Optimization of process parameters on the response of corrosion resistance of electroless Ni-Co-P coating using Box-Behnken Design (BBD)

S Sarkar1*, I Koley2, R K Baranwal1, A Mukherjee1, S Lamicheaney1, GM Majumdar1

1Department of Mechanical Engineering, Jadavpur University, Kolkata-700032, India
2Department of Metallurgical and Materials Engineering, IIEST, Shibpur-711103, India

subha.jumechanical@gmail.com

Abstract.
Ternary Ni-Co-P alloy coating was chosen to improve the corrosion resistance of the Copper substrate. Box-Behnken Design (BBD) of experiment was utilized for the optimization of the effects of different process parameters such as Cobalt Sulphate, Sodium Hypophosphite, and temperature. Electrochemical Impedance Spectroscopy (EIS) was used to study the corrosion resistance behaviour of different samples by altering different parameters. Analysis of Variance (ANOVA) was done to determine the important process parameters and their significant interactions. The surface morphology, microstructures and elemental compositions of the as-deposited coatings were analyzed using Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Energy Dispersive X-Ray Spectroscopy (EDX) respectively. Finally, 15g/L of Cobalt Sulphate, 25g/L of Sodium Hypophosphite, and 85°C of bath temperature were found out to be the optimum conditions for coating deposition in order obtain a corrosion resistance of 1165 ohm-cm².

1. Introduction
During the early 19th century, scientists invented the electroless coating technique [1]. Electroless nickel (EN) coating is indisputably one of the most essential autocatalytic procedures in use today which involves various chemical reactions taking place in an electroless bath. It does not involve the use of exterior electric current unlike conventional electroplating processes. In electroplating or electro-deposition processes, the substrate acts as the cathode, towards which the cations of the electrolyte migrate and due to opposite polarity, the metal ions get deposited on the substrate. On the other hand, in electroless coating, in order to produce enough electrons for the reduction of the substrate, a reducing agent is used. The release of hydrogen gas by the oxidation of the reducing agent denotes the accomplishment of the reaction, thus creating a negative charge on that surface.

Electroless Nickel (EN) coatings can be broadly classified into four categories based on the composition viz. pure nickel, alloy, and poly-alloy coatings, and composite coatings [2]. The alloy and poly-alloy coatings can be further classified into binary alloy coatings, ternary alloy coatings, and
quaternary alloy coatings. As the name suggests, binary alloys consist of two elements in the coating microstructure, for example, Ni-P and Ni-B. Ni-B coatings are known for their high hardness along with the competence to retain lubricants attributable to their cauliflower-shaped surface morphology. On the other hand, Ni-P coatings have a smoother surface with a wavy surface texture. Similarly, in ternary alloys there are three elements present, for example, Ni-Co-P, Ni-W-P, Ni-Cu-P etc. and in quaternary alloys there are presence of four elements, for example Ni-W-Cu-P [3]. EN composite coatings, on the other hand, are formed by the implementation of an inert phase component (PTFE, SiC, Al₂O₃, WC, TiO₂, ZrO₂, etc.) into the metal matrix thereby improving the tribological properties to a greater extent.

In the present scenario, there has been a considerable increase in the requirement of preparation of materials that would be suitable and fit for use to the maximum possible extent in any desired environment along with the best possible aesthetic properties. In automobile, petroleum, aerospace, chemical, electronics, and other industries, there has been a huge problem pertaining to the corroding away of specifically manufactured precision and critical parts resulting in huge loss and increased cost of manufacturing. Hence, corrosion resistance is one of the most vital properties which would help in achieving the aforesaid goal. Now, if we apply a coating on the base material such that the deposited material has high corrosion resistance, then it would act as a sacrificial layer and prevent the base material from getting corroded and hence, would definitely increase the longevity of the sample. The urge for improved mechanical, chemical and tribological properties has motivated researchers to develop alternating compositions of electroless nickel coatings to be deposited over the base substrate. Electroless Ni-P coatings, based on the phosphorous content, provide excellent corrosion, wear, and abrasion resistance and can be applied on irregular shaped structures which led to its great applications in the above-mentioned industries. Heat treatment can also improve some of these properties. Inclusion of a third element, for example W, Co, Cu, Mo etc. in the Ni-P matrix, enhances its properties to a greater extent thereby providing the desired properties to the coated substrates [4,5]. Being a ferromagnetic material, cobalt is considered to be one of the best elements to impart magnetic properties to the sample by increasing the coercive force and decreasing the residual magnetism of the electroless Ni-Co-P deposits. Thus, electroless Ni-Co-P deposits over copper substrate are supposed to have great corrosion, wear, abrasion resistance, electrical and magnetic properties along with properties such as ductility, malleability, thermal stability which are contributed by the copper substrate [6].

