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ADDITIVE MANUFACTURING OF FUNCTIONAL PARTS FROM CERAMICS

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Declaration

I certify that this research work titled *"Additive Manufacturing of Functional Parts from Ceramics"* is my own work. The work has not been presented elsewhere for assessment. The material that has been used from other sources has been properly acknowledged / referred.

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Abstract

Additive Manufacturing has proved to be a tremendous shift in manufacturing and has revolutionized current manufacturing practices. The mentioned technique has some unmatched advantages, including rapid prototyping, the economy of process, less waste production during manufacturing, and freedom of design. Copper oxide is an advanced inorganic material with vast applications, particularly in electronics, medical science, biomedical devices, and gas sensors. It acts as an agent to clear pollutants from the environment. Added to textiles, CuO is an anti-viral, anti-bacterial, and anti-microbial agent. These masks, filters, and textiles are used as an active barrier against several viruses, including Human Corona Virus (229E) and SARS-COV-2. This research aimed at manufacturing cupric oxide Ceramic from Copper powder through a novel Negative Additive Manufacturing Process. The manufactured sample was characterized using six different techniques, including density calculation, porosity calculation, four-point resistivity calculation, SEM analysis, and XRD Analysis. The research experiment confirmed the manufacturing of a monoclinic CuO ceramic sample in the lab having a crystallinity degree of 65.78%.

Key Words: *Cupric Oxide, Copper Oxide, Ceramics, Negative Additive Manufacturing, Ceramic Binder Slurry,*

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Abbreviations

ABS, Acrylonitrile Butadiene Styrene; **CMC**, Carboxymethyl Cellulose; **CO**, Carbon Mono Oxide; **CO_2**, Carbon di Oxide; **CuO**, Cupric Oxide; **DCM**, Dichloromethane; **DI Water**, De-Ionized Water; **FDM**, Fused Deposition Modelling; **H_2,** Hydrogen; **H_2S**, Hydrogen Sulphide; **PLA**, Polylactic Acid; **STP**, Standard Temperature Pressure; **XRD,** X-ray diffraction**; XRF,** X-ray fluorescence**; SEM, ; ZrO_2,** Zirconium dioxide**; AM,** Additive Manufacturing**; JFCA** The Japan Fine Ceramics Association; **PSZ**, Partial Stabilisation of Zirconia; **NMP,** N-methyl-2-pyrrolidone; **Cu_2O,** Cuprous Oxide**; eV, ; NPs,** Nanoparticles**; CAD,** Computer-Aided Design; **MJ**, Material Jetting; **BJ**, Binder Jetting ; **DED**, Direct Energy Deposition; **FFF**, Fused Filament Fabrication; **SLM,** Selective laser melting; **EBM**, Electron Beam Melting; **w/v ratio,** Weight to Volume Ratio; **Mg-PSZ,** Magnesia Partially Stabilized Zirconia; **ID Grinder**, Internal Diameter Grinder;

CHAPTER 1: INTRODUCTION

Research work in this dissertation has been presented in five parts covering the research experiment conducted in the materials lab of the local university to study the negative additive manufacturing of cupric oxide ceramic.

1.1 Background, Scope, and Motivation

The inspiration for this research study was to concentrate on the additive manufacturing of parts from ceramic. A literature review resulted in the identification of a knowledge-based research gap for pure cupric oxide ceramic and a methodology-based research gap for negative additive manufacturing processes, which was the basis of this research to study the manufacturing of ceramic and lead the research to focus on a modern manufacturing technique and advanced ceramics. Cupric oxide material and to develop it using a novel additive manufacturing technique. Further, to confirm and analyse the material properties and microstructure, it was characterized using six different techniques, including:

i. **Density Calculation:** was conducted to study the mass distribution per unit volume in the manufactured CuO Ceramic Sample and confirm the porosity of the sample.

ii. **Porosity Calculation:** was performed to study the porosity of the sample for its potential use as gas sensors.

iii. **Resistivity Calculation:** to understand the electrical properties of the manufactured CuO ceramic sample and its potential application in electronic devices.

iv. **SEM Microscopy:** was conducted to study the microstructure of the manufactured CuO ceramic sample and calculate the porosity using SEM Micrographs.

v. **XRD Analysis** was performed on the manufactured sample to confirm the manufactured ceramic's chemical composition, crystal structure, and degree of crystallinity.

vi. **XRF Analysis:** was conducted to elaborate and confirm the XRD analysis. The purity of the fabricated cupric technique was applied to study a particular property of the cupric oxide ceramic sample, as mentioned earlier. This approach confirmed that the manufactured sample is cupric oxide ceramic.

1.2 Research Questions, Aims, and Objectives

i. Research Questions

The research conducted during the thesis phase comprises of three research questions:

a) Can Pure Cupric Oxide Ceramic be Negatively Additively Manufactured?

b) What will be the porosity of the manufactured Cupric Oxide Sample fabricated using NAM?

c) Is it possible to manufacture a functional Cupric Oxide ceramic part in Local Lab using?

ii. Aims

a) After successful research, we can manufacture the advanced ceramics in the lab using the additive manufacturing process.

b) This research will enable us to manufacture pure copper oxide ceramic.

c) Characterise the manufactured sample and any other sample through the characterization techniques studied in the research experiment.

iii. Objectives

a) Indigenous manufacturing of functional parts from ceramic by additive manufacturing.

b) Analysis and characterization of the manufactured ceramic sample

c) Proposal of manufactured for applications in the modern world.

1.3 Methodology and Scope

The methodology used in this research has the following steps:

A. Literature review focusing advance ceramics and additive manufacturing of ceramics.

B. Initial laboratory experimentation to confirm the availability of necessary resources and test if the manufacturing parameters can be achieved. These parameters include sintering temperature, time, drying equipment, and resources, including optical microscope, SEM, XRD, XRF, ball milling facility, chemical reagents including DCM, Ceramic and metallic powders, and lab equipment.

