Environmental Friendly Electroless Copper Metallization on FDM Build ABS Parts

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Environmental Friendly Electroless Copper Metallization on FDM Build ABS Parts

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by

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based on research carried out

under the supervision of

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May, 2016
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May 25, 2016

Supervisor’s Certificate

This is to certify that the work presented in the thesis entitled *Environmental Friendly Electroless Copper Metallization on FDM Build ABS Parts* submitted by *Sushanta Kumar Sahoo*, Roll Number 214ME2276, is a record of original research carried out by him under my supervision and guidance in partial fulfillment of the requirements of the degree of *Master of Technology* in *Mechanical Engineering*. Neither this thesis nor any part of it has been submitted earlier for any degree or diploma to any institute or university in India or abroad.

Siba Sankar Mahapatra
Professor

Dedicated to

My Parents

And

Sweet nephew "Milu"

Sushanta Kumar Sahoo

Declaration of Originality

I, *Sushanta Kumar Sahoo*, Roll Number *214ME2276* hereby declare that this thesis entitled *Environmental Friendly Electroless Copper Metallization on FDM Build ABS Parts* presents my original work carried out as a postgraduate student of NIT Rourkela and, to the best of my knowledge, contains no material previously published or written by another person, nor any material presented by me for the award of any degree or diploma of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela or elsewhere, is explicitly acknowledged in the dissertation. Works of other authors cited in this dissertation have been duly acknowledged under the sections "Reference" or "Bibliography". I have also submitted my original research records to the scrutiny committee for evaluation of my dissertation.

I am fully aware that in case of any non-compliance detected in future, the Senate of NIT Rourkela may withdraw the degree awarded to me on the basis of the present dissertation.

May 25, 2016
NIT Rourkela

Sushanta Kumar Sahoo

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Abstract

Environment- friendly electroless metallization of copper (Cu) on acrylonitrile-butadiene-styrene (ABS) parts was studied in which the parts are fabricated by fused deposition modelling (FDM) route of rapid prototyping (RP) process. This metallization process eliminates etching as well as the use of high cost palladium (Pd) for activation. For surface preparation aluminium (A)-enamel paste was used. Four different acidic baths were used for electroless Cu deposition and these are 15 wt% copper sulfate ($CuSO_4$) with 5 wt% of individual hydrofluoric acid (HF), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), nitric acid (HNO_3) and acetic acid (CH_3COOH) with different deposition time at room temperature. After successfully deposition of Cu on ABS surfaces in different baths, the electroless Cu deposition on ABS surfaces were characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS). Adhesion assessment of samples in different baths was studied. All baths were capable of formation of Cu crystals on ABS surface. However, better results in terms of electrical conductivity and uniformity in deposition surface is obtained in HF, H_2SO_4 and H_3PO_4 baths.

***Keywords*: ABS Parts, Fused deposition modelling (FDM), Electroless metallization, Conductivity, Adhesion**

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Chapter 1

Introduction

1.1 Background and Motivation

Since plastics have few favorable inherent properties like light weight, resistance to corrosion, high strength-to-weight ratio, good durability, low cost and easy to manufacture, they find wide spread application in industrial and domestics uses. Particularly, industries like automobile, electronics and aerospace extensively use parts made of plastics [1]. But plastic cannot be used directly while considering the properties inherent with metals like electrical conductivity, surface hardness, thermal conductivity etc. However, it becomes absolute necessary to obtain metallic properties on plastic surface to replace metals in industries. A development of conductive layer on a non-conductive material is known as metallization which combines the properties of both plastic as well as metal. Metallization is used to make decorative products, circuit boards and components used in automobile, aircraft, and shipbuilding industries [2-3].

Among different plastics, acrylonitrile-butadiene-styrene (ABS) parts can be metallized with aluminium (Al), gold (Au), copper (Cu), and silver (Ag). Among these, it is difficult to metallize copper (Cu) on ABS parts due to unavailability of suitable activation agent. Therefore, research is going on metallization of copper on ABS parts. There are varieties of metallization processes that include galvanic, flame-spraying, cladding, plating, vacuum metallization, electroless metallization etc. Among these, electroless metallization is the simplest and cheapest method in which metal is deposited over plastic parts by oxi-reduction reaction without the use of electric potential. In general, electroless deposition has certain steps required for metallization such as etching, neutralization, activation and acceleration. For etching, we are normally use chromic acid (Cr_2O_3) or sulphuric acid (H_2SO_4) [4-5]. But these acids are toxic and hazardous to environment. The conventional surface activation process used a solution containing $SnCl_2$ and $PdCl_2$ for sensitization and activation. Due to high cost of palladium, the process becomes very expensive.

Hence, environment friendly electroless metallization is preferred because it eliminates etching as well as the use of palladium (Pd).

1.2 Types of Metallization processes

There are varieties of metallization processes that include vacuum metallization, flame-spraying, cladding, plating, electroless metallization etc.

1.2.1 Vacuum Metallization

Vacuum metallization also called Physical Vapor Deposition or PVD, this innovation is generally used for thin aluminium layer plating over plastic products. The outside and within the part can be covered; be that as it may, in the last case a plastic layer secures the metal covering. The process is totally physical including high-temperature vacuum vanishing took after by buildup. So as to get a polished and reflective covering, there are various examples such as novelties, LED lighting products, interior automotive bezels, novelties, cosmetics, fish lures, point of purchase displays and reflectors. There is also wide variety of household and electronic products.

1.2.2 Electrolytic Plating

Electrolytic plating or electroplating is the procedure of keeping a metallic layer on a conductor with the assistance of an electric current. Before the metallization of a plastic, the plastic surface would to be first made conductive by any technique and after that exclusive would it be able to be electroplated. The parts to be electroplated is submerged in an metal salt solution associated with a present source and goes about as the cathode and another channel produced using the same metal as that of the metal salt is submerged in the bath which serves as the anode and in this manner the circuit is finished. Current streams from the cathode to the anode and the electrons stream the other way and are therefore stored in the cathodic workpiece. The anode gets dissolves during this process and stock up the bath.

1.2.3 Flame and Arc Spraying

These procedures are ease forms where a handheld or programmed firearm is utilized to shower the fluid metal on the parts. A thick metallic layer is developed and the deposition rate is additionally high however the metal quality got is similarly low. The covering is permeable and the surface harshness is high generally.

1.2.4 Electroless Metallization

Electroless metallization is a procedure of metallizing non-conductive substrates without the utilization of electric power. Nickel and Copper are generally used for deposition by this process. In this procedure, the part surface is initially etched with a strong oxidizing agent who makes large voids over the surface for better adhesion. This increment in the surface range makes the surface porous and hydrophilic which helps for better holding between the stored metal and the plastic surface. After the etching process, the part is then activated with an activator generally palladium or stannous chloride is used. Then the activated parts are immersed into the electroless bath to get metallic surface.

1.3 Electroless Metallization

Among these different metallization processes, electroless is the simplest and cheapest one. In this process a thin metallic layer is deposited over the specimen surfaces with the help of oxi-reduction reaction without the use of electric potential. Fig. 1.1 gives some basic steps of electroless metallization.

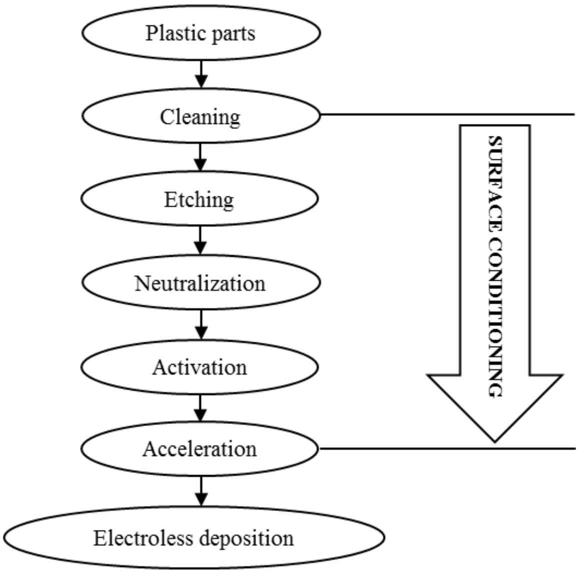


Figure 1.1: Steps involved in electroless metallization of plastics

I. Cleaning

Before surface conditioning in electroless process cleaning of parts is necessary for removing un-wanted materials. The prepared ABS parts were first cleaned by brushing and scour with sand paper. After that the parts are cleaned with soap and then rinsed thoroughly with water to remove oil, grease, dirt etc.

II. Etching

The most important stage in electroless metallization is etching. It is responsible for achieving suitable conditions for better adhesion between metal and plastic. The main purposes for etching are (i) increase of surface area which provides more contact area between metal and plastic, (ii) provides anchoring sites for contamination of activators into the surface, (iii) due to etching, some residual surface contamination get removed. Generally H_2SO_4 and Cr_2O_3 are used as etchant in etching process.

III. Neutralization

This stage is required to remove the oxidant used in the etching process. For this a reducing agent is used to avoid their inhabitation on the electroless deposition of metallic layer on plastic surface.

IV. Activation

This is also known as catalytic stage. In this stage the surface is contacted with an activator or catalysts. The activator particles get deposited into the micro cavities which were formed during etching and these particles initiate electroless metal deposition.

V. Acceleration

In this stage, the absorbed activator particles are activated and subsequently activation power also increases. An acid or base solution is used for accelerator which dissolves excess activator and removes it from the surface.

VI. Electroless deposition

This is the final stage in electroless process. The activated samples are immerged into the electroless bath. The electroless bath contains metal salts either in acid or basic medium. A thin copper layer is deposited over activated plastic surface after some hour. Before and after each stage rinses with water is essential for this metallization process.

1.4 Rapid prototyping

Among the different manufacturing systems such as selective, formative and additive, rapid prototyping (RP) is a group of techniques for additive manufacturing process. Rapid prototyping (RP) is a set of processes that is used to quickly fabricate any given scale model of a physical entity or assembly using three-dimensional computer aided design (CAD) data.

Rapid Prototyping was first used in the late 1980s to produce models and prototype parts. Today there are a lot of applications in rapid prototyping. Such as, (i) design 3D model, (ii) engineering planning and analysis, (iii) tooling and manufacturing. The industries like aerospace, biomedical, automotive, electronics and electrical products use this technology for their parts as well as design and analysis.

The different techniques used in RP fallows some basic steps:

STEP 1

The model of a component is generated on a computer-aided design-computer-aided manufacturing (CAD-CAM) system. This model represents the physical part of the component in an enclosed volume which is to be built. This data must be controlled to create the directions required to control the procedure in the last phase of really manufacturing the part. The input for beginning of RP process can be a point cloud acquired from reverse engineering (i.e. scanning of component) or 3D CAD models produced from different solid modelers.

STEP 2

In this stage, the built model is converted into STL (Stereolithography) file format. The STL file format is generated by tessellating 3D model and then the trassellated model is sliced as shown in Fig. 1.2. Then the standard format of this data is interpreted to the DP machine. Here we can change some parameters like part orientation, slice thickness, building time according to our requirement.

STEP 3

In this stage, the fabrication of physical model takes place. The process in this step varies according to different RP processes and with the basic RP principle i.e. layer by layer deposition.

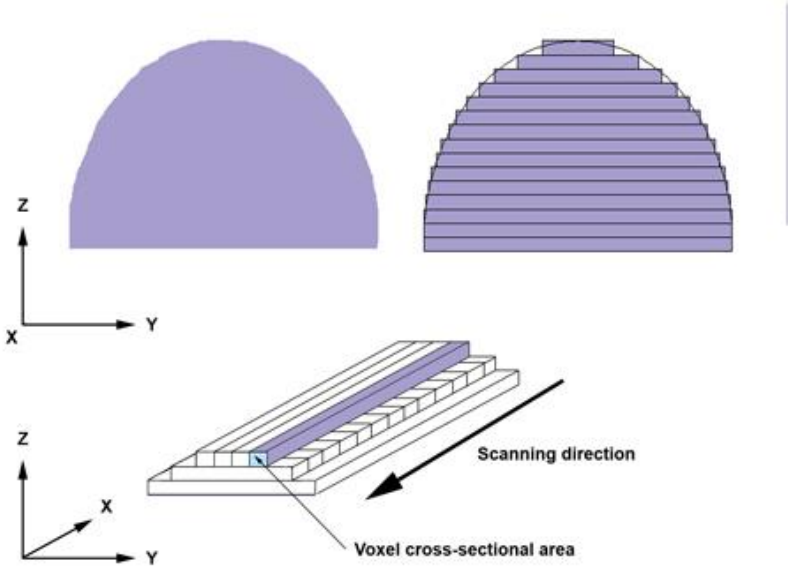


Figure 1.2: 3D Model Slicing.

