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A STUDY ON ELECTROLESS COPPER DEPOSITION FOR DESKTOP STEREOLITHOGRAPHY 3D PRINTING MATERIALS

Electroless deposition is a method of metallizing parts without needing for an electrical source that can be performed on electrically conductive and non-conductive materials. Adhesion quality is an essential aspect of the electroless deposition process that determines the metal deposition conditions. The properties of stereolithography (SLA) 3D printed parts can be improved through the metallization process for various applications. In this study, optimization through the orthogonal design method was used to obtain the optimal processing parameters of electroless copper deposition on desktop SLA material with respect to adhesion quality. Experimental work was carried out according to the L_9 (3^4) orthogonal array, followed by an evaluation of the signal-to-noise (S/N) ratio and analysis of variance (ANOVA). Based on the S/N ratio results, the optimal processing parameters for adhesion quality were potassium hydroxide concentration (400 g/L), etching time (30 min), formaldehyde concentration (3.75 mL/L) and deposition time (30 min). The results of the study are useful for industries such as rapid tooling, rapid prototyping, and semiconductors.

Keywords: Stereolithography; Electroless copper deposition; Optimization; Adhesion quality

1. Introduction

Additive manufacturing technology is an advanced process that has become popular due to its ability to produce complex geometries for various applications directly from digital formats with good dimensional performance [1-3]. Most of the materials used are made of polymers other than metals depending on the technology and purpose of use [4-6]. However, 3D printed parts made of polymers have limited use due to their low hardness and strength [7-9]. Therefore, it is necessary to improve the material properties of 3D printed parts and surface finishes through various processes including electroless metal deposition. Composites consisting of polymers and metals provide additional benefits for many applications such as rapid tooling, rapid prototyping, and semiconductors. Polymer and metal composite materials can be characterized by corrosion resistance, wear resistance, electrical and thermal conductivity including better mechanical properties. Metallization on polymers is a well-known technique used for many applications including molds and dies industries, automotive, aerospace sector, electronics, medical devices, and domestic appliances [10-12]. In general, metallization can be done using several methods such as physical vapor deposition (PVD) [13], chemical vapor deposition (CVD) or electroless metal deposition [14-17]. The electroless metal deposition has many advantages because no special equipment is required to perform the process. Furthermore, the electroless deposition process can produce a more uniform deposition thickness than the electrodeposition process [18]. Various metals and alloys can be used to metallize on the desired materials [19,20]. However, the process requires optimization of processing parameters because each substrate material has unique properties that may influence the yield [21,22]. Currently, there is a lot of research related to metallization on 3D printed parts conducted to improve the material properties for various application purposes [23-25]. In this study, copper was chosen to be deposited on the desktop SLA substrate by electroless deposition technique because it has the necessary soft layer to accommodate the differential thermal expansion between the SLA and the subsequent metal layer [26]. The orthogonal design method was used to obtain the optimum chemical composition and processing parameters of the electroless copper deposition.

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2. Methodology

2.1. Specimen preparation and copper deposition bath

Formlabs high temperature SLA resin (Formlabs Inc., Somerville, MA, USA) was used to print specimens with dimensions of 30×25×3 mm. The specimens were printed with a layer thickness of 100 μm using a Formlabs Form 2 desktop SLA 3D printing machine (Formlabs Inc., Somerville, MA, USA). After completion of the post curing-process, the specimens underwent a pre-treatment process prior to the electroless copper deposition step. The specimens were degreased using a solution consisting of 50 g/L of sodium carbonate, 35 g/L of disodium metasilicate, and 3 g/L of sodium lauryl sulphate. The degreasing process was carried out at a temperature of 25°C for 2 minutes in ultrasonic cleaning equipment. After degreasing, the specimens were immersed in a potassium hydroxide solution that acted as an etchant according to the chemical concentration and etching time as listed in TABLE 1. After that, the activation process was done by dipping the specimens into a solution containing 3 g of stannous chloride, 15 mL of hydrochloric acid and 250 mL of deionized water for 2.5 minutes. The next step was to immerse the specimens in a solution containing 0.0625 g of palladium chloride, 15 mL of hydrochloric acid and 250 mL of deionized water for 2.5 minutes. Specimens were rinsed in deionized water after each process. The composition of the electroless copper deposition bath consists of 20 g/L of potassium sodium tartrate tetrahydrate, 5 g/L copper sulfate pentahydrate as a copper precursor, 5 g/L sodium hydroxide, 5 g/L of sodium carbonate and formaldehyde as a reducing agent in volume quantity as listed in Table 1. The pH value of the bath was adjusted at 12 and the electroless copper deposition processing temperature was maintained at 45°C. The deposition process time was carried out as listed in TABLE 1 and specimens were prepared according to ASTM D3359 [27]. Specimens were then rinsed in deionized water and dried in room conditions.

