JJMIE

Volume 16, Number 5, December. 2022
ISSN 1995-6665
Pages 729– 742

Jordan Journal of Mechanical and Industrial Engineering

Modelling and Prediction of Micro-hardness of Electroless Ni-P coatings Using Response Surface Methodology and Fuzzy Logic

Subhasish Sarkar[a], Rupam Mandal[a], Nitesh Mondal[b*], Shouvik Chaudhuri[c], Tapendu Mandal[d], Gautam Majumdar[a]

[a]Deapartment of Mechanical Engineering, Jadavpur University, Kolkata, India, 700032
[b]Deapartment of Mechanical Engineering, Ghani Khan Choudhury Institute of Engineering & Technology, Malda, India, 732141
[c]Centre for Industrial Mechanics, South Denmark University, Sønderborg, Denmark,6400
[d]Deapartment of Metallurgy and Materials Engineering, Indian Institue of Engineering Science & Technology, Shibpur, India, 711103

Received 8 Jun 2022 Accepted 20 Sep 2022

Abstract

The current study has focused on the electroless deposition of Ni-P alloy over the copper substrate to improve the microhardness of the substrate. Central Composite Design (CCD) has been performed using Design-Expert software for maximizing the microhardness of the coating. Along with that, CCD is also utilized to analyze the influence of various process parameters viz. concentration of Nickel Sulphate, the concentration of Sodium Hypophosphite, and bath temperature. Due to the congruity of the indenter with the coating, the Vickers Hardness Test has been executed for determining the microhardness of each coated sample.33.8223g/L of Nickel Sulphate, 19.6602g/L of Sodium Hypophosphite and 87.6331°C of bath temperature are the optimum conditions for the deposition of coating to achieve a hardness value of 1129.7867 HV_{10g} as obtained from the model analysis of CCD and the same optimum point prediction data of microhardness results to 1070 HV_{10g} . Applying Fuzzy logic, the effect of various parameter onmicrohardness for elcrtroless NI-P coating has been studied. Further, Analysis of Variance (ANOVA) has been implemented which corroborated that the parameter Nickel Sulphate along with the interaction between Sodium Hypophosphite and bath temperature are the significant ones in determining the microhardness of the coating deposited in optimized conditions. Optical Microscopy, Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray analysis (EDX) are conducted to study the surface morphology and the elemental composition of the coated substrate respectively.

Keywords: Electroless Coating; Microhardness; Central Composite Design; ANOVA; Fuzzy Logic; SEM; EDX.

1. Introduction

Since the discovery of Electroless Coating by Brenner and Riddell in 1947[1], there has been a colossal amount of development in this field of research. As the name indicates, the electrons for the deposition of coating are furnished by the reducing agent instead of the electric current. The process comprises of a substrate dipped in an electroless bath comprising of a source of metal ions, reducing agent, complexing agent, bath stabilizer, accelerator, buffering agent, and surfactants[2]. The metallic ions present in the solution are reduced by the reducing agent and get deposited over the substrate as an initial film which further acts as a catalyst for the rest of the process, thus summarizing the entire autocatalytic technique. Owing to the uniformity and evenness of the deposition, electroless coatings have gained ample significance as compared to other surface coating methodologies[3]. In a drive of development during the past few decades, industries thrive for materials with improved mechanical, tribological, aesthetic, and chemical properties. Electroless Nickel (EN) deposits fulfill the above criterion perfectly and hence they have achieved immense usage in aerospace, automobile, marine, mining, electronics, textile industries, etc[4–6].

EN coatings can be classified into pure nickel, alloy and composite coatings[7]. Alloy coatings can be further classified into binary, ternary and quaternary alloy coatings[8]. Phosphorous and Boron are by far the two most extensively used elements along with Nickel to form electroless Ni-P and Ni-B deposits[9]. Ni-B coatings are known for their high hardness along with the competence to retain lubricants attributable to their cauliflower-shaped surface morphology[10].On the other hand, Ni-P coatings have a smoother surface with a wavy surface texture[11]. Due to its excellent wear, abrasion, and corrosion resistance along with significant hardness, electroless Ni-P coating is one of the most popular binary alloys accompanied by well-executed research and widespread development. The phosphorous content in the nickel lattice is a significant criterion that controls the properties and

* Corresponding author e-mail: niteshju@yahoo.com.

microstructures of the electroless Ni-P deposits. Low phosphorous (1-4% P) EN deposits are microcrystalline in nature with high hardness and wear resistance. Medium phosphorous (5-10% P) EN deposits have combined crystalline and amorphous structure and high phosphorous (>10% P) EN deposits have amorphous structure with excellent corrosion resistance and ductility[12]. Inclusion of W, Cu, Co, Mo, Zn, Fe, etc.is done to meet the exigency of the research and development sectors which would impart a high hardness, tensile strength, wear, abrasion, and corrosion resistance along with improved thermal stability[13–16]. EN composite coatings, on the other hand, are formed by the implementation of an inert phase component(PTFE, SiC, Al_2O_3, WC, TiO_2, ZrO_2, etc.) into the metal matrix thereby improving the tribological properties to a greater extent[17–20].

The property that resists localized plastic deformation, abrasion, or scratching is defined as the hardness of a material and it is referred to as microhardness when there is the involvement of hardness testing using a small indenter or when the load is quite less[21,22]. Hardness is one of the most important mechanical properties which requires to be improved to meet the demand of industries syncing with the environment. The salient reason behind this is that this property and the property of wear and abrasion resistance bear a direct relationship. When the crystallization of the amorphous state takes place during heat treatment in an attempt to improve the hardness of the deposits, deposition of the intermetallic Ni_3P phase occurs which is the sole reason for the increase in hardness of the electroless Ni-P deposits[23]. Although, heat treatment of electroless Ni-P deposits [24]is not the solution in every situation whatsoever. In industries, precision instruments, internal surfaces, and other delicate gadgets have to be handled carefully and there is a chance that they might get damaged over severe heat treatment processes due to a lack of precautions.

A lot of work has been done in the past relating to the hardness of electroless Ni-P deposits. Keong*et al*[25] found that the Vickers hardness of the as-deposited electroless substrates increased with the decrease in phosphorous content. They achieved the highest hardness value of 1011 ± 9 $HV_{0.1}$ after heat-treating the substrates at 400-450ºC. They also performed Knoop micro indentation testing on the cross-section of the samples to find the variation of hardness in relation to the depth of the coating. Yan et al. [26] prepared electroless Ni-P substrates with varying phosphorus content by varying the ratio of lactic acid to acetic acid in the electroless bath. They further observed a transition of phase from nanocrystalline to a mixture of nanocrystalline and amorphous and finally to a fully amorphous phase with the increase in phosphorous content of the coating. At a 7.97 at. % Of P, they obtained the highest hardness value of 910 $HV_{0.1}$ for the electroless Ni-P deposits. Zangeneh-Madar and MonirVaghefi[27]studied the effect of thermochemical treatment on the structure and hardness of electroless Ni-P coated low alloy steel. Hardness, roughness tests, phases present, and surface characterization are further performed. They proved that the hardness of the coating increases when complete crystallization occurs.Sivaraos et al.[28] compared Taguchi Method and Response Surface Methodology (RSM),to predicted the near values of average error, the RSM technique is more promising in predicting the response via mathematical modelling than Taguchi technique.A Mukhopadhyay et al.[29] studied the effect of fuzzy logic on NI-P coating to predict the ware depth after using taguchi method. It has been shown that the accuracy of prediction by fuzzy logic is better than the Taguchi method. R. Vinayagamoorthy et al. [30] have built the central composite design (CCD) model and the model is validated by comparing it with the fuzzy model and confirmatory runs. It has been shown that the error is minimum for both central composite design and fuzzy logic. Balaji M et al.[31] observed that Fuzzy TOPSIS prioritization of ASCA of ISM acknowledged driver enablers, emphasized that the priority should start from End to end connectivity had the minimum ranking score and training programme on time management concepts had the maximum ranking score. Azmi Alazzam et al.[32] utilizes adaptive NeuroFuzzy Inference System (ANFIS) which is based on the BPN-ANN structure with two inputs and one output using Matlab software to predict the components' reliability of Lead-free solder process. Qingyong Zhang et al.[33] used Multi-hierarchical Fuzzy system to determine the driving cycle of a Hybrid Electric Vehicles based on four different driving patterns.