1.5 Various rapid prototyping techniques

Based on the material that the prototype or part is built, the RP system is categorized into (i) liquid-based, (ii) solid-based and (iii) powder-based. There are several technologies under these three categories. Some of the well-known techniques are Stereolithography (SL), Laminated object manufacturing (LOM), Selective laser sintering (SLS), Fused deposition modeling (FDM), Multi jet modeling (MJM), 3D printing (3DP), and Solid ground curing (SGC).

1.5.1 Stereo-Lithography (SLA)

It is the primary and first commercial RP machine presented in mid 1980s by 3D frameworks, California, USA. It creates part from a curable liquid resin which is exposed to a laser beam that scan across the resin surface thoroughly and get solidified. After solidification, additional layer of liquid resin is exposed to the laser by lowering of previous solidified layer into a vat. This procedure is rehashed until all cross segments are fabricated into a solid model of the first CAD model. The platform is removed from the vat when all the slices have been followed by the laser and additional liquid resin polymer is washed off the finished part. The finished part is then at last cured into an ultraviolet oven.

1.5.2 Laminated object manufacturing (LOM)

It is a solid-based RP technique introduced in Helisys, California, USA which creates parts using an additive/subtractive process. Here the slices are cut is essential contour from roll of material by using a CO_2 laser beam. The previously deposited slice is attached with a new slice by using a hot roller, which is a heat sensitive adhesive. Apart from the cut undesirable material is removed and the remaining material is placed as a built material. After completion of one slice, the platform is lowered at distance of a layer thickness in negative Z-axis. Then another new layer of material is laid on the platform. This process is continued until the final product come out.

1.5.3 Selective laser sintering (SLS)

It is powder based rapid prototyping system, which used fine polymeric powder like polycarbonate, polystyrene, polyamide etc. The powder is feed by using a powder feed roller over the platform. After scanned by CO_2 laser, the temperature of the bed is rides just below its melting point. The laser is modulated on the selected area according to the part design. Once one slice is cured, bed is lowered and another new layer of powder is feed by the powder feed roller. This process is recycled once the model is completed.

1.5.4 Fused deposition modeling (FDM)

It is also a solid based rapid prototyping process in which a movable (X-Y movement) nozzle on to a substrate deposits molten polymeric material such as ABS, PLC plastics. Here the built material is heated slightly above its melting point temperature. As each layer is extruded, it bonds to the previous layer and solidify. The platform is lowered relative to the nozzle at a distance of layer thickness in negative Z direction and the next slice of the part is put down over the previous one. An additional nozzle is used to build a second material in support structure for complex hanging products. The support structure is broken away from the part once the part is completed.

1.5.5 Multi jet modeling (MJM)

In this RP process a print head enclosing 96 tiny nozzles in a linear array passes into the X-Y plane over the bed. A plane administers a bead of a thermo-plastic polymer where material is to be saved. Any number of the 96 planes can be enacted at the same time giving a quick administer rate when all planes are dynamic. The hot beads of material bond to the past cut of the part that has quite recently been printed. Slender bolster columns should likewise be developed cut by cut in the same material where they are required. At the point when the present cut of the part (in addition to cut of bolster columns) is finished, the stage is brought relative down to the print head and the following cut is printed. When all the cuts have been finished, the part is expelled from the machine and the bolster construction is severed.

1.5.6 3D printing (3DP)

A fiber of material is expelled out of a fine spout in a semi fluid state and stored onto a stage. The spout transfers in the X-Y plane so that the fiber is set down to frame a flimsy cross-sectional cut of the part. As every layer is expelled, it bonds to the past layer also, cement. The stage is then brought relative down to the spout and the following cut of the part is stored on top of the past cut. Another spout is utilized to expel an alternate material to develop bolster constructions for the part where required. When the part is finished, the bolster structures are split far from the part.

1.5.7 Solid ground curing (SGC)

This framework uses photo polymer resins and ultra-violet (UV) light. Information from the CAD model is utilized to create a cover which is set over the resin surface. At the point when the layer has been dried, the overabundance resin is rubbed away and spaces are filled with wax. The wax is chilled and the wax chips expelled. Another layer of resin is connected and the procedure is rehashed. The benefits of SGC are that the whole layer is hardened on the double lessening the part formation time, particularly for multi-part fabricates. Likewise, no post-curing is required. The burdens of this framework are that it is loud, expansive and should be continually kept an eye on. It squanders a lot of wax which can't be reused.

1.6 Literature Gap

In the early of 1939, metallization of plastic was started. Because of non-conductivity of the plastic is very difficult to get metal deposition in electroplating processes. There are many processes in which the surface of plastic was electroplated after making the surface conductivity by applying some conductivity paint. But this is not suitable in terms of uniform deposition as well as the complexity of products. So electroless metallization comes into picture, which is a very simplest process. For this surface conditioning is the most important stage, which is carried by some toxic etchant solutions. Generally in conventional etching, chromium trioxide (Cr_2O_3) is used as an etchant, which is human carcinogen and hazardous to environment. The conventional surface activation process used a solution containing $SnCl_2$ and $PdCl_2$ for sensitization and activation. Due to high cost of palladium, the process becomes very expensive.

The following research gaps have been found out after an exhaustive literature survey:

- The traditional chromic acid etching solution is substituted by some other acids like MnO_2, H_2SO_4 etc. But the process is not completely environmental friendly.
- There are lot of research is going on to avoid the use of high cost palladium, But the substituted activation solutions are more complex and not cost effective.
- In these conventional electroless process the thickness of deposited copper is very small. To increase the thickness electroplating is necessary.
- It is desired to optimization of deposition conditions including the molar concentration of acids and deposition temperature.

In the present study, Environment- friendly electroless metallization of copper (Cu) on ABS parts built by fused deposition modelling (FDM) route of rapid prototyping (RP) process is adopted. For surface preparation, aluminium (A)-enamel paste is used. Four different acidic baths are used for electroless Cu deposition. They are 15 wt% copper sulfate ($CuSO_4$) with 5 wt% of hydrofluoric acid (HF), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), nitric acid (HNO_3) and acetic acid (CH_3COOH) with different deposition time (i.e.2h, 24h, 48h and 72h) at room temperature. After successfully deposition of Cu on ABS surfaces in different baths, their electrical performance, surface characterization by scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS) and adhesion assessment are studied. Conductivity as well as Cu deposition is favorably developed in all electroless acid baths but better for HF, H_2SO_4 and H_3PO_4 baths.

1.7 Research Objectives

The objectives of this study have been outlined completely on the literature survey presented in Chapter 2. Literary works propose that metallization of ABS plastic can help in the lessening of utilization of metals in different applications. Due to simplicity as well as low coast, electroless metallization is preferred. This electroless copper metallization avoid the use of high cost palladium as well as toxic etchants.

To this point, the following are the objectives of this research work:

- To fabricate parts of ABS material through rapid prototyping route based on FDM process.
- To develop an electroless copper deposition method for metallization of ABS parts.

- Applications of this metallization on decorative products build by FDM.
- To test adhesion strength of metallization using a standard ASTM test method.
- To examine the appearance and elemental composition of the copper deposited on ABS surface with the help of scanning electron microscope (SEM) coupled with an energy dispersive X-ray spectronmeter (EDS).

1.8 Summery

The above chapter necessities of metallization over plastics are discussed. The chapter also gives brief idea about different types of metallization as well as different types of rapid prototyping techniques. Basic stages of electroless process and the objective of research work are discussed.

Chapter 2

Literature survey

2.1 Introduction

The current chapter highlights the different types of surface conditioning for electroless metallization and their demerits. To avoid the use of toxic etchants as well as high cost palladium different environmental friendly metallization processes are discussed.

2.2 Electroless metallization

Surface conditioning is very much essential for electroless metallization on plastic before deposition. Among the different surface conditioning operations, etching and activation are the most significant steps for electroless deposition especially for copper. Etching is a surface conditioning process which makes the surface the porus that increase the surface area of the part material and this is essential for good adhesion between metal and plastic. Activation stage is more important for electroless Cu deposition. In this operation the activator particles get deposited into micro cavities which were formed by etching stage.

Equbal and Sood [1] were used H_2SO_4 and CrO_3 acid separately for etching before electroless Cu deposition on ABS parts. For electroless plating they used four acdic baths namely HF, H2SO4, H3PO4 and CH3COOH with different deposition time. They found that conductivity as well as Cu deposition was obtained in all baths except CH_3COOH and better result in terms of uniform deposition in H2SO4 bath due to large availability of hydrogen. They observed that with increase in deposition time, conductivity as well as copper deposition was gradually increased. Among the two etching solution, they found that electrical performance and Cu deposition shows better result in Cr2O3 acid etchant in all baths. Another process of direct copper plating in ABS surface was investigated by **Gui-xiang et al. [2].** They used CrO_3/H_2SO_4 as etching solution with activation by Pd/Sn colloids solution and accelerated with solution containing NaOH, $CuSO_4.5H_2O$, and

EDTANa2 before copper electroplating. They found that Pd/Sn colloid catalyst have good dispersivity with narrow distributing of particle size. Due these smaller particles of catalyst, the dispersivity as well as the activation gives good result. They found that due the disproportionation reaction of Cu2O, metallic copper particles form on the Pd particles. So this results uniform copper deposition over the ABS parts due to the use of Pd/Sn colloid catalyst which having good dispersivity. **Luan et al. [3]** carried the chemical surface preparation for electroless metallization of stereo lithography polymers. For etching solution they used chromic acid and sulphuric acid. In that experiment they conducted the contact angle analysis for assessing the surface hydrophilicity to optimize the preparation process. The results show the applicability of this technology by subsequent metallization process. So it was as an efficient method for metallization of SLA polymers. **Hong et al. [4]** have investigated on autocatalytic electroless copper deposition by Palladium activation with dc magnetron sputtering of tantalum and tantalum nitrides (TaN_X) with different nitrogen content. They found that phase transformation on the deposited TaN_X film with the addition of small amount of nitrogen. With the increase of nitrogen flow rate, the electrical resistivity of the TaN_X deposited films first decreased for the nitrogen flow rate up to 10 standard cubic centimeters per minute (sccm) and then increased for nitrogen flow rate of more than 20 sccm. They also found that the density of palladium nuclei increased with the increase in nitrogen content and the grain size of TaN_X films decreased with the increase of nitrogen flow rate. **Ono et al. [5]** have studied the direct plating of copper on non-conducting resin substrate. Here Pd/Sn mixed catalyst was used to catalyzed the ABS resin substrate and was accelerated in copper ions solution before the direct plating. Due to the migration of direct Cu plating cubic Cu_2O crystals were formed with approximate size of 10-20 nm. The Cu_2O crystals were enhanced the copper deposition by the generation of additive free metallic copper.

The chemical etching of poly (ether ether ketone)/ carbon fiber composites by Cr_2O_3/H_2SO_4 solution performed by **Di et al. [6]** followed by electroless plating with copper ant after that electroplating with nickel. They have studied the effects of chemical etching time and temperature on the adhesive strength of the PEEK/Cf and Cu/Ni layers. They found that the C=O bond increased after chemical etching. More cracks and partially exposed carbon fibers appeared on the surface of the composite with increased in etching temperature and time. Also the electrical resistivity of the metallic layer increased with the increased in etching temperature and time. The composites with etched by temperature at 60^0C for 25 min and at $70\text{-}80^0C$ for more than 15 min have with stand four thermal shocks cycles without bubbling. **Debarnot et al. [7]** have investigated the influence of the polymer pretreatment before the electroless pretreatment. In this work they have used mixed Pd-

Sn colloidal solution for the activation of polyvinylidene fluride (PVDF) surfaces for copper deposition. Here plasma pretreatment was used in presence of N_2 or N_2/H_2 reactive gases. The different parameters to prepare the colloidal solution were reaction temperature, growth time of colloids, plasma processing conditions to obtained metallic palladium with high concentration and good adhesion of copper on the PVDF surface.

