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Modeling of surfactants and chemistry for electroless Ni-P plating

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Abstract

In this work, the effects of the chemical formulation in an electroless nickel phosphorus electrolyte on the physical and mechanical performance of the obtained coating were evaluated. The study paid particular attention to the concentration and type of surfactant (anionic, cationic and nonionic) but also investigated the effect of pH and concentration of sodium hypophosphite in the electrolyte. A three-level Box–Behnken factorial design related to response surface methodology was employed to model the effect of the mentioned parameters and optimize the properties of the coating. Two models fitted with experimental data obtained from microhardness and thickness measurement of the Ni-P coatings. The optimum conditions were determined at pH=5 with 32 g/L sodium hypophosphite and 1.5 g/L anionic surfactant. According to the derived models this formulation would give a Ni-P coating with microhardness of 1080 Hv and thickness of 23 μm .

Keywords: Electroless nickel phosphorus coating; surfactant; response surface methodology.

1. Introduction

The process of electroless coating is well-known and can deposit metals and metal-alloy coatings on a variety of metallic and non-metallic substrates¹⁻³. This technique can be also used for the synthesis of different composite coatings as well as for the metallization of nanotubes and nanowires⁴⁻⁹. A typical example is electroless nickel phosphorus coating (EN-P) which has attracted particular interest due to its unique qualities such as high hardness and outstanding abrasion, wear and corrosion resistance^{5, 10}. The mechanical properties and corrosion resistance of EN-P depositions depend on its composition and thickness, which are functions of the electrolyte formulation and deposition operating conditions^{11, 12}. It has been widely accepted that coating thickness is a determining factor in the performance of metallic coatings for example it is generally true that a thicker coating will lead to greater corrosion resistance. However, higher coating thicknesses can have detrimental effects e.g. increased levels of internal stress and a tendency to crack under tension¹³. The wear resistance of a coating, on the other hand, tends to increase with the coating hardness¹⁴⁻¹⁶. Moreover, the surface morphology of the coating has a great effect on the friction coefficient and electrochemical behavior of the coating as it determines the coating surface roughness¹⁷⁻¹⁹. Therefore, to define the quality and performance of an EN-P coating it is important to determine the microhardness, thickness and morphology of the deposit.

Sodium hypophosphite is used as a reducing agent in the EN-P plating. There are many studies concerning the effect of hypophosphite concentration and pH on EN-P deposition rate¹⁴. It has been reported that the effective molar ratio of $\text{Ni}^+/\text{H}_2\text{PO}_2^-$ should be fixed within a limited range of 0.25 to 0.60, but the suitable range can be 0.30 to 0.45, in order to achieve optimum Ni-P coating properties^{1, 14, 20}. The nickel concentration, of an acidic type EN-P solution (pH=4-6), is normally between 4.5 to 11 g/L (0.08 to 0.19 M)¹⁴. By using this nickel

concentration range and the preferred molar ratio of $\text{Ni}^+/\text{H}_2\text{PO}_2^-$, the sodium hypophosphite concentration range obtained is typically between 0.18 and 0.27 M.

Recently it has been shown that the addition of surfactants to the EN-P bath can enhance the coating morphology²¹⁻²⁵. However, optimization of these additives in the EN-P coating process has not been widely investigated.

In this research, the effects of various surfactants (namely SDS* (anionic), CTAB† (cationic), PVP‡ (nonionic)), pH of the electrolyte and hypophosphite concentration in the coating bath on the properties of the EN-P coating (e.g. the surface morphology, microhardness and coating thickness) have been investigated. Response surface methodology (RSM) was used for modeling and optimizing of the responses to achieve maximum microhardness and coating thickness.

2. Design of experiments

Recently, response surface methodology (RSM) central composite and Box–Behnken design has been used for modeling and optimization of different processes²⁶. The Box-Behnken model can be used for the selection of points from the three-level factorial arrangement, and it could help to produce an effective estimate of the first- and second-order coefficients of the mathematical model²⁷.