C. Final Negative Additive Manufacturing of Cupric Oxide Ceramic in the following three steps:

    a) Slurry Preparation
    b) Negative Additive Manufacturing
    c) Drying, Demoulding, and Sintering

D. Characterization of the manufactured material

The scope of the research is limited to the following two points while keeping the focus solely on the shrinkage of the final ceramic part geometry:

a) Manufacturing of Functional Ceramic parts using the available resources

b) Characterization of the manufactured ceramic sample using the material characterization techniques mentioned above.

1.4 Thesis Structure

This thesis focuses on manufacturing cupric oxide ceramic in the local lab using novel negative additive manufacturing method and covers five chapters. The chapters and their details are:

- **Chapter 1: Introduction**

This chapter briefly introduces the research experiment conducted in the lab. The research questions, aims, objectives, methodology and scope of the research are described in this chapter.

- **Chapter 2: Literature Review**

Literature review systematically reviews all the research literature focusing on the additive manufacturing of cupric oxide material. The literature review defines advance materials and their significance in the modern world. Then it connects ceramics to advance materials and the properties of advance ceramic. Cupric oxide material is then described as an advanced ceramic and is important in today's modern world due to its unmatched applications. Afterward it focuses of the manufacturing process of the ceramic material an. It relates to the general additive manufacturing process for ceramics, stating the advantages of the AM over conventional manufacturing. Then it discusses the additive manufacturing of cupric oxide material in the research literature. At this stage, the methodology-based research gap is identified and the novel negative additive manufacturing method for filling this res is presented.

- **Chapter 3: Materials and Methods**

The research experiment, including the materials used in the experiment, experimental setup and the ceramic manufacturing process is briefly described in this chapter.

- **Chapter 4: Results**

This chapter contains the detailed results of characterization and analysis of manufactured cupric oxide ceramic sample.

- **Chapter 5: Discussions and Conclusion**

This chapter discusses the results of the current research experiment and characterization in contrast to the results in the research literature, extracted during the literature review. It summarizes the research experiment and results. It also recaps the findings, their characterization, research question and its answers, limitations, aspects of the research presented in this document.

References are given at the end of the thesis. The thesis has sixteen figures and six tables.

CHAPTER 2: LITERATURE REVIEW

2.1 Cupric Oxide: An Advance Material

2.1.1 Advance Materials

Advance materials are gaining importance in the modern world due to their unique properties and vast applications. Their properties make them an excellent option to replace conventional materials. These materials are responsible for the fast technological transition over a short period of time. The demand for materials with high performance has created an everlasting need for the emergence of advanced materials. The rapidly increasing population of the world demands products to cater to their needs in the most efficient way. The importance of this problem can be easily understood by analysing population growth and the increase in energy crises. This crisis creates room for enhanced energy harvesting and storage systems. To solve this issue, scientists have researched and manufactured higher-capacity energy devices. These devices include both the batteries and the capacitors. These developed products have a short life span and a short shelf life. Considering the capacitors, the advanced material-based capacitors are high-power capacitors with low weight and a vast operating temperature range with affordable management. These batteries and capacitors are used in different electric vehicles and other devices, resulting in economic, enhanced performance, and low maintenance advantages.[1].

Advance materials are renowned for their resistance to extreme temperatures. These materials have enhanced anti-wear properties as compared to traditional lubricants. They have good thermal insulation properties, which makes them a good choice for thermal barriers. Contradictory to this, some advanced materials possess increased thermal conductivity and, when added to a fluid, enhance its thermal conductivity by 83%.[2]. In today's world, advanced materials, particularly ceramics, have primarily supplanted traditional materials. This technological change is motivated and boosted by the Asian markets in Japan and China[3].

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2.1.2 Ceramics as Advance Materials

The Greek term for ceramics is "Keramicos," which translates as "burned material." Ceramics consist of numerous elements. Composites of ceramic materials are composed of metallic and non-metallic elements. There are two categories of ceramic: traditional ceramics and advanced ceramics. Clay, silica, and feldspar are examples of inorganic non-metallic solids (non-metallic or metallic compounds) used to create traditional ceramics such as tiles, glassware, porcelain, and bricks. Examples of sophisticated ceramics include oxides, nitrate compounds, carbides, and non-silicate glass. Advanced ceramics include, but do not have to be limited to, SiO_2, Al_2O_3, and others such materials.[4]

Advance Ceramics are well known materials among the other inorganic materials for their peculiar characteristics due to the chemical and physical properties. These do not undergo a chemical reaction easily as they are stable compounds. High Hardness, High strength, Low thermal Conductivity and Bio Compatibility are some of the unique characteristics of advanced ceramics. The advanced ceramics when applied in real life give us some drastic benefits compared to traditional materials. These materials have load bearing capability. The cutting tools made up of advanced ceramics reduce the tool consumption to 30% minimising the manufacturing cost. They can operate at 10 times of the conventional cutting speeds. These materials have enhanced resistance to wear, and a unique cutting action governed by their microstructures. With the advanced ceramics we can achieve P4 level manufacturing accuracy for manufacturing of aerospace products. Due to this uniqueness of these materials, they are applied in the field of aerospace, biomedical field, and for other challenging applications replacing the traditional materials. Because of their biologically stable inertia, dental implants and different biomedical scaffolds are manufactured using these materials.

Ceramic bonding can be fully ionic, covalent, or a combination of the two. Ceramics include oxides, silicide, borides, and carbides. Because of their properties, ceramics have increased in favour in the modern world. Ceramic materials have various distinguishing characteristics, including High Melting Point, Resistance to corrosion, Brittle Nature, Resistance to wear, Low Thermal Expansion, High Hardness, High Temperature Bearing Capability, and other such peculiar properties. These properties are the reason that the ceramic materials are used in Solar Cells, Fuel Cells, Heat Exchangers, Turbines, Piezo Electric Devices, and many other devices[5].