2.3 Electroless metallization without use of palladium

To avoid the use of toxic acids in etching process and use of high cost Pd in activation step, a lot of research is going to find environment friendly metallization. **Bazzaoui et al. [8]** investigated a process of copper plating on ABS surface by using polypyrrole. Before copper plating ABS parts were immersed in a solution of 0.3M pyrrole and 0.9M $FeCl_3$. After polymerization the parts were electroplated by using a bath containing $CuSO_4$ $5H_2SO_4$, H_2SO_4, CUFLEX 500 MU base with a 4 cm2 copper wire. This process replaces the use of etching solution as well as use of Pd/Sn catalyst and here the researcher used only one process i.e. the polymerization before electroplating. **Tang et al. [9]** have performed a new surface activation process for electroless Ni/Au plating on ABS plastics. It is Pd-free activation process for the electroless metallization on the ABS plastics that reduced the cost of production. Here the ABS plastic surface was first immobilized by Ni (0) nanoparticles by chitosan (CTS) film followed by deposition of NI and AU on the ABS plastics. Here Au layers were found on the top surface of the Ni layers with stable non-cyanide electroless Au plating. **Qian Ma et al. [10]** investigated a method which replace the use of high cost palladium for activation. They etched ABS parts with a solution containing MnO_2, H_3PO_4 and H_2SO_4 and before this they swelled the parts with tetramethylammonium hydroxide (TMAH), and 1-Methyl-2-pyrrolidinone (NMP) for better etching. Then the substrates were activated with CATAPOSIT44 solution before electroless Cu deposition and electroplated to increase Cu thickness. They studied the surface topography due to swelling and found adhesion strength of 1.04 KNm^{-1} for electroless copper film.

Tang et al. [11] have performed a new method of metallization Ni on ABS plastic. They have used a new palladium free and environmentally friendly surface characterization of Ni by electroless plating on ABS plastic. The surface activation was performed successfully by the immobilizing Ni nanoparticles as catalyst. From the SEM photograph of the Ni plated ABS plastic it was found that Ni nanoparticles were uniformly generated on the substrate with a glossy and smooth Ni-P plating layer. This environmentally friendly metallization process reduces capital cost as well as operational cost in large scale production. **LI et al. [12]** investigated an electroless copper deposition method without the use of etching and Pd/Sn catalyst. They used Al-C paste as a surface pretreatment process before electroless deposition in four different baths such as H2SO4, H3PO4, HNO3 and CH3COOH. They compared results with different deposition time at room temperature and at 60°C of different electroless baths. They founded that except HNO3 bath all baths are capable of formation of Cu crystals and conductivity. H2SO4 and H3PO4 baths gives better result compare to other baths in terms of size of Cu crystals and electrical performance due corrosion of Cu and over-etching of Al seeds by HNO3. They observed that except HNO_3 bath and better result at 60°C compare to room temperature. **Shu et al. [13]** investigated an environment-friendly technics which substitute the use of Cr_2O_3 for etching as well as Pd/Sn catalyst for activation. They used a solution of sulphuric acid and magnesium oxide (H_2SO_4-MnO_2) as an etching solution. They also observed that copper can be successfully deposited on ABS parts by using $CuSO_4$ and with reduction of DMAB (dimethylamineborane, $(CH_3)_2NHBH_3$) which indicates that this process can replace the use of high cost palladium in activation process. They measured the adhesion strength with different temperature and get average adhesion of $1.31 KNm^{-1}$ at 50°C. **Naruskevicius et al. [14]** investigated a Co-based surface activator for electroless metallization of copper on ABS surface. They proved that with the use of colloidal cobalt solution, Co ions can be seeded into the ABS surface which can be able to initiate electroless copper deposition without the use of high cost palladium. They found that due to the presence of a small amount of Cu2+ ions in the colloidal Co-based solution, which catalyzes the reduction based on the dielectric surface producing Co (0) seeds which initiate electroless copper deposition.

A new surface treatment method was developed by **Magallon-Cacho et al. [15]** which can avoid the use of environmental unsuitable CrO_3. In this method they used photocatalytic reaction of TiO_2 on ABS surface. They founded that due to generation of TiO_2 nanoparticles on ABS surface 30µm thick Cu can be developed with excellent adhesion strength. **Luo et al. [16]** investigated a method of copper deposition on PC engineering plastic. They developed a new method of activation process that replace the conventional sensitization and activation (i.e. use of high cost palladium) stages by using aqueous solution of nitric acid, hydrogen peroxide and NH_4F. In that mechanism they analyzed that the reactant (Cu2+) present in the electroless solution was distributed and absorbed by the plastic parts. At a result they founded similar morphology of copper layer as compare to conventional pretreatment process.

2.4 Summary

From the above literature survey different surface conditioning process for electroless are studied. For etching, normally chromic acid (Cr_2O_3) or sulphuric acid (H_2SO_4) are used. But these acids are toxic and hazardous to environment. The conventional surface activation process used a solution containing $SnCl_2$ and $PdCl_2$ for sensitization and activation. Due to high cost of palladium, the process becomes very expensive. Hence, respecters found some environment friendly electroless metallization is preferred because it eliminates etching as well as the use of palladium (Pd).

Chapter 3

Experimentation

3.1 Introduction

FDM route in rapid prototyping has significant advantages over other processes while considering cost of tooling, fabrication of complex shape parts and flexibility. In general electroless metallization process, etching is required for surface conditioning. Here aluminium enamel paste was used for surface preparation as well as for activation for copper deposition. The flow chat for this metallization process and the detail procedure is described below. After successfully deposition of copper crystals on ABS surface, the samples are subjected to various test and observations such as electrical resistance measurement, adhesion test, thickness measurement, SEM/EDS analysis.

3.2 Materials

The material used for sample fabrication is acrylonitrile butadiene styrene (ABS M30) of chemical formula (C_8H_8 C_4H_6 C_3H_3N)m. It is a carbon chain copolymer which contains 90-100% acrylonitrile/butadiene/styrene (Fig. 3.1) resin and also contains mineral oil (0-2%), tallow (0-2%) and wax (0-2%). The mechanical, physical and thermal properties of commercially available extruded and moulded ABS are shown in Table 3.1.

For surface preparation Aluminium (Al) powder (avg. particle size 20 micron), carbon (C) powder and enamel paint are used. For preparation of different copper electroless bath solutions the following chemicals are used such as copper sulfate ($CuSO_4$), hydrofluoric acid (HF), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), nitric acid (HNO_3) and acetic acid (CH_3COOH).

Table 3.1: Properties of ABS plastic

Properties	Unit	Extruded	Moulded
Physical properties			
Density	g/cm^3	0.350 - 1.26	1.02 - 1.17
Viscosity	cP	155000 - 255000 (Temperature 240-260°C)	1.16e+6 - 1.52e+6 (Temperature 240-260°C)
Moisture absorption	%	0.150 - 0.200	0.000 - 0.200
Mechanical properties			
Ultimate Tensile Strength	MPa	27.0 - 52.0	28.0 - 49.0
Yield Tensile Strength	MPa	20.0 - 62.0	13.0 – 65.0
Modulus of elasticity	GPa	1.52 – 6.10	1.00 – 2.65
Rockwell Hardness		90.0 – 121	86 - 115
Flexural Modulus	GPa	1.20 – 5.50	1.61 – 5.90
Elongation at Yield	%	0.620 – 30 0	1.70 – 6.00
Flexural Yield strength	MPa	28.3 – 81.0	40.0 - 111
Charpy Impact, Notched	J/cm^2	0.900 – 5.00	0.400 – 14.0
Thermal properties			
Co-efficient of thermal Expansion (linear)	µm/m-°C	68.0 – 110	0.800 - 155
Thermal Conductivity	W/m-K	0.150 – 0.200	0.128 – 0.200
Glass Transition Temperature	°C	108 – 109	105 - 109

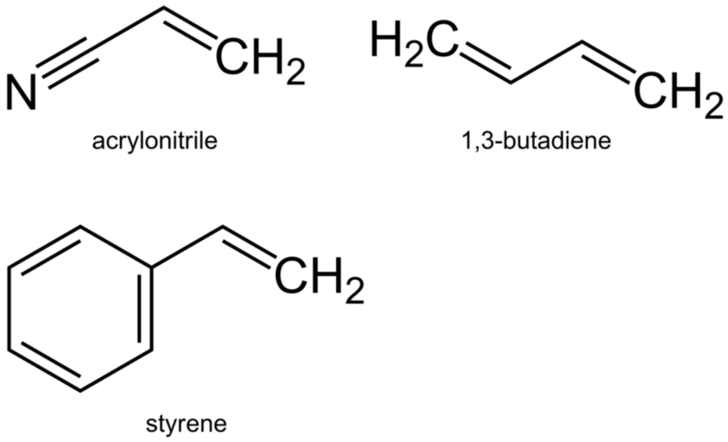


Figure 3.1: Monomers in ABS polymer

3.3 Part Fabrication

The parts were fabricated through rapid prototyping route based on FDM process. The 3D models of specimens are generated by CATIA V5 solid modeling software. After that the 3d parts are exported into insight software to convert into STL (stereolithography) file. After the STL file data send to the FDM software of machine FORTUS 400.

The machine is developed, intended and marketed by Stratasys Inc., 7665 Commerce Way, Eden Prairie, MN 55344, U.S.A. In assessment to the other machines like FORTUS 250mc, 260mc and 360mc, the 400mc offers a larger build chamber (355x254x254 mm). It can use a variety of build materials like ABSi, ABS-M30, ABS-M30i and Polycarbonate (PC). It uses a soluble support material for the ABS based materials and a separate support material for PC. Even though the support material is soluble for ABS, it can still be broken away by hand if the size is small. The parts can be built in four different layer thicknesses which are 0.33 mm, 0.254mm, 0.178mm and 0.127mm. The machine has two auto load model material and support material containers with 14912223 cubic mm of material in each of the four containers.

The material is heated over its solidify temperature by a heated (liquefier) on the administering head and expelled in a semi liquid state on a formerly kept material onto the fabricate stage taking after the outlined instrument way. The head is connected to the gantry that moves the head in the X and Y headings when fabricating a section. The XY framework get together is situated under the top hood of the machine. The whole gantry is outside of the fabricate chamber. Just the base of the head distends into the construct chamber. The fabricate platform travels along the Z course. The drive movement are given to specifically move the fabricate stage and administering head in respect to each other in a foreordained example through drive signals contribution to the drive engines from Computer aided design/CAM framework. For making complex hanging parts we are using support material which is driven by another nozzle as shown in Fig. 3.2.

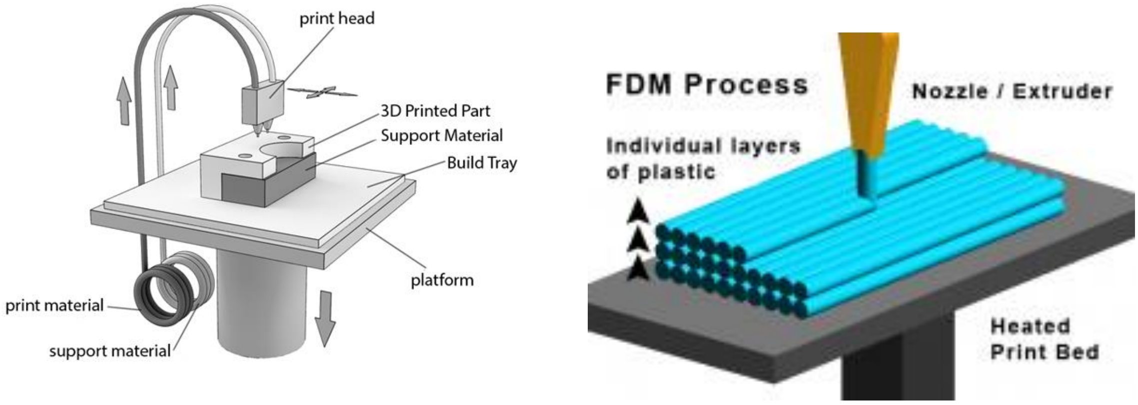


Figure 3.2: Schematic diagram of fused deposition modelling.

3.4 Experimental Procedure for Metallization

An environmental friendly electroless copper metallization is purposed. This purposed methodology is free from toxic hazardous Cr2O3 etching as well as high cost palladium activation. The steps involved in this metallization process are shown in Fig. 3.3.

