NICKEL-COBALT ALLOY DEPOSITION ON IRON SUBSTRATE USING ELECTROLESS DEPOSITION IN DEEP EUTECTIC SOLVENT

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ABSTRACT: Electroless deposition of Ni has been successfully done via deep eutectic solvent (DES) ionic liquid. In this study, a binary Ni-Co alloy is deposited on iron substrate using electroless deposition method in a DES ionic liquid. The DES was made from 2:1 ratio choline chloride-ethylene glycol mixture with various concentrations of nickel and cobalt salts. The coating surface hardness is measured using micro Vickers hardness tester. The coating surface morphology was observed using scanning electron microscope (SEM). Corrosion behavior of the coating in 3.5 wt% NaCl aqueous solution is evaluated using electrochemical measurement method. The thickness of the coating ranged in between 12 μm to 17 μm and shows compact and dense layer above iron surface. The coating made from higher Co to Ni salts ratio concentration in the DES exhibits higher hardness (202.36 Hv) compared to lower Co ratio coatings as well as pure Ni (185.38 Hv) and Co (196.72 Hv) coatings. The corrosion potential of Ni-Co alloy coating from 1:1 Ni to Co salts ratio DES has higher corrosion potential and shows passive oxidation surface compared to iron. Hence, the binary Ni-Co alloy deposition on iron improves the substrate's surface hardness and corrosion resistance.

KEYWORDS: *Electroless Deposition; Displacement Deposition; Deep Eutectic Solvent; Ionic Liquids; Ni –Co alloys*

1.0 INTRODUCTION

Iron is one of the most commonly used metals in various industries usually in the form of alloy. However, iron is very susceptible to corrosion with the existence of oxygen, anions and many more. To prevent corrosion of iron, a coating can be introduced on its surface such as polymer coating, ceramic coating and alloy coating. Alloy coating has the advantages to provide either galvanic protection or barrier protection or both. Also, alloy coating can improves various properties such as hardness, wear resistance and aesthetic appearance. The method of coating varies either dry process or wet process. The wet process such as electrodeposition, electroless deposition and dip coating has better coating coverage compared to dry process, hence, is used for mass production. The electroless deposition uses reducing agent to reduce metal ions without external current density and can be done on various types and complex shapes of a substrate [1]. Alloy deposition can also be done by just adding extra metal ion additives into a plating bath to produce binary alloy, ternary alloy and quaternary alloy such as Ni-P [2], Ni-Cu-P [3] and Ni-Cu-Co-P [4] alloy respectively. However, the reaction mechanism is complex and requires various parameters control including pH, metal ion concentrations, surface activation, temperature, stabilizer and complexing agent. Further study also shows that different metal ions acts differently during reaction such explained the previous study on electroless quaternary nickel alloy deposition's mechanism [5].

Another type of electroless deposition is called displacement deposition where it uses the much noble metallic ions to displace less noble metal surface. The conventional method uses metallic ions in aqueous solvent with metal substrate. Nevertheless, existence of hydroxide ions from the water solvent also promotes oxidation by hydroxide ultimately leads to corrosion to weak substrates such as steel. Gold immersion for examples uses dangerous cyanide substance in aqueous solvent [6]. The DES uses choline chloride and ethylene glycol mixture is a well-known ionic solvent and can be used as a solvent for alloy deposition [7-9]. The addition of metal salts inside the ionic solvent can solved various problems in electrodeposition such as surface oxidation prior to deposition, hydrogen embrittlement due to hydrogen gas evolution during deposition reaction and limitation to maximum metal ion concentration inside the plating bath solution [10]. Rostom et al. [11] shows that, it is possible to deposit Ni and Ag on the surface of copper from choline chloride-ethylene glycol DES by adding Ni salts and Ag salts in the solution. The surface of a substrate, in case of steel, can be activated without corrosion on the surface and the Ni^{2+} ions will be reduced and replacing the Fe atoms on the surface. However, the singular metal element coating surface is relatively soft and susceptible to corrosion compare to binary alloy [1]. The advantages of binary alloy coating are also being applied to electronic component manufacturers to replace the very costly gold deposition on printed circuit board [12]. Nevertheless, the study related to binary alloy formation from DES plating bath is less known and need to be studied.