In our current research, we have employed Central Composite Design (CCD)[34] intending to maximize the micro-hardness by analyzing the impact of the process parameters for the deposition of the coating. Although optimization using CCD analysis has been already performed on a similar experiment[35]and fuzzy logic is also applied to the data evaluated by CCD model, results at the optimization point from both fuzzy and CCD have been compared with the experimental result. Further, to study the surface morphology and the elemental compositions, Optical Microscopy, Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray analysis (EDX) have been performed respectively.

2. Details of Experiment

In this work, at first, the synthesis part has been done with the help of central composite design (CCD) in Minitab software and the effect of input parameters on the output parameter is found. From the output of CCD, the optimization of maximum microhardness has been done and simultaneously the Fuzzy logic is also applied for data prediction and comparsion. The process is completed with the validation test. Figure 1 shows the complete flow chart of this work.

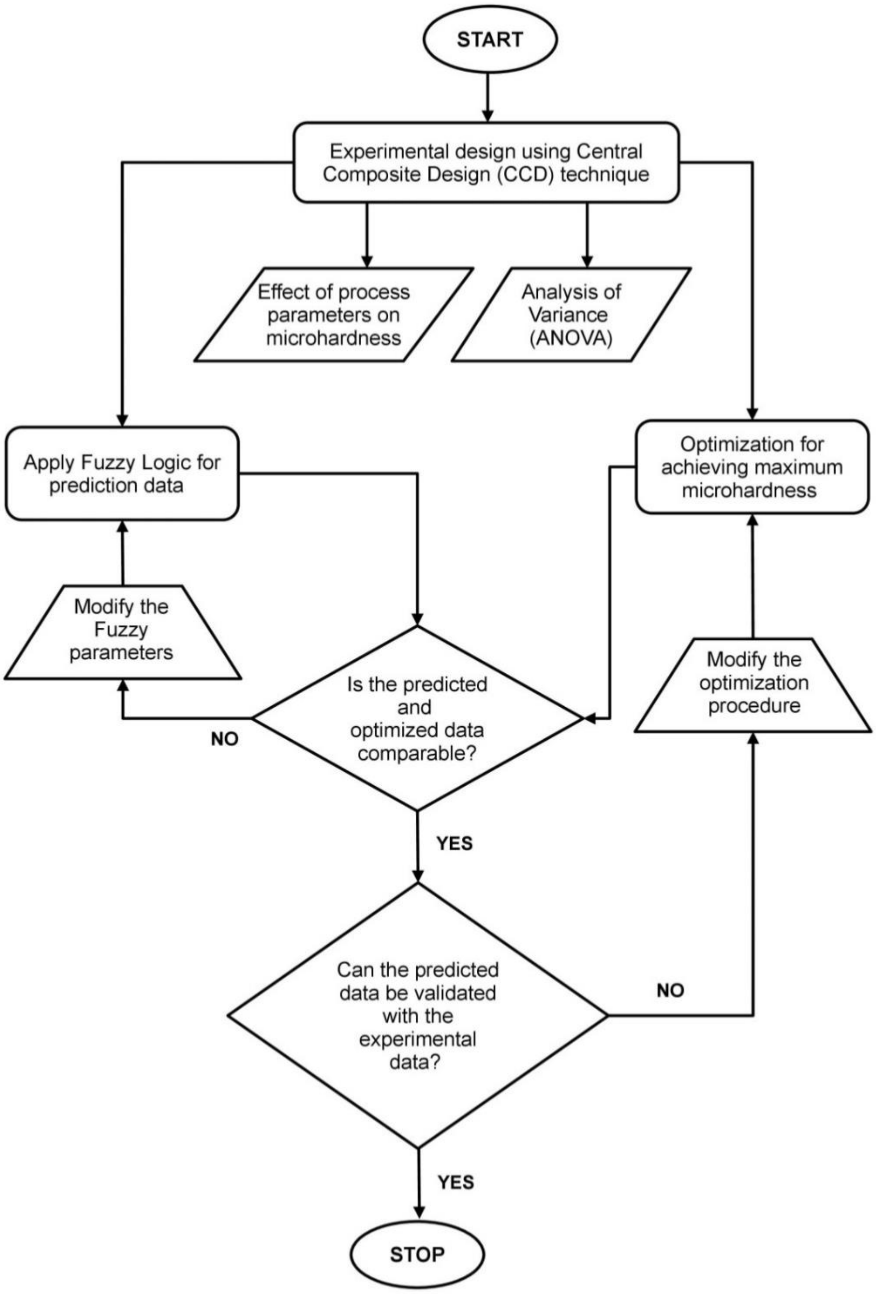

Figure 1. Experimental Flow Chart

2.1. Preparation of substrate and coating deposition

Copper substrates have been cut into pieces of size 20 x 15 x 1mm^3 from a copper foil (99% pure, LobaChemie) in rolled form. In the first place, the copper substrates have been rinsed in distilled water for a couple of minutes. Then, they have been dipped in 25% dilute HCl solution for some time to remove impurities and oxide layers. Then henceforth, the cleaned substrates are subjected to activation using an adsorbing reagent, Palladium Chloride ($PdCl_2$) solution pre-heated at 55^{o}C. Being adsorbing in nature, it forms a fine layer over the substrate thereby initiating the reaction. Great adhesion along with deposition rates are obtained with the help of this activation process.

Nickel Sulphate ($NiSO_4$) is used as the source of nickel ions along with Sodium Hypophosphite (NaH_2PO_4) as the reducing agent for the reduction of nickel ions as obtained from the Nickel Sulphate solution. To slow down the reaction rate to a suitable one by forming metastable nickel complexes, we have used Trisodium Citrate Dihydrate (TCD) as the complexing reagent. Furthermore, we have used Sodium Acetate (CH_3COONa) as the buffering agent to maintain the pH level of the bath to a constant value of 5. The chemical compositions along with the parameters of this electroless bath are displayed in Table 1. In one beaker, the nickel ions source is mixed with the reducing agent, and in another, the remaining chemicals are mixed with 250ml of deionized water distributed proportionately amongst them. The two solutions are separately heated up to 60^{o}C before they are mixed to form the electroless bath.

  - Volume 16, Number 5 (ISSN 1995-6665)

The activated substrates are now dipped in the bath which is in turn heated to a temperature ranging from 85-90°C. After 1hr of electroless deposition, we would observe a bright greyish coating deposited onto the substrate with the solution turning black gradually. It would then be the perfect moment to take out the coated substrates from the bath and clean them by rinsing them in deionized water for a few minutes.

Now, the electroless Ni-P deposited copper substrates are mounted with the aid of epoxy resin because the handling of coatings of such a minute thickness is neither easy nor safe. Finally, they are ready for the hardness measurement procedure.

Table 1. Chemical composition along with process parameters of electroless bath for Ni-P coating deposition over the copper substrate

Factors	Values
Nickel Sulphate	21.59-38.41 g/L
Sodium Hypophosphite	13.27-26.72 g/L
Temperature	76.6-93.41°C
Trisodium Citrate Dihydrate	15 g/L
Sodium Acetate	5 g/L
pH of solution	5

2.2. Hardness Measurement

The mounted electroless Ni-P deposited copper substrates are subjected to the Vickers Hardness Test (VHT) (as displayed in Figure 2) to obtain their microhardness number (HV). The VHT method is carried out as per ASTM standard E384-16 with the help of a right pyramidal-shaped diamond indenter with an apex angle of 136°. The substrate is subjected to a load of 10g with a total time of 15s for loading and unloading. An indentation is left by the indenter whose depth is measured. The lower the indentation depth left by the applied force on the surface of the coated substrate, the harder the tested sample. The microhardness tester provides us with an average of six hardness values. The hardness value (HV) is measured using equation (1) where 'F' is the applied load in grams and 'd' is the average of the two diagonals in mm left by the pyramidal indenter during the impact.

$$HV = \frac{1.8655F}{d^2} \tag{1}$$

VHT is the preferred hardness test because high accuracy is the first priority in our present study. Other hardness tests such as Brinell Hardness Test (BHT) and Rockwell Hardness Test (RHT) are not as accurate enough as VHT since the surface area in contact with the indenter is very small in the case of VHT. Non-destructive hardness tests can be carried out in VHT which is not possible in the other cases. Furthermore, the microstructural constituents can be targeted using VHT after magnifying the surface of the coating and the post-heat treatment options can also be obtained using this technique.