2.2. Selection of factors and levels

Three different levels were selected to investigate the influence of each factor as shown in TABLE 1.

TABLE 1

Factor and level selection for electroless copper deposition process

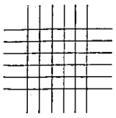
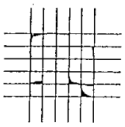
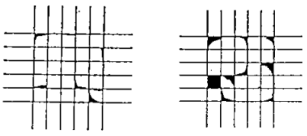
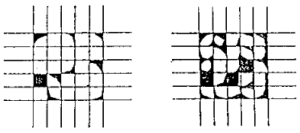
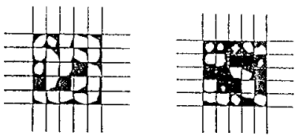
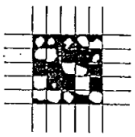
Factors	Label	Level 1	Level 2	Level 2
Etchant concentration (g/L)	EC	200	300	400
Etching time (min)	ET	10	20	30
Reducing agent concentration (mL/L)	RA	10	15	20
Deposition time (min)	DT	30	60	90

2.3. Evaluation of copper deposition adhesion

Adhesion of the metal to the substrate plays an important role in the electroless deposition process. In this study, the adhesion quality between the deposition layer and the substrate was evaluated by the scratching method according to ASTM D3359. The evaluation standards for the adhesion and surface quality of the deposition layer are listed in TABLE 2. In the last step, the optimal deposition processing parameters were verified using the results of main effect plot through a validation test.

TABLE 2

Classification of adhesion test results [12]

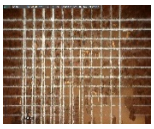
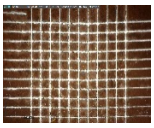
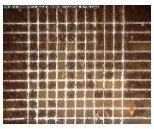
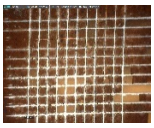
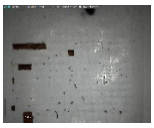
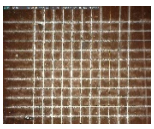
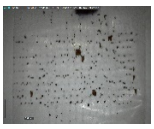
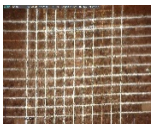
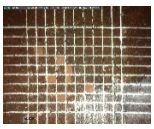
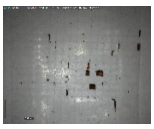
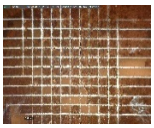
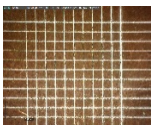
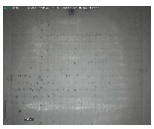
Classification	Percent area removed	Surface of cross-cut area from which flaking occurred for six parallel cuts and adhesion range by percent
5B	0% none	
4B	Less than 5%	
3B	5-15%	
2B	15-35%	
1B	35-65%	
0B	Greater than 65%	

3. Results and discussion

The results shown in TABLE 3 tabulate the percentage removal of copper metal removal area from the SLA substrate and the S/N ratio for each run with the specified electroless copper deposition processing parameters. Experimental work for each set of processing parameters was carried out using laboratory scale electroless copper deposition equipment. Based on the results in TABLE 3, the lowest percentage for area removal was preferred for electroless copper deposition quality characteristics which was approximately 0.50%. The results show minimal copper peeling from the SLA substrate indicating the adhesion quality was satisfactory. The same findings were also

