# Electroplating of FDM Parts: A comparison via two different routes

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## Abstract

Present paper compares the copper electroplating on FDM (Fused deposition modelling) parts through two different routes. The two routes are: (i) Method of electroplating using chromic acid for surface preparation (ii) Method of electroplating using aluminium charcoal (Al-C) paste for surface preparation. Same plating condition is used for both the routes adapted. The result proposes that better copper deposition occurs using the Al-C paste than method using chromic acid for surface preparation. However, it was observed that in few samples, problem of shell cracking occurs in Al-C route, the reason for which is dissolution of paste at high operating condition during electroplating. Finally, the conclusion was made that Al-C paste at suitable operating conditions can be used for electroplating of FDM processed ABS parts. Copyright © 2017 VBRI Press.

**Keywords:** Electroplating, etching, FDM, cracking, deposition, surface preparation.

## Introduction

Advances in research have lead to the development of new smart materials. One of such smart material is metal electroplated plastic material. The combine properties of metal and plastic can be used in metal plated plastic part. This single material will have different attractive properties such as light weight, corrosion resistant, conductivity and abrasion resistant etc. There are varieties of applications where electroplated parts are used such as automotive industries, electronic industries and domestic fitting etc. Electroplated plastic parts are made possible by the process of plating or sometime referred as metallization. Metallization is the process of provide a thin coating to plastic parts. Metallization is further categorized as primary and secondary metallization. Primary metallization provides a thin layer of metallic coating over plastic substrate while the secondary metallization is done to increase the thickness of coating. The primary metallization is done through different methods including electroless plating, brushing a metal paint, spray metal technique, dipping in a metal paint, sputtering and vacuum metallization etc. [**1-2**]. Each process has its own merits and demerits in terms of economic, user friendly and complexity. The process of secondary metallization after primary metallization using any of the possible routes is done mainly by electroplating. Focusing the above mention problem, the present paper uses aluminium charcoal paste route for electroless plating of FDM parts, followed by electroplating for secondary metallization. FDM is a fast-growing RP (Rapid prototyping) process which builds the part by layer-wise deposition principle directly from the CAD model of the part. This process needs no specific process plan and no special tooling is required. For the detail of process literature can be referred [**3**-**5**]. It is very important to mention that FDM uses ABS plastic as part material and according to literature [**6**] ABS has got excellent plating properties. ABS P400 is the material that is used for part fabrication.

Electroless plating is widely used for plating of ABS plastic. This process doesn't require any electrical support and has the advantage of providing uniform plating even in sharp corner without build up [**7**, **8**]. The normal electroless plating process consists of cleaning, etching, neutralization, activation, acceleration and deposition. It is a multi-step process using long deposition time with use of complex chemicals that are costly and environmentally hazardous such as chromic acid used in etching. To eliminate this, number of researchers suggested the use of less costly and environment friendly chemicals. In this direction Li *et al.* [**9**] suggested the use of aluminium-carbon paste to replace chromic acid and made the process environmental friendly. Although, they propose a novel method for electroless plating but the feasibility of their process is not tested for electroplating. As the electroplating process has its own process variables and settings, the feasibility of Al-C paste needs to be tested. Thus, in this paper, electroplating using Al-C paste route of electroless plating is used.

## Experimental

The complete experimental procedure comprises of number of steps which are described as below:

### *Part fabrication*

The part for electroplating is fabricated using fused deposition modelling (FDM) by Stratasys Inc., USA. ABS P400 is the material that is used for part fabrication [**10**]. The part used in this experimental study is of cylindrical shape. Copper (Cu) is used for metallization. Copper is selected for its low cost and excellent conductivity [**9**]. $H_2SO_4$ is used as an electrolyte.

### *Materials/ chemicals details*

For the normal electroless procedure different chemicals used are chromic acid (Assay – 99%, NICE Chemicals, Kochi, India) , sulphuric acid (Assay – 97%, Rankem, New Delhi, India, sodium sulphite ( Assay - 97%, Central Drug house, New Delhi, India), Palladium/tin catalyst powder (Assay: Tin chloride - 95%, Palladium chloride – 99%, NICE chemicals , Kochi, India), sodium hydroxide (Assay – 97%, NICE Chemicals, Kochi, India) and ethylenediaminetetraacetic acid disodium (98% Assay, NICE Chemicals, Kochi, India). The materials used for the aluminium-charcoal route are fine aluminium metal powder (99.5 % Assay, NICE chemicals, Kochi, India), charcoal granules (NICE Chemicals, Kochi, India), enamel paint, distilled water, 320 grit sand paper, brush, beakers and conical flask, sulphuric acid ($H_2SO_4$), Copper sulphate ($CuSO_4.5H_2O$, 99% Assay, Rankem, New Delhi, India)) and hydrochloric acid (HCl, Rankem, New Delhi, India). The different equipment's used in experiments are magnetic stirrer of capacity, 2 litres (made by Remi) and electroplating setup (Rectifier, plating tank and number of hoses).