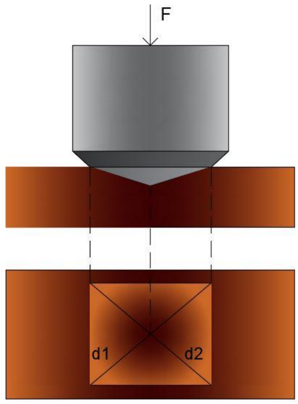

Figure 2. Vickers Hardness Test

2.3. Central Composite Design (CCD)

Central Composite Design (CCD) is a method of response surface analysis based on a two-tiered factorial design. This analysis helps to model and optimize the output response. The behavior of CCD depends on multiple independent variables.It gives three-dimensional surface plots and contour plots through which, the relationship between output and input factors can be effectively analyzed. It also provides regression equations through which feedback for any input value can be effectively predicted. The generalised form of the regression equation has been given in equation 2.

$$x = a_0 + a_1 y_1 + a_2 y_2 + a_3 y_3 + a_{12} y_1 y_2 + a_{13} y_1 y_3 + a_{23} y_2 y_3 + a_{11} y_1^2 + a_{23} y_2^2 + a_{133} y_3^2 \tag{2}$$

where x denotes the output response, all y terms represent the input variables, all a terms represent the constants.

2.4. Fuzzy Logic

Fuzzy Logic is a mathematical theory of the irrational reasoning process that allows the modeling of the human reasoning process in linguistic terms. It does not need any mathematical model to build up. The fuzzy Logic system (madami system) consists of a fuzzyfier, membership function, a fuzzy rule base, an interference engine, and a defuzzifier[36]. Fuzzifier is used to convert crisp values to values. The membership function is a graphical representation of the level of participation of each input. Fuzzy rules use input membership values as weight factors to determine their effect on obscure output values of the final output conclusion[37]. Once the functions are assumed, scaled, and assembled, they are defuzzified to a crisp output that drives the system. Then the Mamdani fuzzy interference system performs obscure arguments in Fuzzy rules to create fuzzy value. Finally, the defuzzifier converts the fuzzy predicted value.

3. Results and Discussions

3.1. Optimization of process parameters using Central Composite Design (CCD)

For several projects working in the field of process parametric optimization, a highly beneficial approach is to go through one of the basic designed optimization processes. These designs are fully based on mathematical modeling. Based on requirements, one such design is chosen. In this paper, the Central Composite Design (CCD) of the experiment has been employed.

The basic design behind the response surface is CCD. Basically, like other designs for optimization, it also shows the interactions amongst the experimental variables. Keeping this into consideration, it increases the replications of central points (keeping all the parameters in their mean values) to check the error of the experiments. The most vital entity of CCD is the increase in the range between two axial points. Thus, it makes a sphere (where a number of parameters are 3) with a radius α (the distance between the central point and any of the corner points). This depicts how the accuracy has been obtained while analyzing the parametric optimization using CCD.

Nickel Sulphate ($NiSO_4$), Sodium Hypophosphite (NaH_2PO_4), and Temperature are the significant factors for optimization. The main constituents of the electroless coating are Nickel and Phosphorous. The quantity of Nickel deposited depends upon the concentration of Nickel Sulphate in the electroless bath which in turn affects the microhardness of the coating to a great extent. Similarly, the concentration of Sodium Hypophosphite decides the amount of Phosphorous deposited over the copper substrate. Temperature, on the other hand, controls the rate of reaction occurring along with the deposition. Thus, they are the most important factors deciding the value of the response, microhardness. The regression equation is the reaction between the response and the process parameters. To obtain a full-factorial regression equation, six central points have been considered and their coded values are displayed in Table 2.

Further, to analyze the problem statistically as well as mathematically, Response Surface Methodology (RSM) have been adopted. The Central Composite Design (CCD) of the experiment is chosen to be the tool based on which response surfaces has been developed. This design encloses 6 central points, 6 axial points, and 8 factorial points. On all of the 20 sets of the experiment, microhardness testing using VHT have been carried out and the obtained results have been provided in Table 3.

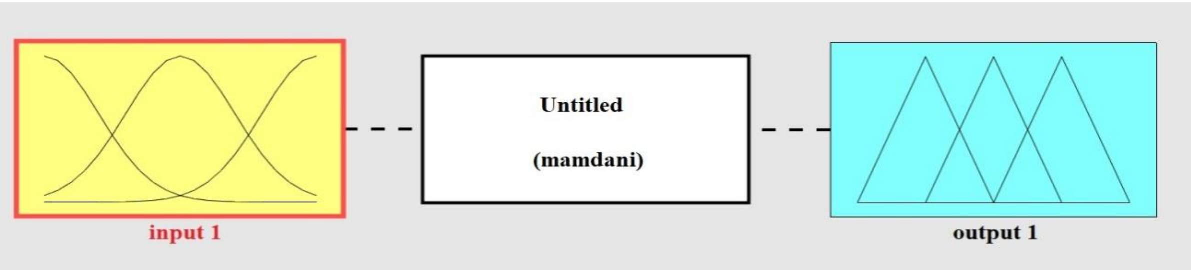

Figure 3. Fuzzy logic controller

Table 2. Coded values of process parameters

Actual Values			Coded Values		
Nickel Sulphate (g/L)	Sodium Hypophosphite (g/L)	Temperature (ºC)	Nickel Sulphate (g/L)	Sodium Hypophosphite (g/L)	Temperature (ºC)
X1	X2	X3	Z1	Z2	Z3
21.59	13.27	76.6	-α	-α	-α
25	16	80	-1	-1	-1
30	20	85	0	0	0
35	24	90	+1	+1	+1
38.41	26.72	93.41	+α	+α	+α

Table 3. 20 sets of Experimental Data for Central Composite Design (CCD) of the experiment for electroless Ni-P deposits

Set of Expt.	Nickel Sulphate (g/L)	Sodium Hypophosphite (g/L)	Temperature (^{0}C)	Micro hardness (HV_{10g})
1	35	16	90	1007
2	35	24	90	1056
3	30	20	85	1107
4	30	20	85	1110
5	30	20	85	1107
6	25	16	80	910
7	25	24	90	920
8	30	20	76.6	895
9	30	20	85	1108
10	30	20	93.41	1015
11	30	20	85	1109
12	35	16	80	980
13	30	20	85	1107
14	25	16	90	840
15	38.41	20	85	1100
16	30	26.72	85	981
17	30	13.27	85	960
18	21.59	20	85	880
19	25	24	80	1023
20	35	24	80	810

The analysis by Design Expert Software suggested the Central Composite Design (CCD) of the experiment evaluated for microhardness with substantial factors to be quadratic in the actual and coded equation which are as follows:

Final Equation in Terms of Coded Factors-

$$\begin{aligned} Micro\ \mathrm{Hardness} &= 1108.65 + 38.81A + 7.80B \\ &+ 22.15C - 39.25AB + 55.75AC + 23.35BC \\ &- 45.98A^2 - 52.92B^2 - 58.42C^2 \end{aligned} \tag{3}$$

Final Equation in Terms of Actual Factors-

$$\begin{aligned} \mathrm{Micro\ Hardness} &= -12916.43746 - 32.19199 \times NS \\ &+ 94.30347 \times SH + 311.54621 \times T - 1.96250 \\ &\times NS \times SH + 2.23000 \times NS \times T + 1.16250 \\ &\times SH \times T - 1.83911 \times NS^2 - 3.30726 \times SH^2 - 2.33686 \times T^2 \end{aligned} \tag{4}$$

Where NS, SH and T stands for Nickel Sulphate, Sodium Hypophosphite and Temperature respectively.

Using the CCD-RSM method for parametric optimization, the optimized value of micro-hardness is 1129.7867 $HV_{10g}$and the corresponding input parameters are 33.8223g/lit of $NiSO_4$, 19.6602g/lit of NaH_2PO_2, and 87.6331^{0}C of temperature.

