3D Printing of Copper Filament for Layered Fabrication

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Abstract: - 3D printing also referred as additive manufacturing is the automated printing methodology for 3D designed models. The layer by layer additive manufacturing possesses numerous benefits right from innovative products to reducing wastage in production. Optimized metal production using non FDM methods is perhaps inevitable in the manufacturing industry, particularly for military and aeronautical areas. It is still a challenge to handle high processing temperatures and multiple metal materials. Printing metal or multiple metals in a substrate is not yet prototyped using any of the 3D printing processes. New metal composite filaments are invented for FDM printers, among which is the Copper-PLA filament. The filament is printed for micro thickness on a glass substrate, which is characterized using inverted type metallurgical microscope for applying in nano sensor fabrication. The average grain size measures 6.5 microns with a total feature count of 82 microns. The minimum feature circumference of particles are 0.075 microns. The porosity count is 119 or 0.04% of the total surface area.

Key-Words: - Copper, PLA, glass, 3D printing, porosity, grain size

1 Introduction

Traditional manufacturing or traditional subtractive techniques rely on the removal of material through cutting, milling and drilling. These results in significant wastage of material [8] and suboptimal geometries. Complex and multistage procedure is involved. The component complexity is limited by process tooling paths. Long product lead times are required. 3D printing is used to describe the technologies that build 3D objects from a digital model by adding layer upon layer of material in different shapes and colors. AM technologies provide the advantages such as material, resource efficiencies along with design flexibility and process wise production compatibility.

The most common plastic materials used in 3D printing are Acrylonitrile Butadiene Styrene (ABS) and Polyacid (PLA) [1]. These thermoplastic polyesters are derived from renewable and recycled materials including corn starch and sugarcane [3]. PLA possesses mechanical properties as polyethylene terephthalate (PET), but has a much lower continuous temperature handling capability.

2 Metal and non metal 3D printing processes

CAD tools play a major role in digital modelling. The CAD tools can be classified as freeform modelling tools and sculpting tools. Exporting happens through a suitable file format, suiting a defined standards methodology and around 30 different file formats are available. Some example file formats are Additive Manufacturing File Format (AMF), Gcode, Initial Graphics Exchange Specification (IGES) and Data Exchange Format (DXF). A slicer software takes a 3D drawing and translates the 3D model into individual layers. It then generates the machine code that is fed into the 3D printer to print [3]. The actual print command is given from the printer head and the micro controller controls the movement of printer head and stepper motors to execute the printing mechanism. The printing commences once the temperature has reached the set temperature. Once printing is complete, the machine and all associated support structures stop printing. The support structures are removed, the surface finishing and polishing are performed.

Vat photo polymerization processes, powder bed fusion processes, extrusion systems, material and binder jetting, sheet lamination processes, directed energy deposition processes are available additive manufacturing technologies. Table 1 lists the metal and non metal printing technologies classified among the available techniques [3]. Metals are processed using powder bed fusion processes, where either lasers or electron beams are used for sintering the metal powder. Binder jetting methods have a binder solution dropped on the metal powder.

Table 1 – Classification of 3D printing processes for metal and non metal type of materials.

NON METAL PROCESSES	METAL PROCESSES
Fusion Deposition Modeling(FDM)	Direct Metal Laser Sintering (DMLS)
Stereolithography(SLA)	Selective Laser Sintering (SLS)
Digital Light Processing (DLP)	Selective Laser Melting (SLM)
Polyjet	Binder Jetting
Multijet	Electron Beam Melting (EBM)
ColorJet	Lost wax Casting – Indirect Method
Mcor Paper 3DP	Shape Deposition Modelling (SDM)
Microstereolithography (MSL)	EOSINT Systems
CMET	LENS. AEROSOL
Bioplotter	Laser Induced Forward Transfer (LIFT)
Benchtop system	Laser Cusing
	Phenix PX
	Laser Structuring systems
	LASFORM

Metal printing processes such as metal powder bed fusion and directed energy deposition are capable of producing high print quality, functional and load bearing parts from a variety of metallic powder materials. It's crucial to know the pros and cons of the processes and hence apply to the suitable chosen material. Low cost metallic powders are the key enablers for 3D printing to realize its potential to provide industrial production revolution. Available metallic powders for additive manufacturing are used for a variety of applications in medical, aerospace, jewellery and automative areas. Processing powders require high temperatures.