3.4.1 Cleaning

Before surface conditioning in electroless process cleaning of parts is necessary for removing un-wanted materials. The prepared ABS parts were first cleaned by brushing and scour with sand paper. After that the parts are cleaned with soap and then rinsed thoroughly with water to remove oil, grease, dirt etc. for better adhesion of Al-C paste.

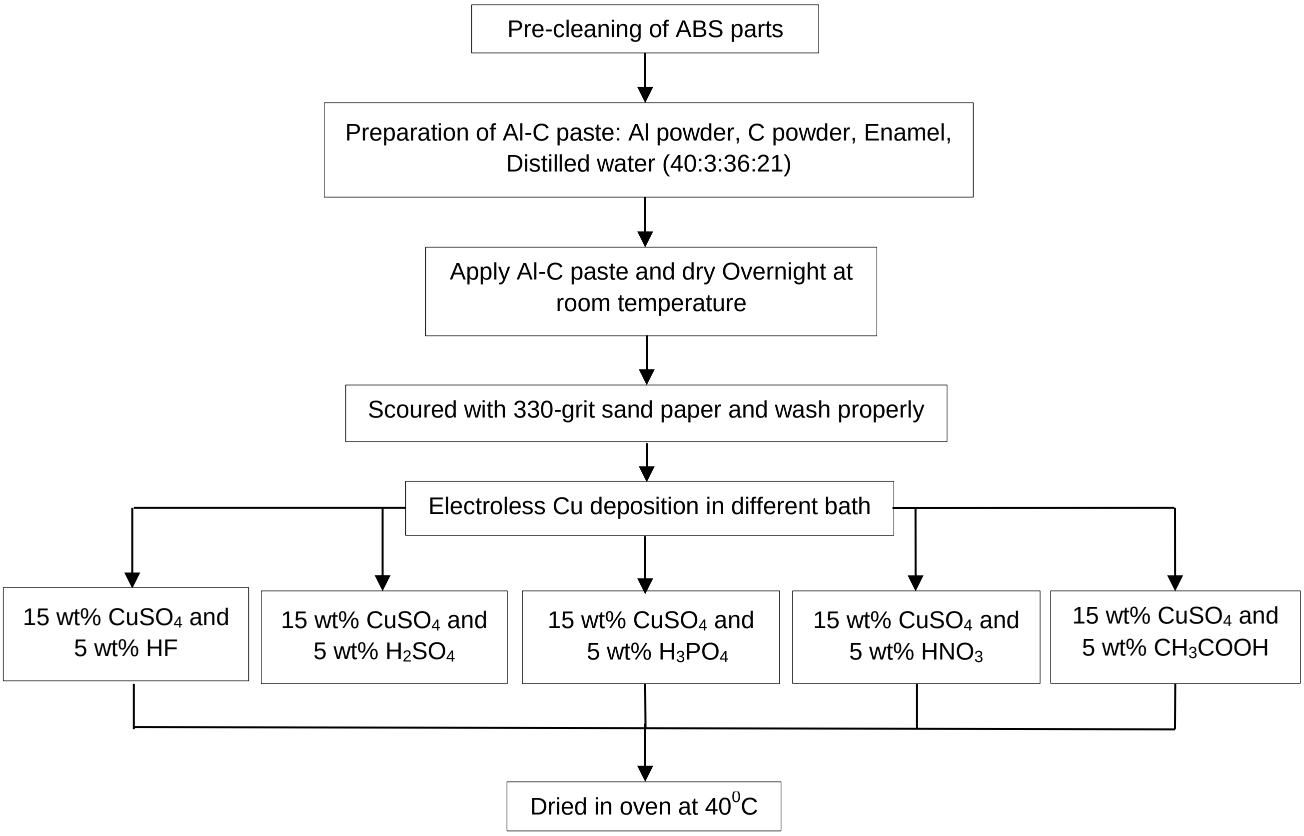


Figure 3.3: Flow chart of experimental procedure.

3.4.2 Preparation of Al-C paste and apply on ABS parts

First the different constituents such as Al powder, enamel, C powder and distilled water are taking separately with a weight ratio of 40:36:3:21. Then all the constituents are mixed together in a 400ml beaker. The mixture is stirred vigorously with the help of a magnetic stirrer for about 50 minutes till the mixture looks like paste. Then the paste was applied on ABS parts carefully with a fine brush. All the pasted ABS parts are allowed to dry through so that there will be no moisture on the surface through whole night at room temperature. The dried examples are then scoured with a 330-grit sandpaper precisely to have full introduction of aluminum over its external surfaces (Fig. 3.4). The parts are then rinsed thoroughly with water and dried in an oven for pre-heat to 40^oC for 30 minutes. This scouring compares to the etching stage required for ordinary electroless methodology.

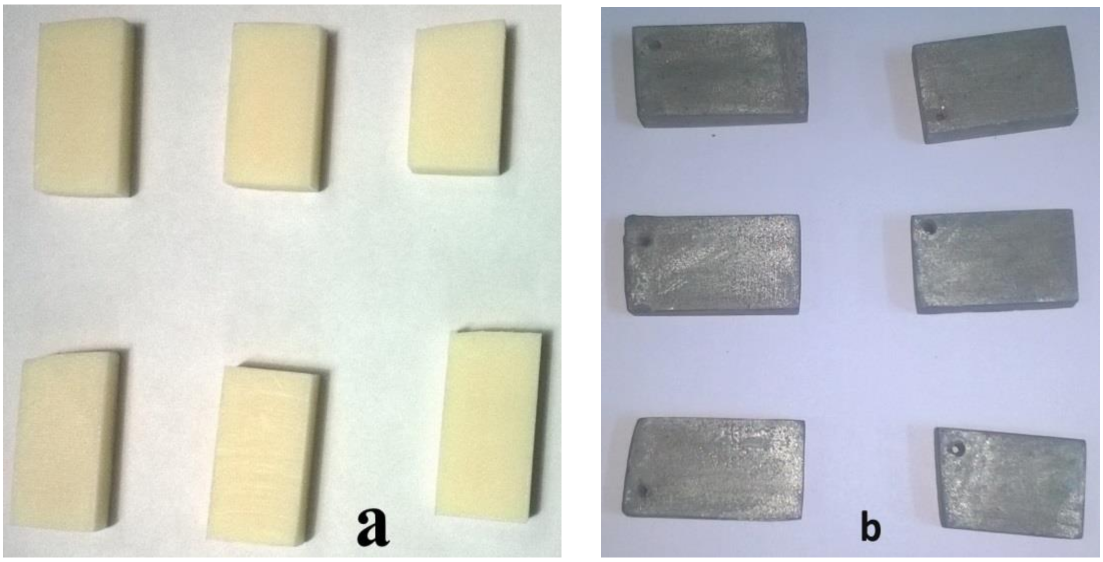


Figure 3.4: ABS Samples for experiment (a) before Al-C paste, (b) after scoured with sandpaper.

3.4.2 Electroless copper deposition

Different electroless bath for copper metallization were prepared with 15 wt% copper sulphate (CuSO4) and 5 wt% of individual acids such as hydrofluoric acid (HF), sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4), nitric acid (HNO_3), acetic acid (CH_3COOH). Then the pretreatment ABS parts were dipped into these electroless copper deposition baths for various times such as 2h, 24h, 48h and 72h. at room temperature as shown in Fig. 3.5. The Cu deposited ABS parts were rinsed with water and dried in an oven at 40^0C for 30 minutes. After that the parts were ready for electrical performance measurement. Fig. 3.6 shows copper deposited ABS parts after dried in an oven.

Figure 3.5: Parts immerged into various electroless baths.

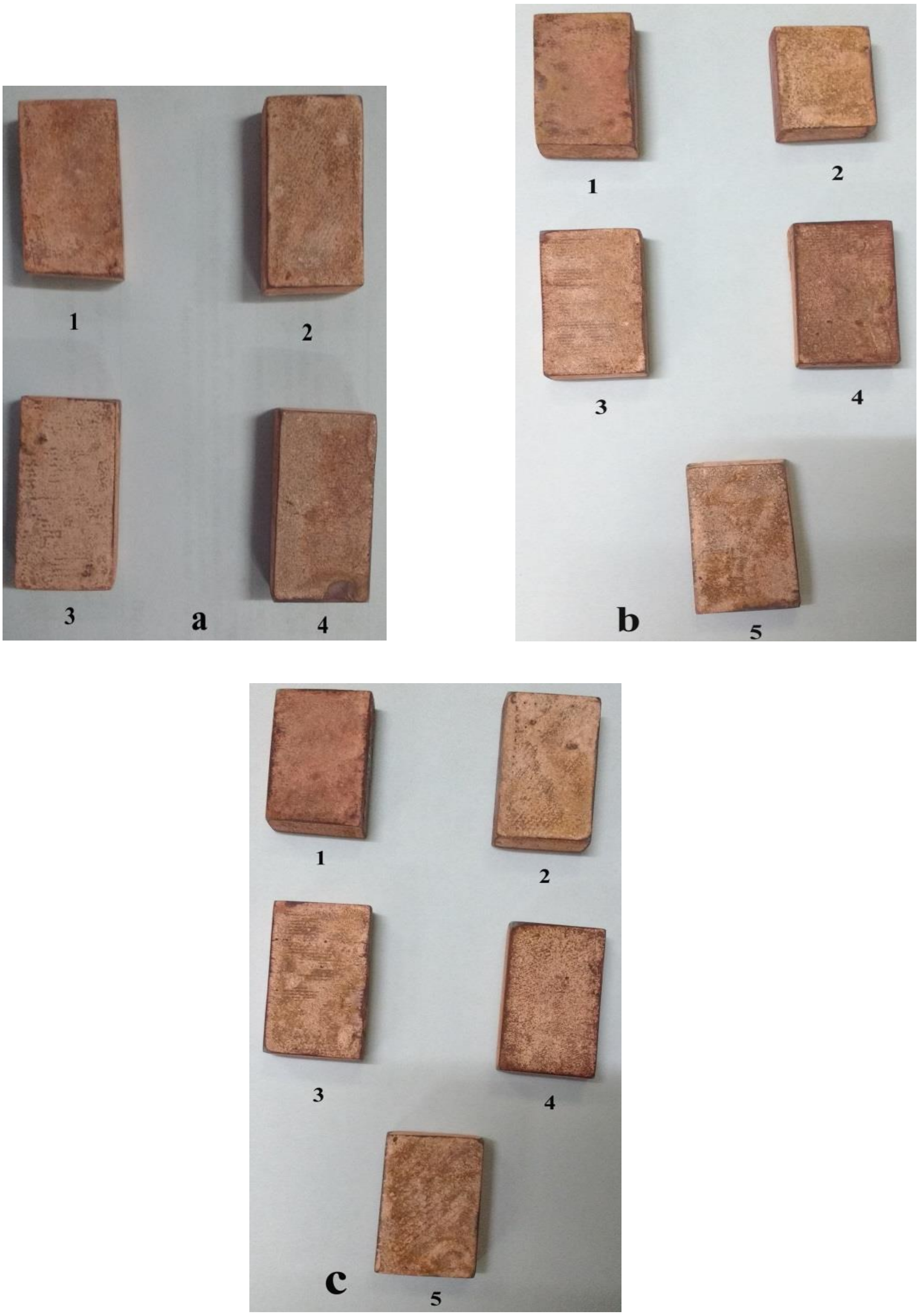


Figure 3.6: Successfully deposited Cu on ABS parts in different deposition time. (a) 24 h, (b) 48 h, (c) 72 h.

1, 2, 3, 4, 5 are respectively for HF, H_2SO_4, H_3PO_4, HNO_3 and CH_3COOH baths.

3.5 Analysis of Copper Deposited ABS Surface

After successfully deposition of copper on ABS surface various analyses are carried out to examine the electrical performance, copper crystal and adhesion for different acidic baths at different deposition time.

3.5.1 Electrical performance measurement

A 4-wire mode method was used to measure the resistance of copper coated ABS parts with the help of a Keithley 2100 digital multimeter for different electroless baths in different deposition times. The resistance was varied from point to point on the surface. So the average resistance ($\overline{R}$) as well as the standard deviation resistance (σ) was measured by taking different readings at different points according to Eq. 1 and Eq. 2. Here the average resistance was measured per area of the ABS surface with unit of Ω/cm^2.

