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Microhardness values optimization of chemically deposited Ni-P thin films using Taguchi method

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Abstract : Ni-P thin films over mild steel were prepared by electroless deposition, using sodium hypophosphite as reducing agent. Taguchi orthogonal array with five process parameters, vis, concentration of nickel ion resource, concentration of reducing agent and complexant and bath operation conditions, pH and temperature of the bath, was used to determine the optimum bath concentrations and operating conditions, to obtain higher values of microhardness in electroless nickel - phosphorus plating. It has been observed that pH, reducing agent and nickel ion concentration have significant influence on microhardness characteristic. The response, microhardness of plates, was analyzed based on signal-to- noise ratio, and analysis of variance (ANOVA). The result obtain from optimum bath composition and bath operating conditions, is quite close to predicted result. The resulting electroless Ni-P coating contain about 9.14wt.% phosphorous with microhardness value of 587 HV (50gr).

Keywords : Taguchi orthogonal design; Microhardness; Electroless nickel plating; ANOVA.

INTRODUCTION

Electroless nickel plating, also known as autocatalytic nickel plating, or as chemical Nickel plating began with Brenner and riddle, using nickel phosphorus bath[1]. The chemically deposited film has many applications in the areas of microelectronic manufacturing, automotive, aircraft and aerospace, chemical and petroleum, food and printing industry and others do to the coatings excellent physical and mechanical properties[2]. Electroless nickel deposit provides very good protection against corrosion[3-5], also it has high abrasion resistance[6], and high values of microhardness[7,8]. This technique not only applied to plating metals, but also used for plating the plastics[9-11]. The deposition rate, properties of coating and the structural behavior of deposits mainly depend upon the plating bath conditions such as the type and concentrations of the reducing agent and stabilizer used pH and the temperature of the bath, etc.

In electroless nickel plating the becoming deposit is not pure Nickel, but it contains the small amount of phosphorus from reducing agent and sometimes other impurities. The design and composition of the chemical solution dictates the phosphorus content and the physicomechanical properties of resulting plates.

The corrosion resistance of the Nickel phosphorous coating depends to phosphorous content of coats. In general, electroless nickel coatings with higher phosphorous content show better corrosion resistance[12]. In order to obtain higher values of microhardness composite materials can be use as reinforcing[13]. Also heat treatment process change the Ni/P matrix phases and has remarkable effect on the microstructure of electroless coatings, which this cause to increase in microhardness and wear resistance of coatings[14].

In order to observe the effect of the process variables changes on one or more response variables, the statistical design of experiments can be used for planning experiments. The obtained data can be analyzed to yield valid and objective conclusions. Experimental design is a careful balancing of several features including power, generalizability, various forms of validity, practicality and cost. In general usage, design of experiments (DOE) or experimental design is the design of any information-gathering exercises where variation is present, whether under the full control of the experimenter or not.

Taguchi technique introduced by Genichi Taguchi in the 1950s and 1960s in order to improve the quality of manufactured goods, and more recently also applied to marketing, photographic, engineering, automotive, biotechnology, in evaluating physical objects, chemical formulations, structures, components, materials and many others industries[15]. This method involves reducing the variation in a process through robust design of experiments, which allows studying the whole parameter space with a limited number of experiments. In Taguchi method, orthogonal arrays are used to organize the process parameters and the levels at which they should be varies.

The aim of this study is to find the optimum concentrations of Nickel ion (Ni), Reducing agent (RED), Complexant (CMP) and also to find the optimum conditions, temperature (T) and pH value, to obtain high values of Ni-P thin film microhardness, using Taguchi approach. The use of Taguchi orthogonal arrays helps determine the minimum number of experiments needed, which may produce the most favorable information for given set of factors.

EXPERIMENTAL

Thin film preparation

The electroless Nickel Phosphorus plating was carried out in bath that contained as followed: $NiSO_4.6H_2O$, 10-40gr/lit, sodium hypophosphite, $NaH_2PO_2.XH_2O$, 15-30gr-lit, sodium citrate as complexing agent, 5-20 gr/lit, the pH value was 4.5-6 and the temperature was 85-91ºC. All the reagents used were of analytic grade.