3.2. Fuzzy Modelling

The basis of a fuzzy model is a linguistic variable, which aims to use fuzzy sets instead of crisp sets. In this study, the fuzzy model uses type-1 fuzzy sets with Mamdani Fuzzy Inference System (FIS) [28, 29] and the centroid defuzzification technique. In the input step, the parameters, viz. the concentration of Nickel Sulphate, Sodium Hypophosphate, and Temperature are fuzzified with triangular membership functions for sake of simplicity. The input space is divided into three obscure subsets, i.e., low (L), medium (M), and high (H). On the other hand, the defuzzifier also employs three subsets viz. low (L), medium (M), and high (H), of triangular membership functions to determine the output value of Microhardness. These membership functions of Nickel sulphate, sodium Hypophosohate, Temperature, and Microhardness are illustrated in Figure 5. The choice of the range of these parameters and their subsets are determined based on the experimental data for CCD design as provided in Table 3. For the concentration of Nickel Sulphate and Temperature, the input range is equally divided into the three subsets. For the concentration of Sodium Hypophosphite, the mid-values of three subsets are equally placed at 16, 20 and 24, respectively. On the other hand, for the output variable, microhardness, the membership function is so designed that the mid-values for the three subsets are equally placed at 900, 1000 and 1100. However, due to constarints on the maximum value,i.e., 1150, the ‘High’ subset is asymmetric.

The rule base for relating microhardness to the process parameters through the Mamdani Inference system is designed based on the qualitative nature of the experimental data for CCD design presented in Table 3. For instance, in table 3, the 6th experimental set depicts that the values for all the three process parameters are in the LOW subset, and the subsequent microhardness takes a value in the MEDIUM subset. Based on this observation, 20 such rules are designed directly from the combination of parameters in CCD-RSM given in Table 3. The IF-THEN rulebase with output is listed in Table 4. When a set of input assumptions is adopted by the FIS, it introduces a certain number of rules, and a fuzzy output is obtained using Mamdani's max-min implication. This fuzzy output is defined using the centroid defuzzification method. A three-input single-output fuzzy model is illustrated in Figure 6. In the present study, the fuzzy modeling has been done using the Fuzzy Logic Toolbox in MATLAB R2018a.

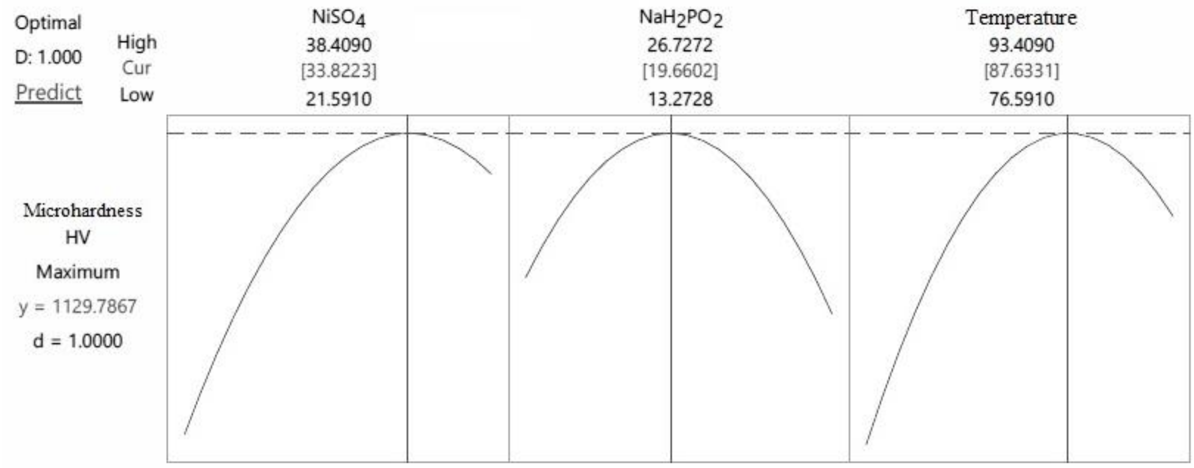

Figure 4. CCD optimized input parameters and output value

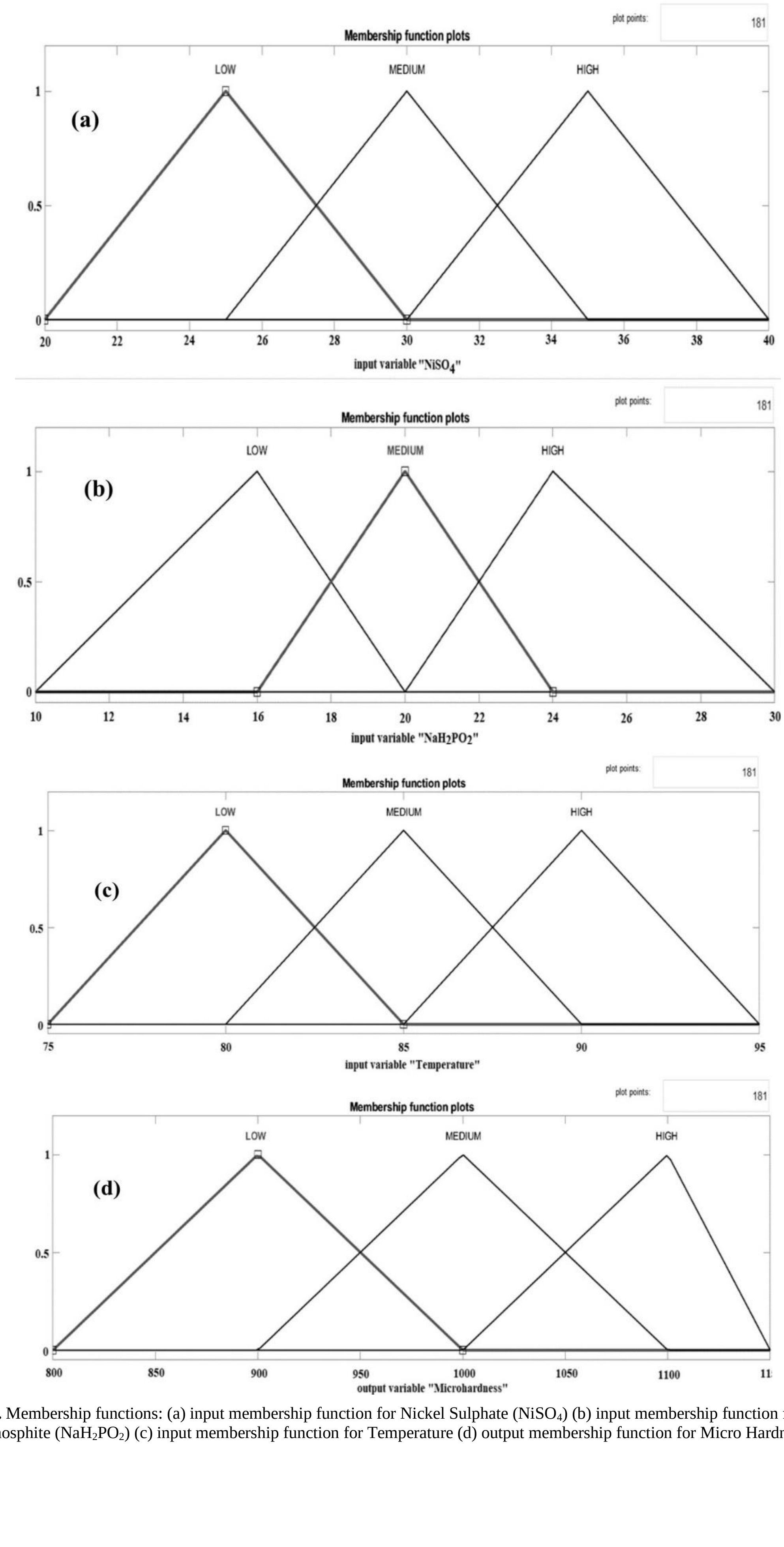

Figure 5. Membership functions: (a) input membership function for Nickel Sulphate ($NiSO_4$) (b) input membership function for Sodium Hypophosphite (NaH_2PO_2) (c) input membership function for Temperature (d) output membership function for Micro Hardness (HV)

Using Fuzzy logic, the prediction value of micro-hardness is 1070 HV_{10g} in input parameters 33.8223 g/lit of NiSO4, 19.6602g/lit of NaH_2PO_2, and 87.6331^{0}C of temperature which is shown in the fig. 7.