Advanced ceramics, also known as "technical," "engineering," or "fine" ceramics, are primarily polycrystalline materials that, unlike conventional ceramics, which are made from natural sources, are almost always synthetic in origin and/or have been engineered (high purity, tailored particle size distribution, small grain size, etc.) to meet the service requirements of increasingly demanding industrial applications in sectors as diverse as aerospace, automotive, biotechnology, and electronics. As a result of their atomic structure, which is comprised of rigid ionic and covalent bonds, they possess a unique set of mechanical, chemical, and physical properties, such as exceptional chemical inertness, high temperature resistance, superior hardness, high stiffness, and a low coefficient of friction. Based on their chemical composition, advanced ceramics are typically divided into two categories: metal oxides, such as alumina (Al_2O_3) and zirconia (ZrO_2), and non-oxides, such as carbides, nitrides, and borides. Based on their intended application, these high-performance ceramic materials can also be categorized as structural ceramics, electro-ceramics (including dielectric, piezoelectric, and pyroelectric performance), opto-ceramics, chemical processing ceramics, ceramic coatings, bio ceramics, and superconductors.

The oxide ceramics most frequently investigated for additive manufacturing are Al_2O (due to its adaptability, affordability, and low sintering temperature) and ZrO_2 (due to its high toughness, low sintering temperature, and broad range of industrial applications). Silica (SiO_2) materials are not considered technical ceramics.

This is because many researchers utilize them as a less expensive alternative to alumina and other sophisticated ceramics in the early phases of AM research projects or biomedical applications. Non-oxygen-containing ceramics have a high hardness and require pressure-assisted firing in a controlled inert atmosphere more frequently than oxide-containing ceramics. Due to their increased hardness and typical sintering temperatures well above 1700 °C, these materials are significantly more difficult to manipulate. While oxide and non-oxide advanced ceramics are typically treated and shaped via the powder processing method, i.e., by shaping and sintering a ceramic component from a dried or wet ceramic powder mixture, they can also be produced via pyrolyzing techniques employing polymers[5]. Japan's advanced ceramics market controls 40 percent of the global market with a 2018 output of $30 billion (an annual growth rate of 6.3%). The Japan Fine Ceramics Association (JFCA) is an organization with 116 members committed to advancing the Japanese fine ceramics industry[6].

2.1.3 Properties of Advance Ceramics

Advance ceramics exhibit a wide range of electrical properties, including those of an insulator, a semiconductor, and a conductive material, making them particularly resistant to high temperatures (up to 2500 °C and beyond). Advanced nanostructured ceramics and partially stabilised zirconia are examples of transformation-toughened ceramics made possible by advancements in processing technology; these materials perform admirably despite having lower fracture toughness and impact resistance than metals and some engineering plastics. Engineers use structurally advanced ceramics when a system's components must tolerate extremely high mechanical, tribological, thermal, or chemical loads. Advance structural ceramics include substances including alumina, cordierite, mullite, spinel, silicon nitride, silicon carbide, boron nitride, titanium nitride, and titanium boride. Zirconia ceramics thrive in high-temperature applications due to their density, bending strength, low thermal conductivity, and lack of thermal expansion. Microhardness and heat conductivity are the strengths of silicon carbide ceramics, yet thermal shock quickly cracks and damages them[7].

These ceramics are perfect for use as heating elements in furnaces since they can withstand temperatures of up to 1600 °C. However, due of its exceptional thermal shock resistance, reasonable strength and hardness, intermediate densities, and thermal conductivity values, silicon nitride is well suited for use in automobile engines. Instead of being dispersed throughout most of the material as they are in structural ceramics, microstructural effects in functional advanced ceramics are restricted to the volume, grain boundaries, or surfaces of conducting or nonconducting ceramics. Examples of these phenomena include superconductivity, piezoelectricity, pyroelectricity, ferroelectricity, piezoelectricity, varistor, and semiconductors. Advance ceramic gas turbines, fuel cells, knock and oxygen sensors, exhaust gas catalysts, and adiabatic turbo-compound diesel engines are just a few of the automotive applications that make use of new ceramic technologies. The severely corrosive body environment renders bio ceramic materials like alumina and zirconia biologically inert due to their outstanding structural stability, in contrast to the advantageous Osseo inductive and osteoconductive properties of hydroxyapatite and tricalcium phosphate [7].

2.1.4 Applications of Advance Ceramics

Partial stabilisation of zirconia (PSZ) ceramics, including mixed oxide zirconia-alumina composite ceramics, have many applications, such as hard and durable knives for high-speed cutting of paper and polymers, wear-resistant roller bearings, ultra-tough femoral ball heads for hip endoprostheses, wire-drawing dies, valve seats, piston heads, and exhaust parts of automotive internal combustion engines, scrapers, and screw-type winding encasements. Advanced ceramics are utilized in numerous products, including ceramic spheres of variable sizes, dental blanks, extrusion tools, wear plates, and press tools. These items include porous ceramic filters, diffusers and adsorbent filter/dryer cores for refrigeration, dispersion components, vacuum chucks, and inkpads[7].

Zirconia is utilized in the pumps' shafts, couplings, and thrust sections due to its high resistance to wear and corrosion. In the chemical industry, high-performance sludge and process pumps are utilized, whereas in the petrochemical industry, pumps operating in sour gases, exceedingly abrasive sand, and high temperatures require valves, seats, sleeves, liners, and nozzles. The abrasion and impact resistance of Mg-PSZ liners is superior to that of tungsten carbide and silicon carbide liners. Dense structural ceramics are precisely ground using an extensive array of grinding equipment, such as diamond cutters and surface grinders, computer numerically controlled milling machines, jig grinders, centre-less grinders, computer numerically controlled lathes, and ID grinders, among others. Due to its high thermal expansion, low thermal conductivity, and high melting point, zirconia is utilized in plasma-sprayed thermal barrier coatings for gas turbine blades in the aerospace industry, tundishes and ladles for liquid metals, and refractory filaments for high-temperature insulation. Paper-cutting blades, scalpels for surgical precision cutting, hairdressing scissors, Kevlar TM fabric-cutting devices, and sushi knives all benefit from zirconia's exceptional retention of edge. As split coupling devices for optical fibres in communications systems, components made of high-strength zirconia with exceptionally precise tolerances and fabricated with diamond tools have been used[7].