The current study is focussed on the optimization of process parameters of Ni-Co-P coatings considering corrosion resistance as a response. The electroless Ni-Co-P coating has been deposited over the copper substrate and the bath parameters have been optimized using Box-Behnken Design [7] of experiment which has been chosen to be the mathematical tool for optimizing the corrosion resistance to the maximum amongst other optimization techniques in this study. The as-deposited samples have been tested by the EIS technique to evaluate their corrosion resistance. Additionally, the observed data have been analyzed statistically for determining the optimized process parameters to improve the corrosion resistance of the coating using Analysis of Variance (ANOVA). The as-deposited substrates have been further characterized using Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Energy Dispersive X-Ray Spectroscopy (EDX) for determining the surface morphology, elemental phases and percentages respectively.

2. Experimental Details:

2.1 Preparation of Substrate

Pre-treated copper samples of dimensions 1.5×1.5 cm² are cut very precisely from a copper foil (thickness 0.1mm, 99% with purity copper). After the selection of substrates for metal deposition, they are subjected to successive cleaning processes in order to get rid of any foreign particles or abrasives. At first, the prepared sample is rinsed with distilled water for 2 minutes to clean off any dirt particles; and then the sample is again acid cleaned with HCl (25% dilute) for 10 minutes to ensure the removal of any surface layer like rust and other oxides. Finally, the acid cleaned sample is dipped in distilled water for a few seconds to remove the acid remains on the surface of the samples. Then the sample is
activated in Palladium chloride (PdCl₂) solution for 8-10 seconds at 55 °C to overcome the initial energy barrier and kick start the deposition process. Then the sample is immersed into the electroless Ni-Co-P bath with compositions as shown in Table 1.

### Table 1. Chemical composition and the agents of the Ni-Co-P electroless bath

| Bath composition                        | Quantity |
|-----------------------------------------|----------|
| Nickel Sulphate (NiSO₄·6H₂O)            | 25g/L    |
| Cobalt Sulphate (CoSO₄·7H₂O)           | 10-20g/l |
| Sodium Hypophosphite (NaH₂PO₂·H₂O)     | 20-30g/l |
| Tri-Sodium Citrate Dihydrate (Na₃C₆H₅O₇·2H₂O) | 15g/L    |
| Ammonium Sulphate ((NH₄)₂SO₄)          | 10g/L    |
| pH value                                | 5        |
| Time                                    | 1hr      |
| Bath volume                             | 250cm³   |
| Temperature                             | 80°C-90°C|

#### 2.2 Design of Experiment

A group of rotatable or nearly rotatable second-order designs that are based on incomplete three-level factorial designs is defined as Box-Behnken Design (BBD) of experiment. Responses and Factors are the two types of variables during the multivariate optimization procedure. The responses are the dependent variables since their values depend on the levels of the factors, which can be classified as qualitative or quantitative. Combined effects of three independent variables, i.e. Cobalt sulphate, Sodium hypophosphite, and temperature are analyzed on corrosion resistance. The independent factor levels were coded as −1 (low), 0 (central point or middle), and 1 (high). The set of experiments are shown in Table 2.