TABLE 3

Results of orthogonal experiments

Trial no.	EC (g/L)	ET (min)	RA (mL/L)	DT (min)	Electroless copper deposit cross-cut	Photo of the tape	% copper metal area removed	S/N ratio (dB)
1	200	10	10	30			60.0	–35.5630
2	200	20	15	60			2.0	–6.0206
3	200	30	20	90			34.0	–30.6296
4	300	10	15	90			12.0	–21.5836
5	300	20	20	30			3.0	–9.5424
6	300	30	10	60			2.0	–6.0206
7	400	10	20	60			8.0	–18.0618
8	400	20	10	90			12.0	–21.5836
9	400	30	15	30			0.5	6.0206

obtained from previous studies that showed copper peeling was affected by the concentration of the reducing agent [16,20]. Meanwhile, the highest value of S/N ratio indicates the best adhesion quality of copper on SLA substrate. The mean square deviation (MSD) for smaller is better can be expressed as shown in Eq. (1) [28].

$$S/N\ ratio, \eta = -10\log\frac{1}{n}\sum_{i=1}^{n} y_i^2 \quad (1)$$

The main effect plot of the S/N ratio for the percentage of copper deposition removal area is shown in Fig. 1. The main effect plot was generated using Minitab 17 statistical software.

TABLE 4 shows the electroless copper deposition processing parameters to obtain optimal copper deposition adhesion quality.

After the S/N ratio and optimal chemical composition and processing parameters of electroless copper deposition were obtained, analysis of variance (ANOVA) was generated using

TABLE 4

Optimal processing parameters for copper deposition adhesion quality

Factor	Etchant concentration, EC (g/L)	Etching time, ET (min)	Reducing agent concentration, RA (mL/L)	Deposition time, DT (min)
Value	400	30	15	30

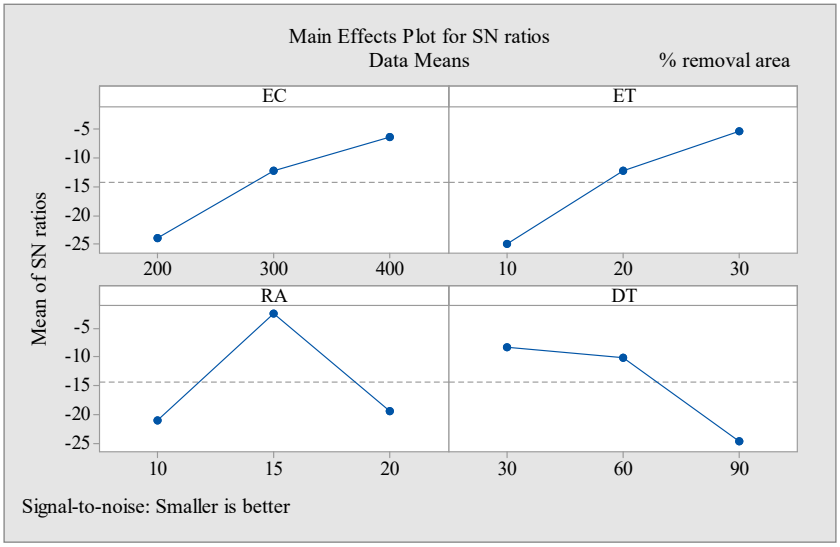


Fig. 1. Main effects plot of S/N ratio for the copper deposition adhesion quality

Minitab statistical software. This analysis can provide significant processing parameters through a statistical method. Based on the ANOVA of the copper deposition adhesion test as shown in TABLE 5, the most significant factor was potassium hydroxide etchant concentration with a contribution of 42.28% followed by etching time, formaldehyde reducing agent concentration and copper deposition time with a contribution of 22.04%, 18.95% and 16.73% respectively. The Formaldehyde reducing agent play an important role in determining the quality of metal adhesion in the electroless deposition process [16,20].

