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Electroless nickel deposition from methane sulfonate bath

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ABSTRACT

Electroless plating is a controlled autocatalytic chemical reduction process for depositing metals. The process involves a continuous build up of a nickel coating on a substrate by immersion of the substrate in a suitable nickel plating under appropriate conditions. In this paper the authors have studied the effect of pH and temperature on the rate of deposition and phosphorous content from nickel methane sulfonate bath. Effect of phosphorous content on hardness, wear resistance and corrosion resistance were also studied. SEM and XRD measurements show nodular and amorphous character of the deposits. As the bath is free from sulfate ions the bath can be operated for more number of turn overs and orthophosphite formed during the process can be removed easily.

1. Introduction

Electroless plating of metals and process technology have important role along with other methods of plating. Today, sophisticated electroless plating systems are in use for many electronic applications. The term electroless plating is defined as autocatalytic deposition of metals/alloys from an aqueous solution of its ions by interaction with a chemical reducing agent. The reducing agent provides electrons for the metal ions to be neutralized. The reduction is initiated by the catalysed surface of the substrate and continues by the self-catalytic activity of the deposited metal/alloy as long as the substrate is immersed in the electroless bath and the operating conditions are maintained. The history of electroless plating began in 1946 when Brenner and Riddel [1] discovered that sodium hypophosphite added as an anti-oxidant to the nickel electroplating bath produced a nickel coating even without passing current. Further investigations revealed that the coating contained phosphorous also. Their discoveries lead to the first commercially usable electroless nickel bath in 1950. Later years witnessed the evolution of electroless copper [2], cobalt [3] silver [4] gold [5] and spectrum of electroless baths capable of producing deposits of improved quality. In 1970 there was an upsurge in electroless deposition of poly-alloys based on nickel–phosphorous, cobalt–phosphorous and nickel–boron. In 1980s a large number of composite coatings with varying engineering properties are being introduced [6]. Electroless plating baths generally comprise nickel salt, complexing agent and a reducing agent. When we use hypophosphite as reducing agent during the process it is oxidized to orthophosphate ions and the nickel cations are reduced to form Ni–P alloy on the substrate surface. As the reaction proceeds the level of orthophosphite ions in the bath increases and often precipitated as insoluble metal orthophosphates. Most electroless nickel solutions use sulfate as the source of nickel ions in solutions and so the sulfate anions also increases during the process. At some critical concentration of these two, i.e. sulfate and orthophosphite ions the electroless nickel solution produces deposits that are rough with variable amount of occluded phosphorous. Martyak [7] has studied the replacement of sulfate ions by methane sulfonate ions and evaluated the various properties of the coatings.

Electroless nickel process based on nickel methane sulfonate show many advantages over the conventional nickel sulfate baths [8]. The solubility of Ni^{2+} in methane sulfonic acid is high >100 g/L and although the methane sulfonate anions increases in concentration with age of the bath the addition of calcium to aged solution allows for the selective removal of orthophosphite thus increasing electroless nickel bath life [9]. This study examines the effect of time, pH and temperature on the rate of deposition in nickel methane sulfonate bath. Effect of phosphorous content on hardness, wear resistance and corrosion resistance was also carried out. Structural investigations were carried out using SEM and XRD measurements.

2. Experimental

2.1. Electrode preparation

Mild steel panels of size 10 cm × 10 cm were mechanically polished, degreased, alkaline cleaned, washed, and dipped in 10% HCl for 2 min, washed, rinsed in deionized water and electroless nickel-plated. These specimens were used for structural

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investigations. For analyzing the phosphorous content, stainless steel panels of the same was used. These panels were etched in hydrochloric acid, washed and activated in a solution containing 0.5 g/L of palladium chloride. After the activation treatment the panels were washed well, rinsed and plated with electroless nickel. Copper panels were used for finding out the rate of deposition, cleaned in sulfuric acid, washed and activated in palladium chloride solution before electroless nickel deposition.

2.2. Bath preparation

Nickel methane sulfonate solution $Ni(CH_3SO_3)_2$ was formulated by dissolving 150 g/L of nickel carbonate into approximately 200 mL distilled water. This slurry was adequately mixed with 70% methane sulfonic acid (MSA) until all the carbonate was removed. Then it was made up to 1 L and used as a stock solution. This stock solution contains 75 g/L of nickel.

Following is the bath composition selected for further studies:

1. Nickel as methane sulfonate: 6 g/L.
2. Sodium hypophosphite: 25 g/L.
3. Tri ammonium citrate: 30 g/L.
4. Stabilizer: 1 ppm.

