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APPLICATION OF DESIGN OF EXPERIMENTS FOR PREDICTING THIN FILM DEPOSITION IN ELECTROLESS NICKEL PLATING

B. Oraon[1], G. Majumdar[1], B. Ghosh[2]

[1] Department of Mechanical Engineering, Jadavpur University, Kolkata – 700 032, India
[2] School of Energy Studies, Jadavpur University, Kolkata – 700 032. India.

ABSTRACT

Electroless nickel plating process has been studied for nickel-boron (Ni-B) deposition considering copper as a substrate material. Deposition thickness has been considered as a response variable and studies have been carried out to observe the effects of various influencing parameters. Statistical analysis has been carried out to identify the significant influencing parameters on response variable. It has been observed that reducing agent ($NaBH_4$), source of metal ($NiCl_2$, $6H_2O$) and temperature significantly affect the deposition thickness. Also the interactions of some of the parameters affect the response variable significantly. Finally predicting regression equation has been developed and analysis of variance for regression equation has been carried out which shows that regression fitting is appropriate and interaction among parameters are also significant.

Keywords: Electroless coating, analysis of variance, design of experiments, substrate material, response variable.

1. INTRODUCTION

Aqueous metal deposition processes can be classified under two headings : electrolytic and electroless. In electorless metal deposition process, no external current supply is required to deposit material on a substrate. The electrons required to bring about the discharge of metal ions are produced by a chemical reaction in solution called bath. The most widely used substrate metals are copper, iron and nickel while the most widely used coating metals are gold or copper. Hence, if an iron part is immersed in copper sulphate solution, it is thinly coated with copper.

In this study, 0.1mm thick copper sheets were used as a substrate material and deposition thickness (in µm) was considered as a response variable. From literature [1] it appears that the deposition rate depends on a number of parameters like temperature, bath composition, pH of the bath, concentrations of chemicals in the bath, concentration of reducing agent, bath loading etc. In our study, nickel chloride ($NiCl_2$, $6H_2O$) was used as source of nickel and sodium borohydride ($NaBH_4$) as a reducing agent. Sodium hydroxide (NaoH) and Sodium Potassium tartrate (Na-K-Tartrate) were used to increase the stability of the bath. Bath pH was kept constant and maintained around 13 (strong alkaline solution).

2. EXPERIMENTAL PROCEDURE

2.1 Initial Study and Bath Composition

After conducting a series of experiments it was observed that $NaBH_4$, $NiCl_2$ ($6H_2O$) and temperature were important parameters which affected the deposition rate. Hence these three factors were considered to perform analysis by design of experiments (DOE). The following tables (Table 1 and Table 2) give the data about the effects of deposition time and deposition temperature on deposition thickness and Fig-1 and Fig-2 show how deposition thickness varies with variation of input parameters.

Fig-1 shows that deposition thickness increases with time and becomes stable at about 60 minute deposition time for a bath. It also shows that deposition rate is more without $K_2S_2O_5$. (stabilizer). Fig-2 shows that deposition thickness increases with temperature; for lower deposition time deposition rate increases steadily but for higher deposition time deposition rate increases upto 70^0C but decreases after 70^0C.

The bath for electroless coating was prepared as follows: the solution on $NiCl_2$ ($6H_2O$), $NaBH_4$, NaOH and Na-K-Tartate were prepared and kept in four different bickers. A clean dried empty bicker was taken. 5 cc of $NiCl_2$ solution, 5 cc of Na-K- Tartrate solution, 5 cc of NaoH solution and 5 cc $NaBH_4$ solution were added to the empty bicker strictly in this order. Then around 20 cc NH_3 solution (25% soln) was added to it which makes a total 40 cc bath for electroless nickel coating. The maximum limits of the parameters were set as follows:

$NiCl_2$ ($6H_2O$) = 20 gm $NiCl_2$ salt/ 100 cc distilled water.
$NaBH_4$ = 0.65 gm $NaBH_4$ /100 cc distilled water.
Temperature = 65^0C

Table1: Deposition time and thickness data at 65^0C with $K_2S_2O_5$ and without $K_2S_2O_5$.