In environments where alumina or mullite would fail due to attrition or thermal stress, zirconia refractory blocks and liners are utilized. Alumina reinforcement is utilized in sliding gate valves, nozzles, and stoppers for steel holding and transfer ladles, as well as tank liners for glass refining. Zirconia becomes unstable in the presence of silicate and aluminium silicate refractories when temperatures exceed 1400°C. Recently, zirconia-based insulating materials with low heat conductivity and density have been used to manufacture filaments, paper, felt, boards, and formed items. The substance is a solid solution of cubic zirconia. It is yttria-stabilized and has a maximal usable temperature of over 2100 ℃. Organic precursor material is impregnated with aqueous zirconium chloride and yttrium chloride solutions to serve as a structural template for the novel manufacturing method. The metallic compounds are imbedded in the organic fibre, where they can be burned off by means of carefully regulated oxidation. The remaining material is then dehydrated at temperatures between 800 and 1300℃ to promote crystallisation, and the oxide particles are sintered to create a ceramic bond. In addition to phase inversion and sintering with N-methyl-2-pyrrolidone (NMP) and water as an internal coagulant, there are additional techniques for producing refractory fibres. The thermal stability of these materials is only one of their outstanding properties. 2600 °C, are resistant to molten metals, and are resistant to corrosion from hot alkalis and a variety of strong compounds. There are numerous applications for zirconia refractory materials, such as electrolysis diaphragms, heated gas filters, and highly effective thermal insulation in aerospace batteries. Its application as a chemical and thermal safety agent may be particularly opportune. It would function as a chemical and thermal buffer if placed beneath the core of a nuclear reactor in the event of a meltdown[7].

Advanced ceramics are used to manufacture gas sensors, biomedical sensors, blood valves, femoral heads, acetabular cups, shoulder buttons, radial heads, dental crowns, scaffolds for tissue engineering, and orthopaedic implants. They are also used in Ballistic armour, vehicle panels, personal protection, and investment casting cores, blades, gear wheels, and bearings are other ceramic items. Grit Blasting, Water Jet Cutting, and Slurry Pumping Nozzles are fabricated using advance ceramics. The electrical components, substrates, connectors, and insulators for spark plugs, as well as high-performance valve components for corrosive and abrasive fluid flows in microwave applications, waveguides, filters, tubes, waveguides, chambers, and spacers for lasers, are all are the products of these materials. Nuclear power plants employ advance ceramic as control rods, shut-off pellets, and shielding rods.[5]

2.1.5 Copper oxides

Throughout human prehistory, history, and even now, copper has played a significant role. Copper has been cold worked for around 10,000 years. Furthermore, copper metal has been purified for around seven thousand years. Its use as a construction material, such as in funnelling, may be dated back to ancient Egypt, and its importance in this industry has not diminished. It has obtained new applications in the modern world, such as model in electrical frameworks and electronic devices. Copper's qualities have been extensively studied and used over its lengthy history, regardless of how much remains unknown about this crucial metal. Specifically, copper oxidation and consumption [8].

Copper oxide occurs in two oxidation states (+1, +2), namely, cupric oxide (CuO) or Copper (II) oxide and cuprous oxide or Copper (I) oxide (Cu_2O), both of which are p-type semiconductors with optical direct band gaps ranging from 1.3 to 3.7 eV for CuO and 1.8 to 2.5 eV for $Cu_2O.$ The cupric oxide has a direct band gap beginning at 1.2 eV, making it an ideal absorber material for solar cell applications [8]. Cuprite is a naturally occurring copper (I) oxide. When exposed to air, copper in its natural state (as an element) reacts slowly. Copper (I) oxide can be synthesized by heating copper metal in an atmosphere abundant in oxygen. It is essential to take measures to prevent copper from completely oxidizing into copper (II) oxide.

2.1.6 Cupric Oxide

CuO is a black-coloured ceramic material known as cupric oxide or copper (II) oxide[9]. It is a transition metal oxide with a high surface-to-volume ratio, porosity[10] and monoclinic crystal structure[11]. It exists in nature as tenorite mineral [12]. It holds unique importance due to its comparable efficiency as a catalytic agent, superconducting property, anti-microbial agent, and energy-storing characteristics[11]. Cupric Oxide is used in various domains today, including electronics, biomedical devices, energy harvesting systems, chemical catalysts for different chemical reactions, solid self-lubricants, and anti-microbial textiles.

Throughout recorded history, ceramics, enamels, porcelain glazes, and synthetic gems have all been coloured with cupric oxide as a pigment. It is also used fumigant, pesticide, to treat potato plants and as a boat hull antifouling treatment. It acts as an antifouling agent stopping barnacles and other organisms from developing on a boat’s hull. When such creatures grow on a boat's hull, they increase the friction that the boat experiences as it moves through the water, slowing it down. It is also applied to wood used in marine platforms and environments particularly on sea walls, decking, roofing, pilings, and fence posts. to prevent fungi and insects from damaging freshwater and marine constructions. The ancient Greeks combined CuO and $CuSO_4$ to treat wounds[13].

2.1.7 Importance of Cupric Oxide

Cupric oxide is the most stable, abundant and the non-toxic oxide having high porosity. This material gains importance due to its distinct properties and characteristics which include high surface area, small energy band gap and good solar rays absorbing property. To exploit the properties of this material it is doped or electrically connected with other materials particularly metals including Gold, Silver, and platinum in an electronic circuit. This doping makes it easy to use CuO in different devices including solar cells, photo detectors, gas detectors, medical sensors, and other such electronic devices [14].It is also an interesting material for its photo-thermal and photoconductive properties[15]. The high porosity of the material makes it a good choice for vapour and gas detection. Its anti-bacterial, anti-viral and anti-cancer properties increase spectrum of application to various medical devices and sensors including sensors, filters, and textiles. It is also used in cancer therapy due to its high chemical reactivity[16].

