Electroless plating of Cu–Ni–P alloy on PET fabrics and effect of plating parameters on the properties of conductive fabrics

Xueping Gan, Yating Wu, Lei Liu, Bin Shen, Wenbin Hu

State Key Laboratory of Metal Matrix Composites, Shanghai Jiaotong University, Shanghai 200030, China

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Abstract

Electroless plating of Cu–Ni–P alloy on polyethylene terephthalate (PET) fabrics and effect of plating parameters on the properties of alloy-coated fabrics were investigated. The deposition rate increased with the increase of temperature, pH and nickel ion concentration. The addition of K₄Fe(CN)₆ to the solution could reduce the deposition rate and make the deposits become more compact. The color of the deposits also had a corresponding improvement, changing from dark-brown to copper-bright with the addition of K₄Fe(CN)₆ to the plating solution. The deposits have an intensified copper (1 1 1) plane orientation with the addition of K₄Fe(CN)₆ to the plating bath. The surface electrical resistance of alloy-coated fabrics increased with increase of nickel ions concentration in the solution. The addition of K₄Fe(CN)₆ to the solution reduced significantly the surface resistance of alloy-coated fabrics. The conductive fabrics with high shielding effectiveness could be prepared at the optimum condition with 0.0038 M nickel ions and 2 ppm K₄Fe(CN)₆. As the deposit weight on the fabric was 40 g/m², the shielding effectiveness of alloy-coated fabrics was more than 85 dB at frequency ranging from 100 MHz to 20 GHz.

Keywords: Electroless plating; Cu–Ni–P alloy; PET fabric; Deposition rate; Crystal structure; Surface morphology; Surface resistance; Shielding effectiveness

1. Introduction

As the use of electronic products and communication instruments increases, electromagnetic interference (EMI) is a problem for the lifetime and efficiency of the instruments. In addition, the regulation of EMI shielding such as by the Federal Communications Commission (FCC) has become more rigorous [1]. Although EMI-transmitted electromagnetic waves can easily damage electronic components, good conductive materials can act as a shield against electromagnetic penetration [2]. Conductive textiles, which are coated with aluminum, copper, silver and nickel, are an important kind of materials for preventing electromagnetic interference. Conductive fabrics coated with different metals have been used in many electronic instruments in a variety of manufactured forms such as fabric tape or foam gaskets. Current metal coating techniques on fabrics are conductive paints and lacquers, sputter coating, vacuum deposition, flame and arc spraying, and electroless plating [3,4].

Among them, electroless plating is probably the preferred way of producing metal-coated EMI shielding textiles. This technique has advantages, such as coherent metal deposition, excellent conductivity, shielding effectiveness (SE) and applicability to complex-shaped materials or nonconductors. It can be applied to almost all fiber substances. It can be performed at any step of textile production such as yarn, stock, fabric or cloth [5].

Because of the high conductivity of copper, electroless copper plating is currently used to manufacture conductive fabrics. The effect of plating process on the SE of copper-coated fabrics has been studied by some researchers [6–8]. The SE of copper-coated fabrics is all not more than 75 dB and electroless copper plating solutions all use formaldehyde as reducing agents [9]. It is operated at pH values above 11 and this bath may release hazardous gases during operation [10]. Therefore, sodium hypophosphite, as the reducing agent, is especially attractive because of its low pH, low cost, and relative safety features [11,12]. Several papers have studied the electroless copper plating solutions using hypophosphite as reducing agent [13–17]. Those researches focused mainly on the effect of additives on the properties of the deposits and the application of electroless copper plating to fabrication of printed circuit boards.
However, the hypophosphite-based electroless copper plating process is more complicated than formaldehyde-based bath because copper is not a good catalyst for the oxidation of hypophosphite resulting in little or no plating on a pure copper surface. One approach to catalyze the oxidation of hypophosphite is to add nickel ions to the bath, resulting in a very small amount of co-deposited nickel and phosphorus in the deposit. The nickel serves to catalyze the oxidation of hypophosphite, enabling continuous copper deposition [9]. Therefore, the deposit of electroless copper plating using hypophosphite as the reducing agent is actually Cu–Ni–P alloy.

