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Thickness of Electroless Nickel Plating

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Abstract

Aqueous acid nickel chloride and alkaline nickel sulfate bath were studied for electroless nickel plating on acrylonitrile-butadiene-styrene (ABS) plastic. Before electroless nickel plating, specimens were etched, sensitized and activated. Effects of sodium hypophosphite and sodium citrate concentrations on the thickness of electroless nickel plating were discussed. Aqueous acid nickel chloride bath comprising, nickel chloride 10 g L^{-1}, sodium hypophosphite 40 g L^{-1}, sodium citrate 40 g L^{-1} at pH 5.5, temperature 85^{o}C with density of 1 Be$^{/}$ in thirty minutes yielded thickest coating. Under comparable conditions, acid nickel chloride bath gave thicker deposits than alkaline nickel sulfate bath.

Keywords: ABS, electroless nickel plating, thickness

Introduction

Electroless plating can be used for special applications for which conventional electrodeposition processes are unsuitable. Interest in electroless nickel plating has numerous applications in varied industries. Since electroless deposits are more expensive to produce than electrodeposits, their use must be predicated on some special advantage [1].

The applications of the polymer composite conductive microspheres, prepared by electroless nickel coating, in thermal sensitive element were introduced [2]. The effect of stabilizer on stability of deposition bath was also studied. The deposit obtained was smooth, bright, and has low porosity and higher hardness [3].

The development of electroless nickel-phosphorous composite coatings was reviewed [4]. It highlights the method of formation, mechanism of particle incorporation, factors influencing particle incorporation, effect of particle incorporation on the structure, hardness, friction, wear and abrasion resistance, corrosion resistance, high temperature oxidation resistance of electroless nickel-phosphorous composite coatings as well as their applications. The improvement in surface properties offered by such composite coatings will have a significant impact on numerous industrial applications and in the future they will secure a more prominent place in the surface engineering of metals and alloys [4].

The electroless deposition of nickel-tungsten-phosphorous alloy coatings onto metal substrates using $H_2PO_2^-$ as reducing agent from solutions containing nickel sulfate, sodium tungstate, sodium citrate, ammonium sulfate and other additives was studied. At most temperatures (60-80°C) and pH (7-11) investigated, bright and coherent coatings uniform in appearance were produced. Phosphorous and tungsten contents ranging from 3.5 to 8 wt % and 0.5 to 6 wt %, respectively, were obtained depending upon solution temperature and pH [5].

The mechanism of electroless nickel plating on ceramic in a bath containing nickel chloride 7.5, sodium hypophosphite 7.5, ammonium chloride 8.75, and sodium citrate 6.25 g L^{-1} at 80 ± 2°C and pH = 5.4 was discussed. The existence of phosphate ions in bath after several depositions was, presumably, due to the oxidation of phosphite ions by divalent nickel ions [6].

Electroless nickel plating is carried out using aqueous solution of nickel salts, hypophosphite of alkali or alkali-earth metals and some organic additions. Different compositions of these solutions have been recommended, but the problem of optimum ratio of these components in the solution still requires continuing study [7].

In this work, electroless nickel plating process on ABS plastic is studied. Two baths of electroless nickel plating are used: (1) acid nickel chloride bath and (2) alkaline nickel sulfate bath. Concentration of reducing agent, sodium hypophosphite, a salt of an organic acid namely sodium citrate, nickel chloride and nickel sulfate were varied, and the effect on the thickness of electroless nickel plating on ABS plastics are examined. The work is designed to find out optimum ratio of these components for obtaining optimal thickness. Tests were carried out to measure the thickness of electroless nickel coatings.

Experimental

Chemicals	Source
Nickel sulfate, $NiSO_4.6H_2O$,	Inco Canada
Nickel chloride, $NiCl_2.6H_2O$,	Inco, Canada
Chromium trioxide, CrO_3,	OXYCHEM, USA
Sulfuric acid, H_2SO_4,	BDH, England
Stannous chloride, $SnCl_2$,	BDH, England
Palladium chloride, $PdCl_2$,	Johnson & Matthey England

Other chemicals, sodium hypophosphite monohydrate, sodium citrate dihydrate, sodium hydroxide, sodium carbonate, ammonium hydroxide, hydrochloric acid, were of laboratory grade and were used as received.

ABS plastic specimens: ABS plastic sheet having smooth surface was cut into small strips of various shapes. These strips were used as a base material for electroless nickel plating process. Before electroless nickel plating ABS surface was rinsed with 10% common detergent solution in order to remove greasy materials.