Hence, in this study, a binary alloy of Ni-Co is deposited on steel substrate from choline chloride-ethylene glycol bath. Ni chloride salts and Co chloride salts are mixed with choline chloride-ethylene glycol DES. The surface morphology was observed using SEM and X-ray diffraction (XRD). The composition of the coating is measured using X-ray Fluorescence (XRF) analysis. Micro Vickers hardness tester is used to determine the coating hardness. Linear scanning voltammetry measurement is done in 3.5 wt% NaCl aqueous solution to investigate the corrosion behavior of the coating.

2.0 EXPERIMENTAL METHOD

Steel substrate (Fe 99.5%, Nilaco, Japan) is first polished with emery paper from grit #400 to #1200 to obtain a mirror-like surface. The substrate is then cleaned and degreased using distilled water and ethanol, respectively. Then, the substrate is immersed into a plating bath solution composed of 1:2 ChCl to EG ratio DES and added with metal salts additives. The composition and the plating parameters are shown in Table 1.

Table 1: Plating bath condition

Bath composition and parameters	**Bath #1**	**Bath #2**	**Bath #3**	**Bath #4**	**Bath #5**
$NiCl_2.6H_2O$	0.10M	-	0.10M	0.10M	0.10M
$CoCl_2.6H_2O$	-	0.10M	0.10M	0.05M	0.03M
ChCl: EG ratio	1:2				
Bath Temperature	373 K				
Deposition time	480 s				

The surface morphology of the coated samples was observed using SEM and measured hardness with microVickers hardness tester (HM-20, Mitutoyo, Japan). The XRD (PW3040/60 X'PERT PRO, PANalytical, Netherland) analysis is done to study its microstructure. The XRD measurement is done using glazing angle mode with incident angle of 0.5° from 10° to 90°.