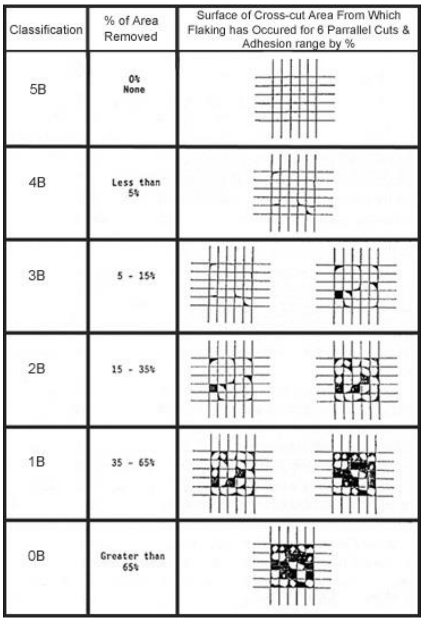
$$\overline{R} = \frac{\sum_{i=1}^{n} R_i}{n} \tag{1}$$

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

Where, R_i is the measured resistance at ith point on the surface and n is the total number of points taken for measurement.

3.5.2 Adhesion assessment

Adhesion assessment of electrolessly Cu deposited ABS parts for different baths was studied on the basis of standard ASTM test method (ASTM 3359-2) at room temperature [22]. Before start the test, the surface was cleaned thoroughly. With the help of a sharp knife two cuts each about 40 mm (1.5 in.) long are made on the surface that intersects near their middle with a smaller angle of between 30 and 45° between the lines. While making the incisions, the straightedge was used to cut through the coating to the substrate in one steady motion. The depth of cut should reach to the ABS surface, otherwise make a new cut, don’t overcut the previous one. The tape was placed at the crossing point of the cuts with the tape running in the same bearing as the littler edges. Smooth the tape into spot by finger in the territory of the entry points and after that rub immovably with the eraser on the end of a pencil. And a weight of 25 kg was placed on it for 5 min. The tape was evacuated by grabbing the free end and pulling it off quickly (not jerked) back upon itself at as near a point of 180° as could reasonably be expected. The resulting surfaces were examined after the tape was taken off and the adhesion performance was rated in accordance with the scale illustrate in Fig. 3.7.



Classification	% of Area Removed	Surface of Cross-cut Area From Which Flaking has Occured for 6 Parrallel Cuts & Adhesion range by %
5B	0% None	
4B	Less than 5%	
3B	5 - 15%	
2B	15 - 35%	
1B	35 - 65%	
0B	Greater than 65%	

Figure 3.7: Adhesion performance scale as per ASTM 3359-02 standard

3.5.3 SEM/EDS characterization

After electroless copper deposition, the surfaces of the specimens are observed directly by scanning electron microscope (SEM) JEOL JSM-6480LV as shown in Fig. 3.8. The JEOL JSM-6480LV is high-performance, scanning electron microscope with a high determination of 3.0nm. The low vacuum mode (which can be gotten to by the snap of a mouse), considers perception of examples which can't be seen at high vacuum because of extreme water content or because of a non-conductive surface. Its non-concurrent five-pivot eccentric stage with compeucentric turn and tilt can oblige an example of up to 8-inches in width. Energy-dispersive X-ray spectroscopy (EDS, EDX, or XEDS), sometimes called energy dispersive X-ray analysis(EDXA) or energy dispersive X-ray microanalysis (EDXMA) is used to examine the elementary analysis of the Cu deposited ABS surfaces for different electroless baths such as HF, H_2SO_4, H_3PO_4, HNO_3 and CH_3COOH.

Figure 3.8: Scanning Electron Microscope (SEM).

3.5.4 Thickness measurement

A Carl Zeiss Microscope as shown in Fig. 3.9 is used to measure the deposited copper layer thickness on ABS surface.

Figure 3.9: A Carl Zeiss Microscope.

3.6 Summary

This chapter highlights different stages of electroless copper metallization on ABS surface. For surface preparation, aluminium (A)-enamel paste is used. Four different acidic baths are used for electroless Cu deposition. They are 15 wt% copper sulfate ($CuSO_4$) with 5 wt% of hydrofluoric acid (HF), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), nitric acid (HNO_3) and acetic acid (CH_3COOH) with different deposition time (i.e.2h, 24h, 48h and 72h) at room temperature. After successfully deposition of Cu on ABS surfaces in different baths, their electrical performance, surface characterization by scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS) and adhesion assessment are studied.

Chapter 4

Copper coating over an artefact

4.1 Introduction

Due to the increase of industrial competition in the present scenario, rapid prototyping not only used for prototype and functional testing but also making patterns, final direct realistic product. So rapid manufacturing, rapid tooling comes into picture. Among the different rapid prototyping processes fused deposition modeling (FDM) is one of the cheapest methods with minimal wastage, easy material change and large build volume. There are some general applications of FDM such as models for conceptualization, patterns for tooling, prototypes for design and analysis, decorative products, customize car body parts, gear box etc.

4.2 Fabrication of an artefact

For the manufactured of the artefact prototypes, a real object was used. The artefact was washed properly with a dry cloth and was then scanned. A 3D scanner manufactured by FARO Technologies Inc., U.S.A, was used for this purpose which can scan 3D real objects and translate the scanned image to a .stl file format. The machine has 7-axis obtainability with infinite rotation for nonstop measuring. There are temperature sensors for higher precision and if the machine is idle for a prolonged period of time then there is an auto sleep mode to help save electricity. The 3D scanner used has been shown in Fig. 4.1.

Figure 4.1: FARO 3D scanner

After scanning of artefact, the file is converted to STL file and then fabricated through FDM route in rapid prototyping as shown in Fig. 4.2.

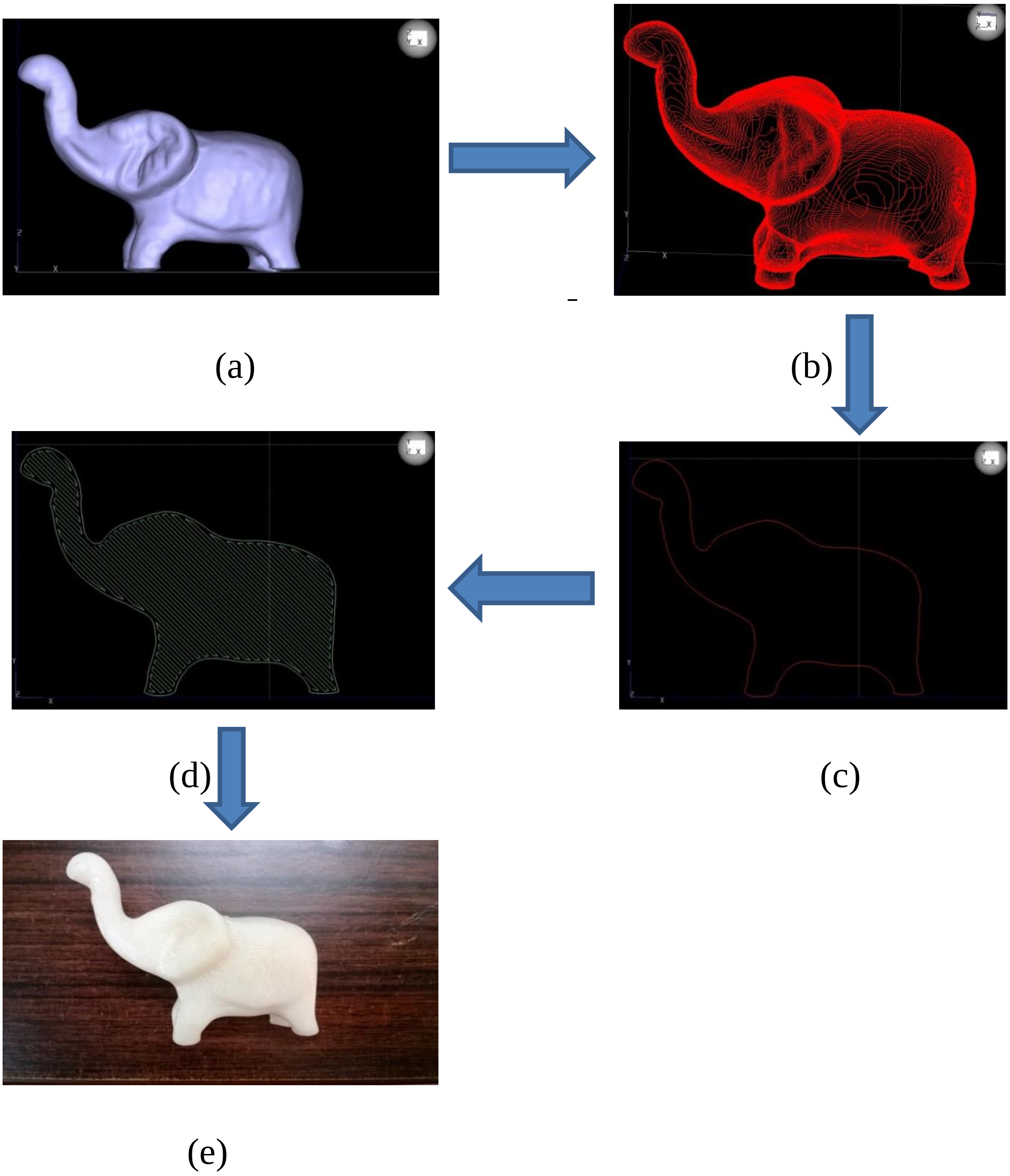


Figure 4.2: Steps involved in artefact fabrication. (a) stl format as visible in Insight 8.0 after scanning, (b) sliced model, (c) contour generation, (d) raster filling pattern, (e) final artefact.

4.3 Electroless Copper coating over an artefact

The same procedure is also followed for the metallization of product. Before metallization surface conditioning is required for this. The fabricated artefact is first scoured smoothly to make the surface smooth and remove dirt. Then wash toughly with soap and water. Al-enamel paste which is prepared as given in chapter 3 is painted with the help of a fine brush and let it to dry toughly. Then the product is scoured with a 330-grit sandpaper precisely to have full introduction of aluminum over its external surfaces. The artefact is then rinsed thoroughly with water and dried in an oven for pre-heat to 40^{o}C for 30 minutes.

For copper coating a electroless bath is prepared with 15 wt% copper sulphate (CuSO4) and 5 wt% of sulphuric acid (H_2SO_4). Then the pretreatment scoured artefact is dipped into the electroless copper deposition bath for 48h. The Cu deposited artefact is rinsed with water and dried in an oven at 40^{0}C for 30 minutes. Fig. 4.3 shows copper coated artifact made by ABS.

Figure 4.3: Elephant made by ABS after electroless Cu coating.

4.4 Summary

This chapter shows that copper is successfully coated in ABS plastic artifact which is made by FDM process in rapid prototyping.

Chapter 5

Result and Discussion

5.1 Electrical performance of copper coated ABS parts

Table 5.1: Electrical performance of electrolessly Cu deposited ABS parts for different acidic baths.

Deposition Time (h)	**Electrical Resistance**									
	HF		**H_2SO_4**		**H_3PO_4**		**HNO_3**		**CH_3COOH**	
	$\overline{R}$ (Ω/cm^2)	σ	$\overline{R}$ (Ω/cm^2)	σ	$\overline{R}$ (Ω/cm^2)	σ	$\overline{R}$ (Ω/cm^2)	σ	$\overline{R}$ (Ω/cm^2)	σ
2	0.157	0.064	>		>		>		>	
24	0.105	0.014	0.125	0.028	0.23	0.196	>		>	
48	0.102	0.01	0.105	0.014	0.12	0.026	1.2	1.083	3.107	1.998
72	0.102	0.01	0.105	0.014	0.107	0.016	0.2	0.104	0.109	0.078

“>” denotes there is no conductivity

Table 5.1 shows measured electrical resistance of copper deposited ABS parts for electroless bath such as HF, H_2SO_4, H_3PO_4, HNO_3, and CH_3COOH at room temperature after 2h, 24h, 48h, and 72h of deposition time. The conductivity was varied between points to points, hence average resistance per surface area (R) and standard deviation (σ) has been calculated. The resistance values after 2 h of deposition time for H_2SO_4, H_3PO_4, HNO_3, and CH_3COOH are so large (i.e. beyond the millimeter range) which indicated by the symbol “>”. The conductivity over Cu layer was developed slowly after 2 h of deposition time only for HF with resistance of 0.157 Ω/cm^2. There is dramatic increase in conductivity in HF, H_2SO_4 and H_3PO_4 baths after 8h, but not for HNO_3 and CH_3COOH baths. After 24 h of deposition time, the minimum resistance was found in HF an H_2SO_4

baths i.e. 0.105 Ω/cm^2 and 0.135 Ω/cm^2 respectively For H_3PO_4 bath it was 0.23 Ω/cm2. In other hand HNO_3 and CH_3COOH baths does not yield any conductivity even after 24 h of deposition time. There was very minor change in resistance for baths HF, H_2SO_4 after 48 h and 72 h with lowest resistance of 0.102 Ω/cm2 and 0.105 Ω/cm2 respectively. The measured resistance of H_3PO_4 bath was found to be 0.12 Ω/cm2 and 0.107 Ω/cm2 after 48 and 72 h respectively. The Cu deposition was still not uniform even after 48 h, but in some places average resistance was found to be 1.2 Ω/cm2. But after 72 h of deposition time it gives good conductivity with resistance of 0.107 Ω/cm2. On the other hand for CH_3COOH bath results resistance of 3.107 Ω/cm2 and 0.190 Ω/cm2 in 48 h and 72 h respectively.