Mild steel was used as substrate with dimension of 20×20×1 mm. before plating the substrate was polished with 800, 1200 and 2000 grade SiC paper then washed and rinsed with distilled water. The substrate was then chemically cleaned using a 15% sodium hydroxide solution at 55 ºC, subsequently rinsed with acetone ant then with double distilled water. The electroless deposition process was carried out in a 300 CC glass vessel for one hour.

Taguchi design

To study the influence of five agents and parameters which were concentrations of bath chemicals, pH and temperature of the solution, against the microhardness value of resulting microfilm, the L-16 orthogonal array of Taguchi design method was used.

With full factorial design, it would require 1024 trial runs for all possible combinations of these factors. By using L-16 orthogonal arrays in this study, the number of trial runs was reduced to 16 experiments. TABLE 1 illustrates the L-16 orthogonal array in which there are five factors with four levels. These factors were assigned to all five columns in the L-16 array. For example in the firs trial, the first level values of each factor are used, in other words the first experiment involved the use of 10gr/lit Nickel source, 15gr/lit reducing agent, 5 gr/lit sodium citrate in pH value of 4.5 and temperature of 85ºC. The same process was applied to the rest of the trials as specified in TABLE 2.

Analysis of signal-to-noise

The undesirable and uncontrollable sources that can cause deviation from target values in products functional characteristics are called noise, and signal to noise ratio measures quality with emphasis on variation. Sig-

TABLE 1 : L-16 orthogonal array in Taguchi experimental design

Trial	level 1	level 2	level 3	level 4	level 5
1	1	1	1	1	1
2	1	2	2	2	2
3	1	3	3	3	3
4	1	4	4	4	4
5	2	1	2	3	4
6	2	2	1	4	3
7	2	3	4	1	2
8	2	4	3	2	1
9	3	1	3	4	2
10	3	2	4	3	1
11	3	3	1	2	4
12	3	4	2	1	3
13	4	1	4	2	3
14	4	2	3	1	4
15	4	3	2	4	1
16	4	4	1	3	2

TABLE 2 : Five factors and four levels in examination

Column	Design Factors	1	2	3	4
1	Nickel source (gr/lit.)	10	20	30	40
2	Reductant (gr/lit.)	15	20	25	30
3	Complexant (gr/lit.)	5	10	15	20
4	pH	4.5	5	5.5	6
5	Temperature (^{o}C)	85	87	89	91

nal-to-noise ratio (SNR) is sometimes used informally to refer to the ratio of useful information to false or irrelevant data. The SNR is a key idea in Taguchi experimental design.

The larger the numerical value of SNR, the more desirable the system is. There are three types of quality characteristic with respect to the target design in Taguchi method. They are 'smaller is the better', 'nominal is the better' and 'bigger is the better'. The SNR for microhardness of coatings is calculated using "bigger is the better" criterion and expressed as below[16];

$$\frac{S}{N} = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right)$$

In which $"n"$ is the repetition number of each experiment under the same condition for design parameters, and $"y\text{i}"$ is the microhardness of coating in an individual measurement at the $"i"$th test.

Taguchi approach tries to reach optimality by maximizing the SNR, and then the effect of noise is minimized.

Analysis of variance (ANOVA)

Analysis of variance, frequently abbreviated to ANOVA, is an extremely powerful statistical technique which can be used to separate and estimate the different causes of variation. It can be used to separate any variation which is caused by changing the controlled factor from the variation due to random errors[17]. ANOVA calculates the F-ratio which is the ratio between the regression mean square and the mean square error. The F-ratio, also called the variance ratio, is the ratio of variance due to the effect of a factor and variance due to the error term. This ratio is used to measure the significance of the parameters under investigation with respect to the variance of all the terms included in the error term at the desired significance level.

RESULTS AND DISCUSSION

Microhardness

Microhardness measurements were performed by Vickers microhardness tester (Shimadzu -HMV 2000 model) with a load of 50gr of diamond indenter for 15 second. Three readings were made on each specimen and the values were then averaged. The results for 16 trial conditions with three run per trial condition are shown in TABLE 3. In this study the higher value for microhardness is the favor, and then the 'bigger is the better' criterion was used.

The corresponding SNR for 16 trials and for each level of factors is given in TABLE 3 and TABLE 4, respectively.