Table 4. Fuzzy rules

Rule No.	IF					THEN
	Nickel Sulphate		Sodium Hypophosphate		Temperature	Microhardness
1	H		L		H	H
2	H		H		H	H
3	M		M		M	H
4	M		M		M	H
5	M		M		M	H
6	L		L		L	M
7	L		H		H	M
8	M		M		L	L
9	M		M		M	H
10	M		M		H	H
11	M	AND	M		M	H
12	H		L	AND	L	M
13	M		M		M	H
14	L		L		H	L
15	H		M		M	H
16	M		H		M	M
17	M		L		M	M
18	L		M		M	L
19	L		H		L	H
20	H		H		L	L

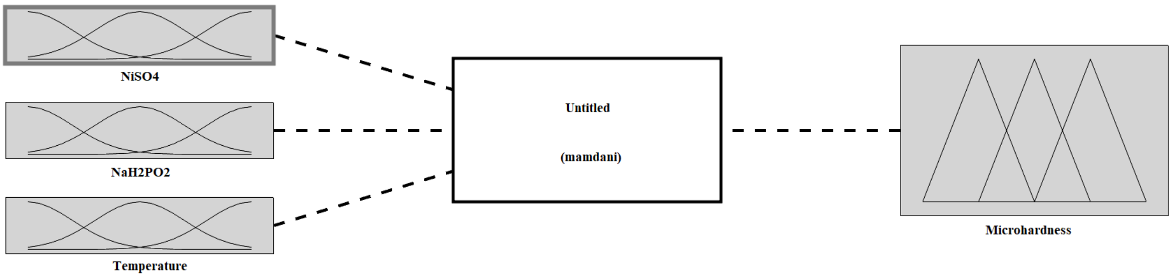

Figure 6. Three input single output fuzzy interference system

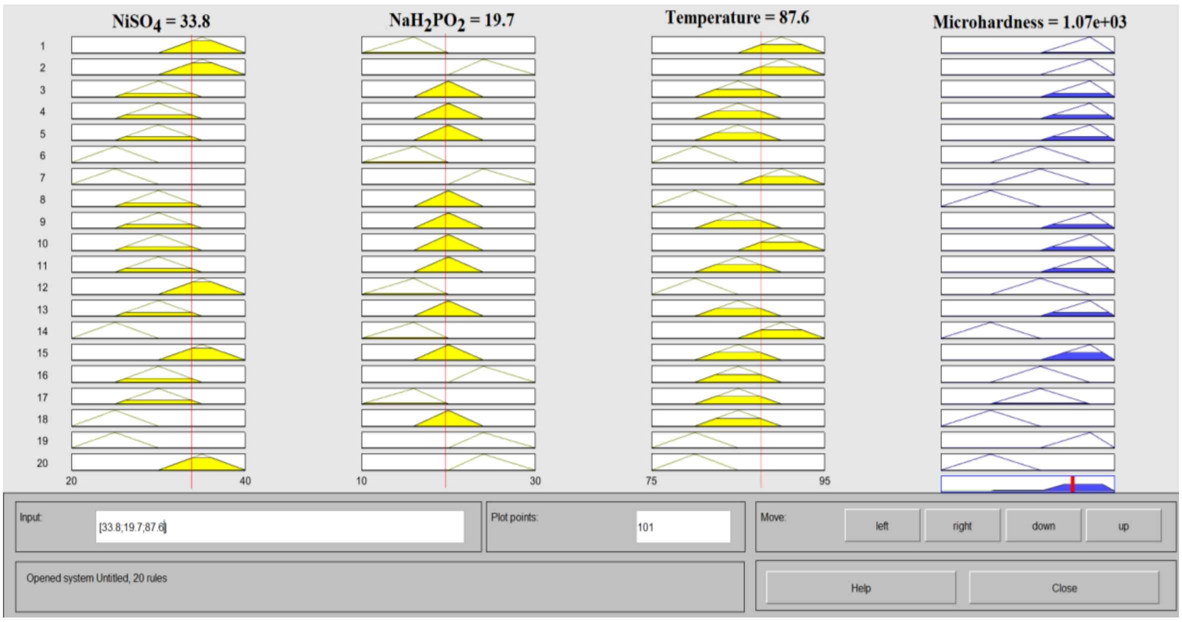

Figure 7. Fuzzy prediction data

3.3. Response Surface Plot Analysis From CCD

Microhardness in this case; the response has been predicted using the response surface plots. 3D surface plots have been analyzed to optimize the response and to interpret the interaction between every single significant process parameter. The surface plots have been obtained by plotting the response, microhardness as the z-axis against two of the three process parameters on the x and y-axes. Thus, on a 2-D plane, we have successfully achieved a 3-D response surface plot.

Figure 8 shows the three-dimensional graphical representation for the variation of microhardness (response) by varying the concentration of $NiSO_4$ and concentration of NaH_2PO_2 keeping the temperature constant. By Figure 8 it can be said that microhardness increased by increasing the concentration of $NiSO_4$ and concentration of NaH_2PO_2. This plot has a more or less symmetric surface with its peak at the center.

Figure 9 shows the three-dimensional graphical representation for the variation of microhardness (response) by varying the concentration of $NiSO_4$ and temperature keeping the concentration of NaH_2PO_2 constant. By Figure 9 it can be said that microhardness increased by increasing the concentration of $NiSO_4$ and temperature. This surface plot also has a nearly symmetric surface with its peak at the center.

Figure 10 clearly shows the three-dimensional graphical representation of microhardness (response) as a function of the concentration of $NaH_2PO_2$and temperature keeping the concentration of $NiSO_4$constant. From Figure 10, it can be said that microhardness increased by increasing the concentration of NaH_2PO_2 and temperature. This surface plot has a perfectly symmetric surface with its peak at the center.

Though from all three RS plots, the huge effect of all three parameters over the response has been observed. The interaction between the bath temperature and sodium hypophosphite for increasing the microhardness is the most significant one by comparing the symmetry of the curvature. It is also concluded from the three surface plots that for obtaining the best-optimized result, $NiSO_4$ should be valued at 30 g/L.

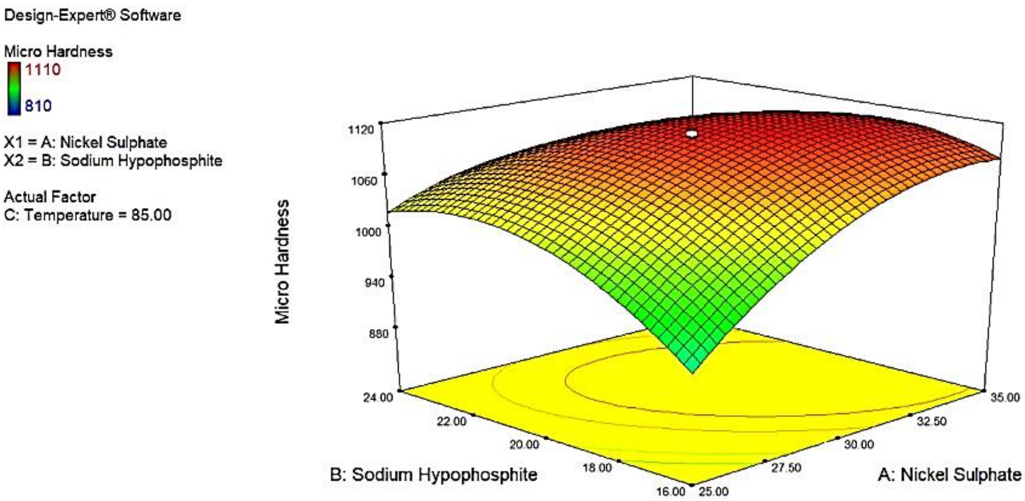

Figure 8. 3D-Response surface plot showing the effect of Nickel Sulphate and Sodium Hypophosphite