The above result shows that there is a dramatically decrease in resistance in all baths except HNO_3 and CH_3COOH baths with increases in deposition hours and reach to the minim resistance. But for HNO_3 and CH_3COOH baths the minimum resistance is found after 72 h. as shown in Fig. 5.1.

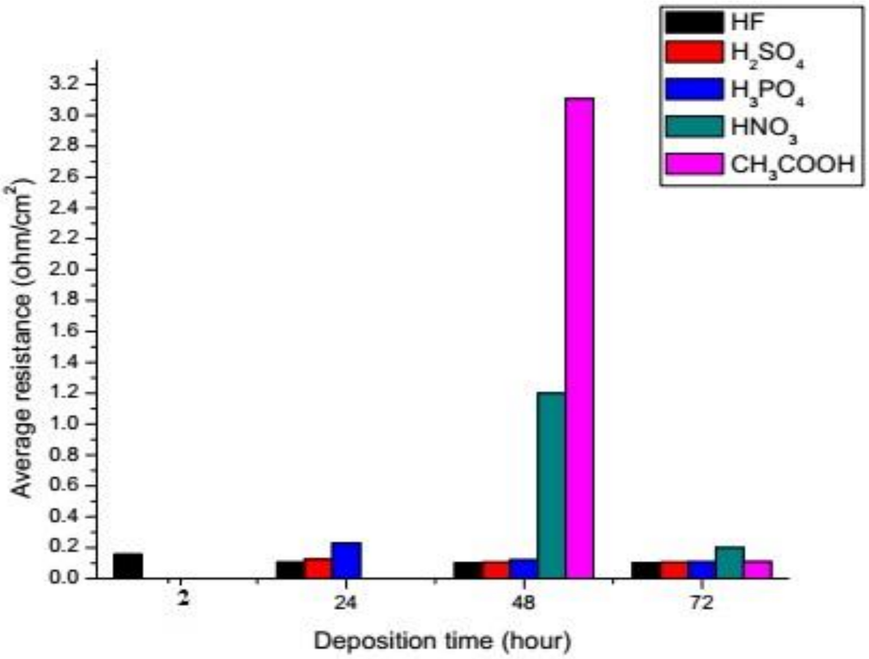


Figure 5.1: Average resistance variation with deposition hour.

5.2 Cu crystal formation on ABS surface

Fig. 5.2 shows the SEM image of copper crystals observed on flat ABS surfaces for HF bath after 2 h of deposition time at room temperature. Only HF bath is capable of formation of Cu crystal on ABS surface after 2 h among the other baths. The micro cavities shows uniformity as well as the size of the copper crystals was not good but this can be increase with the deposition time.

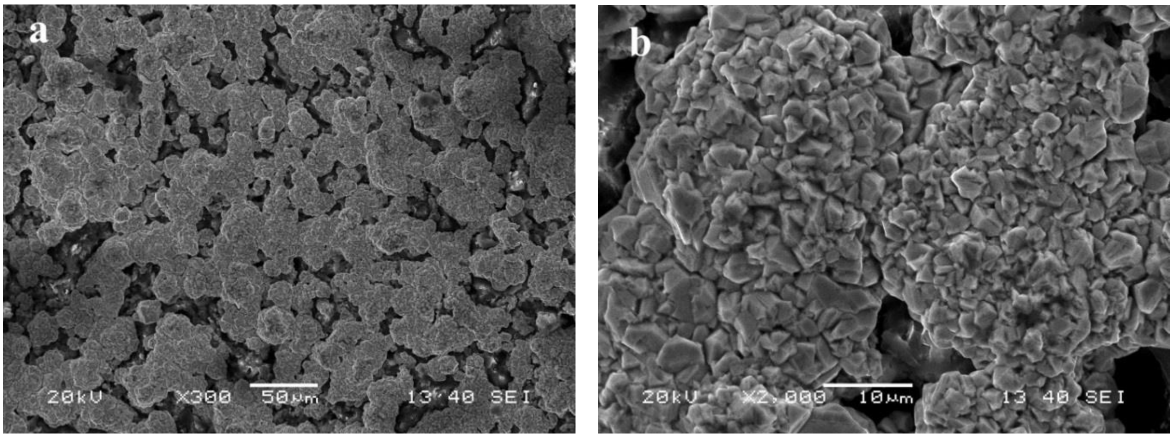


Figure 5.2: SEM image of Cu crystals electrolessly deposited on Al-seeded ABS surfaces after 2 h. for HF bath at room temperature (a) 300 magnification,(b) 2000 magnification.

Fig. 5.3 shows SEM image of Cu crystals electrolessly deposited on Al-seeded ABS surfaces bath at room temperature in 300 magnifications for HF, H_2SO_4, H_3PO_4, HNO_3 baths after 48 h and for CH_3COOH bath after 72 h. The copper crystals are closely combined with uniform copper deposition (i.e. the no void or are very small void size) for HF and H2SO4 baths as shown in Fig. 5.3. For H_3PO4 and HNO_3 baths small size voids are present in the same surface area, so the uniformity was not good as compare to HF and H_2SO_4 baths. 72 h of deposition time is required to achieve uniform Cu crystals on ABS surface for CH_3COOH bath.

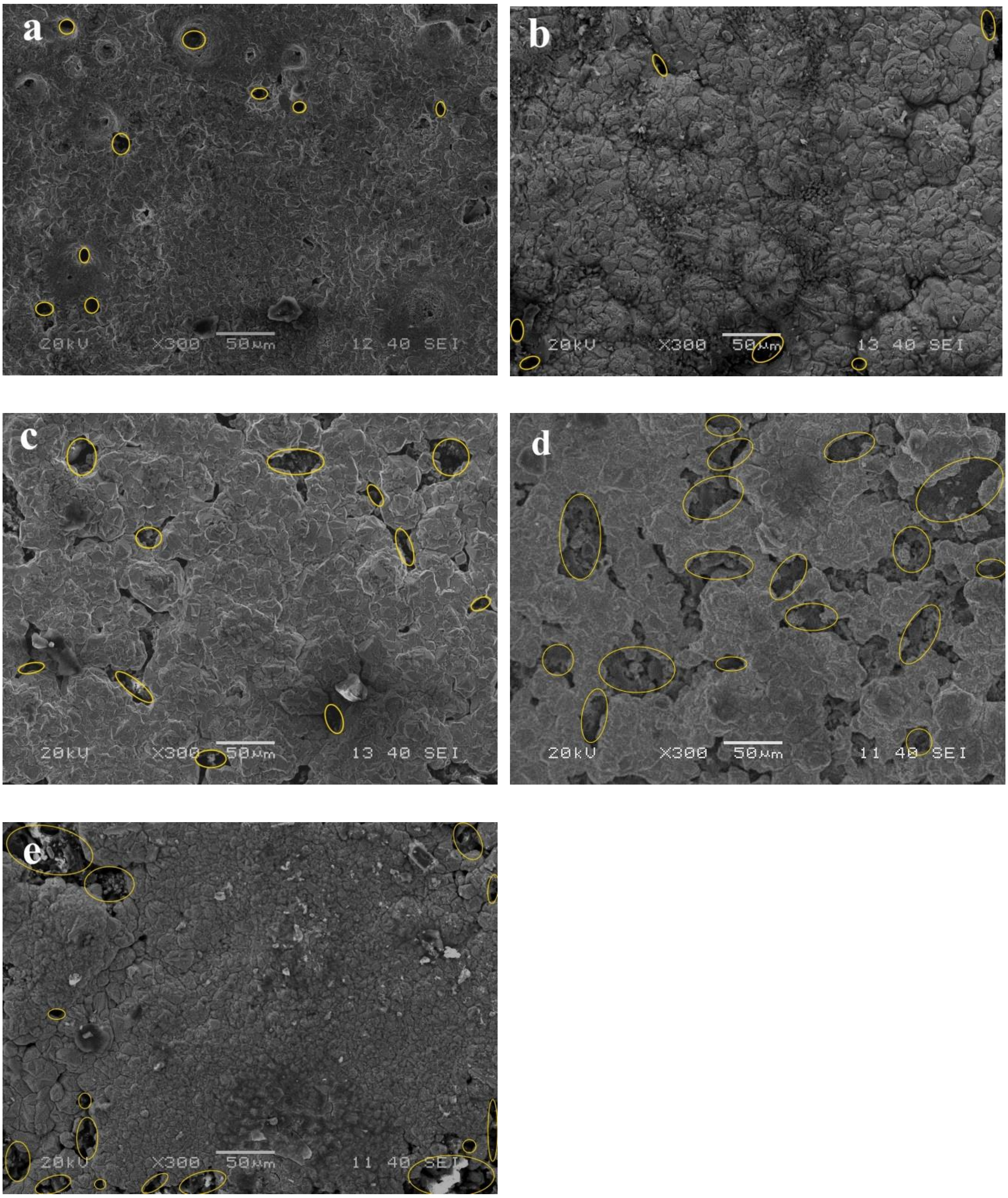


Figure 5.3: SEM images of Cu crystals electrolessly deposited on Al-seeded ABS surfaces bath at room temperature in 300 magnification (a) HF bath for 48 h, (b) H_2SO_4 bath for 48 h, (c) H_3PO_4 bath for 48 h, (c) HNO_3 bath for 48 h, (d) CH_3COOH bath 72 h.