Required amount of chemicals were weighed and dissolved in distilled water. Then filtered the solution through fine filter of 1 μm size and made into 1 L. The pH of the solution was adjusted using ammonium hydroxide solution. After proper conditioning pretreatment, parts to be electroless nickel-plated are simply immersed in a bath after attaining the operating temperature. Mechanical agitation was used. The temperature of the bath was maintained by using temperature controller. The content in the bath was analyzed by EDTA method for every half an hour and replenished.

2.3. Effect of bath variables on the rate of deposition

2.3.1. Effect of temperature on the rate of deposition

Copper panels were etched in 10% sulfuric acid washed with water, dried and weighed. These copper panels were activated and placed in a 250 mL beaker containing electroless bath solution whose pH was 5 and heated for half an hour at 40, 50, 60, 70, 80 °C in a magnetic stirrer.

After half an hour these panels were removed, washed, dried and weighed. From the difference, the weight of nickel deposited was calculated. From the weight of nickel deposited, area of copper panel and density of the deposit, the rate of deposition was calculated.

$$\text{Rate of deposition } (\mu\text{m/h}) = \frac{\text{weight of Ni deposit in g} \times 10^4}{\text{area of copper panel } (\text{cm}^2) \times \text{density}}$$

2.3.2. Effect of pH on the rate of deposition

The pH of electroless bath was changed to 5, 6, 7, 8, 10 using ammonia solution. Activated copper panels were placed in electroless bath at pH values of 5, 6, 7, 8 and 10 at 40, 50, 60, 70, 80 and 90 °C, respectively for half an hour. Then these panels were removed, washed, dried and weighed. From the weight of the deposit, the rate of deposition was calculated.

2.4. Anodic polarization measurements

Anodic polarization measurements were carried out galvanostatically by exposing 1 cm^2 of the plated specimens using constant current regulator. Platinum was used as an auxiliary electrode and saturated calomel electrode as a reference electrode and varied the current from 0 to 100 mA and the corresponding change in the potential was measured against SCE using digital voltmeter. The electrolyte used in the study was 3% NaCl. Graph was drawn between potential and current density.

2.5. Abrasion measurements

Abrasion measurements were carried out using Taber Abraser. The panels were weighed before and after the experiments. 1 kg load was applied in the abrading wheels. Weight loss was found out for 1000 cycles. The experiment was repeated for the second 1000 cycles, the average value was taken. The value gives indication of abrasion resistance of the coating.

$$\text{Abrasion index} = \frac{\text{weight loss in g}}{1000 \text{ cycles}}$$

2.6. X-ray diffraction studies

The X-ray diffraction is widely used to determine the structure and composition of the materials. Diffraction patterns contain information showing various phases of a material and also residual stresses present within the coating material. The X-ray diffraction pattern for the electrolessly deposited nickel specimen obtained from MSA bath was recorded using XRD instrument (make-Panalytical, USA) instruments.

2.7. Scanning electron microscopic studies (SEM)

The morphology of the electroless deposits was examined under high magnification to assess the grain size, deposit nature, heterogeneities and pores present in the deposits using a scanning electron microscope. The scanning electron microscope, which makes use of reflected primary electrons and secondary electrons, enable one to obtain information from regions that cannot be examined by others. The electroless nickel-plated specimens were cut into 1 cm × 1 cm size and mounted suitably and examined under the microscope. The SEM photographs were taken with the magnification range of 1000.

3. Results and discussion

3.1. Effect of temperature on the rate of deposition and phosphorous content in the deposit

Table 1 shows the effect of temperature on the rate of deposition and phosphorous content. It is seen from the table, as the temperature increases rate of deposition also increases. Temperature is the most important parameter affecting the rate of deposition. Most of the oxidation and reduction reaction involved in the overall process required energy in the form of heat and this is true for all baths and at all pH values. While the higher temperature more than 90 °C makes the deposition rate very attractive there is a danger due to possible decomposition of the bath at these temperatures. Hence further experiments were carried out at a temperature of 90 °C.

Apart from the deposition rate, temperature also affects the phosphorous content of the deposit and hence its properties. It is noticed from the table there is a slight increase in phosphorous content as the temperature increases. Hence for these reasons accurate temperature control of the electroless nickel bath is essential to get constant phosphorous in the deposit. In the present study constant temperature controller has been used which maintains the bath temperature with a variation of ±2 °C. Mechanical agitation with a rotation set-up was used to maintain the bath constituents and temperature uniformly through the rotation.