### *Preparation of Al–charcoal paste and plating of ABS parts*

Aluminium powder, charcoal powder, enamel and distilled water were mixed at a weight ratio of 40:3:36:21 in a 200-ml beaker. The prepared mixture was then stirred in a magnetic stirrer vigorously till it appears as thick paste. The paste was then applied carefully with a brush on cylindrical ABS parts precleaned with soap and distilled water. The paste coated ABS parts was allowed to dry at room temperature till it becomes completely dry. Al-Charcoal-pasted samples are scoured with 320 grit sandpaper and rinsed well with distilled water. Electroless bath was prepared by adding 5 wt% of copper sulphate ($CuSO_4$) and 15% of sulphuric acid ($H_2SO_4$). The deposition was done at room temperature for 48 hrs which further eliminate the need of Cole-Parmer StableTemp digital hot plate (Vernon Hills, Illinois) of±2% stability as used by Li *et al.* [**9**]. It is to be noted that the concentration of bath in Li *et al.* work was 15wt% $CuSO_4$ and 5wt% of $H_2SO_4$. Initially the same bath was used but the result obtained was not satisfactory as it was done at normal room temperature which was done at elevated temperature and controlled environment by Li *et al.*

### *Normal electroless copper depositions*

The normal electroless method consists of multiple stages as described below. Chromic acid is used for the etching process. The steps involved are as follows:

**Step 1:** Cleaning- Pumice powder was used for cleaning the ABS parts and then scoured with sand paper to remove oil, dirt, grease, etc., and also to increase surface area by developing micro-cavities.

**Step 2:** Etching - Etching is an important phase for achieving good metal - plastic bond [**11-13**]. Cleaned ABS parts were dipped in an aqueous solution containing chromic acid (600 g/l), Sulphuric acid (150 ml/l) and deionised water, maintained at 60ºC for 10-15 minutes. The samples were then taken out and washed 2-3 times carefully.

**Step 3:** Neutralization - Residual amount of chromium remaining in the ABS surface was removed with a sodium sulphite as a reducing agent to prevent its inhibition in further steps as, even trace amounts of chromium may completely inhibit electroless deposition. The parts were dipped in solution of 10g/l of Sodium sulphite at 25ºC for about 2 minutes and washed with water.

**Step 4:** Activation - An activator consisting of colloidal suspension of palladium/tin (Pd/Sn) catalyst powder was applied over conditioned part surface [**14-15**]. In this study samples were activated at 40ºC for 7 minutes and finally washed with water.

**Step 5:** Acceleration – It dissolves excess Sn and removes it from the surface for exposing the adsorbed Pd. The samples are dipped in a solution mixture containing 30g/l sodium hydroxide (NaOH), 3g/l copper sulphate ($CuSO_4$) and 15g/l ethylenediaminetetraacetic acid disodium ($EDTANa_2$) at 55ºC for about 7 minutes. The samples were finally washed with water followed by acidic bath treatment.

**Step 6:** Electroless deposition - Finally the electroless plating is carried out in electroless bath prepared by adding 5 wt% of copper sulphate ($CuSO_4$) and 15% of sulphuric acid ($H_2SO_4$). The deposition was done at room temperature for 48 hrs.

### *Electrical performance measurement and SEM with EDS*

The resistance of copper plated FDM parts was measured using a VOLTCRAFT M-3850 digital multimeter. The resistance was measured at 30 different points on the different surfaces and average is taken. The average resistance ($\overline{R}$) value together with standard deviation ($\sigma$) was calculated according to Eq. 1 and Eq. 2.

$$\overline{R} = \frac{\sum_{i=1}^{n} R_i}{n} \tag{1}$$

$$\sigma = \frac{\sqrt{\sum_{i=1}^{n} (R_i - \overline{R})^2}}{n-1} \tag{2}$$

where, $R_i$ is measured resistance value at $i^{th}$ point and total number of points are $n$.