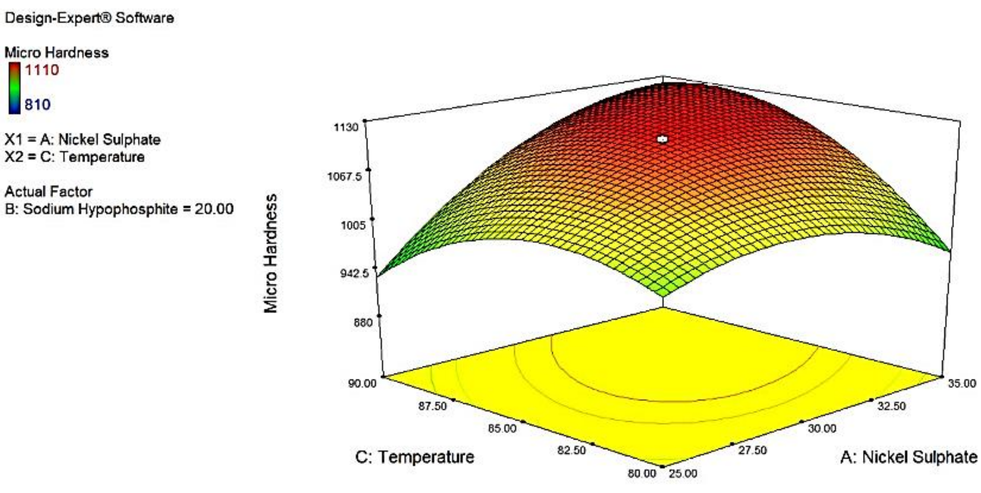

Figure 9. 3D-Response surface plot showing the effect of Nickel Sulphate and Temperature

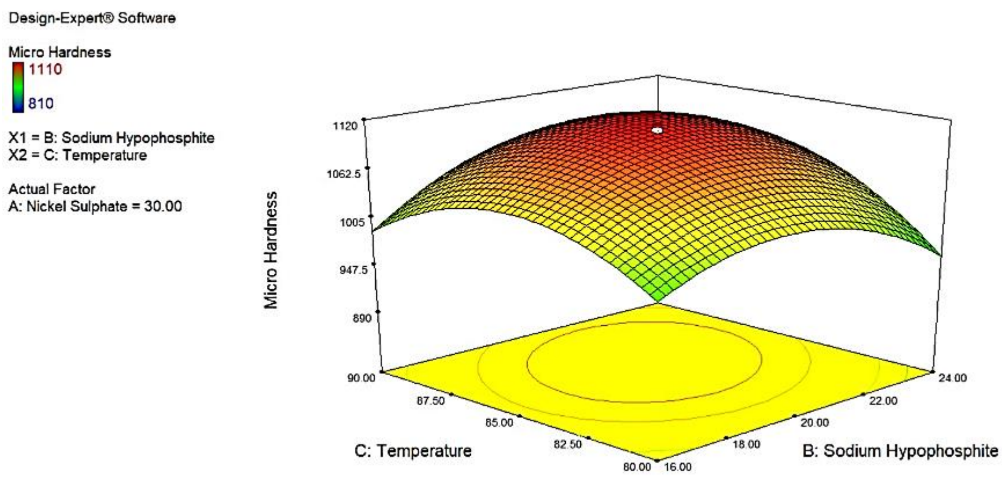

Figure 10. 3D-Response surface plot showing the effect of Temperature and Sodium Hypophosphite

Table 5. ANOVA table for Response Surface Quadratic Model

Source	Sum of Squares	df	Mean Square	F-value	p-value Prob > F	Remarks
Model	169973.56	9	18885.95	10.54	0.0005	
A-Nickel Sulphate	20569.43	1	20569.43	11.48	0.0069	significant
B-Sodium Hypophosphite	831.20	1	831.2027	0.46	0.5112	
C-Temperature	6698.70	1	6698.709	3.73	0.0819	
AB	12324.5	1	12324.5	6.88	0.0255	
AC	24864.5	1	24864.5	13.88	0.0039	
BC	4324.5	1	4324.5	2.41	0.1513	
A^2	30478.64	1	30478.64	17.01	0.0021	
B^2	40313.45	1	40313.45	22.50	0.0008	
C^2	49114.43	1	49114.43	27.41	0.0004	
Residual	17912.18	10	1791.218			
Lack of Fit	17904.18	5	3580.84	2238.02	<0.0001	significant
Pure Error	8	5	1.6			
Cor Total	187885.75	19				

3.4. Analysis of Variance (ANOVA)

From Table 3, it has been found that the maximum microhardness occurs in Experiment 4 with a combination of Nickel Sulphate concentration of 30 g/L, Sodium Hypophosphite concentration of 20g/L, and a bath temperature of 85°C whereas the minimum microhardness has been obtained in Experiment 20 with a combination of Nickel Sulphate concentration of 35 g/L, Sodium Hypophosphite concentration of 24g/L and a bath temperature of 80°C. Hence, to find the perfect combination of these three process parameters for obtaining the maximum microhardness, we have employed a powerful and effective mathematical tool named Analysis of Variance (ANOVA).

The significant combination of factors taking place in an experiment has been determined using this tool. It works on the methodology of the F-value and p-value. The decision about whether we can reject the null hypothesis has been provided by the p-value. When the amount of this p-value is less than 0.05, we can conclude with the affirmation of rejecting the null hypothesis thereby stating that the factor is significant. The ratio of summation of the factors, each raised to the power of two to the variance of errors has been referred to as the F-value. Thus, the amount of F-value is directly proportional to the relative significance of the concerned factor with respect to others. Table 5. displays the CCD analysis results.

From the Model F-value data of 10.54in Table 5, we can conclude that the model is significant. The chance that such a high model F-value would generate is 0.05%. If the values of Prob>F have been found less than 0.05, then we can arrive at the fact that those corresponding factors are significant. Thus, in this case, A, AB, AC, A^2, B^2, and C^2 are the substantial model terms.

From the above facts, it is concluded that the input parameter i.e. the concentration of Nickel Sulphate is significant.Now, the p values have been considered for determining the level of significance of linear main effects and linear interactions of the process parameters Nickel Sulphate, Sodium Hypophosphite, and bath temperature. Therefore, the squared terms have not been considered.

3.5. Surface analysis from fuzzy model

Surface plot is one of the graphical representations to predict the relationship between dependent and independent parameters. Here, the surface plots illustrate the trends in the variation of microhardness for electroless NI-P coating through Fuzzy logic considering the effect of various parameters. The relationship or variation of microhardness, temperature and concentration of $NiSo_4$ have been shown in fig. 11a. It is interesting that microhardness has no such influence in temperature and $NiSo_4$ concentration. Microhardness has maintained a flat surface for any region of the surface plot. An interesting trend has been observed from fig. 11b, when there is a correlation build up among microhardness, temperature and concentration of NaH_2PO_2. The variation of microhardness is very high at high temperature and moderate concentration of NaH_2PO_2. The role of temperature and concentration of NaH_2PO_2 is very prominent to determine the microhardness. Figure 11c. explore the effect of NaH_2PO_2 concentration and $NiSO_4$ concentration together on micro hardness. The hardness is increasing when the concentration of NaH_2PO_2 is between 17 to 22 and the concentration of $NiSO_4$ is near about 35. After increasing the concentration of $NiSo_4$, hardness maintains a constant value for the same concentration of NaH_2PO_2.