### Table 2. Set of experimental data for the Box–Behnken Design of electroless Ni-Co-P coating

| Expt. No. | Cobalt Sulphate | Sodium Hypophosphite | Temperature | R1 (ohm cm²) | R2 (ohm cm²) | C(mF/cm²) |
|-----------|-----------------|----------------------|-------------|--------------|--------------|-----------|
| 1         | 15              | 30                   | 90          | 37.158       | 576.79       | 1.0985    |
| 2         | 10              | 25                   | 90          | 46.643       | 1137.21      | 1.215     |
| 3         | 15              | 20                   | 90          | 37.535       | 927.25       | 1.7164    |
| 4         | 10              | 20                   | 85          | 39.508       | 1173.4       | .856      |
| 5         | 15              | 25                   | 85          | 26.31        | 1072.63      | 4.6322    |
| 6         | 20              | 25                   | 80          | 21.98        | 452.54       | 70.106    |
| 7         | 20              | 20                   | 85          | 36.424       | 436.41       | 28.38     |
| 8         | 15              | 20                   | 80          | 22.55        | 454.5        | 22.092    |
| 9         | 20              | 25                   | 90          | 35.701       | 1198.5       | 8.3785    |
| 10        | 15              | 25                   | 85          | 29.669       | 1023.58      | 0.6894    |
| 11        | 20              | 30                   | 85          | 29.261       | 1101.29      | 0.821     |
| 12        | 15              | 25                   | 85          | 8.8588       | 456.32       | 2.3834    |
| 13        | 15              | 25                   | 85          | 34.794       | 1043.87      | 1.4472    |
| 14        | 10              | 25                   | 80          | 20.743       | 398.64       | 118.88    |
| 15        | 10              | 30                   | 85          | 14.265       | 532.34       | 14.886    |
| 16        | 15              | 25                   | 85          | 14.486       | 420.43       | 49.352    |
| 17        | 15              | 30                   | 80          | 37.516       | 987.34       | 20.915    |
2.3 Experimental details of obtaining corrosion resistance by electrochemical impedance spectroscopy

The electrochemical corrosion analysis of the samples is evaluated by Electrochemical Impedance Spectroscopy (EIS). Electrochemical tests were done in a 3.5 wt. % NaCl aerated aqueous solution using a classic three-electrode cell with a Pt-wire as counter-electrode and an Ag/AgCl electrode (q207 mV vs. SHE) as reference. The sample is enclosed by polyester resin and a certain area is left exposed (approximately 1.5 cm) for testing the series and parallel resistance of the sample. Rs (solution resistance), Rp (polarization resistance), C (double layer capacitance) were monitored during the immersion time and the EIS data is optimized through the different optimization techniques to obtain the best combination of the input parameters.

The experimental results from Potentiodynamic and electrochemical impedance spectroscopy (EIS) in Table 2, were fed into the Design Expert software package to set up mutual relationships between three independent variables according to the following equation:

\[ Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_{ij} \]  

Where X1, X2, and X3 are the coded values. Therefore the predicted responses are influenced by coded values and set of regression coefficients: \( \beta_0 \) (intercept coefficients), \( \beta_i \), \( \beta_{ii} \), \( \beta_{ij} \) (linear coefficients), \( \beta_{11}, \beta_{22}, \beta_{33} \) (quadratic coefficients), \( \beta_{12}, \beta_{13}, \beta_{23} \) (interaction coefficients). The model terms were confirmed or declined in terms of the probability (P) value with a 95% confidence level. Using the Design Expert software, the results were completely analyzed via the analysis of variance (ANOVA).

3. RESULTS AND DISCUSSION

3.1 Data Analysis

A Box-Behnken experimental design with 3 independent variables at 3 different levels was used to study the effects on dependent variables. The second-order response representing the incorporation of Cobalt can be expressed as a function of Cobalt sulphate (X1), Sodium hypophosphite (X2), and temperature (X3) content in the electroless bath.

The dependent variable obtained at various levels of the 3 independent variables (X1, X2, and X3) was subjected to multiple regressions to yield a second-order polynomial equation (full model):

\[ \text{Corrosion Resistance (R2)} = 1085.34 - 143.59 \times X1 + 90.19 \times X2 + 74.57 \times X3 + 198.54 \times X1 \times X2 - 193.62 \times X1 \times X3 - 6.59 \times X2 \times X3 - 46.88 \times X1^2 - 150.03 \times X2^2 - 435.31 \times X3^2 \]  

As obtained from the ANOVA results, the value of the correlation coefficient (R-Squared) of Equation 2 was found to be 0.9279, indicating a good fit. P-Value of the model is 0.0031, which is less than 0.0500 indicate model terms are significant. The Model F-value for this response surface measurement indicates 10.00, which implies the model is significant. In this case, A, AB, AC, C² are significant model terms.