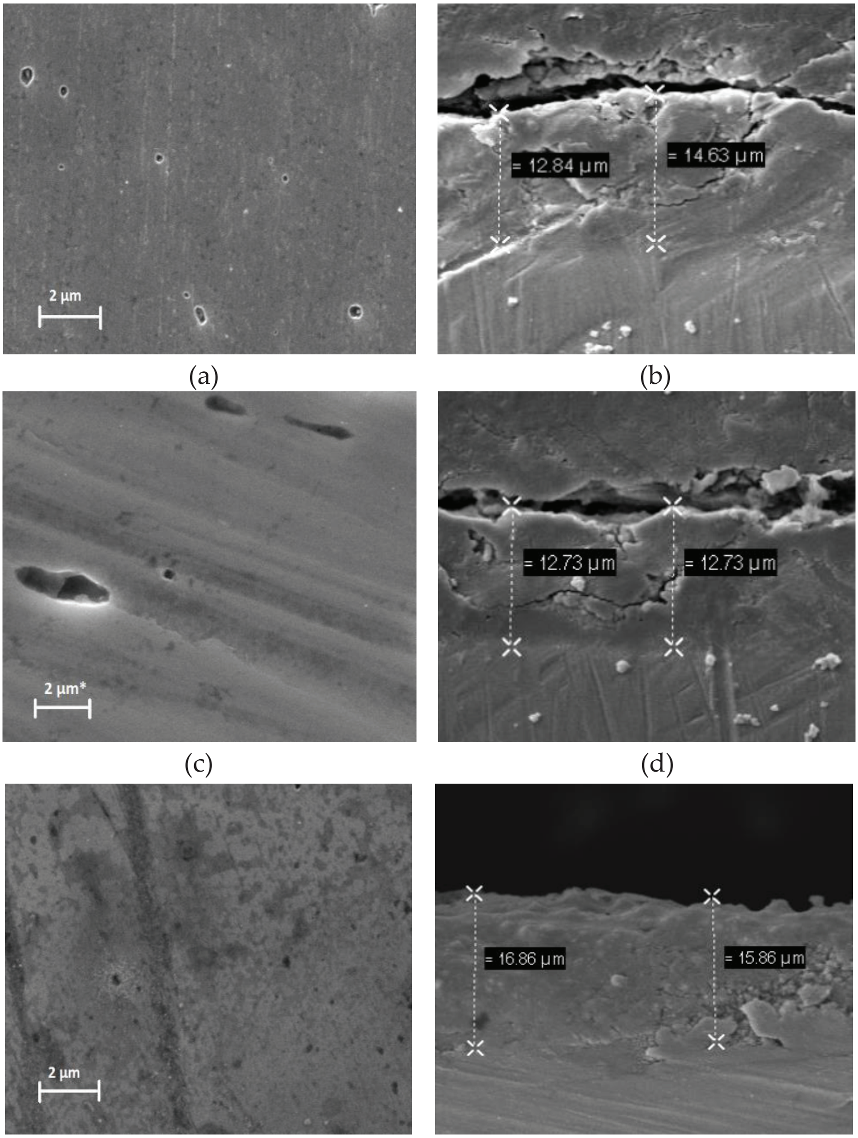
The corrosion behavior of the coated sample is investigated using linear scanning voltammetry (Autolab PGSTAT101, Metrohm, Netherland) method in a 3.5 wt% NaCl aqueous solution. The coated sample surface was used as a working electrode. Graphite rod and Ag/AgCl/KCl(saturated) are used as counter electrode and reference electrode respectively. The measurement was conducted in a classical three electrodes system after natural potential measurement for 1200 s. The scanning range is from -1.00 V to 1.00 V and the scan rate of 1 mV/s. Only one coated sample composition has measured using XRF (X-Supreme 8000, Oxford Instruments, United Kingdom) measurement to proof the existence of Co. The corrosion rate of the samples is calculated using Equation (1) and Tafel extrapolation from the linear scanning voltammetry results.

$$\text{CorrosionRate, CR} = \frac{I_{corr} \times K \times EW}{\rho \times A} \tag{1}$$

3.0 RESULTS AND DISCUSSION

The SEM micrographs of the three coatings are shown in Figure 1. In Figure 1 (e) and (f), the Ni-Co exhibits compact, dense and no micropit surface compare to Ni coating (Figure 1(a) and (b)) and Co coating (Figure 1(c) and (d)). As for the Ni and Co coating, cracks can be observed at the coatings cross section in Figure 1 (b) and Figure 1 (d) respectively. The coating thickness of can be determined by the different shade and microstructure between substrate and the coating. The thickness of the coating varies between 12.73 μm to 16.86 μm for Ni and Co coating. As shown in Figure 1 (e), the Ni-Co alloy coating exhibits the highest thickness compare to Ni and Co coatings.

The Ni-Co coating from Bath #3 composition in Table 2 is 81.4 wt% of Ni and 18.6 wt% of Co. This shows that Ni is preferable to be deposited compared to Co due to the Ni higher reduction potential [15]. Figure 2 shows the XRD measurement results of all Ni, Co and various Ni-Co alloy coating. All the coatings of Ni, Co and Ni-Co alloy main peak are at approximately 44° are slightly shifted to the left from the steel reference peak. The Co coating from Bath #2 has the highest crystallinity followed by Ni-Co from Bath #4. The high crystallinity sharp peaks are influenced by two factors, coating density and background steel substrate. However, in this case, the XRD peaks are influenced from the background steel substrate peak due to low thickness.