2.1.8 Physical of cupric oxide material

a) **Crystal Structure and Material Category:** CuO is categorized as ceramic material[9] having black colour[17] and Monoclinic Crystal Structure[18].

b) **Porosity:** The porosity of pure cupric oxide ceramic is 55%[19] and that of CuO thin films ranges from 39% to 95% [20].

c) **Specific Gravity:** The specific density of the natural occurring tenorite, mineral form of Cupric oxide is 6.5[21]. This value shows that the material is 6.5 times denser that water. The specific density of CuO ceramic varies depending upon the manufacturing method and the several other parameters including the copper loading in the ceramic structure. Literature has reported a value of 4.5 for specific gravity of CuO confirming that the specific gravity of synthesized CuO changes, depending on the synthesis method[22].

d) **Melting Point:** The melting point of CuO is reported to be 1326℃ [23]. It is termed as soft oxide material[23] and is also a self-lubricating material[24].

e) **Thermal Conductivity:** The thermal conductivity range of CuO materials is reported to be 69 to 76 $\frac{W}{mK}$ [25]. The cupric oxide particles addition in water, engine oil, ethylene, ethylene, and glycol enhance the thermal conductivity of mentioned fluids. The addition of 0.75% cupric oxide nanowires has enhanced the thermal conductivity of nanofluids and an increase of 60.78% is reported[26].

f) **Electrical Conductivity:** The cupric oxide material is reported to be a p type semiconductor and its energy band gap is reported to be from 1.2 eV to 2.16 eV[26]. The electrical resistivity of bulk cupric oxide material at an annealing temperature of 900℃ is declared as $8.6x10^4\ \Omega m$ [27]. If the CuO material is manufactured using the Sol-Gel process, then the electrical resistivity is reported to range from 0.84 Ωm to 1.24 Ωm [28]. Another value reported for CuO materials electrical resistivity is 5 Ωm when manufactured using wet ball method[29]. These findings confirm that the electrical resistivity value for CuO varies as the manufacturing process is changed.

2.1.9 Chemical properties of cupric oxide material

a) **Chemical Composition:** Chemical formula of cupric oxide is CuO[30].

b) **Dissolution:** CuO is insoluble in water but is highly soluble in ammonium chloride and potassium cyanide. It can be dissolved in acids including HCL, HNO_3 and $H_2SO_4$to render $CuCl_2$, $Cu(NO_3)_2$ and $CuSO_4$ salts[31].

c) **Stability:** No biodegradation of Cupric Oxide is reported in the research literature [31].

d) **Toxicity:** Modified and Green Synthesized CuO nanoparticles are efficient material for drugs used in treatment of pancreatic, gastric, colon cancers[32] and breast cancer[33] in humans. This is due to their cytotoxicity which enables the CuO nanoparticles to be toxic to cells in the human body preventing the growth and replication of the cancerous cells and even killing the cells[32,33].The bulk Cupric Oxide material is reported to be nontoxic and safe contradicting the nature of CuO nanoparticles[32,34–38].

e) **Adsorption:** The Cupric oxide nanoparticles are reported to have an adsorption capacity of 3152 mg/g for fluoride in aqueous media. This value shows that it can remove fluoride from water more than three times its weight. The CuO nanoparticles are considered efficient adsorbing materials due to small particle size, economical manufacturing, copper material natural abundance, nontoxic nature and , increased surface area[39]. The CuO material with feather morphology has the greatest adsorption efficiency of 99% as compared to leaf and dendrite morphologies[40]. Studies show that the CuO material can be regenerated three times before losing the properties and performance when working with CO_2 adsorption and desorption. Among different morphologies studied for the adsorption and desorption for CO_2 gas it is reported that the sphere flower morphology of CuO particles depicted remarkable performance which was also comparable and better if compared with that of cuprous oxide particles [41].

f) **Cupric Oxide as Catalyst:** Cupric oxide acts as catalyst for several chemical reactions. It is added as additive in diesel and biofuels to increase the fuel efficiency and reduce the fire point of the fuel. They are employed as an oxidizing agent and minimize the CO and Hydrocarbon emissions from the vehicles[42,43]. CuO is used as catalyst to degrade different dies including Methylene Blue[44], Methyl Orange[45], Azo Dyes[46], MB Dyes and MR Dyes[47]. It is an economical photocatalyst material with effective antibacterial deactivation property to treat dyes present in the industrial wastewater and degrade the pollutants present in it. It is used as an additive in Solid Propellent and increase the burning rate by three times[48]. CuO material is also known for its Sono catalytic and photocatalytic degradation of organic pollutants including cationic and anionic dye which are Victoria Blue and Direct Red 18 respectively[49]. Gold dopped CuO nanoparticles are reported for enhanced gas detection response including ethanol, methanol, acetone, acetone, xylene, and formaldehyde[50]. CuO coatings function as catalysts and decrease 80% of the HC, CO and NO_X emissions. Further these coatings are capable of detection, and later conversion of these emission gases into benign gases[51].

2.1.10 Applications of cupric oxide

CuO, commonly known as cupric oxide, is a material that has distinctive properties which render it beneficial in an extensive variety of applications, including electronics, biofuel additives, catalysts for chemical reactions, gas detection probes, and products that belong to the biotechnology and medical industries. The porosity of the material makes it ideal for perceiving multiple gas molecules and aiding in the elimination of environmental contaminants. This is possible because of its adsorption property. Several CuO material applications are described in detail below:

a) Application of Cupric Oxide as Catalyst

CuO is used as a catalytic agent for the oxidation of Carbon mono oxide, conversion of Carbon dioxide to methanol, and for the water gas shift reaction[52]. Rocket propellant often contains Cuo as a burning rate catalyst. It's a superior catalyst for AP composite propellant and may drastically increase the burning rate of homogenous propellant while decreasing pressure inde.x[53]. One new noble-metal-free and environmentally friendly reaction procedure for synthesis of carbonyl compounds involves the use of CuO as a cheap and efficient heterogeneous catalyst under aerobic conditions[54]. Degradation of organic contaminants by peroxymonosulfate activation is aided by CuO's catalytic characteristics.It's a reliable catalyst that can be produced with little effort. In terms of catalytic performance, the CuO material with a significantly larger surface area demonstrated outstanding degradation of phenolic organic pollutants[55].