Adhesion assessment of the Al pasted FDM samples was performed after electroless copper deposition in $H_2SO_4$ bath by following the standard ASTM test method ASTM D 3359-02 (Standard Test Methods for Measuring Adhesion by Tape Test) [**16**]. The test was done only for aluminium pasted parts to evaluate the proper adherence of paste over ABS parts as the copper is deposited over aluminium seeds exposed during scouring of parts and presence of aluminium seeds is only insured by presence of paste. The test was not required for normal electroless route since this does not involve any paste. Further, the activator (Pd/Sn catalyst powder) got deposited only in the micro cavities formed during etching stage and further deposition is possible only because of these catalysts.

A ZEISS EVO- MA10 SEM scanning electron microscope (SEM) coupled with an energy dispersive X-ray spectrometer (EDS) was used to examine the appearance and elemental composition of the copper in samples prepared by both routes.

### *Electroplating*

Electroplating also referred as electro deposition, can be described as a chemical deposition process in which electric current is used to deposit thick metallic coating onto another conductive surface. Electroplating of metallic alloy coatings is generally practised to modify the substrate surface in order to produce a wide range of useful materials with improved mechanical, decorative, electrochemical, electrical, magnetic or optical properties [**17**]. Metal alloy coatings electro deposition is a more complex process than a single metal one and involves the control of several chemical and operational parameters such as plating current density, metal ion thickness, rotation speed and the chemistry of the plating solution. Electroplating not only enhances the look of a part but it also produces a hard, durable surface and dramatically increases the strength of an electroless plated FDM part. The complete electroplating process consists of number of parts and equipments. The electrolytic tank is connected to two filters. The two filters are namely plate and cartridge filter. Plate filter is consists of polypropylene layer in the cylindrical housing for filtering the heavier and bigger impurities. Cartridge filter is also polypropylene filter in form of thread for separating the smaller impurities which remains while passing through plate filter. These two filters are connected to electrolytic tank for continuous filtration of the electrolytic solution which is re-circulated between filters and electrolytic tank. The rectifier provides the current density and voltage to the setup. In our study since we desired the copper electroplated part, the plating is done with copper. The electrolytic bath composed of mixture of Copper sulphate ($CuSO_4$), Sulphuric acid ($H_2SO_4$) and Hydrochloric acid (HCl). The Bath is prepared by adding 200 gm/lts of Copper sulphate, 60 gm/lts of Sulphuric acid and 120 ml/lts of Hydrochloric acid.

When the potential difference is applied the cu from copper plate (anode) dissolves into medium in form of $cu^{2+}$ ions. Since the substrate or job is negatively charged it accepts the copper ions and copper ions start depositing in the job and thereby building the layer. The reactions are:

At Anode $Cu \rightarrow Cu^{2+} + 2^{e1-}$

At Cathode $Cu^{2+} + 2\ ^{e1-} \rightarrow Cu$

In our study, the optimized condition was obtained at 2.5 Volt. The plating was done for 3 hours to ensure thick deposition of copper layer onto electrolessly processed FDM parts. It is to be noted that for both the route the composition and operating conditions are same. **Fig. 1** and **Fig. 2** shows the electroplating setup (tank with filters) and rectifier (uday industries made).

**Fig. 1.** Two filters connected to the electrolytic tank.

**Fig. 2.** Rectifier

## Results and discussion

The resistance value of electrolessly plated part was measured and standard deviation was calculated. Average resistance ($\bar{R}$) values together with standard deviation ($\sigma$) obtained after electroless copper deposition for chromic acid route and Al-C route at room temperature for 1 hr, 24 hr and 48 hr of deposition time are presented in **Table 1** and **Table 2**. It was observed that resistance value decreases with time which insures improvement in conductivity of part [**2**]. It can be clearly observed from the table that better conductivity was achieved after 48 hrs of deposition time. It was noticed that after 48 hrs of deposition, blue copper sulphate crystals get spread over part surface and creating its own layer and no conductivity was noted. Thus, best conductivity was obtained at 48 hours of deposition time. It is also observed that the resistance values are in ohms for aluminium pasted samples when compared with samples of conventional chromic acid route. This means that the result obtained after electroless plating is better for the aluminium pasted route than conventional chromic acid.

As good conductivity was achieved after 48 hrs of deposition the SEM images are presented for 48 hrs of deposition time. **Fig. 3** (**a**), (**b**) and (**c**) presents the SEM image, EDS mapping and EDS spectra of Cu deposition on samples of conventional chromic acid route after electroless Cu deposition in $H_2SO_4$ bath at room temperature. **Fig. 3** (**a**) is the SEM image in which large Cu crystals can be clearly observed. A localised copper distribution in the sample is presented as in EDS image (**Fig. 3b**). 88.83 % Cu, 5.39 % O, 0.78 % C and 5% beryllium is observed in elemental analysis of the corresponding tested sample (**Fig. 3c**).