2.1 Miniaturized sensors

Sensors are miniaturized and multi layered structures having surface modifications on the top layer for environmental sensing. Micro sized air flow sensor, air pressure sensor, capacitive sensor, force sensor, printed microlenses, opto fluidic sensors can be 3D printed [2]. Layering and layered compatibility plays a major role in sensor fabrication.

The structure of sensor which is to be 3D printed using nanoscale resolution is shown, in Fig 1. The figure describes the sensor layers for 3D printing, wherein the base substrate, such as silicon (1.4cmx1.4cm) is prepared and centered below the nozzle. The titanium adhesive layer (10 nm) is printed on substrate. The copper layer (100 nm) is printed on the adhesive, where it gets set without any oxidation [7]. The potassium gold cyanide (PGC) is sprayed using 3D printer nozzle, where nano porous gold is formed on the surface. Potassium gold cyanide reacts with copper to form gold cyanide, cuprous cyanide, nano porous gold along with potassium cyanide. The reaction is maintained to be in alkaline medium for a better plating rate. Gold undergoes reduction process to form nano porous gold on copper surface. The Electroless plating method [7] is followed for the mentioned electrochemical process. A suitable stepper motor is analyzed and selected for the newly designed 3D printing process, where nano scale resolution is required.

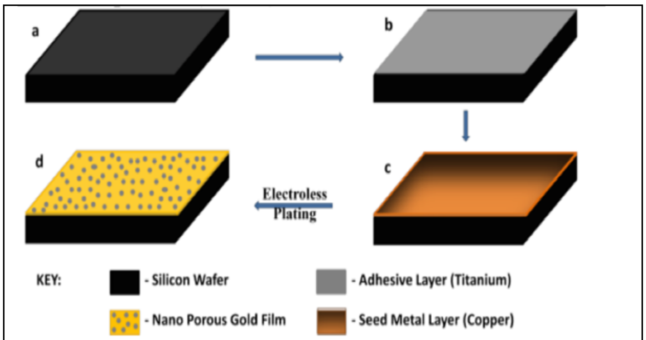


Fig 1 – Layering material in pictorial representation for sensor structure with nano scale resolution to be 3D printed. a . Silicon b. 3D printed titanium layer c. 3D printed copper on layered structure d. Formation of nano porous gold and layering structure

3 Printing copper in FDM process

The Fig.1 describes metal materials to be printed. The metals involved are copper and titanium. For printing copper, various methodologies are analyzed. Mechanical behaviour of sintered nano structured copper has been analyzed for multiple applications in the literature. Thermo physical properties and microstructural investigations of copper and copper oxide composites are vital for sensing applications. For example, for a longer dwell time at the maximum temperature, the oxidation influence leads to a significant reduction of product life time [5]. Among the methodologies analyzed, 3D printing using existing filament structures are performed and tried to match with the sensor requirements for making the fabrication less complex. Various 3D printing processes are studied. The fused filament fabrication process has the capability of printing copper PLA filament using micro resolution. The same is being verified using 3D printing process. The copper – PLA filament has 4g/cm^3 specific gravity, 0.15-0.35% mould shrinkage, tensile strength of max 25 MPa, 10^{11}ohms/square surface resistivity. The processing parameters such as drying condition is 4 hours @ 60^{0}C. Melting temperature is 160-230^{0}C [11]. Injection pressure can be kept to a minimum.