In Box–Behnken designs, the experimental runs are selected from an equidistant hypersphere from the central point. This model has two major requirements, which are as following:

1. Experiment numbers, which can be calculated by

$$N = 2k(k-1) + C_p \quad (1)$$

* - sodium dodecyl sulfate
† - cetyltrimethylammonium bromide
‡ -polyvinyl pyrrolidone

Where k is the number of factors and (C_p) is the number of the central points;

2. Factor levels, which should be ordered at three surface $(-1, 0, +1)$ with equally spaced intervals between these levels²⁸.

It is noted that Box–Behnken designs (with $N=2k(k-1)+C_p$ experiments) are more economical and efficient compared with the original design with $3k$ experiments²⁹.

In this work the chosen deposition variables were designated by X_1, X_2, X_3 as the numeric factors and X_4 as a non-numeric factor (i.e. the surfactant type), and the predicted responses, microhardness and coating thickness, are designated as Y_1 and Y_2 , respectively. Table 1 depicts the coded values and actual levels of variables that were used in the present study.

3. Materials and methods

3-1 Coating deposition

The substrate employed in these experiments was mild steel (AISI 1040) with dimensions of $(20 \times 10 \times 6 \text{ mm}^3)$. The substrates were pre-treated before EN-P plating by degreasing in acetone and ethanol, followed by acid pickling for 1 min in 8 Vol.% H_2SO_4 . The samples were rinsed by deionized (DI) water and dried using air flow after each of the mentioned pretreatment stages.

The chemical formulations of the electrolytes and their operating conditions are shown in Table 2. It can be seen that the source of Ni ions was nickel sulfate whilst sodium hypophosphite was utilized as the reducing agent. SDS, CTAB and PVP were used as anionic, cationic and nonionic surfactants, respectively. The pH of the bath was kept constant by adding either hydrochloric acid or ammonia as appropriate. After electroless plating, the samples were rinsed with DI water followed by ethanol. After drying the Ni-P coated

specimens were heat treated at 400 °C under argon atmosphere for 1 hour. All chemicals were analytical reagent grade (Merck) and were used without further purification.

3-2 Methodology

The Box–Behnken factorial design was used to determine the relationship between the response functions (microhardness and coating thickness) and four variables (surfactant type, surfactant concentration, hypophosphite concentration and pH) in the EN-P coatings. The levels of these variables were chosen based on the Box–Behnken experimental design, whereas the other operational parameters were kept constant (21 g/L NiSO₄, deposition time of 60 minutes, bath temperature = 90±2 °C, and annealing temperature = 400 °C). The level of four deposition variables studied was given in Table 1 in the previous section.

3-3 Measurements of coating properties

Surface morphology and phase composition of the EN-P coatings were characterized by using scanning electron microscopy (SEM) (CamScan MV2300) and XRD analyzer equipment (Philips X'pert, X-ray diffraction, Cu K α radiation) with X'pert Highscore 1.0d software respectively. Coating thicknesses were measured by Elcometer 355 probe and optical microscope (Leica make, Model DMIRM). A Microhardness tester (Struers-Duramin), with a diamond pyramid as an indenter in 50 g load, was used for microhardness estimation of the EN-P deposits. The average of five measurements is reported as the final result for each sample.

4. Results and Discussion

51 sets of experiments with appropriate combinations of X₁, X₂, X₃ and X₄ were performed by using the Box–Behnken method. Table 3 lists the experimental design matrix of the variables in actual levels of experimental design and the responses.