**Table 1**: Electrical performance after electroless Cu deposition for aluminium charcoal pasted samples.

| **Deposition time (Hour (hr))** | **Acidic bath** <br> **$H_2SO_4$** <br> $\bar{R}$ **(Ω)** | $\sigma$ |
|---|---|---|
| 1 | - | - |
| 24 | 0.11 | 0.03 |
| 48 | 0.09 | 0.01 |

">" denotes readings that are beyond the maximum measuring range (100 MΩ) of the multimeter; "-"denotes there is no conductivity.

**Table 2**. Electrical performance after electroless Cu deposition for chromic acid etched samples.

| **Deposition time (Hour (hr))** | **Acidic bath** <br> **$H_2SO_4$** <br> $\bar{R}$ **(MΩ)** | $\sigma$ |
|---|---|---|
| 1 | > | > |
| 24 | 1.36 | 0.14 |
| 48 | 0.92 | 0.15 |

">" denotes readings that are beyond the maximum measuring range (100 MΩ) of the multimeter; "-"denotes there is no conductivity.

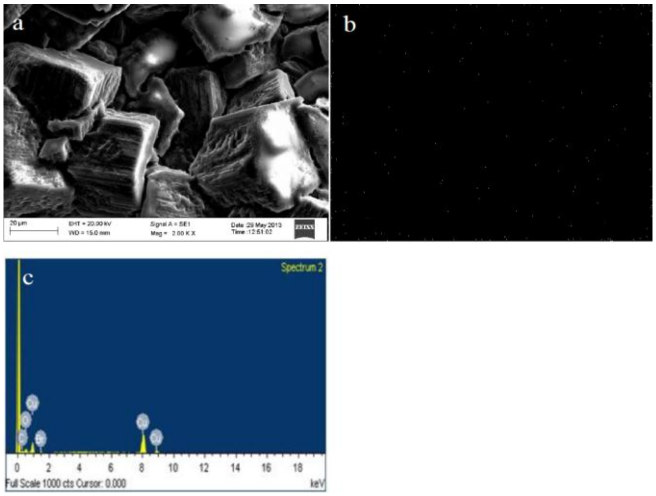

**Fig. 3.** (a)SEM image (b) EDS mapping (c) EDS spectra of conventional route after electroless copper deposition in $H_2SO_4$ after 48 hrs.

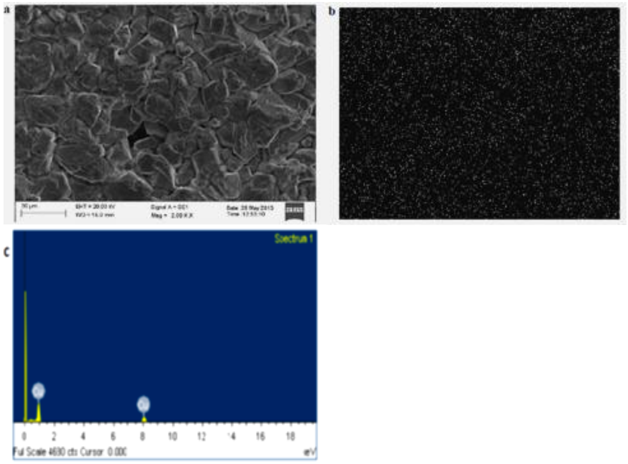

**Fig. 4.** (a) SEM image (b) EDS mapping(c). EDS spectra of aluminium charcoal pasted samples after electroless plating in $H_2SO_4$ bath after 48 hr.

**Fig. 4**(**a**), (**b**) and (**c**) presents the SEM image, EDS mapping and EDS spectra of Cu deposition on Al-C pasted samples after electroless Cu deposition in $H_2SO_4$ bath at room temperature after 48 hr. Cu crystals are closely connected and provide smooth appearance. This is further justified by their EDS mapping indicating more Cu after 48hr of deposition time. Further, in the EDS mapping it can be observed that copper crystals are widely spread over whole area of sample covered in SEM. The EDS spectra shows the peaks indicating copper at that region and elemental composition was 100 weight% copper and 100 atomic % copper.

The reason for more copper deposition in aluminium charcoal pasted samples is uniform distribution of aluminium throughout the part by the application of Al-paste. As the Cu gets deposited over the aluminium seeds exposed during etching and its growth increases with the deposition time thus uniform Cu deposition is obtained after 48 hr of deposition time.