3.1 Borosil glass substrate

Borosil glass is a low alkali borosilicate type 3.3 glass. It is virtually free of magnesia lime-zinc group [6]. It is completely free of arsenic and other heavy material. As the Coefficient of thermal expansion of glass is low, the thermal stresses under a given temperature gradient are consequently low [6]. The glass can withstand higher temperature gradients. Minute scratching of glass surface can however reduce its thermal resistance. In general, “Strain Point” should be regarded as the maximum safe operating temperature of glassware. The glass may incur permanent stresses when heated above 500 ºC and then cooled. The typical thermal properties of glassware are: Coefficient of Linear Expansion is 32.5 $x10^{7}$/ºC; Strain Point is 515 ºC; Specific Heat is 0.2 to 3; Thermal Conductivity 0.0027 Cal/cm/ºC/sec); Annealing Point is 565 ºC; Softening Point 820 ºC. Borosil glass is highly resistant to water, neutral and acid solutions, concentrated acids and their mixtures as well as to chlorine, bromine, iodine and organic matters. Even during extended period of reaction and at temperatures above 100 C, its chemical resistance exceeds that of other materials and most metals [6]. It can withstand repeated dry and wet sterilization without surface deterioration and subsequent contamination. Borosil glass is resistant to attack of various chemicals [6]; only hydrofluoric acid, very hot phosphoric acid and alkaline solutions increasingly react with the glass surface and this reactivity increases with rising concentration and temperature. Consequently, it appears clear and colorless.

3.2 3D printing of copper filament

Deposition Process - The borosil glass plate of thickness 0.16 mm (No.1 type of glass is 0.13 to 0.16 mm thick) and of dimension (22 mm x 22mm x 0.079mm) is cleaned with Millipore water and dried at room temperature. Once no water droplets are seen, the plate is placed in the print bed of 3D printer (Witbox 3D Printer). The STL file with dimension 10 mm x 10 mm is input to the slicer software (Cura15.04.4) from 3D design plotted by COMSOL software and exported to STL file. The 3D printer nozzle is heated to 220 deg ºC. The Nozzle dimension of diameter 0.4 mm is used to extrude. It takes about 4 minutes to print a 1 mm thick layer. The 3D print processing is stopped after 1 minute to obtain a 50 µm layer. The grain size, phase, particle distribution, coating thickness along with phase is measured using metallurgical microscope. Glass is a potential material for substrates, as it offers good dimensional stability and coefficient of thermal expansion similar to silicon.

Fig 2 shows the 3D Print of Copper PLA filament using a Witbox type 3D printer. The printed dimensions are 10 mm x10 mm x 0.016 mm while the substrate dimensions are 22 x 22 mm x 0.16 mm. The substrate melting temperature is 500 ºC, which can withstand the filament melting temperature. Surface is shown flat, but it is not a polished one having some deviations in the sides, which can be manually processed. The concern is of dimensional accuracy.

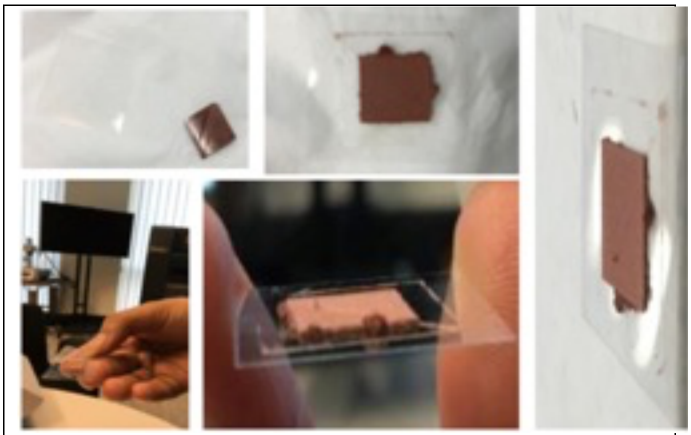


Fig 2 – 3D Print of Copper PLA filament using a witbox 3D printer. The printed dimensions are 10 mm x10 mm x 0.016 mm while the substrate dimensions are 22 x 22 mm x 0.16 mm. The substrate melting temperature is 500 ºC.

Characterization is important for the print, to find the suitability of surface to match for sensor fabrication. The resolution or thickness, porosity, granularity, feature dimensions, phases or maximum material content and conductivity are key parameters for selecting the filament. Hence the parameters are analyzed.

3.3 Characterization of micro resolution 3D print for forming nano sensor

Microstructural analysis is used to determine if the structural parameters are within required specifications [12]. The analysis is used to determine the microstructural changes that occur as a result of varying parameters such as composition, heat treatment or processing steps.