Deposition time (min)	Deposition thickness (μm) (with $K_2S_2O_5$)	Deposition thickness (mm) (without $K_2S_2O_5$)
10	0.116	1.787
20	0.466	3.463
30	0.974	4.109
40	1.230	4.653
50	1.288	4.780

Table 2 : Deposition temperature and thickness data for 10 minutes and 20 minutes deposition time (without $K_2S_2O_5$.)

Deposition temperature (^{0}C)	Deposition thickness (μm) (Deposition time 10 min)	Deposition thickness (μm) (Deposition time 20 min)
55	0.720	1.748
60	1.182	2.700
65	1.787	3.463
70	2.173	3.918
75	2.621	3.344

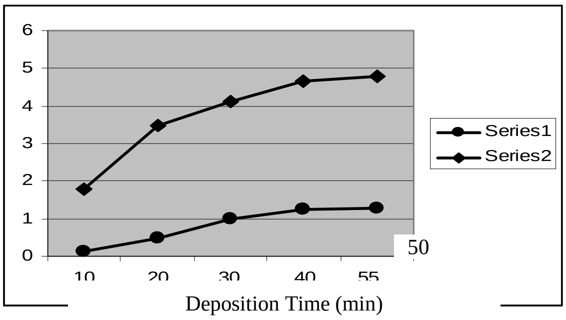

Fig -1 Deposition time vs thickness curve

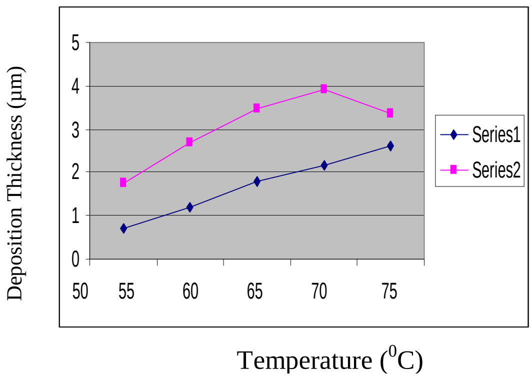

Fig – 2 Deposition Temperature vs thickness curve

2.2 Design of Experiments and Observations

A mathematical model which takes into account the main effects as well as interaction effects among the parameters can be written (for 3 parameters) [2] :

$$h = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{23} x_2 x_3 + \beta_{13} x_1 x_3 + \beta_{123} x_1 x_2 x_3 \ldots\ldots\ldots (1)$$

The following table gives the parameters and their levels :

Parameter	Levels		
	Lowest	Centre	Highest
$NaBH_4$ (gm / 100cc DW)	0.2	0.3	0.4
$NiCl_2$ $(6H_2O)$ (gm/100cc DW)	12	15	18
Temperature ($_0$C)	50	55	60

The following table gives the details of experimental layout and observations on deposition thickness. Here a full factorial experimental layout with six additional centre points were considered [3]. This type of experimental layout can also be used to perform further analysis for second order response curve to develop an appropriate response surface for predicting response variable for different settings of input variables. The table shows the actual values as well as the coded values of the variables.

Transformation equations used are as follows:

$$x_1 = \frac{z_1 - 0.3}{0.1}, \quad x_2 = \frac{z_2 - 15}{3}, \quad x_3 = \frac{z_3 - 55}{5}$$

The experiments were carried out in random order and the results are as follows:

Sl. No.	z_1	z_2	z_3	x_1	x_2	x_3	h
1	0.2	12	50	-1	-1	-1	1.27
2	0.4	12	50	1	-1	-1	1.793
3	0.2	18	50	-1	1	-1	1.723
4	0.4	18	50	1	1	-1	2.480
5	0.2	12	60	-1	-1	1	1.842
6	0.4	12	60	1	-1	1	3.162
7	0.2	18	60	-1	1	1	1.350
8	0.4	18	60	1	1	1	4.253
9	0.3	15	55	0	0	0	2.869
10	0.3	15	55	0	0	0	2.742
11	0.3	15	55	0	0	0	3.151
12	0.3	15	55	0	0	0	2.819
13	0.3	15	55	0	0	0	2.543
14	0.3	15	55	0	0	0	2.543

2.3 Results and Discussions

The coefficients of the regression equation were estimated and obtained as follows : [4]

$$\beta_0 = 2.467, \quad \beta_1 = 0.688, \quad \beta_3 = 0.418$$
$$\beta_{12} = 0.227, \quad \beta_{13} = 0.368, \quad \beta_{23} = -0.068,$$
$$\beta_2 = 0.217, \quad \beta_{123} = 0.169$$

