Optimization of Electroless Ni-P, Ni-Cu-P and Ni-Cu-P-TiO₂ Nanocomposite Coatings Microhardness using Taguchi Method

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Abstract. This paper studies the electroless (Ni-P) deposition which is used in different engineering applications due to their ability to modify and enhance the surface properties of the steel substrate. The electroless plating process was used to prepare (Ni-Cu-P), (Ni-P) and (Ni-Cu-P/ Nano TiO2) alloys in this research. Deposition process parameters based on (L28) Taguchi orthogonal configuration with three process parameters, viz., stirring speed, temperature, time, are designed for optimum microhardness. Under the Taguchi series, the microhardness activity of electroless (Ni-P-TiO2) nanocomposite deposition was measured. The findings revealed that the integration of TiO2 into the coating allows micro-hardness cause an increase. Finally, optimum conditions were achieved as A2B1C2 (i.e. Speed of stirring = 1000 r.p.m, Temperature = 90 °C and Time = 70 min).

Keywords. Electroless deposition, Microhardness, Taguchi method

1. Introduction

The coating Electroless Ni-P, first developed by Riddell and Brenner, has commonly been used in electronic, chemical, and industrial applications because of its great mechanical, electrical, physical, tribological, and corrosion properties. [1,2,3] The electroless deposition is a self-catalytic chemical technique used to deposit one layer of metal in a non-electric tank onto the other. The electroless bath creates watery solutions of complexing agents, metal ions, stabilizers which all work or run at stable temperature, in specific (pH) range. Electroless deposition possesses have many benefits in terms of electrolytic depositions; they improve the physical properties of materials such as the uniform thickness of the deposition, improved hardness, corrosion resistance, and abrasion. The electroless deposition may be added to any form of substrate, such as glass, steel, aluminum, and alloys, etc.[4]. In recent years, the efficiency and longevity of the nickel-phosphorus bed have been improved by the combination of various metal elements in the (Ni-P) matrix. Choosing certain elements depends on the properties and applications required. Copper, Tungsten, Cobalt, Molybdenum, and Iron are common elements that strengthen the various properties of the substrates. The properties of (Ni-P) deposition by the electroless operation on (Ni-P) matrix are enhanced by the presence of copper increases different characteristics, like wear and corrosion, surface hardness, thermal resilience, and solderability [5]. The addition of more than one factor to the bath is often intended to acquire a deposit with distinct unique properties. The development of nanomaterials will increase the enhancements due to their unusual mechanical, magnetic, and optical properties in nanocomposite depositions with a
metal matrix [6]. These nanomaterials are used as an additive in electroless (Ni-P) plating, which can make several developments for many applications in various fields. These electroless depositions (Ni-P) did improve the mechanical properties for the substrate surfaces [7]. Hardness is a property of a material that was important for specific applications. Surface hardness is especially important for the management of tear and wear processes in components or products. For some engineering products, stiffness property was improved also by that additives, which is it is imported for some engineering systems and structures. Electroless nickel is currently considered a hard deposition for tribological applications. The hardness of the electroless deposition increases with the heat treatment to a certain temperature. The toughness of (Ni-P) depositions reduces with an extreme annealing temperature. The longevity of electroless (Ni-P) composite depositions is improved by the inclusion of ceramic particles and decreased by the inclusion of soft composite particles [8]. The microhardness of the surface has a significant impact on mechanical properties such as fatigue behavior, resistance to corrosion and creep life. As a result, improvement in the modeling of surface microhardness and optimization of control parameters is required to achieve the desired degree of surface microhardness. It is therefore necessary to maximize the mean microhardness of the products. In the past, numerous optimization methods have been used to refine input characteristics to achieve an optimal response. In this research, the Taguchi method was used for optimization [9-10]. The present study aims to investigate the effect of solution composition on deposition surface microhardness, and hardness of the final surface with the use of (L_{28}) orthogonal array in the Taguchi technique.

2. Experimental work

2.1. Substrate deposition and preparation

Low carbon steel samples with the dimensions of diameter of height (1 cm × 1 cm ± 1 mm) were used as substrates. The chemical structure of the low carbon steel is shown in table (1) using Spectra Max at (The General Company for Engineering Inspection and Rehabilitation):

| Element | C    | Si   | Mo   | S    | P   | Ni   | Cr  | Mn  | Cu  | Fe |
|---------|------|------|------|------|-----|------|-----|-----|-----|-----|
| Wt%     | 0.07 | 0.105| <0.002| 0.014| 0.0242| 0.0227| 0.0376| 0.356| 0.0292| Bal |

Table 1. Chemical composition of low carbon steel.

