Investigation of electroless copper plating on polyurethane foam, as an initial step of open cell foam production process

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Coating of polymeric foams is known as a method for production of metallic foams, which produces foams with high volume of porosity and controllable pore size. In this research, this method was employed to produce open cell copper foam by use of polyurethane foam with an average pore size of 0.4 mm as the substrate. Since polyurethane foam as a non-conductive material is not able to be coated directly by electrolytic deposition, the substrate was initially metallised by electroless copper plating. In the electroless plating process, the effects of the main parameters such as bath chemical composition, solution pH and temperature on deposition rate and thickness of the coatings obtained were investigated. The results showed that the optimum condition of the process is obtained when CuSO$_4$ concentration in the deposition bath is 12 g L$^{-1}$, pH is 13 and plating temperature range is 55–60$^\circ$C.

Keywords: Copper, Deposition rate, Electroless plating, Metallic foam, Polyurethane foam

Introduction

Metallic foams are a new generation of materials and have received a great deal of attention in recent years. This popularity is a result of their unique properties such as high surface/weight ratio, high-heat transfer coefficient and good recycling capability. Open cell metallic foams are used as mechanical energy absorbers, filters, silencers, flame inhibitors, catalytic reactors, thermal converters, flow filters among others. Electrolytic deposition is one of the open cell metallic foam production methods. In this procedure, polymeric foam is used as the substrate, which will be plated by a desirable metal such as copper and nickel; always considering that electrolytic plating requires enough electrical conductivity in the polymeric foam as the substrate. In this study, polyurethane foam, which is a non-conductive material and cannot be electroplated directly, was used as the substrate, to produce open cell copper foam. Therefore, electroless plating, which is one of the common procedures of polymer metallisation, was used. Electroless plating is widely used in order to form a conductive layer over 3-D non-conductive substrates currently. Copper electroless plating on polyurethane requires the following steps:

1. Chemical etching
2. Surface sensitisation
3. Usage of special salts in order to activate the surface of a polymeric substrate
4. Application of specific compounds to achieve conductivity on the polymer surface

According to the above steps, once the surface is cleaned, it must be ‘activated’ by pre-plating treatments designed to make the surface active to the plating solution. Sensitisation and activation steps are carried out in dilute acidic solutions of SnCl$_2$ and PdCl$_2$ or AgNO$_3$, respectively. When AgNO$_3$ is used, the following reaction occurs at the polymer surface:

$$\text{Sn}^{2+}(aq) + 2\text{Ag}^+(aq) + \text{Sn}^{4+}(aq) + 2\text{Ag}(s) \quad (1)$$

On the basis of this reaction, Sn$^{2+}$ ions reduce Ag$^+$ ions leading to attachment of Ag particles to the polymeric substrate, and precipitation of copper occurs in these catalytic points. Then precipitated copper atoms act as a catalyst and result in acceleration of the coating process. In this study, polyurethane foam was coated by electroless copper plating and parameters affecting the rate of deposition and coating thickness, including bath composition, pH and temperature, were investigated. The purpose of this work is to optimise the conditions of electroless copper plating in order to establish a more stable and higher deposition rate bath, and greater thickness to produce a higher quality deposit.

Experimental methods

Materials

Polyurethane foam with an average pore size of 0.4 mm was used as the substrate and the electroless copper plating bath contained 3–16 g L$^{-1}$ of copper sulphate (CuSO$_4$·5H$_2$O) as a source of copper ions, 3 g L$^{-1}$ formaldehyde (HCHO) as reducing agent, 42 g L$^{-1}$ ethylenediamine tetra acetic acid (EDTA) as complexant and various amount of sodium hydroxide (NaOH) to reach the pH values of 10–14.
Electroless plating process

The whole electroless plating process comprised five major steps: cleaning, chemical etching, sensitisation, activation and, finally, electroless plating. In the cleaning step, polyurethane substrate was soaked in ethanol 98% for 15 min at room temperature to wash and degrease the surface of the polymeric foam, and then it was rinsed in distilled water. In the next step, the polymeric specimen was etched by a solution composed of 350 g L$^{-1}$ chromic acid and 200 g L$^{-1}$ sulphuric acid. The subsequent stage was sensitisation in which the etched sample was rinsed in distilled water and then was immersed in a solution of 50 g L$^{-1}$ SnCl$_2$ and 80 mL L$^{-1}$ HCl 37% for 15 min at 35°C. Then, the sensitised polymeric substrate was rinsed in distilled water to proceed to the activation step. The activator solution contained 20 g L$^{-1}$ AgNO$_3$ and 60 mL L$^{-1}$ HCl 37%. After the activation step, the specimen was rinsed in distilled water, and was immersed in the electroless plating solution. In the electroless copper plating baths, which use formaldehyde (HCHO) as a reducing agent, the most critical reaction is:

$$\text{Cu}^{2+} + 2\text{HCHO} + 4\text{OH}^- \rightarrow \text{Cu} + 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2$$

This reaction can be considered as two opposite electrode processes or involving two half-cell reactions:

Anodic half cell reaction

$$2\text{HCHO} + 4\text{OH}^- \rightarrow 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2 + 2\text{e}^-$$

(3)

Cathodic half cell reaction

$$\text{Cu}^{2+}_{\text{solution}} + 2\text{e}^- \rightarrow \text{Cu}_{\text{lattice}}$$

(4)

Based on the above reactions, a uniform layer of copper covers the polymeric foam ligaments.