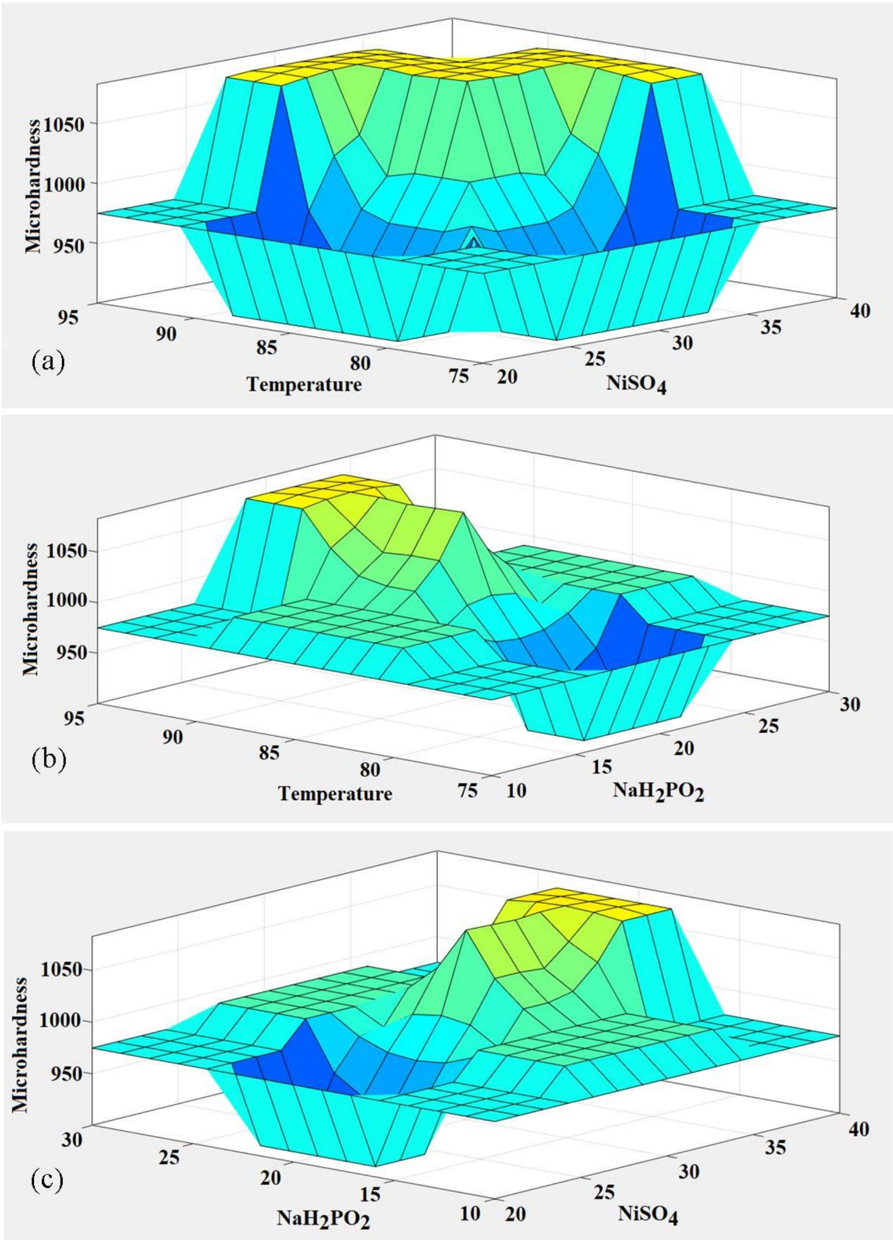

Figure 11. Surface plot showing the variation of Microhardness with (a)Temperature and concentration of $NiSO_4$ (b) Temperature and concentration of NaH_2PO_2 (c) concentration of NaH_2PO_2 and concentration of $NiSO_4$

4. Comparision and validation test

Based on the advanced CCD model and the Fuzzy model, the validity of the model has been tested.They have been carried out with different input values of concentration of Nickel Sulphate. The concentration of sodium hypophosphate, and temperature, and the experimental, CCD optimized result, and fuzzy predicted results have been compared.The value of the concentration of Nickel Sulphate, concentration of sodium hypophosphate, and temperature considered for the validation tests have been selected from within the range of the parameters considered ($NiSO_4$ =33.8 g/L, NaH_2PO_2 = 19.7 g/L, Temperature = 87.6331°C).

Figure 12 shows the results of verification tests, and it is observed that both models can predict microhardness values with high accuracy. However, the accuracy obtained from the fuzzy model is about 2.02% compared to -3.46% of the CCD model, where the negative sign is an indication of overprediction. Therefore, we conclude that the fuzzy model is more accurate and can be used effectively to predict the microhardness of the electroless Ni-P coating. This observation regarding the fuzzy model is corroborated by other studies as well [28].

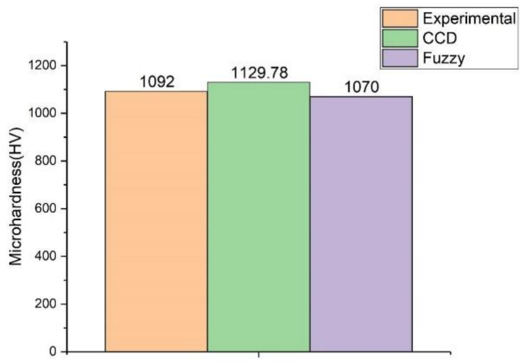

Figure 12. Validation test result

5. Characterization of the electroless coated Ni-P substrate deposited in optimized condition

5.1. Surface Morphology using Optical and Scanning Electron Microscopy

Round nodules of non-uniform sizes but uniform shapes have been observed throughout the Optical micrograph of the electroless Ni-P coating deposited in optimal condition (Figure 13). The particles have been scattered throughout the micrograph but in some portions, clusters of Ni-P have been observed.

Coarse globular uniform microstructures of varying sizes ranging from 5-30µm have been spread throughout the scanning electron micrograph (Figure 14) of the as-deposited optimized electroless Ni-P substrates. The few white spots present in the micrograph depict that the porosity of the deposition is very less, thus signifying higher hardness of the as-deposited substrate. No cracks or holes are observed throughout the micrograph suggesting that the coating is dense with negligible defects. The grain boundaries are well-defined.

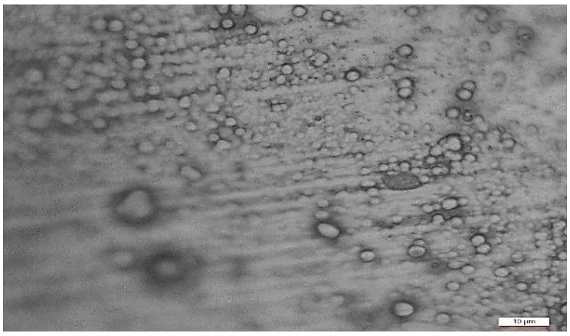

Figure 13. Optical Microstructure of electroless Ni-P coating deposited in optimal conditions

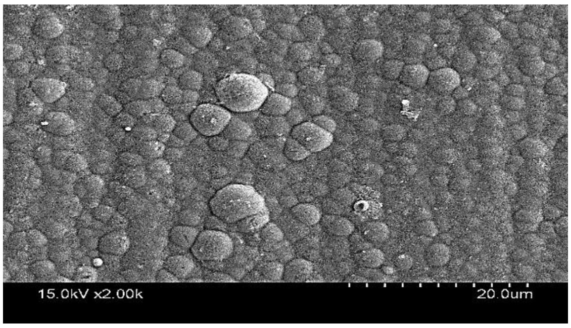

Figure 14. Scanning Electron Micrograph of the as-deposited optimized Ni-P coating

5.2. EDX study of the as-deposited optimized sample

Figure 15 depicts the EDX spectra of the as-deposited optimized coating. The peaks of Ni and P are observed, and thus arrive at the conclusion of the confirmed presence of Nickel and Phosphorous in the coating. From the EDX analysis, the elemental compositions are obtained as Ni - 90.39% and P - 9.61%. This data signifies that the coating is a medium Phosphorous content and thus it has a high hardness value.

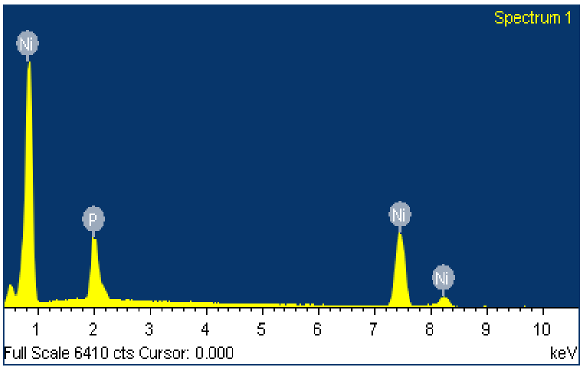

Figure 15. EDX spectra of the as-deposited optimized coating

6. Conclusion

Electroless Ni-P coating has been successfully deposited over the copper substrate with a 9.61 wt. % of Phosphorous as determined from EDX analysis. From the Response Surface Methodology Based on CCD design and the ANOVA analysis, it is prominent that Nickel Sulphate along with the interaction between Sodium Hypophosphite and Bath Temperature are the most significant factors in maximizing the microhardness of the coating. The optimized conditions for obtaining the maximum hardness are 33.8 g/L of Nickel Sulphate, 19.7 g/L of Sodium Hypophosphite, and 87.6 ^oC of bath temperature under these conditions, the microhardness of the coating is found to be 1129.78 HV_{10g} from CCD model and for fuzzy and experimental results are respectively 1070 HV_{10g} and 1092 HV_{10g} whereas the microhardness of the copper substrate is originally 651 HV_{10g}. Thus there is an increase in the microhardness of the coating SEM micrograph of the as-deposited optimized coating revealed the presence of globular structures and the lower porosity of the coating which is a vital reason for its high hardness.