3.2. Effect of pH on the rate of deposition and phosphorous content

Table 2 shows the effect of pH on the rate of deposition and phosphorous content at a bath temperature of 90 °C. It is seen from the table as the bath pH increases the rate of deposition increases and phosphorus content decreases in the deposit. The following is

Table 1
Effect of bath temperature on the rate of deposition and phosphorous content at a pH of 5.

S. No.	Temperature (°C)	Rate of deposition (μm/h)	Phosphorous content
1	40	3.5	6.8
2	50	5.3	7.2
3	60	6.6	7.0
4	70	8.2	7.5
5	80	10.9	8.2
6	90	11.5	8.5
7	100	18.2	9.0

Table 2
Effect of pH on rate of deposition and phosphorous content at a bath temperature of 90 °C.

S. No.	pH	Rate of deposition (μm/h)	% of phosphorous content
1	4	10	10
2	5	11.5	9
3	6	12.5	8.5
4	7	15	6.5
5	8	18.62	6.4
6	10	22.53	5

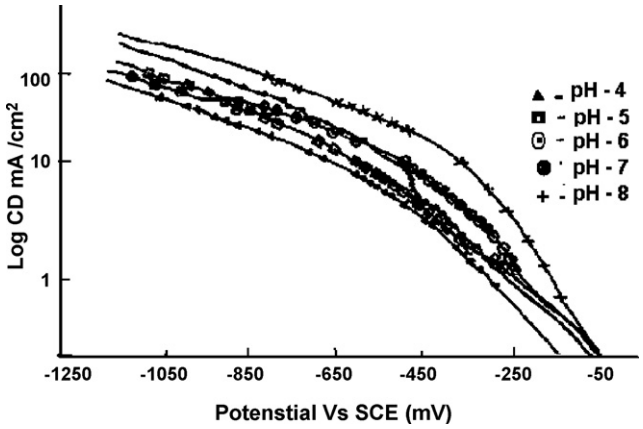

Fig. 1. Anodic polarization behavior of electroless nickel deposited at various bath pHs.

the overall reaction in the hypophosphite reduction of nickel ions:

$$Ni(CH_3SO_3)_2 + 3NaH_2PO_2 + 3H_2O \rightarrow Ni^0(P) + 3NaH_2PO_3 + H_2 + 2NaH_3SO_3 \quad (1)$$

Also producing H_2PO_3 and methanesulfonate $CH_3SO_3^-$.

The same reaction has been written as

$$2H_2PO_2^- + Ni^{2+} + 2H_2O \rightarrow 2H_2PO_3^- + H_2 + 2H^+ + Ni^0 \quad (2)$$

or

$$Ni^{2+} + H_2PO_2 + H_2O \rightarrow Ni^0 + H_2PO_3^- + 2H \quad (3)$$

It is seen from the equations that the H^+ ion concentration increased as nickel ions are reduced to form the metal. The practical implications of this are that pH will drop as the process proceeds.

Because of the OH^- ions must be supplied by controls dosing with NH_4OH to maintain the pH of the bath. pH of the solution has great effect on the rate of deposition and phosphorous content. There are three competing reactions in the electroless processes hydrogen evolution, nickel reduction, and phosphorous reduction as per the following partial reactions

$$H_2PO_2^- + H_2O \xrightarrow[\text{energy}]{\text{catalytic}} H_2PO_3^- + 2H^+ + 2e \quad (4)$$

$$Ni^{2+} + 2e \rightarrow Ni^0 \quad (5)$$

$$2H^+ + 2e \rightarrow H_2 \quad (6)$$

$$H_2PO_2^- + e \rightarrow 2OH^- + P \quad (7)$$

With increase in acidity of the bath probability of interaction of protons with electrons is increased leading to the reduction of coefficient of utilization of hypophosphite. So the rate of reduction of nickel decreases (5) and there will be more hydrogen evolution (6). Further hydrogen ion present in the electrolyte favors reaction (7) leading to the formation of more phosphorus content in the deposit.

Table 3
Effect of pH, hardness and phosphorous content at a temperature of 90 °C.

S. No.	pH	Hardness Hv load 100 g
1	4	581
2	5	500
3	6	449
4	7	449
5	8	431
6	10	400

Table 4
Wear resistance of electroless nickel coatings deposited at various pH values.