b) Application of Cupric Oxide in the field of Medical Science, Cancer Therapy and prominently against SAR – CoV-2

The Importance of Copper oxide in medical sciences as a Microbial Warfare Agent[56] gains importance, as the world is now prone to several new viruses, including Corona Virus. It has several excellent properties, including antifungal, anti-viral, anti-bacterial, and anti-cancer [57]. This material is used for focused cancer therapy to treat cancer patients[56]. The infusion of the Copper Oxide in the textiles induced a particular property in the textile fibers, which hold viral deactivation properties. This property is advantageous in manufacturing textiles, masks, and respirators as virus filters. Respirators and masks manufactured by doping copper oxide material resulted in an anti-influenza (H9N2) avian influenza virus mask. Filters holding Copper Oxide media were reported to minimise viruses, including Para Influence 3, HIV-1, Type 1 Adenovirus, Cytomegalovirus, and Measles[58]. Cupric oxide added to Polyester/Cotton Fabric deactivated the Human Corona Virus (229E) and SARS-COV-2[17]. CuO nanoparticles induce cell mortality at low concentrations by inducing cytotoxicity.CuO NPs synthesized with folic acid were an effective alternative treatment for triple-negative breast cancer cells, according to in vitro investigations [59]. Tumour stem cells, also referred to as tumour initiating cells (TICs), are a subset of cancerous tumour cells that have the ability to self-renew and disseminate cancer to other parts of the body. Due in large part to the TIC's inherent resiliency, pancreatic tumors can recur following treatment. We demonstrate the lethality of copper oxide nanoparticles (CuO-NPs) using TIC-enriched PANC1 human pancreatic cancer cell cultures. In TIC-enriched PANC1 cultures, the effects of CuO-NPs on cell viability and apoptosis are more pronounced than in normal PANC1 cultures. These effects are associated with decreased mitochondrial membrane potential and elevated levels of reactive oxygen species (ROS). In addition, we demonstrate that CuO-NPs inhibit tumor growth in a murine model of pancreatic cancer. Tumors from treated animals contained significantly more apoptotic TICs than tumors from untreated mice, demonstrating that CuO-NPs target TICs in vivo. Our findings imply that CuO-NPs may be useful as an innovative treatment for pancreatic cancer [60]. Intriguingly, new research suggests using alumina granules coated with copper oxide nanoparticles for water filtration to treat viruses in effluent water from healthcare facilities. In vivo biocompatibility assays utilizing Zn-doped CuO nanoparticles immobilized on catheters via the sonochemical method revealed increased biosafety and effective action against biofilm formation. Copper (I) oxide and metallic copper were 99.9 % effective at removing bacteriophage MS2 from wastewater, whereas copper (II) oxide was utterly ineffective. According to the authors, the oxidation state of copper is associated with the elimination of viruses as a result of electrostatic interaction between viruses and the material surface [61].

c) Application of Cupric Oxide as Biomedical Sensors

Due to its high surface-to-volume ratio and porous structure[10], CuO is used to sense gases in the atmosphere and in different biomedical sensing devices[62]. It is used to sense Carbon di Oxide[62], Nitrogen di oxide[56], Hydrogen[63], Hydrogen Sulphide[10], Carbon mono Oxide[10], Benzyne Alcohol[64], Ethanol and Methanol [65]. Because of its high chemical reactivity, CuO is a catalytic agent in focused cancer treatment and anti-cancer, anti-viral, anti-microbial, and anti-bacterial medications. CuO-based biomedical instruments detect blood protein patterns and blood glucose levels. It has significant anti-viral and catalytic effects. It serves as a heterogeneous catalyst. CuO aids in the rapid detection of glucose by catalysing glucose oxidation to create gluconolactone, which is then converted into glucose acid by additional oxidation using CuO[66].

d) Application of Cupric Oxide in Electronics

CuO is used as a p-type semiconductor and magnetic storage media and finds its application in capacitors, electrodes, and in different gas-sensing probes[66]. It is employed in different energy harvesting devices, particularly in light energy harvesting systems and solar cells, because its narrow energy band gap having a value of 1.2ev. It finds its applications in supercapacitors. Electrical, Optical, and photovoltaic devices. Studies show that CuO can replace the anodes made of graphite in Lithium-Ion Batteries. Graphite is less expensive, safer, and more environmentally favourable than graphite. The only drawback is the quick decay of capacity due to the irregular, massive, and uneven variations in the volume during the release and absorption of lithium ions in the battery[67].

e) Application of Cupric Oxide as Self-Lubricating Solid

Copper oxide material is also being studied for its solid self-lubricating property[24]. Due to its high friction coefficient and low wear per nanoparticle, it is added to Oil, forming a lubricating suspension with an enhanced anti-wear property[68]. As an additive for biodiesel, it supports effective heat transfer and low nitrogen oxide emission. This addition in biodiesel enhances combustion and engine performance, resulting in improved emission characteristics[43].

f) Application of Cupric Oxide as Environment Cleaning Agent

Due to its worth noting adsorption[69] and desorption properties[70], Copper Oxide also serves the environment by removing pollutants, including fluorides[71], arsenic[69], Benzene[72], and Toluene[72] from the aqueous environment. CuO serves the environment by removing different pollutants through adsorption and desorption properties. Its adsorption property removes arsenic, Lead, Fluoride, Acrylic Acid, and Ciprofloxacin from different media, making the CuO material a good choice as a water-treating agent[73]. Other studies show that CuO can filter Arsenic[69], Fluoride, Benzene, and Toluene[72] from an aqueous environment. In the Elution process, CuO is used as an Adsorbent to obtain several Eluents, including Sodium Hydroxide, Ethanol, Sodium borohydride, and HCL using different absorbate materials, including different dyes[73]. CuO is also considered a good fit for visible light or UV-assisted semiconductor catalysts used for water treatment[67].