Then specimens were washed at room temperature in an alkaline solution (1 M KOH) and then successively rinsed with appropriate deionized waters for 15 minutes. Before the deposition, the steel sample cleaning was carried out as follows:

The samples have been mechanically polished to (2000) grade with emery papers, and carefully processed at a (50%) dilute (HCl) solution. Specimens were washed with water, dried manually by a piece of cotton and then washed by methanol. Samples after washing with methanol were rinsed and dried in an oven. The samples then were immersed in the (Ni-P) deposition bath instantly. Table (2) indicates the tank composition for the (Ni-P) electroless deposition. The tank is run at (70 °C to 90 °C) with a (pH = 5) solution for (60 minutes to 120 minutes) of plating time.

Table 2. Bath composition for (Ni-P) deposition.

| Substance           | Concentration (g/L) |
|---------------------|---------------------|
| NiSO_{4}.6H_{2}O     | 30                  |
| NaH_{2}PO_{4}        | 25                  |
| Na_{2}C_{6}H_{5}O_{7}.H_{2}O | 20 |
| Thiourea            | 0.002               |

Table (3) gives the composition of the bath for (Ni-Cu-P) electroless deposition. During the deposition, magnetic stirring was performed at a steady rate. Operation at (70 °C to 90 °C) was conducted in the bath with a (pH = 10 ± 0.2) solution for (60 minutes to 120 minutes) of plating time.
Table 3. Bath composition for (Ni-Cu-P) deposition.

| Substance                  | Concentration (g/L) |
|----------------------------|---------------------|
| NiSO₄·6H₂O                 | 25                  |
| NaH₂PO₄                    | 25                  |
| CH₃COONa.3 H₂O            | 20                  |
| Na₃C₆H₅O₇.2H₂O            | 60                  |
| CuSO₄·5 H₂O               | 1                   |
| Thiourea                   | 0.005               |

Table (4) shows the bath of composition for (Ni-Cu-P) Nano (TiO₂) electroless deposition. The bath was operated at (70 °C to 90 °C) with a (pH = 5) solution for (60 minutes to 120 minutes) of plating time.

Table 4. Bath composition for (Ni-Cu-P) Nano (TiO₂) deposition.

| Substance                  | Concentration (g/L) |
|----------------------------|---------------------|
| NiSO₄·6H₂O                 | 25                  |
| NaH₂PO₄                    | 25                  |
| Sodium acetate            | 20                  |
| Sodium citrate            | 60                  |
| CuSO₄                     | 1                   |
| Thiourea                   | 0.005               |
| Nano TiO₂                 | 15                  |

In each experiment, (200 mL) of fresh bath solution was selected.

2.2. Microhardness measurements

For evaluating the microhardness of electroless (Ni-P), (Ni-Cu-P) ternary, and (Ni-Cu-P) Nano (TiO₂) coatings, a microhardness tester with a Vickers indenter was used. To cause the indentations in all deposits, a constant load of 100 g was applied and the hardness values were averaged out of five such determinations. The test was conducted in (Department of Materials Engineering - University of Technology - Baghdad - Iraq), as shown in figure (1):

![Microhardness test device](image)
2.3. Taguchi method

Taguchi modeling is a very effective way to optimize input parameters by the (signal/experiment) output using the signal-to-noise ratio (S/N). The (S/N) ratio works in three different ways depending on the response. If it is necessary to optimize the response in the area of maxima, then the option selected will be "The bigger, the better". In the case of surface microhardness, the (The bigger, the better) option is used. A higher (S/N) ratio indicates less unwanted noise and more signal required [11-12].

3. Results and discussions

Table(5), which contains data for the substrate for purposes of analysis, provides the structure of the Taguchi orthogonal array system and the effects of micro-hardness tests for the various deposition on (low carbon steel). There is greater hardness in all coated samples relative to the substrate (low carbon steel).