S. No.	pH	Weight loss in grams for first 1000 cycles	Weight loss in grams for second 1000 cycles
1	4	0.007	0.012
2	5	0.015	0.024
3	6	0.024	0.026
4	7	0.033	0.045
5	8	0.04	0.72

3.3. Anodic polarization studies

Fig. 1 shows the anodic polarization behavior of Ni–P deposits obtained at various pH ranges. It is seen from the figure that there is an increase in anodic polarization as the pH of the bath decreases or P content increases in the deposit. Thus there is an increase in corrosion resistance behavior of the deposit with increase in P in the deposit.

3.4. Effect of phosphorous on hardness and wear resistance of the deposit

Tables 3 and 4 show the hardness and wear resistance values of the deposits. It is clear from the tables that both wear resistance and hardness of the deposits increases with increase in phospho-

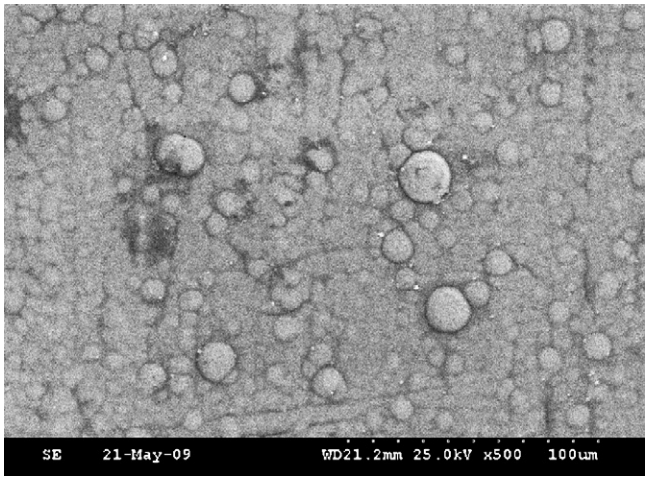

Fig. 2. SEM photomicrograph of electroless nickel deposit (1000×).

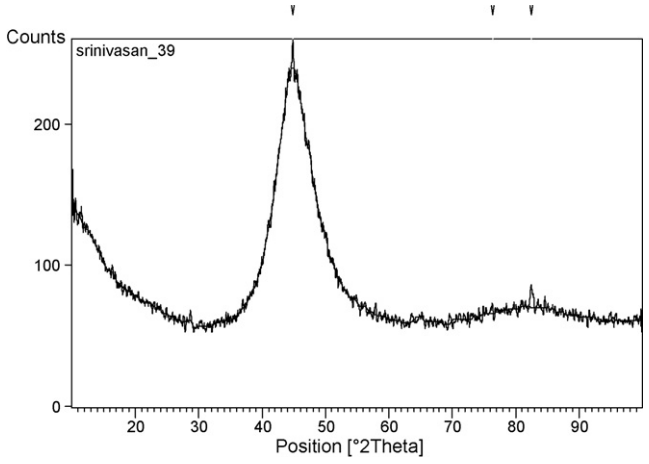

Fig. 3. XRD pattern of electroless nickel deposit obtained at a pH of 5.

rous content in the deposit which is in agreement with polarization behavior.

3.5. SEM and XRD studies

Figs. 2 and 3 show the SEM and XRD pattern of the deposits obtained from MSA bath at a pH of 5 and at a temperature of 90 °C. It is seen from the XRD pattern there is broadening of XRD lines which indicates amorphous nature of the deposits. SEM micrograph shows that the deposits are nodular in nature.

4. Conclusions

A new electroless bath has been formulated based on nickel methanesulfonate as the source of metal ions. The absence of sulfate ions increases the bath life of the electroless nickel solution. Only little nickel sulfonate is required for replenishments due to higher solubility of nickel sulfonate. Electroless nickel process based on nickel methane sulfonate show many advantages over the conventional nickel sulfate baths. The solubility of Ni^{2+} in methane sulfonic acid is high. Although the methane sulfonate anions increases in concentration with age of the bath, the addition of calcium to the aged solution allows for the selective removal of orthophosphite thus increasing electroless nickel bath life. Further replenishments of the solutions require only little nickel sulfonate due to higher solubility of nickel sulfonate. The small replenishment volume maintains a constant operating temperature, which in turn produces uniform and high quality coatings. Following is the optimum concentration of bath and operating conditions to get quality nickel deposits:

Nickel methanesulfonate:	6 g/L (as Ni).
Ammonium citrate:	30 g/L.
Sodium hypophosphite:	25 g/L.
Stabilizer:	1 ppm.
pH (ammonia):	5.
Phosphorous content:	9%.
Temperature:	90 °C.

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