Etching: Then thoroughly washed with distilled water and etched in chromic plus sulfuric acid solution; chromium trioxide 300 g L^{-1}, sulfuric acid 200 ml L^{-1}, density 24 Be$^{/}$, at temperature 65-70°C and immersion time ten minutes. Specimens were immersed in acid solution for one minute at temperature 30°C to remove any traces of chromic acid etch solution left on the surface

Sensitization: Aqueous acidic colloidal stannous chloride solution was used to sensitize the previously etched ABS specimens. Sensitization was carried out from solution, stannous chloride 3 g L^{-1}, hydrochloric acid (10%) 20 ml L^{-1}, at temperature 40°C for immersion time five minutes.

Activation: For activation the specimen were immersed in palladium chloride solution, palladium chloride 0.3 g L^{-1}, hydrochloric acid (10%) 20 ml L^{-1}, at temperature 40°C for five minutes. The pH of the solution was 2.9.

Accelerating: Acceleration of palladium activated ABS specimens was done in an aqueous sulfuric acid (20%, volume/volume) solution at temperature 40°C, for three to five minutes.

Electroless nickel plating: Electroless nickel was plated on previously activated ABS specimens from aqueous solutions of nickel chloride/nickel sulfate, sodium hypophosphite and sodium citrate.

Electroless nickel chloride bath: Nickel chloride bath for electroless nickel plating was prepared from nickel chloride, sodium citrate and sodium hypophosphite. The concentration of each substituent was varied from 5 to 40 g L^{-1} and their effect was studied. In all the experiments the solutions were prepared in distilled water. The plating conditions were, temperature 85°C, pH 5.5, density 1 Be$^{/}$ and deposition time thirty minutes. The pH of the bath was maintained by the addition of ammonium hydroxide. The plating conditions were kept constant in all the experiments.

Electroless nickel sulfate bath: Nickel sulfate bath for electroless nickel plating was prepared from nickel sulfate, sodium citrate and sodium hypophosphite. The concentration of each substituent was varied from 5 to 40 g L^{-1} and their effect was studied. In all the experiments the solutions were prepared in distilled water. The plating conditions were, temperature 40-45°C, pH 9, density 5 Be/ and deposition time thirty minutes. The pH of the bath was maintained by the addition of ammonium hydroxide and sodium carbonate. The plating conditions were kept constant in all the experiments.

Drying: After electroless nickel coating, ABS specimens were immersed in warm water for one minute to wipe out completely traces of chemicals left on the finished surface. Double water rinsing was done before drying the finished ABS plastics.

The saw test: The metallic nickel layer was not peeled off during sawing across the electroless nickel plated ABS component. The nickel coatings obtained were stable.

Appearance test: Electroless nickel deposit was grey in color with smooth surface. Bright deposits were obtained at higher nickel concentration. The nickel coatings showed satin finish.

Thickness measurement: The thickness of electroless nickel coating was measured by difference in thickness of nickel coated and uncoated ABS component automatically in five seconds and recorded by (Echometer, an ultrasonic thickness gauge) a hand-held instrument. A few drops of fluid (for example, grease, water or glycerine) were applied to the location on the work-piece where the measurement was to be made. The probe was attached and thickness was recorded [8].

Results and Discussion

Two types of electroless nickel plating baths were studied: (1) acid nickel chloride bath, (2) alkaline nickel sulfate bath, for electroless nickel plating on ABS plastic specimens.

Effect of sodium citrate and sodium hypophosphite on thickness of electroless nickel coating from acid chloride bath was investigated. Results obtained are shown in Fig. 1. The concentration of sodium chloride was maintained at 10 g/L in this set of experiments. The electroless nickel coating was carried at temperature 85°C, pH 5.5, and solution density 1 Be/. The plating conditions were kept constant in all sets of experiments. Dotted line in Fig. 1 showed that maximum thickness was obtained at sodium citrate/sodium hypophosphite ratio 1:1. Also by increasing the concentration of both sodium citrate and sodium hypophosphite, keeping the ratio 1:1 constant, the thickness of electroless nickel coating was also increased, Fig. 1.