Deposition rate measurement

It is difficult to calculate the surface area of the foam materials because of the complex surface. In this study, the deposition rate is defined as the mass gain of unit mass foam substrate and unit time. The deposition rate was calculated by the following equation

$$V = \frac{(m_2 - m_1)}{m_1 \cdot t}$$

(5)

Where $m_1$ and $m_2$ are the masses of the specimen before and after the electroless plating procedure, respectively; $t$ is the stabilising time of the electroless plating bath.

According to this equation the unit for deposition rate is milligrams per milligram-minute, as given in the Results section (Figs. 1, 4 and 6).

The experiments were repeated five times and the mean of these five sets of data for each point was applied to calculate the deposition rate at that point.

Deposition thickness measurement

In the present research study, to measure the copper layer thickness, the samples were mounted and sanded, so that the ligaments of the foam presented as a clear cross-section. Finally, the samples were imaged by using an electron microscope and the thickness of copper layers was measured. Each reported result is the mean of 10 measured datum points.

Results and discussion

The effect of CuSO$_4$ concentration

Figures 1 and 2 show the effect of CuSO$_4$ concentration on the deposition rate and coating thickness. As the diagrams imply, increasing CuSO$_4$ concentration in the electroless plating solution results in increase of deposition rate and thickness of the coating. When CuSO$_4$ concentration exceeds 12 g L$^{-1}$, the bath stability decreases and the grains of the resulting coating are coarse. On the other hand, when CuSO$_4$ is <8 g L$^{-1}$, the deposition rate is insignificant and the resulting coating is grey. As shown, the CuSO$_4$ concentration of 12 g L$^{-1}$ is required to obtain the maximum deposition rate and coating thickness. It should be noted that the resulting coating at this CuSO$_4$ concentration had the brightest appearance.

Figure 3 shows an SEM image of the cross-section of an electroless plated polymeric foam ligament.

The effect of bath temperature

Bath temperature plays an important role in the electroless plating process and determines the structure and properties of resulting coatings. As Fig. 4 implies, in the temperature range of 30–60°C, increasing the temperature improves the deposition rate significantly. This behaviour originates from the effects of two reactions in the electroless copper plating process, including the cathodic reaction, which
reduces copper ions and the anodic reaction which produces water (reactions 3 and 4).

The kinetics of electroless plating is controlled by the above reactions. Increasing the temperature accelerates those reactions and as a result the deposition rate increases. In temperatures higher than 60°C, the deposition rate subsides, because at higher temperatures cathodic and anodic reactions happen throughout the solution (solution decomposition). In fact, in temperatures higher than 60°C, dynamic and thermodynamic conditions are more favourable inside the solution and consequently, solution deposition speeds up and leads to reduction of the deposition rate.16 As shown in Fig. 5, elevation of bath temperature increased the thickness of the resulting coating, but at temperatures higher than 60°C, the thickness of the coating decreased.

The effect of pH

According to Fig. 6, elevation of pH in the plating solution from 11.0 increases the deposition rate, but at pH values higher than 13, no further increase occurs.

5 Effect of bath temperature on coating thickness

6 Dependence of deposition rate on pH

7 Dependence of coating thickness on pH

This behaviour is because of the presence of $4\text{OH}^-$ ions in the overall reaction

$$\text{Cu}^{2+} + 2\text{HCHO} + 4\text{OH}^- \rightarrow \text{Cu}^+ + 4\text{H}_2 \uparrow + 2\text{H}_2\text{O} + 2\text{HCOO}^-$$

(6)

As pH varies, the proportional concentrations of methylene glycol and hydroxide ions change during the
decomposition of methylene glycol. In fact, at higher pH values, OH$^-$ ions are consumed during the hydroxylation of formaldehyde. Formaldehyde is converted to methylene glycol and will be oxidised. Subsequently, this oxidation leads to formation of ions\textsuperscript{15}
\[
\text{HCHO} + \text{OH}^- \rightarrow \text{CH}_2(\text{OH})\text{O}^- \\
\text{CH(OH)O}^- + \text{OH}^- \rightarrow \text{CHOO}^- + \text{H}_2\text{O} + e^- \tag{8}
\]
There is a direct relation between deposition rate and coating thickness variations with solution pH. As shown in Fig. 7, the maximum coating thickness is obtained in a plating solution with pH $= 13$, and no trace of copper was observed in the sample treated at pH $= 10$.

Figure 8 displays the structure of polyurethane foam used as substrate, before and after electroless plating. As is shown, the foam retains its structure during the plating process and variation of pore size is negligible, too.

Conclusion

1. Increasing the CuSO\textsubscript{4} concentration in electroless copper plating solution causes a drastic improvement in deposition rate, but when CuSO\textsubscript{4} exceeds 12 g L$^{-1}$, deposition rate decreases. The highest deposition rate, coating thickness and brightness were observed in the specimen plated in solution with CuSO\textsubscript{4} concentration of 12 g L$^{-1}$. It can be concluded that the best CuSO\textsubscript{4} concentration value for the bath used in this study is 12 g L$^{-1}$.

2. Deposition rate decreases with increase in the solution pH. At pH values lower than 10, no surface coverage was observed and at pH values higher than 13, copper particles were formed inside the solution leading to reduction of the deposition rate. On the basis of these results, the best pH value for the bath used in this study is 13.

3. In the temperature range of 30–65°C, elevation of temperature results in a noticeable improvement of deposition rate. At temperatures lower than 30°C, the resulted coating is dark and at temperatures higher than 60°C, deposition rate decreases because of bath instability. At temperatures between 55 and 60°C, the plating solution has the most stability, and deposition rate and deposit thickness are at their maximum; thus, the best temperature for operation of the electroless plating bath, used in this work, ranges from 55 to 60°C.

References