The objective of this study is to apply the electroless plating of Cu–Ni–P alloy on PET fabrics using hypophosphite as the reducing agent to the preparation of conductive fabrics and investigate effects of operating parameters on the deposition rate, composition and properties of deposits such as the crystal structure, surface morphology and surface resistance.

2. Experimental

Polyethylene terephthalate (PET) fabrics (51 × 38 count/cm², 64 g/cm², taffeta fabric) were used as substrates. The surface area of each specimen is 100 cm².

Electroless plating was carried out by a multistep process, which included: scouring, rinsing, etching, rinsing, sensitization, rinsing, activation, electroless plating, rinsing and drying. The specimens were scoured in 10 g/L NaOH solution (1 L) at 70 °C for 3 min prior to use. The samples were then rinsed in distilled water and etched in a mixture of 15 g/L KMnO₄ and 40 mL/L H₂SO₄ solution (1 L) for 3 min. Surface sensitization was conducted by immersion of the specimens into an aqueous solution (1 L) containing 10 g/L SnCl₂ and 40 mL/L 38% HCl at 30 °C for 3 min. The specimens were then rinsed in distilled water and immersed in an activator solution (1 L) containing 0.50 g/L PdCl₂ and 20 mL/L 38% HCl at 60 °C for 3 min. The specimens were then rinsed in a large volume of deionized water for more than 5 min to prevent contamination of the plating bath. Afterward, the specimens were then immersed in the electroless plating bath for 10 min. The volume of the plating bath was 3 L. The electroless plating bath contained: 0.032 M copper sulfate, 0.0019–0.0076 M nickel sulfate, 0.283 M sodium hypophosphite, 0.071 M sodium citrate, 0.493 M boric acid and 0–6 ppm K₄Fe(CN)₆. Deionized water was used to prepare the solutions. The pH was adjusted using NaOH or H₂SO₄ to a final value of 8.5–10.5. The temperature was held at 60–75 °C.

Deposition rate was calculated from the weight gain of the specimen before and after plating, the surface area and plating time. The units are expressed as g/(m² min).

A PARSTAT model 2273 potentiostat was used for electrochemical measurements. The linear sweep voltammetry (LSV) experiments were carried out at 70 °C and at a scan rate of 10 mV/s. The working electrode was pure copper with 1.0 cm² surface area; the counter electrode was a platinum foil, and the reference electrode was a commercial Ag/AgCl electrode saturated with KCl.

The crystal structure of the deposits was investigated using X-ray diffraction (XRD, Cu Kα radiation and graphite filter at 40 kV and 100 mA). Scanning electron microscope (SEM, JEOL JSM-6460) was used to characterize the surface morphology of the deposits. The chemical composition of the deposits was determined using energy dispersive X-ray (EDX) analysis attached to the SEM.

The surface resistance Rₛ was measured by the four-probe method as described in ASTM F 390. Rₛ is considered to be the resistance of a square sample, the units of Rₛ are commonly expressed as ohms-per-square or Ω/sq.

The coaxial transmission line method as described in ASTM D 4935-99 was used to test the EMI shielding effectiveness of the conductive fabrics. A number of researchers have described the detailed set-up and test procedure using a plane-wave electromagnetic field [18–20].

3. Results and discussion

3.1. Deposition rate

The effects of bath composition, pH and temperature on the deposition rate were studied.

As mentioned above, nickel ions were added to the bath to catalyze the oxidation of hypophosphite. When the nickel ions concentration in the bath is low, the deposition rate of the plating decreased with time, and finally stopped because the surface catalytic activity was not replenished. Thus, it was necessary to maintain the nickel ions concentration above a critical value in the bath to sustain the deposition rate. The effect of nickel ions concentration on the deposition rate at different temperature is shown in Fig. 1. It shows that the deposition rate increased when the nickel ions increased from 0.0030 to 0.0076 M at 65–75 °C. However, when nickel ions concentration was lower than 0.0030 M, a thin layer of deposits was obtained, and then electroless plating stopped. Therefore, 0.0030 M is the critical point of nickel ions concentration in the solution.

The dependence of deposition rate on pH for different temperature is shown in Fig. 2. At 60 °C, pH had little influence.
on deposition rate and the deposition rate is very low. As the temperature is 65 °C and above, the deposition rate increased obviously with the increase of the solution pH.