(a) (b)

(c) (d)

(e) (f)

Figure 1: SEM micrograph of DES electroless alloy coating (a) Ni coating, (b) Ni coating cross section, (c) Co coating, (d) Co coating cross section, (e) Ni(81.4 wt%) Co(18.6%) coating and (f) Ni(81.4 wt%) Co(18.6 wt%) coating cross section

Table 2: Composition of coatings

Bath #	Composition (wt%)	
	Ni	Co
Bath #1	100	-
Bath #2	-	100
Bath #3	81.4	18.6

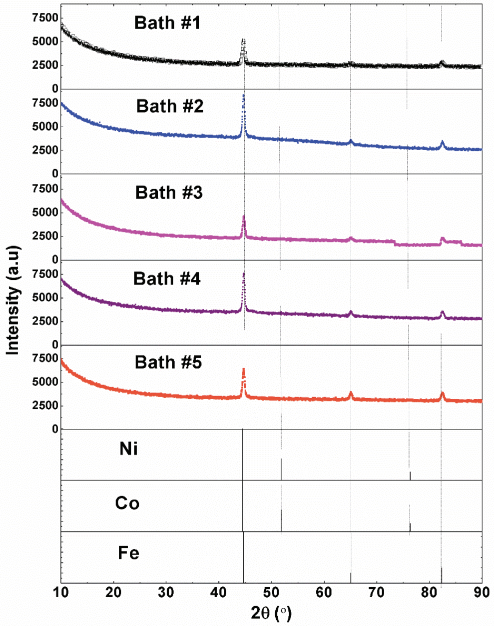


Figure 2: XRD measurement results of alloy coatings from various plating bath

Nevertheless, despite the differences in the XRD results, the surface hardness of the Ni, Co and Ni-Co alloy coating show differences. The higher Co^{2+} ion ratio in the plating bath, the Ni-Co alloy coating surface hardness is also gradually increased (Figure 3). The highest Ni-Co coating hardness achieved is from Bath #3 (202.36 Hv), where the ratio of Ni^{2+} and Co^{2+} ion concentration in plating bath is 1:1. The Ni-Co alloy coating hardness from Bath #5 is the lowest (185.12 Hv), slightly higher than the steel substrate (180 Hv). Thus, it can be deduced that the increases of Co content in the Ni-Co alloy coating improves the surface hardness and possibly improve wear resistance.

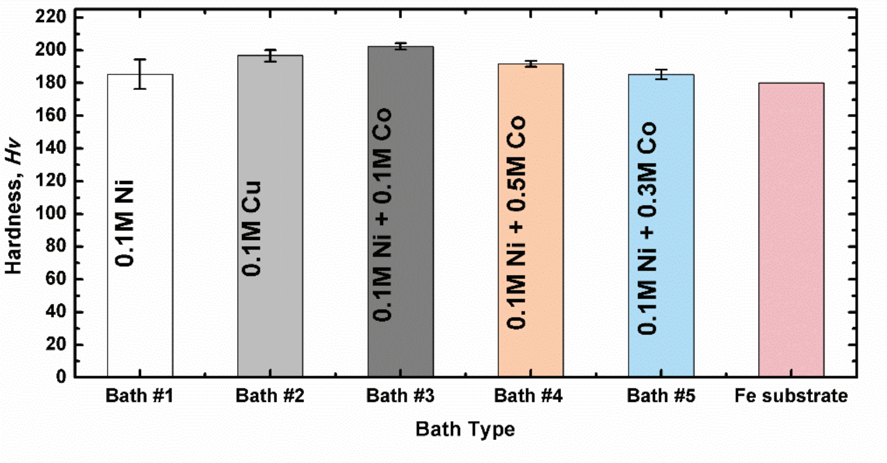


Figure 3: Surface hardness of alloy coating from various plating bath

The corrosion behavior of the steel substrate, Ni, Co, and various Ni-Co alloy coatings in 3.5 wt% NaCl aqueous solutions is depicted in Figure 4. In Figure 4(c), the surface oxidation potential of Ni-Co alloy coating from Bath #4 is the noblest compare to other coatings. The Co coating has the lowest corrosion potential compared to Ni and Ni-Co alloy coating. The existence of micropits and cracks in the Co coating could be causes of the lower oxidation potential compare to steel. Passive film behavior can be seen for Ni, Co and Ni-Co alloy coatings except Ni-Co alloy coatings from bath #5 (Figure 4(b)). The Ni-Co alloy coating from bath #5 exhibits similar characteristic as steel substrate confirming the effect of cracks and micropits on its corrosion behavior.