4-1 Determination of a model equation for the microhardness value

Using multiple regression analysis, the experimental results that are listed in Table 3 were fitted to a full quadratic (second order) model for microhardness by employing Design Expert V.7 software. The regression coefficients for the selected terms in the model were determined and found to be significant. This analysis enabled a model equation for microhardness (Y1) to be determined which included expressions for pH(X1), sodium hypophosphite concentration (X2) and surfactant concentration (X3) for each surfactant as shown below:

For anionic surfactant:

$$Y_1 = 646.183 + 818.269X_1 - 150.747X_2 + 121.768X_3 + 5.517X_1.X_2 - 0.864X_1.X_3 - 2.660X_2.X_3 - 89.096X_1^2 + 2.445X_2^2 - 18.950X_3^2 \quad (2)$$

For cationic surfactant:

$$Y_1 = 623.335 + 924.148X_1 - 171.830X_2 + 133.709X_3 + 5.5170X_1.X_2 - 0.864X_1.X_3 - 2.660 X_2.X_3 - 89.096X_1^2 + 2.445X_2^2 - 18.950X_3^2 \quad (3)$$

For nonionic surfactant:

$$Y_1 = 933.545 + 838.222X_1 - 163.757X_2 + 94.431X_3 + 5.517X_1.X_2 - 0.864X_1.X_3 - 2.660 X_2.X_3 - 89.096X_1^2 + 2.445X_2^2 - 18.950X_3^2 \quad (4)$$

4-2 Construction of the model equation for the coating thickness

Among different models, software suggested a linear model for the coating thickness results presented in Table 3. The model equation representing the coating thickness (Y2) was shown as follow:

For anionic surfactant:

$$Y_2 = -9.145 + 5.750X_1 + 0.069X_2 + 0.217X_3 \quad (5)$$

For cationic surfactant:

$$Y_2 = -17.020 + 5.750X_1 + 0.069X_2 + 0.217X_3 \quad (6)$$

For nonionic surfactant:

$$Y_2 = -14.337 + 5.750X_1 + 0.069X_2 + 0.217X_3 \quad (7)$$

To estimate the significance of the model, the analysis of variance (ANOVA) was conducted in the confidence interval of 90%. The P-Values, shown in Table 4, clearly indicate that the model fits the results very well.

4-3 Optimization studies for microhardness and coating thickness

Quadratic programming of the Design Expert V.7 software was employed to optimize the model equations to maximize microhardness and coating thickness within the investigated experimental array. The optimum deposition variables were found to be pH=5, 32 g/L sodium hypophosphite and 1.5 g/L anionic surfactant (SDS), which resulted in the maximum microhardness and maximum coating thickness. At these optimum conditions, the model predicted a coating with microhardness value of 1080 Hv and thickness of 23 μm .

The models were validated by selecting three EN-P plating conditions and comparing the observed and the predicted as shown in Table 5. It can be seen that the model gave results which were very close to the actual results and the model could describe 90% of the total variations in the investigated method.

4-4 Three-dimensional (3D) response surface plots

The three-dimensional (3D) plots were employed to gain a better description of the effects of the electrolyte and deposition conditions on the coatings microhardness and thickness. These graphs were plotted based on the model equations. Fig. 1 (a) displays the 3D response surface relationship between pH (X_1) and Sodium hypophosphite concentration (X_2) on microhardness at the center level of the surfactant concentration (X_3). The graphs indicate a

good relationship between dependent and independent parameters. While the model processes three factors, one of them was kept constant at the center level for every plot. Consequently, the whole of three response surface plots were created. According to Fig. 1(a), the coating microhardness could be significantly raised with the increasing pH (X_1) and sodium hypophosphite concentration (X_2). Fig. 1 (b) displays the 3D response surface relationship between pH (X_1) and surfactant concentration (X_3) on microhardness at a center level of hypophosphite content (X_2). Unlike what was shown in Fig. 1(a), Fig. 1(b) indicates that the microhardness value decreased beyond the mid-point concentration of surfactant. Fig. 1(c) shows the 3D response surface correlation between sodium hypophosphite concentration (X_2) and surfactant concentration (X_3) on the microhardness at the center level of pH (X_1). These results demonstrate that the maximum microhardness value was obtained with the middle level of surfactant concentration (X_3) and maximum levels of pH (X_1) and the sodium hypophosphite concentration (X_2). The reason for this result can be explained according to the theoretical effects of each parameter. The pH and surfactant acts as accelerator and decreases the grain size thus improving the morphology of EN-P coatings. Sodium hypophosphite according to the mechanism of EN-P deposition, has two main effects. First, it acts as an electron provider and second, it is the source of phosphorus elements. By increasing its concentration, the deposition rate can increase since it can support the need for extra electrons. The deeper explanation of the effect of each parameter is given in the next section.