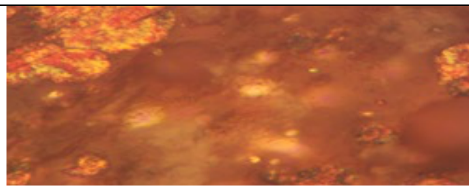


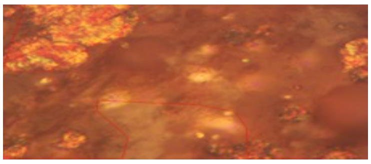
Fig 3 – Image of the 3d printed metal structure on glass. The image is taken from inverted metallurgical microscope through *Envision* software

The Image of the 3d printed metal structure on glass is shown in Fig 3. The image is taken from inverted metallurgical microscope through Envision software. The image shows plastic in a brighter contrast and copper in normal brownish colours. The PLA resists conductive nature, which has to be removed through chemical processing. The image is a portion of a microscopic light pointed on the 3D printed object. Here a flat or smooth surface is not preferred. Porosity adds to more conductive nature of a surface.

Fig 4 provides the coating thickness of the 3D printed layer through a mechanical mounting technique and measured through envision software. The average thickness measured is 79 microns. The maximum thickness is 115 microns whereas the minimum thickness among the measured point of microscopic light is 42 microns. The micron thickness is achieved through a FDM type of 3D printer. Research is underway for a nano resolution thickness print under a similar type of process.

Coating Thickness Measurement Result

Calibration : 24 μm/pixel
Unit : microns
Mag : 400
Measurement Result



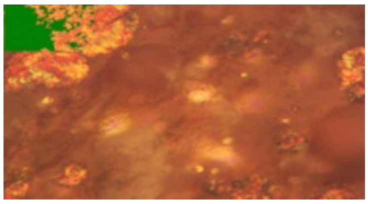
Maximum Thickness = 115
Total field count = 1
Minimum Thickness = 42
Average Thickness = 79
Standard deviation = 21

Fig 4 – *Envision* software measures the coating thickness through a proper mounting technique. The average thickness is 79 microns.

The particle analysis report provided with Fig 5 demonstrates the minimum, maximum feature areas and counts for a 53% total feature area, which indicates the statistics on particles' geometrical nature. There is a relation between particle size, distribution and coating thickness. Roughness decreases with increasing particle size [13]. Elasticity increases with decreasing particle size. Here the features range from 0.075 to 1 micron circumference for a feature count of 82. As roughness is a phenomenon of interest, and increased roughness is required for making the surface conductive, decreased particle sizes and feature sizes are preferred. Based on the particle distribution, the surface resistance is correlated.

Particle Analysis Report

Calibration : 24 μm/pixel
Unit : microns
Mag : 400
Measurement Result



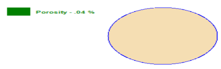
Total Field count	1
Total Feature count	82
Total Feature Area	9541
Total Area	17789
Total Feature Area %	53.63
Min Feature area	1
Max Feature area	8650
Min Feature Length	1
Max Feature Length	122
Min Feature Width	0
Max Feature Width	115
Min Feature Circ	0.07545258
Max Feature Circ	0.9991752

Fig 5 – The green portion of the microscope has been selected by the *Envision* software for particle analysis in Fig 3. In the above figure, the processed image is displayed. The minimum feature width, length, area, circumference is obtained consequent to this analysis.

Porosity is the measure of void spaces in a material. Porosity is related to conductivity. The material shows higher similarity and hence the porosity is very less. Porous structure and transport properties in a surface increases conductivity [10]. Optical method of determining porosity is optimal, by determining the area of the material versus the area of the pores visible under the microscope, as detailed in Fig 6 of porosity analysis report.

Porosity Analysis Report

Calibration : 24 μm/pixel
Unit : microns
Mag : 400
Measurement Result



Total Field count	1
Total Porosity count	119
Total Area	285649
Total Porosity Area	111
Total Porosity Area %	0.04
Length - Smallest	1
Length - Largest	3
Length – Average	1

Fig 6 – In the above figure, *Envision* processed image is shown, for the image in Fig 3. The porosity count is 119 and the porosity is 0.04% of the total surface area.