References

[1] Brenner A, Riddell G. Deposition of nickel and cobalt by chemical reduction. J Res Natl Bur Stand. 1947 Nov;39(5):385.

[2] Sudagar, Jothi, Jianshe Lian, and Wei Sha, "Electroless nickel, alloy, composite and nano coatings–A critical review". Journal of alloys and compounds, Vol. 571, 2013, 183-204.

[3] Wang, Sheng-Chang, and Wen-Cheng J. Wei. "Kinetics of electroplating process of nano-sized ceramic particle/Ni composite". Materials Chemistry and Physics, Vol. 78.3, 2003, 574-580.

[4] Xu, Yong, et al. "Flexible shear-stress sensor skin and its application to unmanned aerial vehicles". Sensors and Actuators A: Physical, Vol. 105.3, 2003, 321-329.

[5] Trudgeon, M. A., and J. R. Griffiths. "Corrosion resistance of electroless nickel coatings in mining environments". British Corrosion Journal, Vol. 21.2, 1986, 113-118.

[6] Liu, Xi, Jia-Qiang Gao, and Wen-Bin Hu. "Application of electroless Ni-P alloys in electronics industry". Diandu yu Jingshi(Plating & Finishing), Vol. 28.1, 2006, 30-34.

[7] Agarwala, R. C., and Vijaya Agarwala. "Electroless alloy/composite coatings: A review". Sadhana, Vol. 28.3, 2003, 475-493.

[8] Sharma, S. B, "Characterization of carbon fabric coated with Ni-P and Ni-P-ZrO2-Al2O3 by electroless technique". Journal of materials science, Vol. 37.24, 2002, 5247-5254.

[9] Oraon, B., G. Majumdar, and B. Ghosh. "Improving hardness of electroless Ni–B coatings using optimized deposition conditions and annealing". Materials & design, Vol. 29.7, 2008, 1412-1418.

[10] Oraon, B., G. Majumdar, and B. Ghosh. "Parametric optimization and prediction of electroless Ni–B deposition". Materials & design, Vol. 28.7, 2007, 2138-2147.

[11] Krishnan, K. Hari, et al. "An overall aspect of electroless Ni-P depositions—A review article". Metallurgical and materials transactions, Vol. A 37.6, 2006, 1917-1926.

[12] Narayanan, TSN Sankara. "Deposition of electroless Ni–P graded coatings and evaluation of their corrosion resistance". Surface and Coatings Technology, Vol. 200.11, 2006, 3438-3445.

[13] Bangwei, Zhang. "Preparation, formation and corrosion for Ni-WP amorphous alloys by electroless plating". Transactions of the IMF, Vol. 74.2, 1996, 69-71.

[14] Kumar, Anuj. "Study on thermal stability of electroless deposited Ni-Co-P alloy thin film". Journal of Materials Science: Materials in Electronics, Vol. 22.9, 2011, 1495-1500.

[15] Armyanov, S. "Electroless deposition of Ni-Cu-P alloys in acidic solutions". Electrochemical and solid-state letters, Vol. 2.7,1999, 323.

[16] Chou, Yu Hsien."Studies on Ni-Mo-P coatings by electroless deposition". Key Engineering Materials, Vol. 364. Trans Tech Publications Ltd, 2008.

[17] Ger, Ming-Der, and Bing Joe Hwang. "Effect of surfactants on codeposition of PTFE particles with electroless Ni-P coating". Materials chemistry and physics, Vol. 76.1,2002, 38-45.

[18] Song, Y. W., D. Y. Shan, and E. H. Han. "Comparative study on corrosion protection properties of electroless Ni-P-ZrO2 and Ni-P coatings on AZ91D magnesium alloy". *Materials and Corrosion, Vol.* 58.7, 2007, 506-510.

[19] Szczygieł, B., A. Turkiewicz, and J. Serafińczuk. "Surface morphology and structure of Ni–P, Ni–P–ZrO2, Ni–W–P, Ni–W–P–ZrO2 coatings deposited by electroless method". Surface and Coatings Technology, Vol. 202.9, 2008, 1904-1910.

[20] Ma, Chunyang. "Effect of heat treatment on structures and corrosion characteristics of electroless Ni–P–SiC nanocomposite coatings". Ceramics International, Vol. 40.7, 2014, 9279-9284.

[21] Gadhari, Prasanna, and Prasanta Sahoo. "Effect of process parameters on microhardness of Ni-P-Al2O3 composite coatings". Procedia Materials Science, Vol. 6, 2014, 623-632.

[22] Mejias, A. "Hardness evaluation from a bilayer coating system of Ni-P deposited on carbon steel plates by multicycle indentation tests". Surface and coatings technology, Vol. 334, 2018, 410-419.

[23] Kumar, P. Sampath, and P. Kesavan Nair. "Studies on crystallization of electroless Ni□ P deposits". Journal of Materials Processing Technology, Vol. 56.1-4, 1996, 511-520.

[24] Sarkar, Subhasish. "Optimization of process parameters for electroless Ni–Co–P coating deposition to maximize micro-hardness". Materials Research Express, Vol. 6.4, 2019, 046415.

[25] Keong, K. G., Wei Sha, and Savko Malinov. "Hardness evolution of electroless nickel–phosphorus deposits with thermal processing". Surface and Coatings Technology, Vol. 168.2-3 ,2003, 263-274.

[26] Yan, M., H. G. Ying, and T. Y. Ma. "Improved microhardness and wear resistance of the as-deposited electroless Ni–P coating". Surface and Coatings Technology, Vol. 202.24, 2008, 5909-5913.

[27] Zangeneh-Madar, K., and SM Monir Vaghefi. "The effect of thermochemical treatment on the structure and hardness of electroless Ni–P coated low alloy steel". Surface and Coatings technology, Vol. 182.1, 2004, 65-71.

[28] Milkey, K. R., et al. "Comparison between Taguchi Method and Response Surface Methodology (RSM) in Modelling CO 2 Laser Machining." Jordan Journal of Mechanical and Industrial Engineering, Vol. 8.1, 2014.

[29] Mukhopadhyay, Arkadeb, et al. "Wear analysis of electroless Ni-P coating under lubricated condition using fuzzy logic". Portugaliae Electrochimica Acta, Vol. 34.1, 2016, 63-83.

[30] Vinayagamoorthy, R. "A central composite design based fuzzy logic for optimization of drilling parameters on natural fiber reinforced composite". Journal of Mechanical Science and Technology, Vol. 32.5, 2018, 2011-2020.

[31] Balaji, M. "A fuzzy approach for modeling and design of agile supply chains using interpretive structural modeling". JJMIE, Vol. 10.1, 2016, 67-74.

[32] Alazzam, Azmi, and Tariq Tashtoush. "Lead-Free Solder Reliability Modeling Using Adaptive Neuro-Fuzzy Inference System (ANFIS)." Jordan Journal of Mechanical and Industrial Engineering, Vol. 15.2, 2021.

[33] Zhang, Qingyong, et al. "Driving Pattern Recognition of Hybrid Electric Vehicles Based on Multi-hierarchical Fuzzy

Comprehensive Evaluation." Jordan Journal of Mechanical and Industrial Engineering, Vol. 14.1, 2020.

[34] Manousi, Natalia. "Determination of rare earth elements by inductively coupled plasma-mass spectrometry after dispersive solid phase extraction with novel oxidized graphene oxide and optimization with response surface methodology and central composite design". Microchemical Journal, Vol. 152, 2020, 104428.

[35] Sarkar, Subhasish. "Parametric optimization of process parameters on the response of microhardness of electroless Ni-P coating". Journal of Molecular and Engineering Materials, Vol. 6.01, No. 02, 2018, 1850003.

[36] Daws, Kasim M., Zouhair I. Al-Dawood, and Sadiq H. Al-Kabi. "Selection of metal casting processes: a fuzzy approach". JJMIE, Vol. 2.1, 2008.

[37] Moneim, Ahmed Farouk Abdul. "Fuzzy genetic prioritization in multi-criteria decision problems". Jordan Journal of Mechanical and Industrial Engineering, Vol. 2.4, 2008, 175-182.