

Electroless Ni-P-Cu-CuO composite coatings on mildsteel with zwitterionic surfactant

R. Muraliraja*, R. Elansezhian

Department of Mechanical Engineering, Pondicherry Engineering College, Pondicherry University, Puducherry, India.

*Corresponding e-mail: muralimechraja@gmail.com

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ABSTRACT – Binary, ternary and composite coatings were prepared by using alkaline based electroless bath on low carbon steel substrate. Nickel sulphate, copper sulfate, nano copper oxide was used as nickel, copper and nano copper particle sources, respectively. The deposits were characterized using SEM, XRD and EDS. SEM micrograph reveals the presence of proper coating and nano particles in the composite coating. EDS measurements showed that the phosphorus content in the deposit varied, due to the presence of copper. Zwitterionic surfactant was added into the electrolyte to increase the deposition rate and disperse nano particle effectively during coating. The wear resistance and friction behavior of all the coated substrates were investigated using pin on disc machine. The composite Ni-P-Cu-CuO coating exhibited better wear resistance than other binary and ternary coating in protecting the mild steel substrate.

1. INTRODUCTION

Variety of routines were found to deposit the protecting layer like paint coating, galvanization, chemical vapour deposition, physical vapour deposition, chrome plating, electroplating and electroless plating. Among these, electroless plating may be a guaranteeing in numerous commercial enterprises with novel attributes like corrosive resistance, uniform deposits and wear resistance. From the observations in the literature survey [1-6], there were no relevant research data reported on the electroless coating of Ni-P-CuO and Ni-P-Cu-CuO deposits on low carbon steel substrate, which is worthwhile attempt in our present investigation. Till now, the effect of zwitterionic surfactant (C14SB) to disperse the nano particles in electroless coating has not been studied.

This present research work focuses on development of deposits with zwitterionic surfactant and nano copper oxide, which may be referred as a comparatively new finding in the electroless coating process. The newly formulated deposits are analyzed for their morphology, structure, composition of metallic elements, surface roughness and friction and wear resistance.

2. EXPERIMENTAL DETAILS

The substrates of mild steel disc were prepared to the size of 20mm diameter and 7mm thickness. The machined substrates were mechanically polished by surface grinding followed by disc polishing. Before

coating process, pretreatment was done to evacuate the impurities and to activate the substrate surface. Three steps are concerned in pretreatment process (i) degreased by using acetone for 3min. (ii) cleaned with ethanol for 3 min. and (iii) dipped in 20% H₂SO₄ solution for 30 s. Once every stage, the substrates were rinsed in deionised water. Finally, it was placed into the electroless solution for coating on the substrate. Analytical grade chemicals of nickel sulphate, sodium hypophosphite, sodium citrate, ammonium acetate were used as source of nickel, reducing agent, complexing agent and buffering agent respectively. Zwitterionic surfactant namely 3-(n,n di-methyl myristylammonio) propane sulphonate (C14-SB) and Copper oxide nano particle (<50nm particle size) were procured from Sigma Aldrich. pH of the electrolyte is maintained at 8 by adding liquid ammonia solution. Electroless coating was carried out in a 250 ml glass beaker at 85°C for 1 hr. During co-deposition of nano copper oxide, the electrolyte was stirred magnetically to maintain the suspension of nano particle throughout the process. The specimens were rinsed with deionised water for 5 s, dried and preserved for further testing. The procedure to estimate the deposition rate of coated substrates is given in previous publication of Sudagar *et al.* [4] The surface morphology of the deposits were observed using scanning electron microscope (SEM) with voltage of 15 kV (Hitachi, Model: S-3400N), and an energy dispersive X-ray analysis (EDS) attachment was used for element identification. The structure of deposits was characterized using X-ray diffraction (XRD), Rigaku Ultima IV X-ray diffractometer with Cu anode. Retractable type surface roughness measurement tester (model: SJ-210) was used for analysis. The evolution profile was recorded in computer using SurfTest SJ USB Communication Tool software (Version 5.006).