To calculate the SNR for each level and for each factor Equation (1) was used.

$$MD4 = \frac{1}{4}\left(\frac{S}{N_{tw}} + \frac{S}{N_{tx}} + \frac{S}{N_{ty}} + \frac{S}{N_{tz}}\right) \quad (1)$$

In which S/N_{tw}, S/N_{tx}, S/N_{ty} and S/N_{tz} are the same SNR for any trial which the factor appeared in.

For example the Reductant factor was at level two for trial condition 2, 6, 10 and 14 in the array. Then for computing the average effect of Reductant, which was denoted by $MD4$, is shown below, Equation (2):

$$MD4 = 1/4(53.655+52.988+52.061+52.408) = 52.778 \quad (2)$$

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TABLE 3 : Results of Ni-P microhardness values and the S/N ratio for each trial

	sample≠1	sample≠2	sample≠3	averages	S/N ratio
trial≠1	376	378	374	372.666	51.425
trial≠2	492	469	485	482	53.655
trial≠3	385	359	368	370.666	51.368
trial≠4	230	239	235	234.666	47.405
trial≠5	470	469	457	465.333	535.353
trial≠6	457	436	446	446.333	52.988
trial≠7	435	414	424	424.333	52.548
trial≠8	424	424	413	420.333	52.469
trial≠9	537	516	524	525.666	54.41
trial≠10	404	395	404	401	52.061
trial≠11	482	457	476	471.666	53.465
trial≠12	289	280	280	283	49.032
trial≠13	470	470	465	468.333	53.41
trial≠14	424	414	414	417.333	52.408
trial≠15	414	404	404	407.333	52.197
trial≠16	394	387	385	388.666	51.79
average	-	-	-	411.208	52.124

TABLE 4 : The S/N ratio for each level of five factors

Factors	Level 1	Level 2	Level 3	Level 4
Ni	50.963	52.84	52.242	52.451
RED	53.149	52.778	52.395	50.174
CMP	52.417	52.059	52.664	51.356
Ph	51.353	53.25	52.143	51.75
T	52.038	53.101	51.7	51.658

This result is presented in TABLE 4 column 3 and row3.

The average effects of five factors for each level were shown in TABLE 5. It can be seen that the first factor, concentration of nickel ions, has highest effect at level two.

ANOVA is very useful to revealing the level of significance of influence of factors. TABLE 6 shows the ANOVA result for microhardness of electroless nickel plating and it shows the percentage contribution of each parameter. It is seen that parameters 'reducing agent' and 'pH' and nickel ion have got the most significant influence on the microhardness value at the confidence level of 90%. The microhardness of Ni/P alloy is dependent upon the P content and then the most important factor that affects the hardness of the alloy is the reducing agent concentration (sodium hypophosphite). The microhardness of Ni/P film increasing with decreasing of the P content[18]. From TABLE 5 it is evident that the microhardness of Ni/P alloy reduced as the concentration of reducing agent increases.

TABLE 5 : Main effects (average effects of factors)

Factors	Level 1	Level 2	Level 3	Level 4
Ni	364.999	439.083	420.333	420.416
RED	458	436.666	418.5	331.666
CMP	419.833	409.416	433.5	382.083
Ph	374.333	460.583	406.416	403.5
TMP	400.333	455.166	392.083	379.25

TABLE 6 : ANOVA table

Factors	DOF	Some of sqrs.	Variance	Pure sum.	percent
1. NI	3	7.916	2.638	7.916	16.964
2. RED	3	21.416	7.138	21.416	45.893
3. CMP	3	3.882	1.294	3.882	8.319
4. pH	3	8.009	2.669	8.009	17.162
5. T	3	5.343	1.811	5.343	11.646

TABLE 7 : Optimum levels for five factors

Factors	Level description	level	contribution
1. NI	20	2	27.875
2. RED	15	1	46.791
3. CMP	15	3	22.291
4. pH	5	2	49.375
5. TMP	87	2	43.958
Total contribution from all factors			190.289
Current grand average of performance			411.208
Expected result at optimum condition			601.498

OPTIMUM POINTS AND LEVELS

The output of Taguchi approach is a set of optimum level for each of the given factors. TABLE 7 shows the optimum levels for five factors examined in this study. Also the performance of the optimum conditions and the amount of expected microhardness for electroless nickel plating are given in this table. The value of microhardness that resulted from optimum bath composition, 573 HV(50gr), is quite close to the predicted value from Taguchi approach, 601.498 HV(50gr).