Fig 7 provides an analysis report on phases, meaning the composition of material that is 3D printed. The major portion is highlighted to be the area in % by envision software. The filament contains 80% of copper and for the particular point of light by the microscope, 95% is represented as copper. Minor portion of PLA in the highlighted area gives more scope for possibility on chemical treatment to reduce resistivity of the surface.

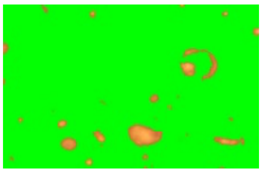
Phases Microstructure Analysis Report

Calibration : 24 μm/pixel

Unit : microns

Mag : 400

Measurement Result



Phase data		
Element	Area	Area%
copper	16416	95.65000153

Fig 7 –The Image in Fig.3 is the raw image from the inverted metallurgical microscope. The above given figure is the processed image from Envision. The color coding in above figure, highlights that Copper constitutes a very high percentage (95.65%) of the total material.

Metallographic examination of copper revealed that the specimens with high impact strength (113 to 115 ft-lb) had small grains while those with low impact strength (57 to 84 ft-lb) had large grains. The grain size analysis report with a magnification unit of 400 microns provides a measurement result of average grain size to be 6.5 microns, for a 25 number of horizontal intercept lines. Fig 8 has 25 intercept lines for approximately 1-micron length. The relation between grain size and conductivity is analyzed in the literature. This will be useful for sensor fabrication.

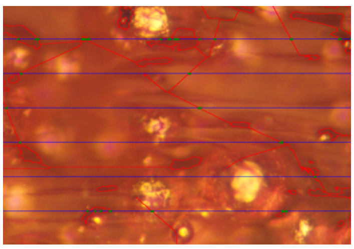
Grain Size (HAYN Intercept) Analysis Report

Calibration : 24 μm/pixel

Unit : microns

Mag : 400

Measurement Result



ASTM Standard - E112

Average Grain Size - 6.5

Total Line Length(mm) - 0.9085714

No. of Intercepts - 25

Fig 8 – Fig 3 is the raw image from the inverted metallurgical microscope. Above figure is the processed image from Envision. Grain size is computed using HAYN Intercept method. Average grain size is 6.5 microns.

The overall summary report for 3D printing of copper and its analysis through inverted metallurgical microscope is provided in Table 2. The coating thickness measured for the printed object is 79 microns. Porosity is 0.04%, grain size is 6.5 microns, material phase % is 95.65. Particle size measured is 122x155 microns. The conductivity requires a higher porosity and PLA material has to be removed by further chemical treatment. The PLA can be made conductive, which is the scope of further research [19, 20].

TABLE 2 - (OPTICAL) METALLURGIAL MICROSCOPE STUDY RESULTS OF 3D PRINTED COPPER STRUCTURE ON GLASS

DESCRIPTION	SOFTWARE USED – ENVISION 5.0 METCO – INVERTED METALLURGICAL MICROSCOPE MAGNIFICATION CHOSEN – 400X				
	COATING THICKNESS (MICRONS)	POROSITY	GRAIN SIZE	PHASE	PARTICLE SIZE
3D PRINTED PLA MIXED COPPER FILAMENT ON BOROSIL SUBSTRATE	*79*	*0.04%*	6.5	*95.65%*	122x155 (FEATURE LENGTHXWIDTH)

4 Conclusion

The micro range thickness or resolution can be achieved using the fusion deposition model type of 3D printer. The copper layer deposited has an average thickness of 79 microns and minimum thickness of 42 microns. The grain size is 6.5 microns. The porosity is only 0.04%. The low porosity implies low conductivity. The conductivity can be increased by applying suitable chemicals on the printed surface to react and remove the plastic content leaving behind only Copper. Alternatively, a higher purity of the source material can be used. Hence the characterization is performed for the 3D printed layer to fabricate the sensor further. There is a future scope of research on conductive polymers in order to convert normal PLA to conductive PLA on the surface.

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