4-5 Properties of the EN-P coatings

SEM micrographs of the EN-P deposits produced under different operating conditions are presented in Fig. 2, which shows the effects of the mentioned surfactants. It can be seen that the morphology of the EN-P coating which was fabricated in the presence of SDS is spherical, nodular and fine. The coatings morphologies also revealed a more uniform coating obtained in presence of SDS compared to PVP and CTAB. For the deposit obtained with PVP in the

electroless nickel formulation (Fig. 2(c)) a cluster shape can be seen to have appeared. This cluster shape was also seen when the surfactant CTAB was used although they were of a smaller size. However, there were no clusters observed in the coating which were plated from an electroless nickel solution that contained SDS as a surfactant. The positive influence of SDS on the surface roughness and surface morphology of EN-P coating has been previously shown by Lin and Duh³⁰. Sudagar et al.³¹ also reported a 50% increase in the smoothness of Ni-P coating through addition of surfactant to the electrolyte.

It seems that SDS improves formation of EN-P coating by promoting the adsorption of Ni²⁺ ions. The hydrophobic groups of SDS ions get close to the surface and the hydrophilic group interacts with the aqueous phase. Thus, the adsorption of Ni²⁺ ions in the coating bath by the hydrophilic group of SDS can improve the precipitation process. In addition, Chen et al.³² reports that the surfactant can remove hydrogen bubbles (H₂) during the deposition process leading to a pit-free nickel coating. Fig. 3a displays their suggested mechanism for hydrogen bubble removal.

The performances of CTAB and PVP surfactants, however, are not comparable with that of SDS in this regard. According to Fig. 1, the microhardness of the EN-P coatings increased with hypophosphite concentration and pH value, and surfactant concentration until the critical micelle concentration (CMC) was obtained. The enhanced performance of SDS regarding the coating microhardness compared to that of CTAB was also reported by Sudagar et al.³¹ and it is proposed that this is due to the anionic nature of SDS enabling it to more readily interact with positively charged Ni and H ions.

Fig. 4 shows EDS spectra of the coatings that were obtained under conditions 4 and 9 listed in Table 3. These EDS spectra demonstrate that an increase in the hypophosphite concentration caused larger phosphorus content in the coating. Consequently, the fraction of Ni₃P, as a hard

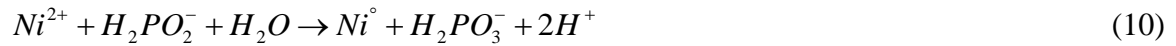
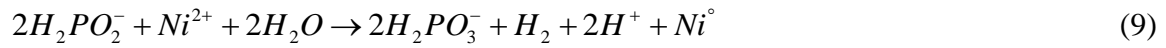
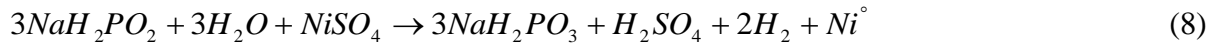
phase in Ni-P coating, increased and contributed to the higher microhardness which was determined after heat treatment³³.

Fig. 5 reports the XRD patterns of the EN-P coatings that were obtained under the particular conditions for runs 1, 6 and 7 in Table 3. Comparing these results with results of other studies^{21-24, 31, 32} revealed that adding of SDS to the deposition bath caused the microstructure of the Ni-P coating to change from more crystalline to a nano-crystalline/amorphous. The change in deposit morphology described might explain the higher microhardness which was found when SDS was added to the electrolyte.