3. RESULTS AND DISCUSSION

The effects of CuSO₄.5H₂O (1.5 g/L) presence in the plating solution on the deposition rate are shown in Figure 1. As per DIN 50988 standards, the deposition rate of Ni-P matrix is (34.38) measured. The co-deposition of Cu in Ni-P matrix reduces the deposition rate from 34.38µm/h to 24.89 µm/h. Further addition of copper nano particle in Ni-P-Cu diminishes the deposition from 24.89 to 18.97 µm/h. It is reported from the present study that addition of copper sulfate reduces the deposition rate. This trend matches with earlier data of Liu and Zhao [6]. Till now the deposition rate of

composite coating was not reported by researchers from our observation. The deposition rate of composite coating without surfactant was measured; it varies between $10 \pm 2 \mu\text{m/h}$ for the same chemical composition except surfactant concentration. But after addition of zwitterionic surfactant into the bath, it increases the deposition rate to $20 \pm 4 \mu\text{m/h}$. The mechanism to improve the coating thickness after adding C14-SB surfactant was reported, it double the deposition rate of Ni-P binary coating. A monomer layer was formed by added zwitterionic surfactant, which comprises of positive and negative head. Negative head of the surfactant monomer attracts more metallic nickel particles and pulled all the metal particles towards the substrate. Nickel deposit is also facilitated with repulsive force from the positive head of surfactant, which restrict the nickel particle to cross the monomer layer. This surfactant allows the nickel particle to coat only on the substrate surface prompting to enhance the coating thickness on the substrate.

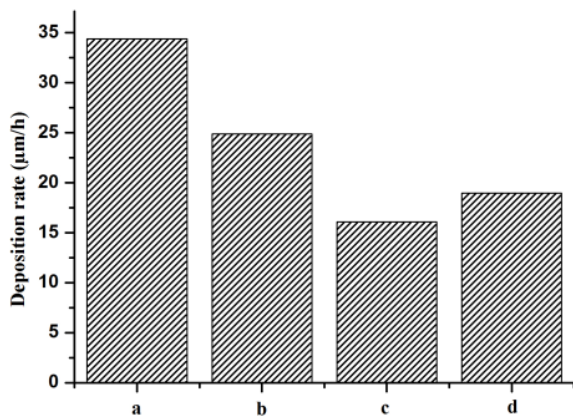


Figure 1 Deposition rate of the deposits. (a) Ni-P (b) Ni-P-Cu (c) Ni-P-CuO (d) Ni-P-Cu-CuO.

The average surface roughness (R_a) of the deposits was measured and the evolution profiles are portrayed in fig. 4. High R_a value was obtained on Ni-P deposit ($2.29 \mu\text{m}$) due to the presence of high nickel content (92.3 wt. %). These values follow an analogous trend reported by earlier researchers Elansezhian *et al.* [7]. The R_a values of Ni-P-Cu, Ni-P-CuO, Ni-P-Cu-CuO are 1.512, 1.956 and $1.510 \mu\text{m}$ respectively. From perception through SEM micrograph, the roughness of the deposit decreased with the co-deposition of copper. Introduction of copper in the deposit appears to stifle the development of the nodules by inhibiting further development. This could be the principle reason for getting very smooth deposits of ternary Ni-P-Cu and quaternary Ni-P-Cu-CuO. Incorporation of nano copper oxide in the Ni-P deposit has resulted in more nodular and rough deposit having roughness of $1.956 \mu\text{m}$.

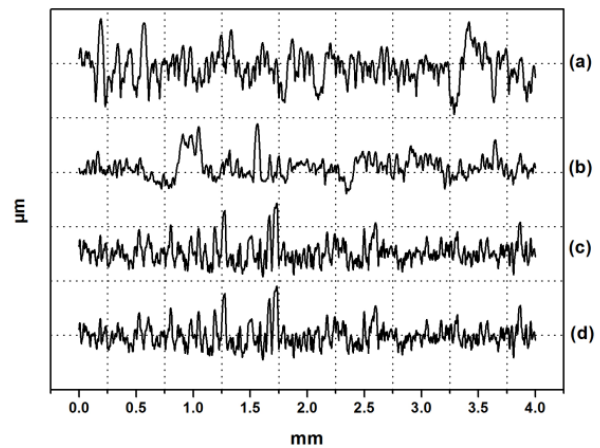


Figure 2 Evaluation profile of electroless coated deposits for roughness measurement.

4. CONCLUSION

The electroless coating with co-deposition of copper and copper nano particles are obtained using electroless coating process. The C14-SB surfactant improved the deposition rate of composite coating and helped to disperse the nano particle effectively for distribution over the substrate. R_a value of the deposit decreased after addition of copper into the Ni-P matrix. The nano copper particles have some influence in improving wear of the coatings. Due to insufficient page, wear behavior of the substrates will be discussed in full paper.

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