From the Tafel extrapolation, the corrosion rates in mm/year of all coatings including steel substrate are displayed in Table 3. As a reference, steel substrate has the highest CR of 6.42 mm/year, followed by Ni-Co coatings from Bath #5 and Bath #4. The Ni-Co alloy coating from Bath #3 has higher CR compare to Co coating, but better than Ni coating. Although the Co coating has the lowest CR compared to all, its corrosion potential is the lowest of all. It can be concluded that the Ni-Co alloy coatings from Bath #3 has the best corrosion resistance performance due to the noble corrosion potential and the passive film formation. Hence, with proper adjustment to the plating bath compositions, the Ni-Co coatings various properties can be improved by increasing the Co^{2+} concentration in the bath.

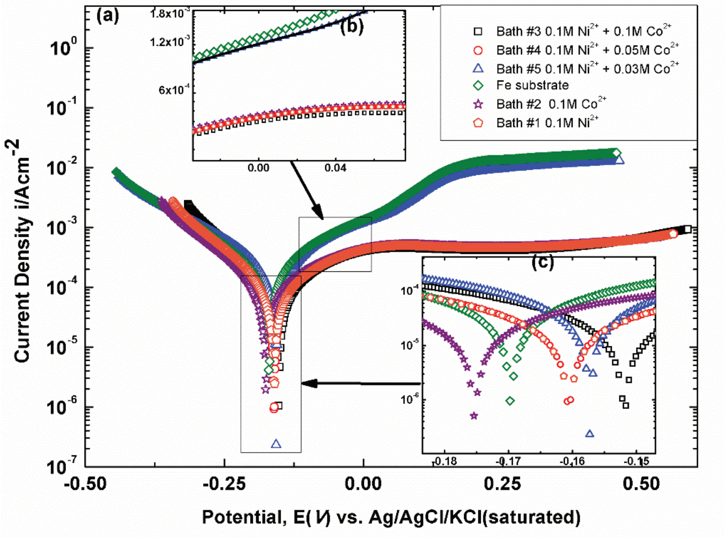


Figure 4: Corrosion behavior of steel substrate, Ni, Co and Ni-Co alloy coatings: (a) overall, (b) passive area and (c) corrosion potential

Table 3: Corrosion rate for all coatings and steel substrate in 3.5 wt% NaCl aqueous solutions

Sample	**Corrosion potential, *E_{corr}* (*V*)**	**Corrosion current density, *I_{corr}* (*A/cm²*)**	**Corrosion rate, *CR* (*mm/year*)**
Steel substrate	-0.46	5.53×10^{-4}	6.42
Bath #1 (0.1M Ni^{2+})	-0.33	2.19×10^{-4}	2.55
Bath #2 (0.1M Co^{2+})	-0.36	1.62×10^{-4}	1.15
Bath #3 (0.1M Ni^{2+} + 0.1M Co^{2+})	-0.30	1.34×10^{-4}	1.88
Bath #4 (0.1M Ni^{2+} + 0.05M Co^{2+})	-0.32	3.60×10^{-4}	5.52
Bath #5 (0.1M Ni^{2+} + 0.03M Co^{2+})	-0.35	4.89×10^{-4}	5.68

4.0 CONCLUSION

The Ni-Co alloy coatings from plating bath with Ni^{2+} to Co^{2+} ratio 1:1 has the best corrosion resistance compare to other samples due to much noble potential and passive oxide film formation. The Ni-Co alloy from the same bath has the highest hardness due to smooth, dense, micropit-free surface and cracks compare to others. The higher Co^{2+} content inside the plating bath, the Ni-Co coating hardness increases gradually and improving its wear resistance. In addition, the coating method using electroless deposition in DES can be used to deposit binary alloy on steel.

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