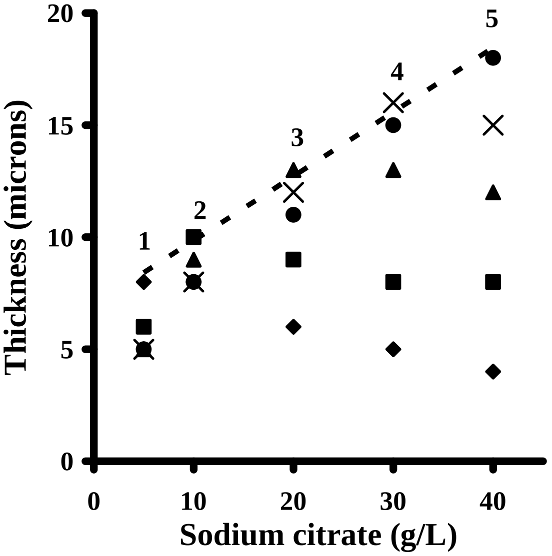

Figure 1. Effect of concentration of sodium citrate and sodium hypophosphite on thickness of electroless nickel plating from nickel chloride bath. Nickel chloride 10 g L^{-1}. 1-sodium hypophosphite 5 g L^{-1}, 2-sodium hypophosphite 10 g L^{-1}, 3- sodium hypophosphite 20 g L^{-1}, 4- sodium hypophosphite 30 g L^{-1}.

The effect of nickel chloride concentration on coating thickness is shown in Fig. 2. It was seen that, Fig. 2, nickel chloride 10 g L^{-1}, gave the maximum thickness in all cases of sodium citrate/sodium hypophosphite , 5/5, 10/10, 20/20, 30/30, 40/40 g L^{-1}.

Electroless nickel coating was also carried out from alkaline nickel sulfate bath. The effect of nickel sulfate's concentration on thickness of electroless nickel coating is shown in Fig. 3. The effect was studied at different concentrations of sodium citrate and sodium hypophosphite but there ratio was kept 1:1. The electroless nickel plating was carried out at temperature 40-45°C, pH 9, density 5 Be/ and deposition time thirty minutes. The plating conditions were kept constant in all the experiments.

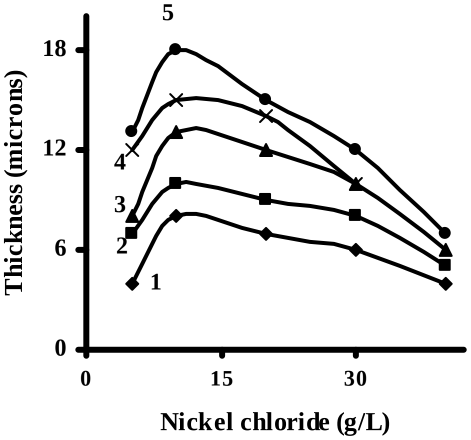

Figure 2. Effect of concentration of nickel chloride on thickness of electroless nickel plating from nickel chloride bath. 1-sodium citrate/sodium hypophosphite 5/5 g L^{-1}, 2-sodium citrate/sodium hypophosphite 10/10 g L^{-1}, 3-sodium citrate/sodium hypophosphite 20/20 g L^{-1}, 4-sodium citrate/sodium hypophosphite 30/30 g L^{-1}, 5-sodium citrate/sodium hypophosphite 40/40 g L^{-1}.

At nickel sulfate 30 g L^{-1}, maximum thickness was obtained in all cases; at sodium citrate/sodium hypophosphite 5/5, 10/10, 20/20, 30/30, 40/40 g L^{-1}. Alkaline nickel sulfate bath containing nickel sulfate 30 g L^{-1}, sodium hypophosphite 40 g L^{-1}, sodium citrate 40 g L^{-1} at pH 9, temperature 50°C and density of 5 Be/ gave good thickness, 10 microns, Fig. 3. At pH < 7, electroless nickel sulfate bath was not operated properly because hydrogen ions are a by-product, and the pH of the electroless nickel bath decreases during operation. The pH of the bath was maintained by the addition of ammonium hydroxide and sodium carbonate. Acid nickel chloride bath had a greater stability, wide operating range and better thickness results than alkaline nickel sulfate bath. The acid nickel chloride bath gave better thickness than alkaline nickel sulfate electroless nickel bath.

The interaction between the hypophosphite ion and water leads to the formation of a hydride ion, H^-, which then acts to reduce the nickel ions in solution. The hydride ion does not remain as a proton, but it is reduced to its atomic state. The atomic hydrogen forms molecules which are subsequently liberated as hydrogen gas. The reactions may be represented by the following equations.

