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Optimizing microhardness of electroless Ni-P coated copper substrate using PSO

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The present study is conducted to expedite an experimental investigation on optimizing the microhardness of electroless nickel-phosphorous (Ni-P) coating over thin copper substrates. The deposition is executed considering the concentration of nickel sulphate (g/l) and concentration of sodium hypophosphite (g/l) acted as coating variables. The concentration of the complexing agent such as trisodium citrate ($Na_3C_6H_5O_7$) is kept constant in all the coatings and the temperature of the bath is kept at 85°C. After the coating of the specimens, they are subjected to heat treatment at 300°C for one hour. The microhardness testing of the heat-treated specimens is carried out using Vickers microhardness testing machine. The experimentally obtained data is optimized using particle swarm optimization (PSO) to maximize the hardness. The optimized value of hardness obtained is 1241.15 VHN at the concentration of 35.1937 gm nickel sulphate per litre and 24.9304 gm sodium hypophosphite per litre. The improvement in the surface hardness has created much impact to use this coating technique in many industrial applications.

***Keywords*:** Electroless coating, particle swarm optimization, microhardness.

1. Introduction

The term electroless deposition was first introduced by Brenner and Riddell in 1946. It is a type of coating which is suitable for all simple/complex geometries having uniform coating throughout its surfaces without the requirement of the electricity. The increased use of this coating is because of its unique physicochemical and improved material properties. Excellent corrosion resistance, wear resistance, improved hardness and low coefficient of friction properties of this coating enhance wide range use of this technique to develop components in automotive, aerospace, chemical industries, electrical and electronics, marine industries. The metals like Ni, Cu, Co, Ag are being coated on the activated substrate, which enhances the hardness and strength without sacrificing ductility and toughness [1]. The coating takes place in an electroless bath which consists of an aqueous solution of metallic ions, a complexing agent(s), a reducing agent(s), and bath stabilizer(s) operating in a specific metal ion concentration, temperature, and pH ranges [2]. Temperature excites the reaction mechanism that starts the ionization process in the solution resulting charge transfer process from the source to the substrate [3]. The electroless deposition is different from electrolytic plating technique as the deposition of the metal doesn't require electrode and surface nucleation has begun over the surface due to its autocatalytic nature of the reaction while the later plating technique which is a displacement reaction process requires electricity [1, 2]. When the current is supplied, it displaces the metal ions of the substrate by a more noble metal in the solution. Also, the coating doesn't seem uniform throughout its surfaces. The advantages of electroless coating include its quality of deposits, improvement in mechanical properties. The only disadvantage of this coating is the life of its electroless bath. The bath needs to change after a certain period as the metal ions get consumed during the deposition and as its concentration decreases which slow down the deposition and makes poor adhesion over the substrates [3]. Oraon et al. [4] used the optimized deposition conditions and different annealing temperature for coating of

Ni-B over copper substrates to obtain the variation of hardness with a change in temperature ranging 100°C to 500°C. From the result obtained using response surface method and regression analysis, they concluded that there was a significant improvement in hardness with the increasing temperature up to 300°C and then starts decreasing. Krishnaveni et al. [5] studied the hardness and wear resistance of the Ni-B coating, both in as-plated and heat-treated conditions. They used Leitz microhardness tester and a pin on disc wear test apparatus to determine the hardness and wear rate. They observed that the heat-treated substrate offers better wear resistance than the as-plated substrates. From the XRD patterns, they observed that the amorphous structure of the as-plated specimen, when subjected to heat treatment, changed its structure to undergo crystalline nickel and nickel borides. Grosjean et al. [6] used nickel and ceramic particles for electroless coating on the brass substrate. After the coating done, they used a Vickers hardness test to determine the optimized hardness value and the optimized coating conditions. Also, they conducted a friction test using a ball on disk tribometer. They obtained a huge improvement in anti-corrosion and tribological performances due to the presence of ceramic particles. Cai and Sun [7] incorporated MoS_2 nanoparticles into nickel phosphorus coating over medium carbon steel and obtained that MoS_2 particles covered by Ni-P matrix when observed under X-ray photoelectron spectroscopy. They also conducted corrosion testing using weight loss method containing an aqueous solution of NaCl, NaOH and, HCl with the bare substrate, Ni-P substrate and Ni-P-MoS_2 composites and obtained that the Ni-P-MoS_2 coating substrate showed better corrosion resistance than the other two substrates. Modelling of electroless co-deposition was performed by Veeraraghavan et al. [8]. They designed their experiments in two factor two level factorial to determine the effects of variables individually. They also developed second order polynomial using five factors as variables (metallic ions, reducing agent, pH, temperature and complexing agents) and deposition rate. With the generated polynomial, they optimized the deposition rate with the minimized variables. Chang and Wang [9] worked on the corrosion behaviour of nickel coated steel boosted by titanium ion embedding. They imparted Ti ions using an ion implantation apparatus operated at 100 KeV. They observed the increase in hardness up to 10-15 percent and the ion implemented electroless nickel coating develop the best corrosion resistance at maximum polarization resistance (3×10^5 Ω/cm^2) and at minimum capacitance (1×10^5 F/cm^2).