From the EDX analysis, the phosphorous content of the thin film was obtained about 9.14%wt. Figure 1 shows the X-ray diffraction pattern of Ni/P thin film after annealing at 300 °C which indicates crystalline structure of Ni at 2θ=45 and good crystalline structure

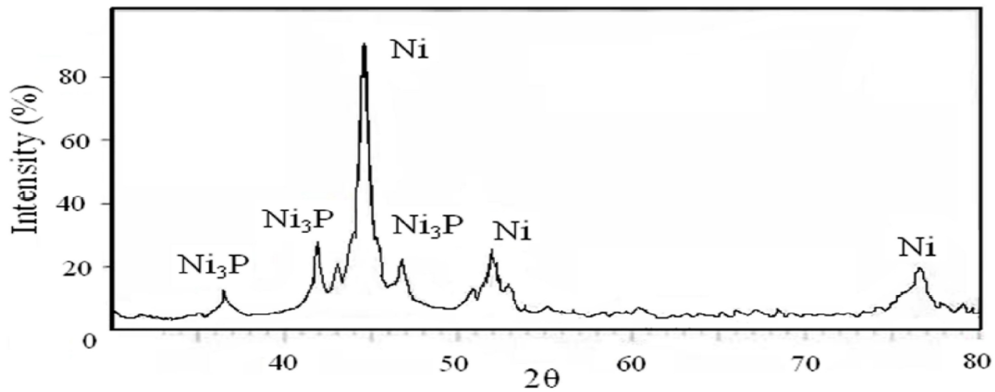

Figure 1 : XRD pattern of Ni/P thin film after annealing at 300 °C

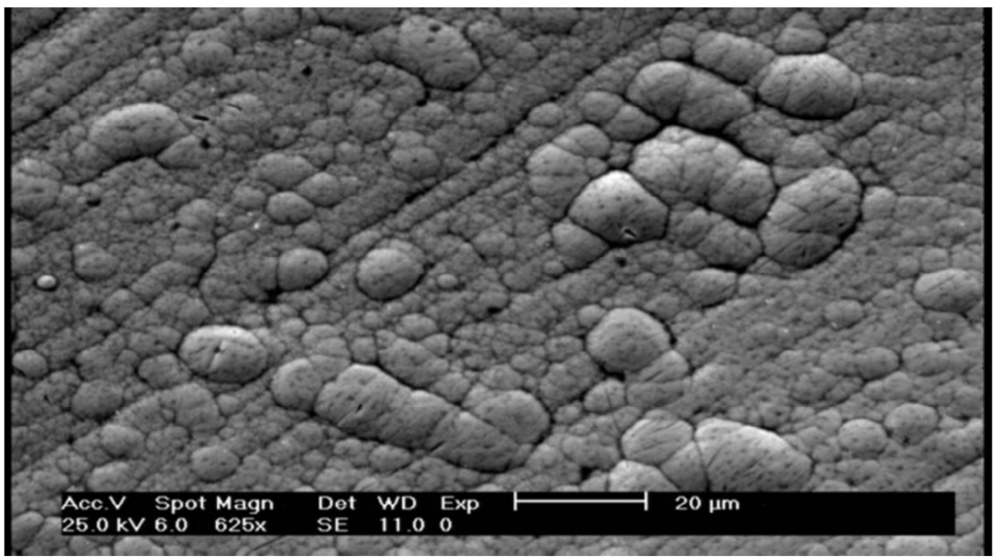

Figure 2 : Scanning electron microscopy image of Ni/P thin film plated from baths with optimum composition and condition

of Ni_3P. The SEM micrographs of resulting film are presented in Figure 2 which shows a dense and fine crystalline structure.

CONCLUSION

The optimum bath formulation for electroless Ni/P plating was resulted by using Taguchi orthogonal array design to maximize the microhardness value of thin films. Taguchi method prediction, in this work just considered the microhardness, as the "bigger is the better" quality characteristic. The result obtained from optimum bath composition and bath operating conditions, is quite close to predicted results. The ANOVA analysis approved that the concentration of reducing agent, pH value, and Ni source concentration have the most significant influence on the microhardness of Ni/P films.

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