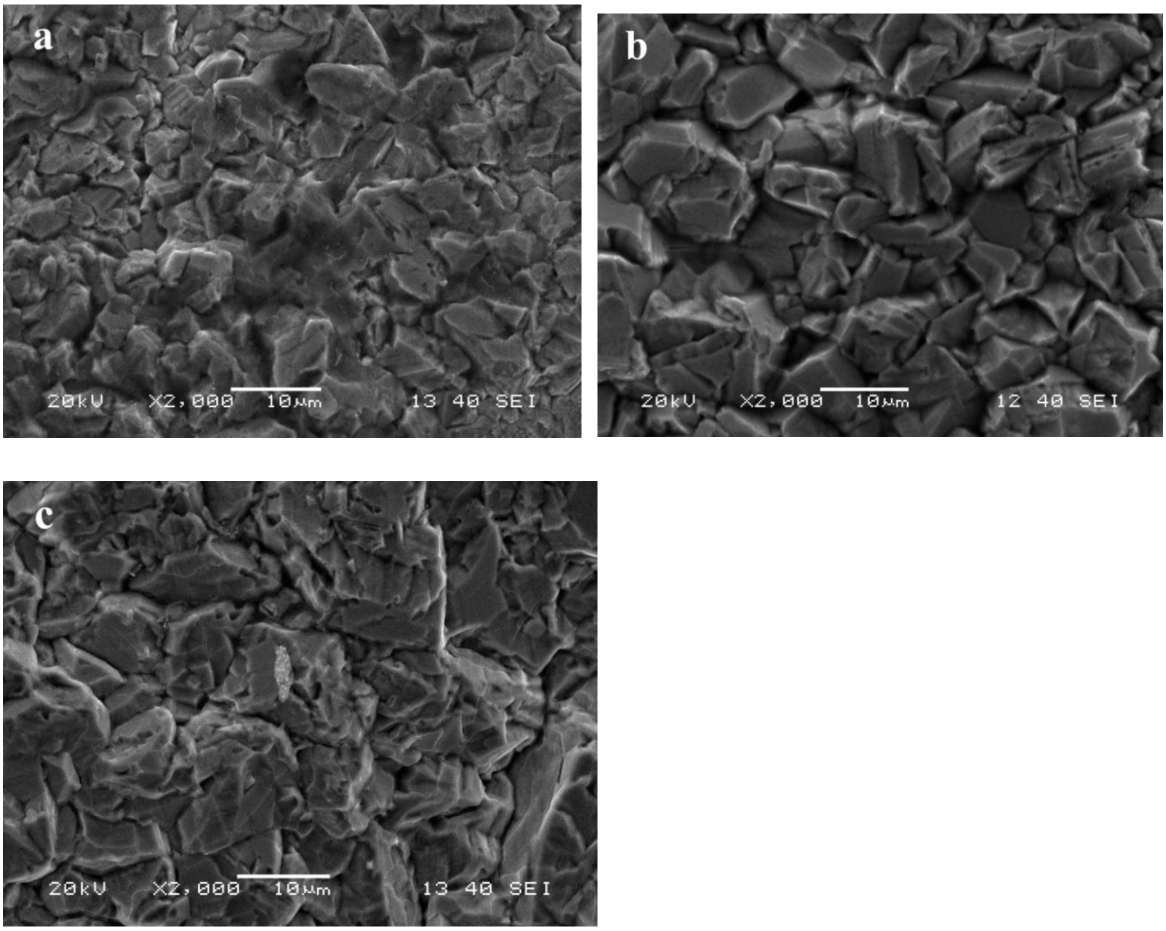


Figure 5.4: SEM images of Cu crystals electrolessly deposited on Al-seeded ABS surfaces after 24 h.at room temperature (a) HF bath, (b) H_2SO_4 bath, and (c) H_3PO_4 bath.

After 24 h of deposition time, uniform Cu deposition was observed in HF, H_2SO_4 and H_3PO_4 baths as the morphology shown in Fig. 5.4 with regular diamond pyramid structure. The uniformity as well as compactness of copper crystals is achieved after 24 h of deposition time for HF, H_2SO_4 and H_3PO_4 baths. But uniformity archived for HNO_3 and CH_3COOH baths after 48 h and 72 h respectively. As the deposition time gradually increases, the size of Cu crystals goes on increasing as shown in Fig 5.5. Here large uniform Cu crystals observed for HNO_3 and CH_3COOH baths (Fig. 5.5 c and Fig. 5.5 d). So after long deposition time due to the formation of large uniform Cu crystals on ABS surface metallic shining were observed.

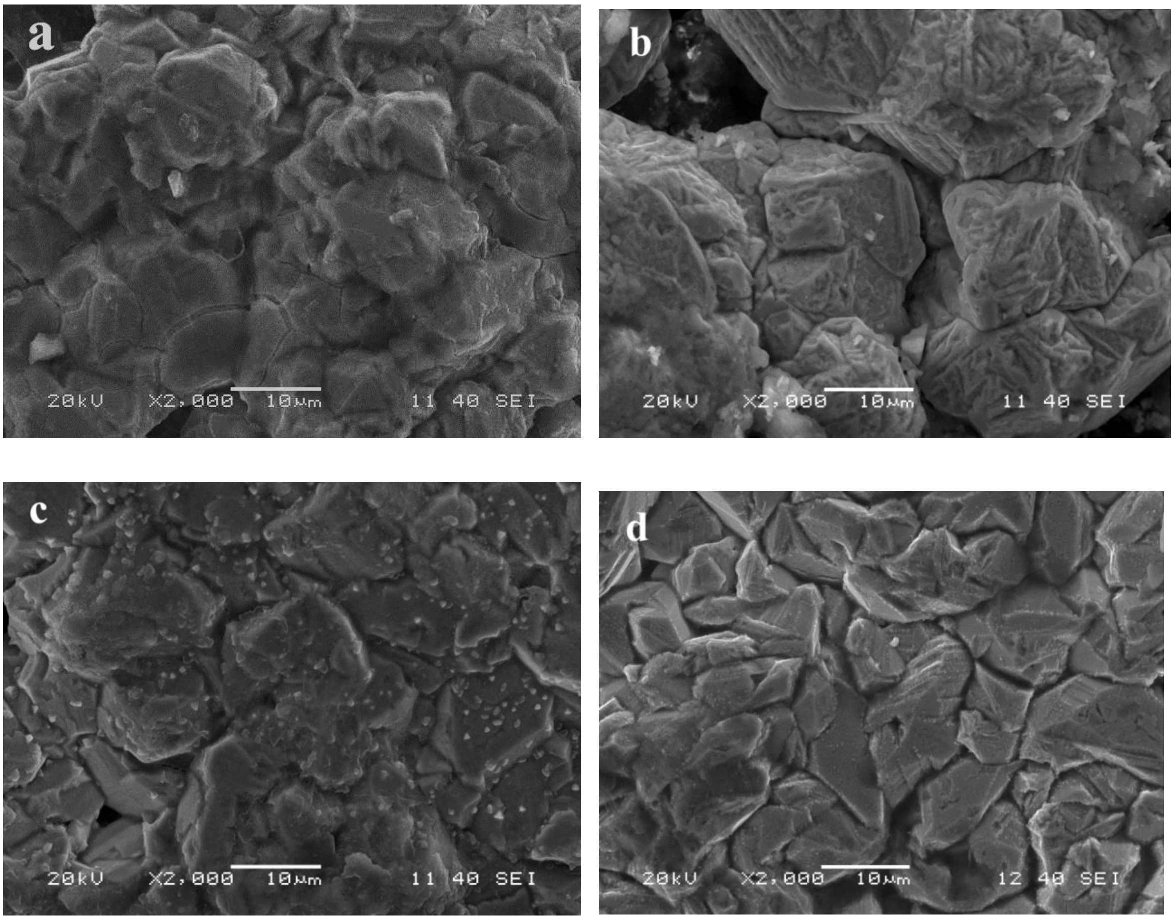


Figure 5.5: SEM images of Cu crystals electrolessly deposited on Al-seeded ABS surfaces after 24h.at room temperature (a) H_2SO_4 bath for 48 h, (b) H_3PO4 bath for 48 h, (c) HNO_3 bath for 48 h, (d) CH_3COOH bath 72 h.

5.3 EDS characterization

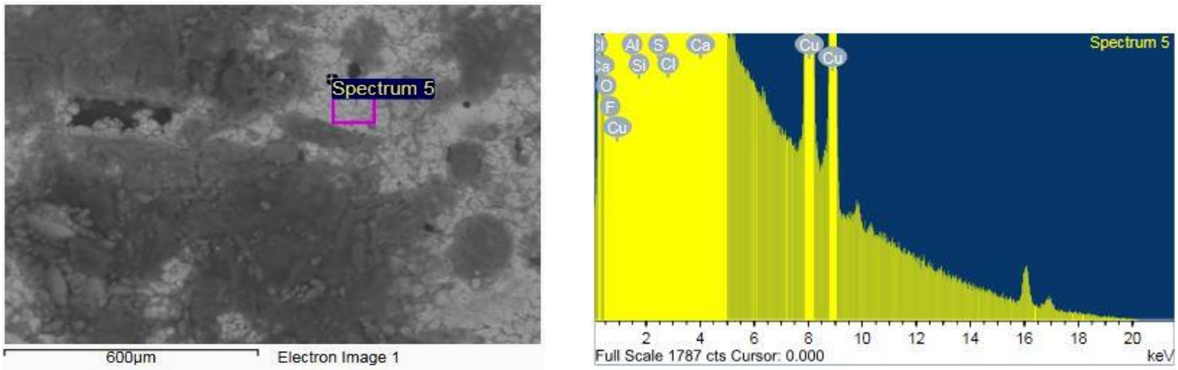


Figure 5.6: EDS spectra of Cu deposired ABS sample whose surface is prepared in HF bath.

Table 5.2: Elementary analysis of Cu coated ABS surface in HF bath.

HF Bath								
Element	O K	F K	Al K	Si K	S K	Cl K	Ca K	Cu K	Total
Weight%	11.55	3.25	1.44	0.33	0.92	1.02	0.38	81.11	100
Atomic%	31.36	7.44	2.32	0.51	1.25	1.25	0.41	55.47	

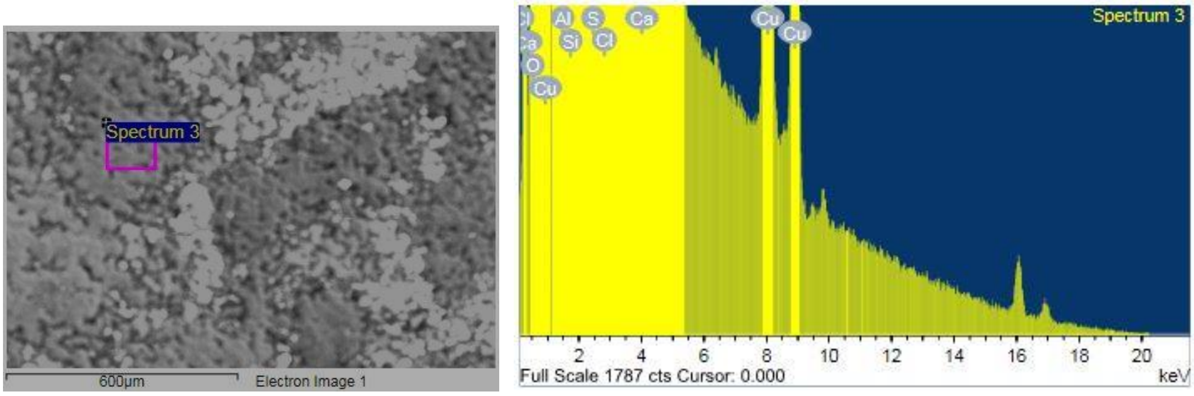


Figure 5.7: EDS spectra of Cu deposired ABS sample whose surface is prepared in H_2SO_4 bath.

Table 5.3: Elementary analysis of Cu coated ABS surface in H_2SO_4 bath.

H_2SO_4 Bath								
Element	O K	Al K	Si K	S K	Cl K	Ca K	Cu K	Total
Weight%	12.27	1.67	0.72	0.62	0.77	0.37	83.58	100
Atomic%	34.54	2.79	1.15	0.87	0.98	0.42	59.25	

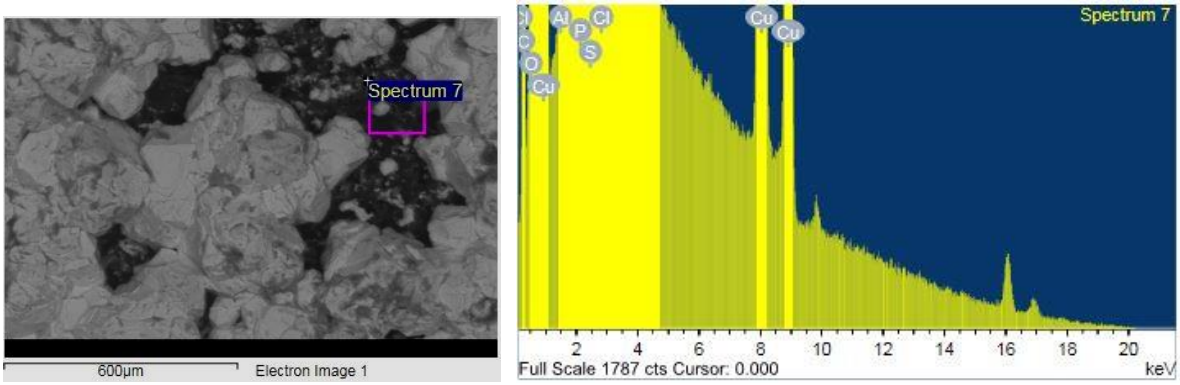


Figure 5.8: EDS spectra of Cu deposited ABS sample whose surface is prepared in H_3PO_4 bath.

Table 5.4: Elementary analysis of Cu coated ABS surface in H_3PO_4 bath.