2. Fundamental aspects

2.1. Electroless components and their functions

The electroless bath consists of the solution of metal ions, reducing agents, bath stabilizers, of which further pH and temperature are controlled. The reducing agents provide electrons to minimize the metal ions. Generally, four types of reducing agents used including sodium hypophosphite, hydrazine, amine boranes, and borohydride. Sodium hypophosphite is commonly used as a reducing agent because of ease of its control and lower cost. Amino borane seems effective over a wide range of pH but only dimethyl and diethylamino boranes are commercially used. Sodium borohydride acts as a powerful reducing agent in both acidic and alkaline bath. Hydrazine has the tendency of depositing pure nickel over the substrate, but because of its instability at higher temperature tends the bath to be unstable. A complexing agent like sodium citrate maintains the stability of the electroless bath. With the continuing of deposition, the concentration of metal ion decreases and there is a chance of formation of nickel phosphite which decomposes the electroless bath [1,10].

2.2. Effect of plating parameters

The reaction occurs in the bath is endothermic so with the increase in temperature, the deposition rate rises exponentially and the optimum range for an acidic solution is found between 80-90°C. Although, the alkaline bath can be functioned at a lower temperature as compared to the acidic bath. pH accelerates the chemical reaction and increases the deposition rate. Zhao and Liu [11] concluded that adhesion increases up to four times when the pH range of the solution lies in between 4.5-5.2. High pH retards the reduction of hypophosphite and slows the chemical reaction. Also, the concentration of metallic ion and reducing agent ion should be in a proper ratio. When the ratio of metallic and hypophosphite ion is low, decomposition reaction occurs due to lack of metallic ions and high ratio decreases the phosphorus content and makes the coating dull.

2.3. Microhardness measurement

The microhardness of a specimen is generally measured using a Vickers microhardness testing machine. A diamond indenter of tip angle 136° indents the surface of the specimen by applying a certain amount of load. The microhardness is measured by applying 10gram load on the coating with the loading time of 15 sec. Generally, 10-20 % of the deposited thickness is indented to keep away the effect of the substrate.

3. Particle Swarm Optimization

PSO is an intelligent artificial optimization algorithm. Kennedy and Eberhert developed this technique to optimize the social behaviour of a flock of birds and shoal. A family of particles is generated and started with random solutions. The particles move in search space according to the given mathematical function over the particle's position and velocity. The position and velocity get updated after every iteration. Every particle has its own local best position known as personal best or "pbest" and is influenced to move towards the whole population's best position known as global best or "gbest"[12]. The particles follow the same procedure to obtain the optimized function value. The flowchart of the procedure is described as:

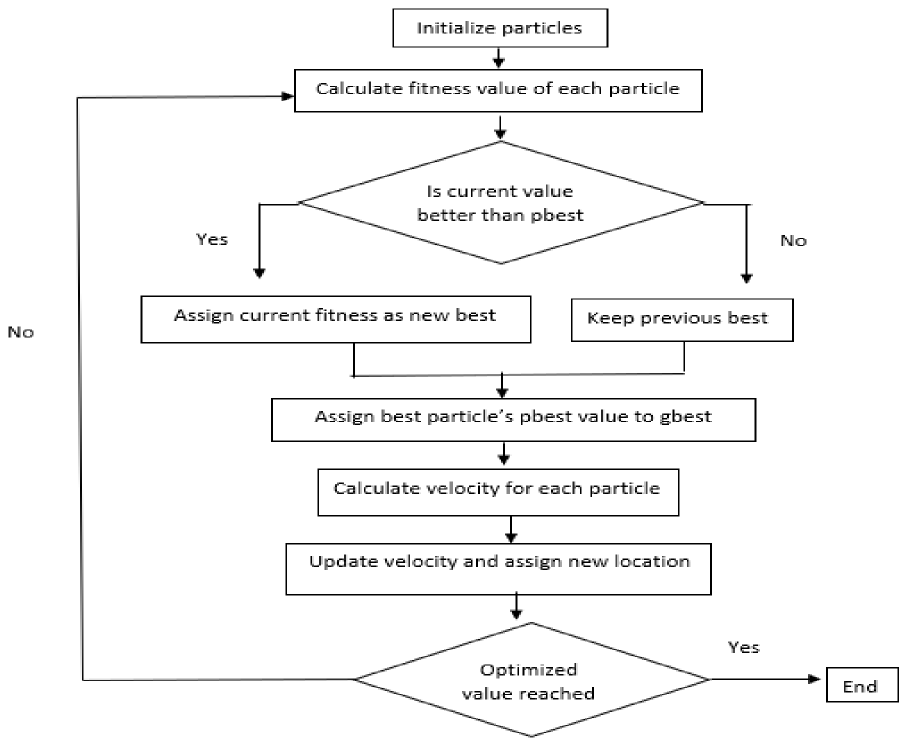

Fig. 1. The flowchart of Particle Swarm Optimization.