| Exp. No. | Coating Type        | Speed of stirring (r.p.m) | Temperature °C | Time Min. | Microhardness |
|----------|---------------------|--------------------------|----------------|-----------|---------------|
| 1        | Ni-P Coating        | 500                      | 70             | 60        | 187.8         |
| 2        | Ni-P Coating        | 500                      | 70             | 90        | 156.8         |
| 3        | Ni-P Coating        | 500                      | 70             | 120       | 183.6         |
| 4        | Ni-P Coating        | 500                      | 80             | 60        | 212.2         |
| 5        | Ni-P Coating        | 500                      | 80             | 90        | 191.9         |
| 6        | Ni-P Coating        | 500                      | 80             | 120       | 168.4         |
| 7        | Ni-P Coating        | 500                      | 90             | 60        | 166.5         |
| 8        | Ni-P Coating        | 500                      | 90             | 90        | 184.6         |
| 9        | Ni-P Coating        | 500                      | 90             | 120       | 185.3         |
| 10       | Ni-P Coating        | 500                      | 90             | 60        | 206.1         |
| 11       | Ni-P Coating        | 500                      | 90             | 90        | 202.8         |
| 12       | Ni-P Coating        | 500                      | 90             | 120       | 205.2         |
| 13       | Ni-P Coating        | 500                      | 70             | 90        | 373.1         |
| 14       | Ni-P Coating        | 500                      | 70             | 120       | 344.5         |
| 15       | Ni-P Coating        | 500                      | 80             | 60        | 259           |
| 16       | Ni-P Coating        | 500                      | 80             | 90        | 218.2         |
| 17       | Ni-P Coating        | 500                      | 80             | 120       | 229.9         |
| 18       | Ni-P Coating        | 500                      | 90             | 60        | 316.9         |
| 19       | Ni-P Coating        | 500                      | 90             | 90        | 264.4         |
| 20       | Ni-P Coating        | 500                      | 90             | 120       | 225.5         |
| 21       | Ni-P Coating        | 500                      | 70             | 90        | 311.3         |
| 22       | Ni-P Coating        | 500                      | 70             | 120       | 182.5         |
| 23       | Ni-P Coating        | 500                      | 80             | 60        | 172.1         |
| 24       | Ni-P Coating        | 500                      | 80             | 90        | 207.7         |
| 25       | Ni-P Coating        | 500                      | 80             | 120       | 191.7         |
| 26       | Ni-P Coating        | 500                      | 90             | 60        | 190.2         |
| 27       | Ni-P Coating        | 500                      | 90             | 90        | 177           |
| 28       | Ni-P Coating        | 500                      | 90             | 120       | 188.5         |

Table (6) shows a comparison of the microhardness ratios determined by the mean (S/N). It displays the (S/N) response table, indicating micro-hardness. This is a description of the mean ratio (S/N) for each factor stage (time, temperature, and string speed). In the same way, the cumulative mean ratio (S/N) is determined and displayed in Table (7) of the (28) experiments. The solution table indicates the average function chosen for each factor stage. The solution table contains rankings that compare the relative significance of the outcomes depending on delta statistics. The delta is the highest average for each factor below the lowest average for each factor. Delta-based ranks are allocated; the largest delta value is assigned to rank 1, the second-highest delta value to rank 2, and so on. Ranks are also seen in figures (2 and 3) showing the related key plots between the method parameters. When the line
for a given parameter is nearly horizontal in the main effect plot, there is no noticeable effect on the parameter.

Table 6. Response table for signal to noise ratios.

| Level | Speed of stirring | Temperature | Time |
|-------|-------------------|-------------|------|
| 1     | 46.13             | 46.35       | 46.03|
| 2     | 46.22             | 46.06       | 46.37|
| 3     |                   | 46.11       | 46.06|
| Delta | 0.09              | 0.29        | 0.34 |
| Rank  | 3                 | 2           | 1    |

Table 7. Response table for means.

| Level | Speed of stirring | Temperature | Time |
|-------|-------------------|-------------|------|
| 1     | 217.2             | 235.0       | 208.2|
| 2     | 204.7             | 205.7       | 224.4|
| 3     |                   | 207.8       | 209.6|
| Delta | 12.5              | 29.3        | 16.2 |
| Rank  | 3                 | 1           | 2    |

Figure 2. Main effects for (S/N) ratios.

Figure 3. Main effects for means.
In contrast, the most important impact would be a parameter for which the line is the highest inclined. The key plot of effects reveals that the most critical parameters are (time, temperature), and the relatively minor factors are those parameters (speed) (Fig. 2). A2B1C2 (stirring speed = 1000 r.p.m., temperature = 90 °C, and time = 70 min.) provides the optimum process parameter mix for full microhardness. The efficiency of variance analysis (ANOVA) will determine the contribution of each component to the corrosion current density. Table (8) summarizes the findings of the variance analysis (ANOVA). Table (8) data reveal that the contribution of the four variables, i.e., speed, temperature, and time as (1%, 82%, 17%) respectively. The selected considerations demonstrate that the temperature of the bath has a significant effect on microhardness deposition parameters.

4. Conclusions
The orthogonal array of Taguchi is used for optimizing the process parameters for deposition of low carbon steel nanocomposite deposition compounds with electroleess (Ni-P-TiO2) microhardness behavior. Bath temperature and time have the biggest effect on electroleess (Ni-P-TiO2) deposition hardness regulation features. A2B1C2, i.e. speed = 1000 r.p.m, temperature = 90°C and time = 70 min, gives the optimum balance of the coating parameter for optimal hardness.

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