3.2 Discussion on 3-D and Contour Plot for Corrosion resistance (R2)

The response surface plot in Figure 1 shows that the corrosion resistance has a high influence of X2 and less of X1. This can be inferred from the fact that the corrosion resistance ameliorated with the impact of X2 (higher contour values are observed for X2). Figure 2 shows that the corrosion resistance has a huge impact of X3 and slight effect of X1. The contour plot suggests that the surface is not symmetrical and the peaks are not in the center. Figure 3 indicates that the corrosion resistance increases with the increase of X2 and X3. From the contour plots, we can optimize the process parameter of cobalt sulphate 15gm/L, sodium hypophosphite 25gm/L and temperature 85°C, with optimized surface response (corrosion resistance) of 1165 ohm cm².
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Figure 1: Second order 3-D and Contour plot showing the interaction effect of X1 and X2 with response to corrosion resistance

Figure 2: Second order 3-D and Contour plot showing the interaction effect of X1 and X3 with response to corrosion resistance

Figure 3: Second order 3-D and Contour plot showing the interaction effect of X2 and X3 with response to corrosion resistance

3.3 SEM and EDX analysis of the as-deposited optimized electroless Ni-Co-P coating

The study of surface morphology of the as-deposited coated substrates was done with the aid of Scanning Electron Microscopy (SEM) in order to analyze the effect of electroless Ni-Co-P deposits in improving the corrosion resistance of the copper substrate by providing a sacrificial layer over it. Figure 4 shows the SEM micrograph of the optimized as-deposited surface at an optimal combination of the parameters A, B, and C. It depicts a compact coating with well-marked grain boundaries and minimum defects having no cracks and holes. Due to the low porosity of the coating as observed from the SEM micrograph, we can conclude that the coating will prevent any foreign particles or abrasives from seeping in and reaching the substrate thus acting as a protective barrier thereby increasing its corrosion resistance. It is well observed that there are many globular particles on the surface of the substrate which are quite spherical in shape and with sizes varying in the range 3-5µm. The reason for this kind of shape is the formation of grain boundaries which usually takes place radially during the deposition of the coating. Particle clustering is observed in many places even though there are some granules of large sizes (8-10µm). Similar micrographs with minimum defects of deposition were
obtained by Huo et al [8]. The thickness of this deposit was obtained in many previous pieces of literature with similar surface morphologies and chemical composition and on average it ranges from 1-2µm [9,10]. The Energy Dispersive X-ray (EDX) analysis confirms that the major elements of the material are Ni, Co, and P with a weight percentage of 71.78%, 12.94% and 15.28% respectively.

3.4 XRD analysis of the optimized electroless Ni-Co-P coating

Figure 5 shows the XRD analysis, which confirms that the peaks of Ni$_3$P, Ni$_2$P, Ni$_{12}$P$_5$, CoP$_2$, and Cu$_2$P feature in the electroless Ni-Co-P alloy coatings. The presence of the phases (Ni$_3$P, Ni$_2$P, Ni$_{12}$P$_5$, CoP$_2$) completely depends on the concentration of the three process parameters, Cobalt Sulphate, Sodium Hypophosphite and bath temperature. These phases clearly depict a microcrystalline structure. The presence of the phases (Ni$_3$P, Ni$_2$P, Ni$_{12}$P$_5$, CoP$_2$) is one of the sole reasons for the decrease in corrosion rate or the increase of corrosion resistance. The presence of Co$_2$P phase can also bring about suitable improvement in the corrosion resistance of the as-deposited coating. As confirmed from the EDX analysis, the coating is a high phosphorous content coating (15.28%). Hadipour et al depicted the presence of similar phases at the diffraction angles in the case of high-phosphorous Ni-P coatings quite similar to our study [11].

4. Conclusion

Electroless Ni-Co-P ternary coating was deposited onto Copper substrate. In this present work, the effects of different process parameters with three design factors such as Cobalt Sulphate, Sodium Hypophosphite, and temperature were studied. All three design factors at different levels were analyzed and optimized with the help of Box-Behnken Design of experiment. Through the regression equation, the optimized surface response (corrosion resistance) obtained for the best set of parameters for Ni-Co-P electroless alloy coating (Cobalt Sulphate (CoSO$_4$.7H$_2$O) =15g/L, Sodium Hypophosphite (NaH$_2$PO$_2$.H$_2$O) =25g/L, Temperature=85°C) is 1165 ohm⋅cm$^2$. Maximum corrosion resistance signifies the minimum corrosion rate of the as-deposited substrate. ANOVA analysis showed that Cobalt Sulphate and Sodium Hypophosphite were the important factors and the interaction between Temperature and Sodium hypophosphite was the most significant one in determining the corrosion resistance of the coating. SEM analysis displayed the deposition of the Ni- (12.94 wt. %) Co- (15.28 wt. %) P coating in granular structures. XRD analysis depicted the presence of Ni-Co-P amorphous alloy peaks and also showed the presence of Co$_2$P phase in the amorphous state. The corrosion resistance of the copper substrate increases significantly with the deposition of electroless Ni-Co-P coating.

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