$H_2PO_2^- + H_2O \longrightarrow HPO_3^{2-} + 2H^+ + H^-$
(in acid solutions) (1)
$H_2PO_2^- + 2\,OH^- \longrightarrow HPO_3^{2-} + H_2O + H^-$
(in alkaline solutions) (2)

$Ni^{2+} + 2\,H^- \longrightarrow Ni^0 + 2\,H$

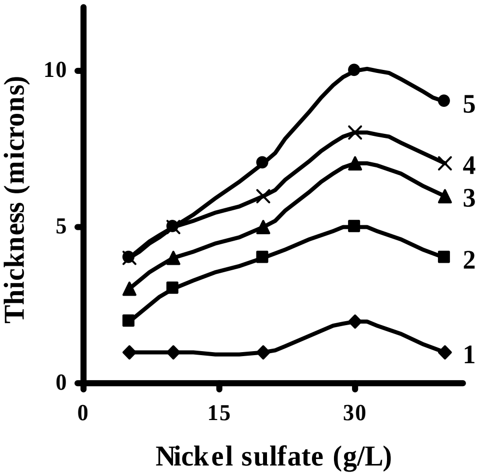

Figure 3. Effect of concentration of nickel sulfate on thickness of electroless nickel plating from nickel sulfate bath. 1- Sodium citrate/sodium hypophosphite 5/5 g L^{-1}, 2-sodium citrate/sodium hypophosphite 10/10 g L^{-1}, 3-sodium citrate/sodium hypophosphite 20/20 g L^{-1}, 4-sodium citrate/sodium hypophosphite 30/30 g L^{-1}, 5-sodium citrate/sodium hypophosphite 40/40 g L^{-1}.

Sodium hypophosphite reduces the nickel ions in solution to their elemental form. During this reduction process, the hypophosphite anion decomposes to orthophosphite with the production of gaseous hydrogen. The general mechanism of solution operation may be written as follows [9].

$$Ni^{+2} + \text{Sodium hypophosphite} + \text{Complex or} \xrightarrow{\text{Catalytic surface}} (Ni + P)\ \text{deposit} + H_2 + \text{Sodium orthophosphate}$$

The bath comprising, nickel chloride 10 g L^{-1}, sodium hypophosphite 40 g L^{-1}, sodium citrate 40 g L^{-1} at pH 5.5, temperature 85°C and density of 1 Be/ for thirty minutes gave best thickness of electroless nickel coating in micrometer, 18 microns, Fig. 2. Acid nickel chloride bath gave better thickness (16 µm/thirty minutes) than alkaline nickel sulfate bath (10 µm/thirty minutes). The stability of the solution is very important for the solution to operate properly.

Stability of bath: Selection of parameters for electroless nickel plating

(a) Acid nickel chloride bath: Electroless acid nickel chloride bath was operated at pH 5.5, temperature 85°C with density of 1 Be/. Early experiments showed that slight changes in pH and temperature beyond these values adversely affected the performance of the bath. For example, no deposition was observed below temperature 60 °C, between 60-80 °C, only islands of nickel coatings were deposited on ABS substrate. Color of the solution was light green when properly operated. Below 60°C, and pH < 5.0, precipitates were found. The problem was solved by raising temperature of the bath and adjusting pH of the solution with sodium carbonate, sodium hydroxide/sulphuric acid (20%).

(b) Basic nickel sulfate bath: Under basic conditions, the clarity and color of the solution served as criteria for ensuring its stability. A clear and dark green solution was consistent only with density 5 Be/, pH close to 9, and temperature controlled within the narrow range of 45-50 °C. In other words, the bath failed to furnish nickel coating below 45 °C. When pH was higher than 9, precipitation resulted in the bath, presumably from particulate nickel or its hydroxide. At the same time, the solution turned light green from a darker shade of the same color necessary for satisfactory deposition of nickel. Repeated use of the same bath causes it to become unsuitable for electroless nickel deposition.

The stability of the solution was maintained by removing the residual metallic nickel in the solution. The metallic nickel residues are removed by filtering the solution, twice. The pH was adjusted mostly by sodium carbonate. At lower concentration of nickel ion, the reduction rate of the solution is impaired. When the concentration of reducing agent, sodium hypophosphite decreases from the optimum concentration the blistered deposits may result, as bath does not initiate deposition immediately. When the concentration of the sodium hypophosphite increases from optimum concentration, the deposition rate of the solution drops until a concentration at which the bath spontaneously decomposes is attained. Similarly, the higher concentration of any one complexors greater the loss in plating speed [9].

Conclusion

Effect of nickel chloride, sodium hypophosphite and sodium citrate concentrations for aqueous acid nickel chloride bath and effect of nickel sulfate concentrations in alkaline nickel sulfate bath was studied for electroless nickel plating process on ABS plastic. It was found that acid nickel chloride bath had a greater stability, wide operating range and better thickness results than alkaline nickel sulfate bath. Best nickel chloride concentration was found 10 g $L^{-1}$and that of nickel sulfate 30 g L^{-1}. Concentrations of sodium hypophosphite 40 g L^{-1} and sodium citrate 40 g L^{-1} gave best thickness results for each bath. The electroless nickel coatings were bright, have satin finish and good adhesion.

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