Hence the regression equation becomes:

$$h = 2.467 + 0.688x_1 + 0.217x_2 + 0.418x_3 + 0.227x_1x_2 + 0.368x_1x_3 - 0.068x_2x_3 + 0.169x_1x_2x_3$$

The significance of the coefficients can be tested using the students t- test : [2] :

$\hat{\sigma}^2 =$ Estimate of error
= sample variance of central points
= 0.0522

$\therefore \hat{\sigma} = 0.2284$

Again [4], $\sigma_{\beta_j} = \frac{\hat{\sigma}}{\sqrt{N}} = \frac{0.2284}{\sqrt{8}} = 0.08075$

$t_0 = 2.467$, $t_1 = 8.520$, $t_2 = 2.687$,
$t_3 = 5.176$, $t_{12} = 2.811$, $t_{13} = 4.557$,
$t_{23} = 0.842$, $t_{123} = 2.093$,

Here the degrees of freedom = n-1 =6-1=5

Taking level of significance as 5%, 2.5% and 1%. We have,

$t_{0.05;5}$=2.015, $t_{0.025;5}$=2.571, $t_{0.01;5}$=3.365,

The comparisons among estimated values and tabular values of test statistics 't' for coefficients of main effects as well as interactions indicate that all the main effects and interactions x_1x_2, x_1x_3 and $x_1x_2x_3$ are significant at 5% significance level while the main effects of factor x_1, x_3 and interaction x_1 x_3 at 1% significance level.

Hence the final predicting regression equation becomes

$$h = 2.467 + 0.688x_1 + 0.217x_2 + 0.418x_3 + 0.227x_1x_2 + 0.368x_1x_3 + 0.169x_1x_2x_3$$

2.4 Analysis of Variance for Regression Equation

The analysis of variance (ANOVA) gives appropriate picture about the fitting of the data. The ANOVA table for the given data is shown below.

Sources of variation	Sum of square	Degrees of freedom	Mean sum of square	F_0
Regression $(\beta_1, \beta_2, \beta_3)$	5.56	3	1.8533	6.11 a
Residual	3.0325	10	0.30325	
(Interaction)	(1.7575)	4	0.4394	8.42 a
(Pure quadratic)	(1.014)	1	1.0140	19.425 b
(Pure error)	(0.261)	5	0.0522	
Total	**8.5925**	**13**		

a : Significant at 5% level
b : Significant at 1% level

The analysis of variance of multiple regression model indicates that regression and interactions significant at 5% level and residual due to pure quadratic is significant at 1% level.

It further indicates that experiments were carried out at near optimum points where quadratic regression model will be more appropriate to fit the data.

3.0 CONCLUSION

It has been observed that reducing agent ($NaBH_4$), source of metal ($NiCl_2$, $6H_2O$), temperature and pH of the of bath significantly affect the deposition thickness. Reducing agent ($NaBH_4$) affects the deposition thickness most significantly. Also the interactions of some of the parameters affect the response variable. Finally the non-significant factors have been isolated and approximate predicting equation has been determined by using multiple regression analysis.

4. REFERENCES

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5 NOMENCLATURE

Symbol	Meaning	Unit
z_1	Actual value of $NaBH_4$	Gm/100cc distilled water
z_2	Actual value of $NiCl_2$, $6H_2O$	Gm/100cc distilled water
z_3	Actual value of temperature	^{0}C centigrade
x_1	Coded value of $NaBH_4$	-
x_2	Coded value of $NiCl_2$, $6H_2O$	-
x_3	Coded value of temperature	
β_i	Regression Co-efficient of i^{th} parameter	
β_{ij}	Regression Co-efficient of interactions of i^{th} and j^{th} parameter	
$\hat{\sigma}$	Standard deviation of error estimate	
σ_{β_j}	Standard deviation of estimate of j^{th} regression co-efficient.	
$t_{\alpha,\nu}$	Value of student's 't' distribution at α significance level and ν degrees of freedom.	
$F_{\alpha;\nu_1,\nu_2}$	Value of F-distribution at α significance level and ν_1 (upper), ν_2 (lower) degrees of freedom	
h	Deposition thickness (both sides)	micron (μm)