2.2 Manufacturing of Advance Ceramics

Ceramics can be made through various manufacturing processes, each with its own advantages and disadvantages. Here are some of the most common methods of ceramic production:

a) **Powder compaction**: In this method, ceramic powders are compacted into a desired shape using a mould and pressure. The mould can be made from a variety of materials, including metal, plastic, or rubber. The powder is pressed into the mould using a hydraulic press or other mechanical means, and the resulting green body is then sintered in a furnace to form a dense ceramic object. This method is commonly used for making simple shapes like tiles and bricks[74].

b) **Slip casting:** This process involves creating a slurry of ceramic particles and a liquid binder, which is then poured into a porous mould. The liquid is drawn out of the mould, leaving behind a solid ceramic object. Slip casting is commonly used for making objects with complex shapes, like decorative ceramic figurines and vases[75].

c) **Extrusion:** In this method, ceramic material is forced through a die to create a continuous shape. The extruded material is then cut to the desired length and fired in a kiln. This process is used to create tubes, rods, and other objects with a uniform cross-section[76].

d) **Tape casting:** Tape casting involves spreading a slurry of ceramic particles and a liquid binder onto a flat surface, such as a glass plate. A doctor blade is used to smooth the surface and control the thickness of the tape. The tape is then cut to the desired shape and fired in a kiln. This process is used to create thin sheets of ceramic material, which can be used for electronic components and other applications[77].

e) **Injection moulding:** In this method, ceramic material is melted and injected into a mould using high pressure. The mould is cooled, and the resulting part is removed. Injection moulding is commonly used for creating complex shapes with tight tolerances, like ceramic engine parts and other precision components[78].

Each of these manufacturing processes has its own advantages and disadvantages. For example, powder compaction is a simple and cost-effective method for making simple shapes, but it may not be suitable for creating complex objects. Slip casting and tape casting are useful for making objects with complex shapes and thin walls, but the firing process can be time-consuming and may result in uneven shrinkage. Injection moulding is a precise and efficient method for creating complex shapes, but it may not be cost-effective for small production runs. The method used to manufacture ceramics depends on the specific requirements of the object being produced. Each manufacturing process has its own advantages and disadvantages, and the selection of a particular method depends on factors such as the desired shape, size, and material properties of the finished object, as well as the available resources and cost constraints[79].

2.3 Additive Manufacturing

2.3.1 Overview of Additive Manufacturing

Additive Manufacturing (AM) is a Modern Manufacturing Technique. Additive Manufacturing (AM) is done by successive layer deposition of stock material using the 3D CAD Models. 3-dimensional (3D) CAD Models are created using CAD Software. The products manufactured can be functional prototypes as well as batch products. AM is also referred to as layer manufacturing, additive fabrication, additive processes, freeform fabrication, and solid freeform fabrication[80].

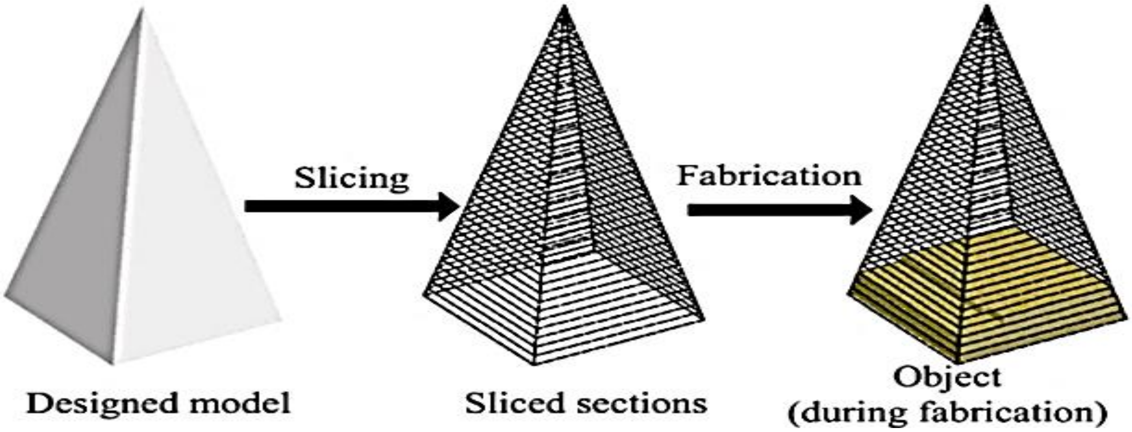


Figure 2.1: Additive Manufacturing Process

Additive Manufacturing can reduce lead times, waste, energy use, and spare parts inventories, as well as improves system readiness and sustainability of armed forces, specifically during military and humanitarian missions abroad. Results showed that AM can solve a range of problems and improve production by customization, rapid prototyping, and geometrical freedom. Advantage of opting for AM techniques for macro scale production is mass customization. AM reduces the Tooling Cost[81].

AM is also known as layer manufacturing, layer manufacturing, additive fabrication, additive processes, techniques, freeform fabrication, and solid freeform fabrication. There are both functional prototypes and production products. Additive Manufacturing for Ceramics is more cost-effective than injection moulding for low-volume production. This is due to the lack of economies of scale and/or the fact that hardware and tooling modifications are not required when manufacturing excessively complex parts [5].

Using digital models, additive manufacturing (AM), commonly referred to as 3D printing, creates goods and parts layer by layer. In contrast to conventional manufacturing, which produces parts by removing material from a raw block, additive manufacturing (AM) builds parts up layer by layer. This enables the development of elaborate shapes and complex geometries that would otherwise be challenging, if not impossible, to produce using conventional techniques[82].

The ability of AM to build parts with astounding precision and accuracy is one of its main benefits. Due to the process's digital nature, components can be designed to exact specifications, and the machine can produce those components with astounding accuracy. As a result, AM is the perfect method for producing items that need to be extremely precise, such medical implants or aerospace components. Another benefit of additive manufacturing is its capacity to produce parts more quickly and inexpensively than conventional manufacturing processes. Because additive manufacturing (AM) is a digital process, parts can be instantly designed and produced without the use of costly tooling or setup expenses. Because of this, AM is a great option for generating small batches of parts or unique items that would be costly or time-consuming to fabricate using conventional techniques[83].