4. Experimental procedure

In this experiment copper specimens of 20*20 mm^2 with thickness 1 mm are taken for electroless coating. The specimens are subjected to precleaning, to remove any layer of surface oxides present over them. For cleaning, the specimens are first subjected to distilled water for 5 minutes followed by cleaning in 35% dilute hydrochloric acid in room temperature for 10 minutes. The specimens are again dipped in distilled water for 2 minutes. Some materials like copper require activation for the initiation of electroless deposition. Palladium chloride solution at 55°C is used as an activator where the substrates are dipped for 10 seconds. The substrates are again dipped in distilled water for some time. The substrates are now ready for coating which are poured in the electroless bath for 1 hour. The electroless bath which consists of nickel sulphate, sodium hypophosphite, tri-sodium citrate maintained at temperature 85°C. The lactic acid is added into the electroless bath to keep the pH in the range 4.5-5 as it helps in accelerating the deposition rate. A bright thin layer of Ni-P coating is observed over the activated substrates after 1 hour. The configuration of the electroless bath is shown in Table 1.

Table. 1. Electroless bath composition

Bath Composition	**Reagents**	**Concentrations(g/l)**
Nickel sulphate	$NiSO_4$	30,35,40
Sodium hypophosphite	NaH_2PO_2	15,20,25
Tri-sodium citrate	$Na_3C_6H_5O_7$	15
Lactic acid	$C_3H_6O_3$	10

The coating conditions are:
pH maintained: 4.5-5.
Bath Temperature: 85°C
Coating time: 60 minutes
Bath Volume: 250mL
The following reactions take place during the Ni-P coating over the Cu specimens:

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H^+ + 2e^- \quad (1)$$
$$Ni^{2+} + 2e^- \rightarrow Ni \quad (2)$$
$$2H^+ + 2e^- \rightarrow H_2 \quad (3)$$
$$H_2PO_2^- + 2H^+ + e^- \rightarrow P + 2H_2O \quad (4)$$

The catalytic action of hypophosphite which yields H^+ ions and electrons around the activated substrate which reduces nickel and hydrogen ions. Nickel gets deposited over the substrate and hydrogen gas comes out of the electroless bath in the form of bubbles.

5. Results and Discussion

To achieve the maximum hardness using PSO, an objective function is created from the experimental data using fit regression model from MINITAB software. A different combination of process parameters such as the concentration of $NiSO_4$"x(1)" and concentration of NaH_2PO_2,"x(2)" is considered. The obtained equation of regression for hardness is given as:

$$\text{Hardness (VHN)}=73.0*x(1)-44.82*x(2)-1.284*x(1)^2+0.66*x(2)^2+1.105*x(1)*x(2)$$

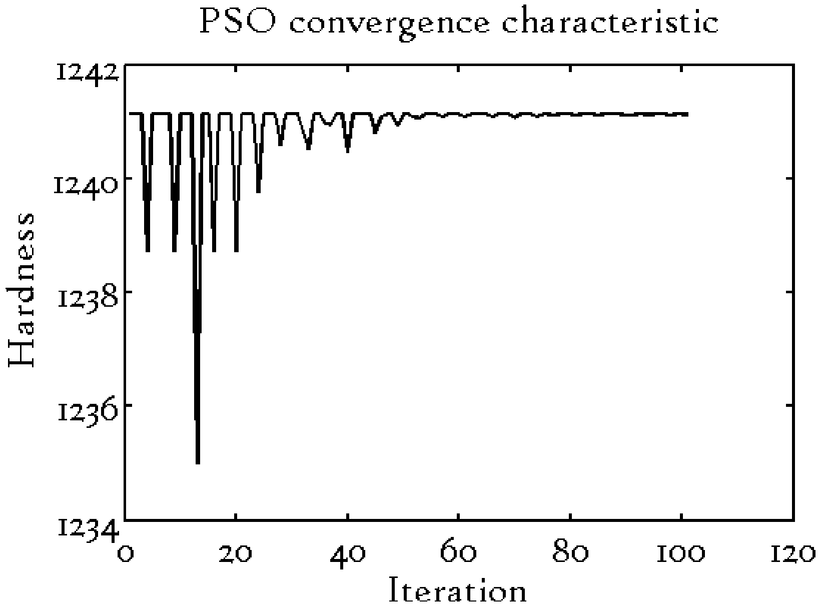

Fig.2. PSO convergence plot of best run.

The plotted graph between hardness and iteration converges after 60 iterations and the maximum value of hardness obtained is 1241.15VHN at the concentration of nickel sulphate is 35.1937(g/l) and concentration of sodium hypophosphite is 24.9304(g/l).

6. Conclusion

This paper presents the electroless Ni-P coating on the Cu specimen and an efficient approach of optimizing the microhardness of electroless coated Ni-P by varying the concentration of metallic ions and reducing agent in a suitable range. The main advantages of PSO are its computational efficiency without considering any assumptions. A fit regression polynomial equation is generated from the experimental data and is maximized using the PSO program in MATLAB. Maximum hardness obtained is 1241.15VHN at 35.1937(g/l) concentration of nickel sulphate and 24.9304(g/l) concentration of sodium hypophosphite.

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