Therefore, a continuous deposition could be obtained as the nickel ions concentration and temperature were 0.0030 M and 65 °C, respectively, and above. According to the experimental results, it was a good condition that the ions concentration and temperature were 0.0038 M and 70 °C, respectively. However, the deposition rate is high and the color of the deposits is dark-brown. The dark appearance of the deposits usually indicates poor mechanical and electronic properties [12]. Thus, K₄Fe(CN)₆ was used to improve the properties of the deposits. The influence of K₄Fe(CN)₆ on deposition rate is shown in Fig. 3. The deposition rate decreased from 1.47 to 1.2 g/(m² min) as the concentration of K₄Fe(CN)₆ changed from 0 to 2 ppm. There is little difference in deposition rate at higher K₄Fe(CN)₆ concentration. The effect of K₄Fe(CN)₆ concentration on the oxidation of hypophosphite was also investigated to explain the function of K₄Fe(CN)₆, as shown in Fig. 4. The result shows that addition of 2 ppm or above K₄Fe(CN)₆ reduced the oxidation current significantly, which resulted directly in the decrease of deposition rate with the addition of K₄Fe(CN)₆ to the plating bath. It is possible that the reduction in the deposition rate and oxidation current of hypophosphite with the addition of K₄Fe(CN)₆ results from its adsorption on the electrode surface causing a lower rate of electron transfer or nucleation. The effect slows down with further addition of K₄Fe(CN)₆ as the surface adsorption reaches saturation.

3.2. Composition

The composition of the deposits as the function of nickel ions and K₄Fe(CN)₆ concentration in the bath was investigated using energy dispersive X-ray analysis. The deposits consisted mainly of copper with small amounts of nickel and phosphorus. As shown in Table 1, the nickel content of the deposits increased significantly with the increase of nickel ions concentration in the solutions, which resulted in higher deposition rate. As shown in Table 2, when the nickel ions concentration was 0.0038 M, the nickel content was 3–5 wt% and decreased slightly with the increase of K₄Fe(CN)₆ concentration.

3.3. Surface morphology

The morphology of the alloy-coated fabrics was studied by SEM. SEM photographs of the alloy-coated fabrics obtained at different K₄Fe(CN)₆ concentration are shown in Fig. 5. Fig. 5a shows that the deposits on the PET fibers were loose and the surface was very rough in the absence of K₄Fe(CN)₆ in the solution, which resulted in dark-brown deposits mentioned above. The surface morphology is similar with that of copper deposits on PET fabrics obtained from formaldehyde bath [6]. As shown in Fig. 5b–d, the deposits became more compact and smoother with the increase of K₄Fe(CN)₆ concentration in the bath, and the deposits at the presence of K₄Fe(CN)₆ in the solution were better than that obtained from formaldehyde bath. The color of the deposits also had a corresponding improvement, changing from

<table>
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<th>Deposits</th>
<th>K₄Fe(CN)₆ concentration (ppm)</th>
<th>Ni + P/P content (wt%)</th>
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<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>4.0/0.3</td>
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<tr>
<td>2</td>
<td>1</td>
<td>4.5/0.4</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>3.9/0.3</td>
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<tr>
<td>4</td>
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Table 1 Nickel and phosphorus content in the deposits from the bath with different nickel ions concentration (K₄Fe(CN)₆ concentration: 0 ppm; pH 10; T: 70 °C)

Table 2 Nickel and phosphorus content in the deposits from the bath with different K₄Fe(CN)₆ concentration (Ni ions: 0.0038 M; pH 10; T: 70 °C)
Fig. 5. SEM photographs of the alloy-coated fabrics obtained at different K₄Fe(CN)₆ concentration in the bath (Ni ions: 0.0038 M; pH 10; T: 70 °C): (a) 0 ppm; (b) 1 ppm; (c) 2 ppm; (d) 4 ppm.

dark-brown to copper-bright with the addition of K₄Fe(CN)₆ to the plating solutions. The bright appearance of the deposits usually indicates better mechanical and electrical properties.