The obtained results indicated that the positive effect of the surfactant on deposit properties was improved with pH of the coating bath. The results suggest that addition of the surfactant caused a greater adsorption of Ni²⁺ and consequently higher deposition rates, effects that were also described by Chen et al.³² and Kumor²⁵. In addition, Chen et al.³² found that addition of low concentrations of surfactants to the electroless solution caused higher deposition rates (up to 26% greater than the deposition rate from a surfactant-free bath). This effect can be due to the ability of surfactants in increase the wettability of the substrate by reducing the surface tension between the catalytic surfaces and coating solution. Fig. 3.b shows this mechanism which was suggested by Elansezhian et al^{21, 22} and authors previous reports^{23, 24}.

An increase in the pH of the coating bath accelerated the deposition rate and improved both the surfactant effect and the coating microstructure. As was mentioned previously, an increase in the pH value of the electrolyte leads to a harder deposit. According to Xinyu Mao³⁴ et al, with increasing pH value of the plating bath, a decrease in the phosphorus content of the coatings was found whilst the microstructure changed from amorphous to nano- crystalline. They explained the pH effect by the fact of the hardness of amorphous phase is lower than nanocrystalline phase. In addition, the pH increased the deposition rate and as a consequence, the obtained coating was finer grain size. The following reactions¹ displays the nickel

electroless deposition. As it shown the main productions are H^+ and Ni. So by increasing the pH, the tendency for H^+ production increased because of decreasing H^+ content and as result the deposition rate can be increased. The same trend may be seen here but other parameters have contributed to the improvement of properties and these cannot distinguished clearly.



Under these conditions, the effects of the surfactant decreased significantly. It was shown in this study that the surfactants mainly affect the grain size, microhardness, uniformity and morphology of the EN-P coatings.

4. Conclusion

In this study a Box–Behnken factorial design was employed with Response Surface Methodology in order to model four variables in the chemistry of an EN-P coating solution formulation (types and concentration of surfactant, hypophosphite concentration and deposition bath pH) and to optimize the microhardness and thickness of the EN-P coatings. Mathematical software was used to extract model equations for the coatings microhardness and thickness derived from data obtained from a designed experiment. It can be concluded from this investigation that agreement between the predicted and observed values was very good using the model equations. Quadratic programming was utilized to optimize these equations to elucidate the conditions required to achieve maximized microhardness and coating thickness. It was found that the optimum operating conditions for the Ni-P were

pH=5, 32 g/L Sodium Hypophosphite and 1.5 g/L Surfactant. The anionic surfactant performed better than the cationic and nonionic surfactants regarding the microstructure, surface morphology, thickness and microhardness of the EN-P coatings.

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Tables:

Table 1. Variables and levels used in the Box–Behnken designed experiment

Table 2. Electrolyte composition and operating conditions.

Table 3. Box–Behnken design with the experimental results

Table 4. Analysis of variance (ANOVA) for response surface quadratic model to predict microhardness and coating thickness

Table 5. Experimental and predicted values for Coating's microhardness and thickness

Table 1

Variable	Symbol	Coded variable level		
		Low -1	Center 0	High +1
pH	X1	4.0	4.9	5.8
Sodium hypophosphite concentration (g /l)	X2	24	28	32
Surfactant concentration (g /l)	X3	0.50	1.25	2.00
Surfactant type	X4	Anionic	Cationic	Nonionic

Table 2

Bath Composition		Operating conditions	
Nickel sulphate (g /l)	21	pH	4.0 - 5.8
Sodium hypophosphite(g /l)	24-32	Deposition temp (°C)	90± 2
Lactic acid (g /l)	23	Bath vol. (ml)	250
Picric acid (g /l)	2.2	Annealing. Tem. (°C)	400
Surfactant (g /l)	0.50 – 2	Deposition time	60 min

Table 3.

