardness [hv]	Ni-Co-Cu-P alloy hardness [hv]
8.50	184.0	444.9
9.00	184.0	521.1
9.50	184.0	553.3

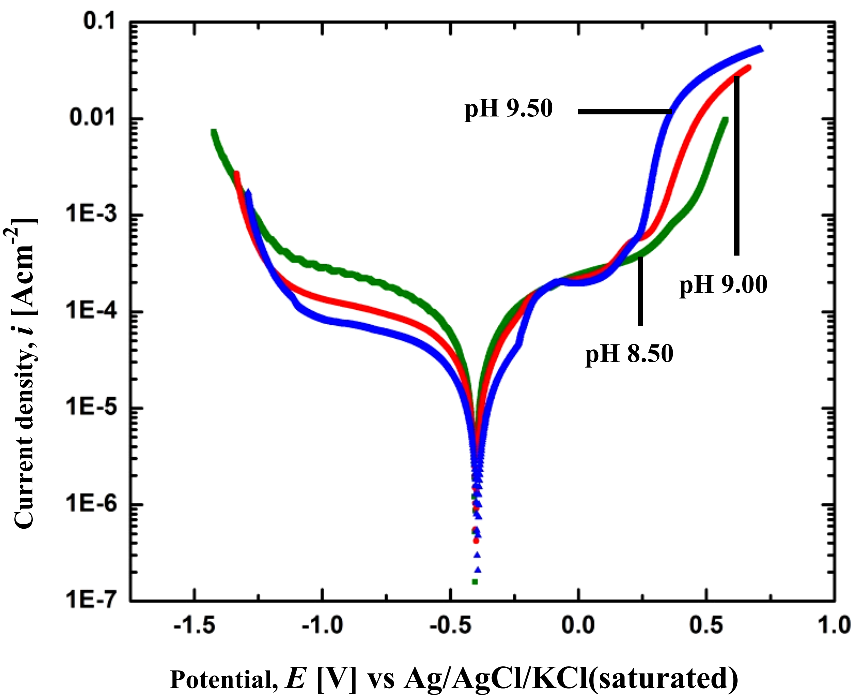

Fig. 2 Corrosion behavior of electroless Ni-Co-Cu-P alloy coating produced at various plating bath pH in 3.5wt% NaCl aqueous solution by polarization curve measurement.

Table 3 Corrosion potential and current density of substrate and electroless Ni-Co-Cu-P alloy coatings

Samples	Corrosion potential, E_{corr},[mV]	Corrosion current density, i_{corr} [μAcm^{-2}]
Fe (99.5%)	-595	41.3
Ni-Co-Cu-P (pH 8.5)	-397	673.8
Ni-Co-Cu-P (pH 9.0)	-395	185.9
Ni-Co-Cu-P (pH 9.5)	-389	23.5

From the polarization curve measurement results, the Ni-Co-Cu-P alloy coatings from all plating bath display almost similar corrosion potential (Fig. 2 and Table 3). The most noble corrosion potential is at -389 mV is from the coating produced at bath pH 9.50 and reduces very slowly at lower bath pH. Although the corrosion current density of the Ni alloy coating is higher from bath pH 8.50, its polarization curve shows slightly broader passive area compared to others (Fig. 2). The greater Cu and Co content in the Ni alloy coating may influencing the formation of much stable corrosion product with the assistance of P content.

Conclusions

The increase of electroless Ni alloy plating bath pH accelerates the deposition rate while decreases the Co, Cu and P content in the alloy coatings. The elecroless Ni-Co-Cu-P alloy coating with higher thickness and Ni content has higher hardness than the lower thickness coating. The coating with the highest Co, Cu and P content exhibits broader passive area despite having almost similar corrosion potential with the highest corrosion current density compared to others. Co, Cu and P content have significant effect on the corrosion behavior of the Ni alloy coating in neutral media.

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