Adhesion evaluation of the entire Al pasted samples is done according to the scale defined by ASTM D 3359-02. All the ABS test samples after tape test shows no flaking and yield results in a scale 4B or 5B, meaning excellent adhesion strength. Finally, the electroplating was carried at 3 volts for 5 hours. Few cylindrical electroplated parts obtained after electroplating using chromic acid for etching at given parameters are shown in **Fig. 5**.

**Fig. 5**. Electroplated cylindrical ABS part using chromic acid for etching.

It can be clearly seen from the **Fig. 4** that copper deposited over cylindrical part are very good and uniform despite of having the resistance values in MΩ after electroless deposition. The wires at the centre of the parts are used for holding the part while immersing it in electrolytic bath. To determine the thickness of the deposited copper layer the diameter of electroplated electrode was subtracted from raw ABS cylindrical part. The thickness was measured at different point and compared with raw ABS part and the average value was 0.220 mm. **Fig. 6** and **Fig. 7** shows copper deposited ABS parts using Al-charcoal paste. Furthermore, the different steps in normal electroless plating are eliminated making it cost effective. Good and comparable copper deposition can be observed on the cylindrical ABS parts using aluminium charcoal paste. The thickness of deposition was found to be around 0.30 mm on average which shows better copper deposition on comparison. The only problem observed was shell cracking at some regions in few samples and non-uniform deposition at edge.

**Fig. 6**. Electroplated cylindrical ABS part using aluminium charcoal paste.

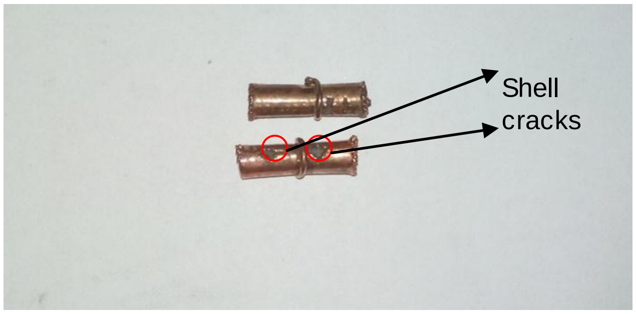

**Fig.7**. Electroplated ABS part using aluminium charcoal paste showing shell cracking.

The reason for the shell cracking is dissolution of aluminium paste in electroplated bath because of such high voltage in samples subjected to less drying time after the application of paste. Since, the electroless samples are carried at room temperature no external force or heat is applied. During, the electroplating process because the current pass through the plated part it got heated and because of that paste dissolves at certain regions which was not dried completely. Thus, the problem of shell cracking occurs.

## Conclusion

Two different routes are employed for electroplating of FDM processed ABS parts. These routes are:

1. Conventional electroless deposition method using chromic acid for surface preparation.
2. Use of Al-charcoal paste as surface preparation agent for copper deposition.

This deposition was further confirmed with the conductivity via resistance value and SEM with EDS images. Important conclusions drawn from the study are:

1. Copper deposition is achieved through both the routes.
2. In Al-C method, resistance was obtained in all the measured points but resistance values were not obtained in all the measured points in chromic acid route [**18**].
3. After electroless deposition Al- seeded samples (route 1) gives the best performance when compared with route 2 both in terms of electrical conductivity and Cu deposition. The reason for the better conductivity in Al- seeded samples is uniform distribution of aluminium by application of Al paste. Cu crystal gets deposited in the region where aluminium seeds were present and the growth of Cu becomes denser with increase in deposition time. Hence Al used in paste for surface preparation itself acts as catalyst in the electroless Cu deposition process.
4. The resistance obtained for chromic acid route is higher (in MΩ compared to Ω for route 1). The resistance is higher for this route because deposition occurs only in the micro cavities formed during etching. During etching micro cavities are formed by removal of softer butadiene from ABS parts and increasing the surface area. It is in these cavities where catalyst (Pd/Sn) is absorbed during activation. The etching may not be able to create cavities throughout the part which leads to non-uniform or localized deposition of Cu leading to higher resistance.”
5. Conductivity varies because of non-uniform distribution and different size of Cu in each route. Also, conductivity improves with the deposition time.
6. After electroplating good and uniform deposition occurs in route 1(Chromic acid route) instead of such poor conductivity after electroless plating.
7. Route 2 (Al-C pasted route) provides better and thick deposition of copper after electroplating at the same operating condition. The only problem of shell cracking and non-uniform deposition of copper at edges occurs which can be controlled by adjusting the parameters during plating.

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