Run	Actual level of variables				Observed results	
	X ₁	X ₂ (g /1)	X ₃ (g /1)	X ₄ (surf. charged)	Microhardness (HV)	Coating Thickness (μm)
1	4	24	1.25	Anionic	816	11.71
2	5.8	24	1.25	Anionic	988	27.84
3	4	32	1.25	Anionic	1010	11.82
4	5.8	32	1.25	Anionic	1047	33.29
5	4	28	0.5	Anionic	784	15.59
6	5.8	28	0.5	Anionic	1012	24.65
7	4	28	2	Anionic	752	17.41
8	5.8	28	2	Anionic	1024	24.13
9	4.9	24	0.5	Anionic	1016	20.61
10	4.9	32	0.5	Anionic	1078	21.51
11	4.9	24	2	Anionic	1044	17.99
12	4.9	32	2	Anionic	1045	26.03
13	4.9	28	1.25	Anionic	1063	24.54
14	4.9	28	1.25	Anionic	930	20.67
15	4.9	28	1.25	Anionic	977	21.33
16	4.9	28	1.25	Anionic	968	20.38
17	4.9	28	1.25	Anionic	984	21.42
18	4	24	1.25	Cationic	845	12.98
19	5.8	24	1.25	Cationic	990	15.54
20	4	32	1.25	Cationic	556	10
21	5.8	32	1.25	Cationic	959	19.77
22	4	28	0.5	Cationic	571	15.88
23	5.8	28	0.5	Cationic	1001	12.93
24	4	28	2	Cationic	566	6.69
25	5.8	28	2	Cationic	1059	22.02
26	4.9	24	0.5	Cationic	983	11.18
27	4.9	32	0.5	Cationic	960	11.89
28	4.9	24	2	Cationic	976	15.3
29	4.9	32	2	Cationic	960	11.44
30	4.9	28	1.25	Cationic	954	11.34
31	4.9	28	1.25	Cationic	906	13.02
32	4.9	28	1.25	Cationic	983	12.54
33	4.9	28	1.25	Cationic	952	11.77
34	4.9	28	1.25	Cationic	963	12.75
35	4	24	1.25	Nonionic	856	12.19
36	5.8	24	1.25	Nonionic	1171	23.34
37	4	32	1.25	Nonionic	742	7.17
38	5.8	32	1.25	Nonionic	1173	20.34
39	4	28	0.5	Nonionic	944	5.87
40	5.8	28	0.5	Nonionic	1055	26
41	4	28	2	Nonionic	895	12.67
42	5.8	28	2	Nonionic	891	14.34
43	4.9	24	0.5	Nonionic	939	13.67
44	4.9	32	0.5	Nonionic	964	17.34
45	4.9	24	2	Nonionic	971	17.34
46	4.9	32	2	Nonionic	956	15.67
47	4.9	28	1.25	Nonionic	949	16.67
48	4.9	28	1.25	Nonionic	947	17
49	4.9	28	1.25	Nonionic	935	17.34
50	4.9	28	1.25	Nonionic	973	18
51	4.9	28	1.25	Nonionic	952	17.71

Table 4.

	Source	Sum of Squares	DOF	Mean Square	F Value	p-value
Microhardness	Model	6.099×10 ⁵	17	35874.07	6.00	< 0.0001
	Residual	1.973×10 ⁵	33	5978.43	-	-
Coating thickness	Model	1190.32	5	238.06	24.22	< 0.0001
	Residual	442.22	45	9.83	-	-

Table 5.

Run	Actual level of variables				Observed results		predicted results		Error%
	X ₁	X ₂ (g/l)	X ₃ (g/l)	X ₄ (Surf. charged)	Microhardness (HV)	Coating Thickness (μm)	Microhardness (HV)	Coating Thickness (μm)	
1	5	32	1.5	Anionic	1080	23.0	1110	24.0	Max 5%
2	5	32	1.5	Cationic	1178	15.0	1125	16.5	Max 10%
3	5	32	1.5	Nonionic	1008	17.0	965	18.0	Max 6%