3.4. Crystal structure

The XRD patterns of the deposits obtained at different K₄Fe(CN)₆ concentration are shown in Fig. 6. The peaks that appeared at 2θ = 43.3°, 50.5°, 74.2°, and 89.9° represent (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of copper, respectively. The copper oxide phase was not detected in the deposits. The relative intensities of the diffraction peaks from the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes are listed in Table 3. It can be seen that the deposit has an intensified copper (1 1 1) plane orientation with the addition of K₄Fe(CN)₆ to the plating bath.

3.5. Surface resistance and shielding effectiveness

As we know, the surface resistance of alloy-coated fabrics is related to the weight of alloy coating on the fabrics. Thus, in order to study the influence of plating parameters on the surface resistance, the weight of alloy coating was kept at 30 g/m². The effect of nickel ions concentration on the surface resistance of alloy-coated fabrics is shown in Fig. 7. It shows that the surface resistance increased obviously with the increase of nickel ions concentration. As mentioned above, higher nickel ions concentration in the solutions led to higher content of Ni–P alloy in the deposits. The Ni–P alloy has high electrical resistivity (120 μΩ cm) [21] and the nickel atoms in the copper lattice increase the crystal defects in the deposit. Fig. 8 shows that the addition of K₄Fe(CN)₆ reduced significantly the surface resistance of the alloy-coated fabrics, which should result from the more compact and smoother deposits with intensified copper (1 1 1) plane orientation than that in absence of K₄Fe(CN)₆.

Thus, the electroless plating solution using hypophosphite as reducing agent with 0.0038 M nickel ions and 2 ppm K₄Fe(CN)₆ can be used to prepare conductive fabrics with smooth deposits and low surface resistance. Fig. 9 shows the SE of alloy-coated
fabrics with different weight of alloy coating. The SE increased greatly with the increase of deposit weight on the PET fabric, which is in good agreement with the Schelkunoff theory about electromagnetics. According to the Schelkunoff theory [22], better conductivity of the fabrics leads to higher SE. As the deposit weight on the fabric was 40 g/m², the SE of alloy-coated fabrics was more than 85 dB at frequency ranging from 100 MHz to 20 GHz, which is a very good SE. The conductive fabric with SE more than 85 dB can be used in advanced electronic products and national defense field.

Electroless plating of Cu–Ni–P alloy on PET fabrics and effect of plating parameters on the properties of alloy-coated fabrics were investigated. The deposition rate increased obviously with the increase of temperature, pH and nickel ion concentration. However, high deposition rate resulted in loose deposits and the surface of the deposits was rough. The addition of K₄Fe(CN)₆ to the solution could reduce the deposition rate and make the deposits become more compact. The deposit has an intensified copper (1 1 1) plane orientation with the addition of K₄Fe(CN)₆ to the plating bath. The color of the deposits also had a corresponding improvement, changing from dark-brown to copper-bright with the addition of K₄Fe(CN)₆ to the plating solution. The surface resistance of alloy-coated fabrics increased obviously with increase of nickel ions concentration in the solutions because of high nickel content in the deposits. The addition of K₄Fe(CN)₆ reduced the surface resistance significantly, which resulted from the more compact and smoother deposits than that in absence of K₄Fe(CN)₆. The conductive fabrics with high SE could be prepared at the optimum condition with 0.0038 M nickel ions and 2 ppm K₄Fe(CN)₆. When the coating weight on the fabric was 40 g/m², the SE of alloy-coated fabrics was more than 85 dB at frequency ranging from 100 MHz to 20 GHz.

4. Conclusions

Fig. 7. The effect of nickel ions concentration on the surface resistance of alloy-coated fabrics (K₄Fe(CN)₆: 0 ppm; pH 10; T: 70 °C).

Fig. 8. The effect of K₄Fe(CN)₆ concentration on the surface resistance of alloy-coated fabrics(Ni ions: 0.0038 M; pH 10; T: 70 °C).

Fig. 9. The shielding effectiveness of alloy-coated fabrics with different weight of alloy coating: (a) 10 g/m²; (b) 20 g/m²; (c) 40 g/m².

Fig. 9. The shielding effectiveness of alloy-coated fabrics with different weight of alloy coating: (a) 10 g/m²; (b) 20 g/m²; (c) 40 g/m².

References