TABLE 5

ANOVA results for copper deposition adhesion test

Factors	DF	SS	F value	Cont. (%)
Etchant concentration (g/L)	2	1334.6	0	42.28
Etching time (min)	2	695.7	0	22.04
Reducing agent concentration (mL/L)	2	598.2	0	18.95
Deposition time (min)	2	528.1	0	16.73
Error	0	—	—	—
Total	8	3156.6	—	100.00

The optimal processing parameters obtained from the ANOVA results require validation to ensure that the smallest percentage of the copper removal area during the adhesion test was achieved. A validation test was performed according to the optimal chemical composition and electroless copper deposition processing parameters. TABLE 6 shows the result of the electroless copper deposition validation test. The validation test proved that the result of the optimized processing parameters was within the allowable range. The percentage margin of error was calculated using Eq. (2) [29].

$$Margin\ of\ error\ (\%) = \frac{Experiment - Confirmation}{Experiment} \times 100 \quad (2)$$

Based on Fig. 2 and TABLE 7, it can be concluded that the percentage of copper peeling during the copper adhesion test have a margin of error of around 10%. Therefore, the validation

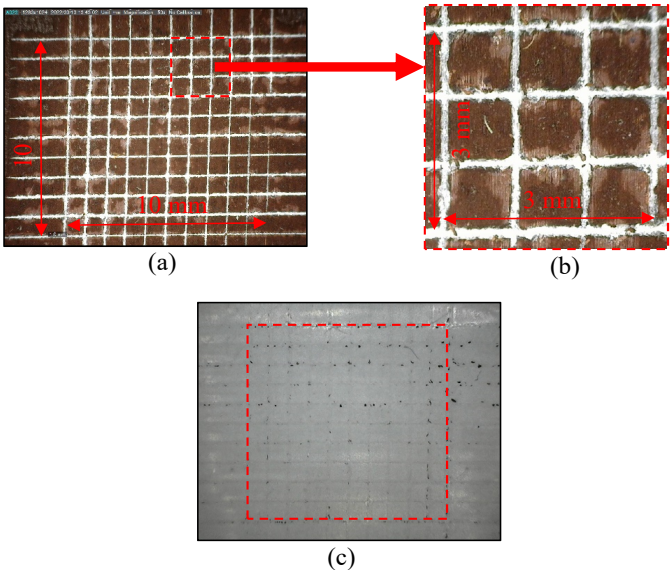


Fig. 2. Image of (a) Validation test of copper metal cross-cut, (b) Magnified condition, (c) Tape image after peeling

TABLE 6

Copper metal adhesion quality confirmation test result

Factor	Etchant concentration, C (g/L)	Etching time, T (min)	Reducing agent concentration, RA (mL/L)	Deposition time, T (min)	% Copper metal area removed
Value	400	30	15	30	0.55

test was accepted because the margin of error was within the allowable percentage [29].

TABLE 7

Margin error for experimental and confirmation of copper adhesion test

Response	Experiment (%)	Confirmation (%)	Margin error (%)
% Copper metal area removed	0.50	0.55	10

5. Conclusion

This study is useful to obtain the optimal electroless copper deposition processing parameters on desktop SLA 3D printing material with respect to the adhesion quality of copper deposition. The results also demonstrated:

i. The order of significant factors influencing the processing parameters of electroless copper deposition were etchant concentration, etching time, reducing agent concentration, and deposition time.
ii. The optimal formula for electroless copper deposition process was 400 g/L potassium hydroxide, 30 min etching time, 15 mL/L formaldehyde and 30 min deposition time.
iii. The result of the validation test using the optimal processing parameters show the minimum percentage of the copper removal area which indicates the satisfactory adhesion quality of copper deposition.

Hence, the experimental results of electroless copper deposition on SLA 3D printed parts provide significant findings that benefit SLA 3D printing applications, including for plastic injection rapid molds. The electroless copper deposition on the SLA 3D printed parts in this study was intended to act as a metal base layer. Therefore, subsequent metal deposition can be applied to improve the properties of SLA metal-coated parts for relevant applications.

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