H_3PO_4 Bath								
Element	C K	O K	Al K	P K	S K	Cl K	Cu K	Total
Weight%	15.09	6.75	1.33	0.19	0.23	0.17	76.24	100
Atomic%	42.66	14.32	1.68	0.21	0.24	0.17	40.73	

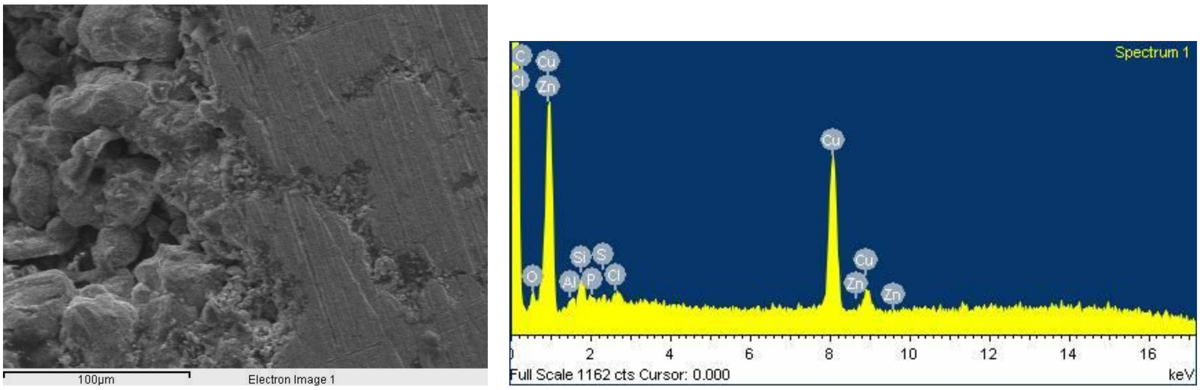


Figure 5.9: EDS spectra of Cu deposited ABS sample whose surface is prepared in HNO_3 bath.

Table 5.5: Elementary analysis of Cu coated ABS surface in HNO_3 bath.

HNO_3 bath										
Element	C K	O K	Al K	Si K	P K	S K	Cl K	Cu K	Zn K	Total
Weight%	14.98	4.9	1.49	3.49	0.94	0.67	1.22	70.69	1.61	100
Atomic%	42.19	10.36	1.87	4.21	1.03	0.71	1.17	37.64	0.83	

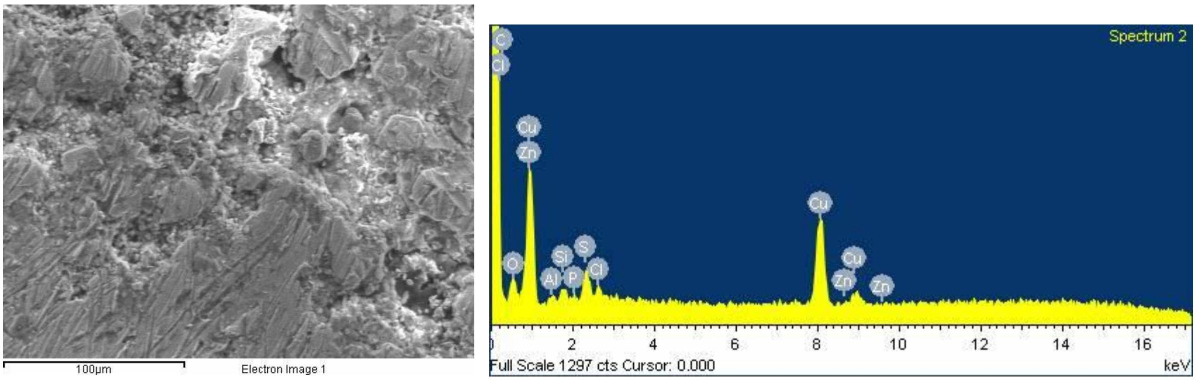


Figure 5.10: EDS spectra of Cu deposited ABS sample whose surface is prepared in CH_3COOH bath.

Table 5.6: Elementary analysis of Cu coated ABS surface in CH_3COOH bath.

CH_3COOH bath									
Element	C K	O K	Al K	Si K	P K	S K	Cl K	Cu K	Zn K	Total
Weight%	17.49	12.63	1.44	2.25	0.75	4.76	1.72	57	1.94	100
Atomic%	41.28	22.38	1.51	2.27	0.69	4.21	1.38	25.43	0.83	

The EDS spectra of electrolessly Cu deposited ABS samples in different baths at room temperature are examined as shown in (Fig. 5.6 to 5.10). For HF, H_2SO4, H_3PO4, HNO_3 the EDS is done after 48 h of deposition time and for CH_3COOH after 72 h. All elements on the surface are analyzed through EDS mapping by looking the peaks. The result shows that Cu is dominated the surface in all electroless baths, but considerable high in HF, H_2SO_4, H_3PO_4 and HNO_3 baths.

The elemental analysis of Cu deposited ABS surfaces are also carried out and the elementary compositions are shown in Table 5.2 to 5.6. For the HF and H_2SO_4 baths the Cu content appears to level off 81.11 and 83.58 weight % respectively. While for H_3PO_4 and HNO_3 baths, the copper content appears to a weight % of 76.24 and 70.69 respectively. Even after 72 h of deposition time the result foe CH_3COOH bath is 57.00 only. These results reflect the electrical performance of the samples. So the electrical resistance of CH_3COOH bath is high compare to others. The non-uniform and non-measurable resistance of HNO_3 bath samples is due to over etching of Al seeds by HNO_3. The comparison between weight percentages of copper with different electroless baths is shown in Fig. 5.11. Except CH_3COOH bath all are capable to yield more than 70 % weight percentage of copper over the ABS surface.

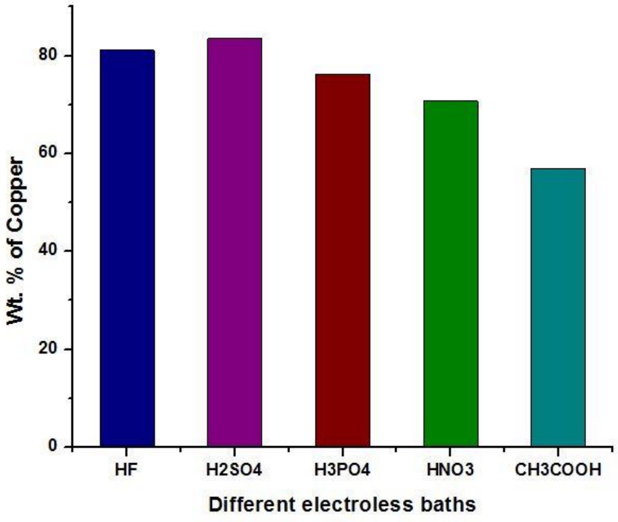


Figure 5.11: Wt % of copper for different acidic baths.

5.4 Thickness measurement of Cu deposited ABS parts

A Carl Zeiss Microscope was used to measure the deposited copper thickness on Al seeded ABS surface. The thickness was varied from 50 to 65 micron in different location on the surface. Fig.5.12 Shows the Al enamel paste and Cu layer clearly with Cu thickness of 64.04 micron. The Cu thickness is further increased by electroplating.

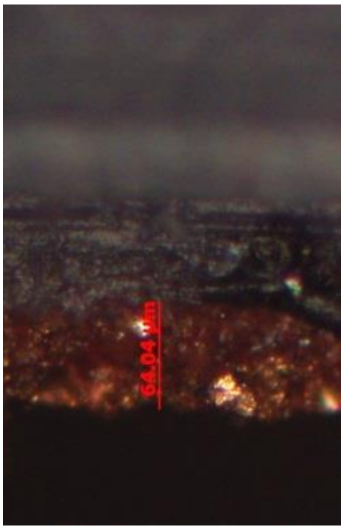


Fig.5.12: Thickness of Cu layer on ABS surface

5.5 Adhesion evaluation of Cu deposited ABS parts

Adhesion evaluation of the electrolessly Cu deposited ABS parts for different baths such as HF, H_2SO_4, H_3PO_4, HNO_3 and CH_3COOH was carried out based on ASTMD 3359-02 standard tape test as shown in Fig.5.12. The adhesion performance was rated according to the scale defined by ASTM D 3359-02 as given in Table 5.7. Except CH_3COOH and HF baths all samples yield a scale of 5 i.e. no removal of Cu and for CH_3COOH and HF it is 4 i.e. the removal is less than 5%. So this indicates excellent adhesion strength on Cu deposited ABS parts.

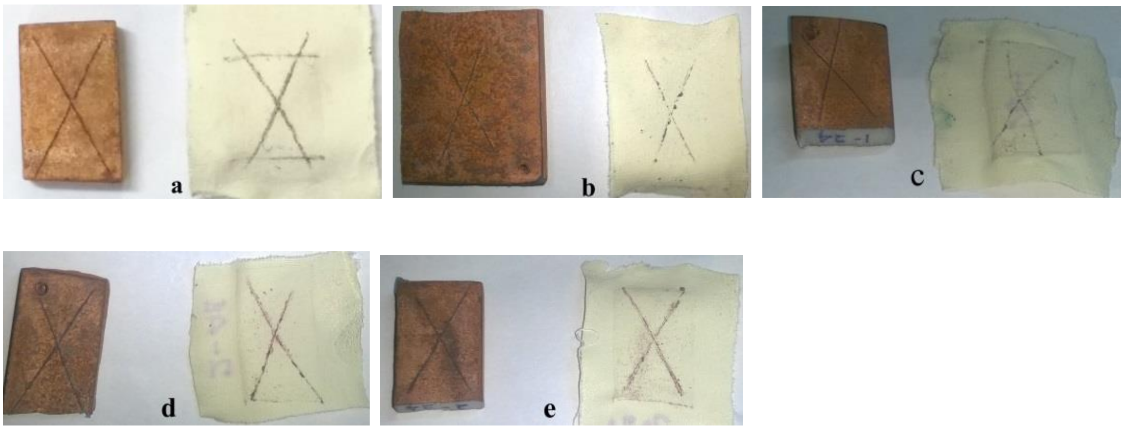


Fig.5.13: Standard tape test results of electrolessly Cu deposited ABS parts for different baths. (a) HF, (b) H_2SO_4, (c) H_3PO_4, (d) HNO_3 and (e) CH_3COOH.

Table 5.7: Adhesion performance analysis of electroless deposited Cu layers on ABS parts.

Deposition conditions	**Bath**				
	HF	**H_2SO_4**	**H_3PO_4**	**HNO_3**	**CH_3COOH**
Scale	4	5	**5**	5	4

5.5 Summary

Conductivity as well as copper appearances for different acidic baths are studied in different deposition time. HF, H_2SO_4, H_3PO_4 baths result better result compare to HNO_3 and CH_3COOH baths in terms of uniformity of copper deposition and conductivity. All baths result excellent adhesion strength over ABS.

Chapter 6

Conclusion

6.1 Summary of the findings

After carrying out a systematic study the following extrapolation can be summarized:

I. Electroless metallization of Cu on FDM build ABS parts has been studied with five acidic electroless baths namely HF, H_2SO_4, H_3PO_4, HNO_3 and CH_3COOH. All baths prompted development of Cu crystals on the Al-seeded ABS surfaces through this electroless metallization process.

II. Just the HF, H_2SO_4, H_3PO_4, and CH_3COOH baths were fit for creating conductive Cu layers on ABS to change over the non-conductive plastic surface into conductive because of large availability of hydrogen, while conductive surface was not uniform for HNO_3 bath, which was theoretically credited to the erosion of Cu and over-etching of Al seeds by HNO_3.

III. It was observed that the conductivity as well as size of Cu crystals varies from point to point on ABS surface and this improves with increase in deposition time for all baths. At room temperature, after 24 h of deposition time HF, H_2SO_4 and H_3PO_4 baths results maximum conductivity i.e. minimum resistance. But for HNO_3 and CH_3COOH baths the minimum resistance was achieved after 72 h of deposition time.

IV. Copper is successfully deposited on decorative product and results good adhesion. So the acidic baths developed in this study may provide more alternative options for plating of plastics.

6.2 Recommendation and Future scope

From the current work it was found out that future work can carried out in the following direction:

I. Optimization of deposition conditions including the molar concentration of acids and deposition temperature is desired.
II. How to overcome the corrosion of Al with HNO3, so that the conductivity for HNO3 bath can be improved.
III. Apply proposed metallization process for making an EDM electrode and compare the results with copper electrode.

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