AM does have certain disadvantages, though. The narrow range of materials that can be employed in the process is one of the main obstacles. Although there are many materials that can be used in additive manufacturing, their strength, durability, and other qualities are frequently constrained. Because of this, designing components for use in demanding settings like aerospace or automotive applications may be challenging[84].

The high cost of materials and equipment is another issue with AM. Even though the cost of AM technology has decreased recently, most businesses still need to make a sizable investment. Additionally, the price of materials for AM can be expensive, particularly for materials with high performance like ceramics[84].

The production of ceramics could undergo a transformation because of additive manufacturing (AM). Unlike the labour- and time-intensive technique used in traditional ceramics manufacture, additive manufacturing (AM) enables the precise and accurate production of complicated designs and complex geometries. A major benefit of employing AM for ceramics is its capacity to produce parts with a high degree of accuracy and precision. This is crucial for applications like medical implants where the part's exact shape and size are essential to its operation. The capacity to produce parts with a high level of customisation is another benefit of AM for ceramics. Because additive manufacturing (AM) is a digital process, parts can be created to exact specifications, offering a high level of customization and flexibility. Nevertheless, there are some drawbacks to using AM for ceramics. The narrow range of materials that can be employed in the process is one of the main obstacles. While there are many materials that can be used in additive manufacturing, ceramics frequently have restricted properties and performance traits[83,84].

Furthermore, AM for ceramics can be expensive, especially for high-performance ceramics. Smaller companies or startups may find it challenging to invest in the technology as a result. There are several significant distinctions between making ceramics with AM and traditional methods. The production of parts and products for traditional ceramics is a labour- and time-intensive process that calls for trained artisans. AM, on the other hand, is a digital procedure that can be finished fast and effectively with no need for human involvement. The degree of customisation and flexibility that is feasible between additive manufacturing (AM) and conventional ceramics manufacture is another difference. It can be challenging to manufacture items with complicated designs or complex geometry using conventional production techniques. However, with AM, components can be created to exacting standards, offering a high level of customization and flexibility. Overall, AM offers several benefits over conventional manufacturing techniques and has the potential to transform the way that ceramics are produced[5].

The process of additive manufacturing has various benefits over traditional ceramic manufacture. The capacity to build complicated geometries that are impossible to produce using conventional methods is one of the key advantages. Additionally, additive manufacturing can significantly cut down on waste materials and the number of steps required for production. Cost savings and a lessening of the impact on the environment can result from this[83]. Making specialized parts is one of additive manufacturing's many important benefits. It is challenging to produce unique or one-of-a-kind pieces in traditional ceramic production since moulds or tools are frequently needed. However, using additive manufacturing, each part can be created from scratch without the use of costly tooling. This can be especially helpful in sectors like healthcare where specialized parts are frequently needed[5].

Additionally, additive manufacturing has some disadvantages. Achieving the necessary level of accuracy and surface smoothness is one of the key issues. The choice of materials that can be employed may also be constrained because some materials are more challenging to work with when employing additive manufacturing techniques. The production rate, which may be slower than with conventional manufacturing techniques, is another drawback. Additive manufacturing, in relation to ceramics specifically, is a quickly developing technology that is garnering greater attention as researchers and engineers examine its potential. The capacity to produce complicated shapes that are not feasible using conventional ceramic manufacturing techniques is a significant advantage of additive manufacturing for ceramics. For instance, complicated shapes or intricate lattice structures that are impossible to construct using conventional techniques can be produced with additive manufacturing. The capacity of additive manufacturing for ceramics to produce intricate ceramic parts with exceptional accuracy and precision is another important benefit. This is crucial for sectors like aerospace and healthcare where parts must adhere to highly exact tolerances and specifications[85]. The usage of additive manufacturing for ceramics has some restrictions as well. Getting the necessary degree of material characteristics and performance is one of the biggest hurdles. Materials can be handled and treated in the standard ceramic manufacturing process to attain material qualities, such as strength, hardness, or thermal conductivity. These qualities, especially for high-performance ceramics, can be more challenging to achieve with additive manufacturing. The variety of materials that can be utilized for ceramic additive manufacturing is another restriction. Using additive manufacturing, some ceramics, like alumina, have been successfully printed, but others, like zirconia, are more difficult to work with[5].

Additive manufacturing is a quickly developing technology that has several benefits over conventional production processes. A few advantages of this technique include the capacity to produce intricate geometries, lower waste, and modify parts. Particularly for ceramics, additive manufacturing can produce intricate and precise parts that are impossible to make using conventional techniques. However, there are some difficulties when applying this technology to ceramics, especially when trying to achieve the necessary material characteristics and performance. It is expected that additive manufacturing will become more widely used in the ceramics industry as this technology develops[5].

2.3.2 Types of Additive Manufacturing

The use of additive manufacturing (AM), a game-changing technology, has completely changed how we design and produce things. To generate a 3D item from a computer model, materials are built up layer by layer. Compared to conventional production methods, additive manufacturing (AM) technologies provide several advantages, such as the capacity to generate complicated geometries, lower waste, and increase design flexibility. There are seven primary categories of AM technologies, each having a special method and benefits. These are the technologies: Material Extrusion Material Jetting Powder Bed Fusion Sheet Lamination Vat Photopolymerization Binder Jetting Direct Energy Deposition Material[86]. The detail of the seven additive manufacturing methods is given below.

a) **Material Jetting:** An additive manufacturing (AM) technique called material jetting (MJ) works similarly to inkjet printing. Droplets of a liquid substance are deposited onto a build platform using print heads, and these droplets are then cured or hardened using a variety of processes, including UV light, heat, or chemical reactions. The droplets are placed in a predetermined pattern that gradually adds layers to the object. High-precision material jetting may create components with exquisite features and complex shapes. It can print numerous materials at once and produce gradients of different materials or colours inside of a single item. The size of the pieces that can be generated and the variety of materials that can be printed, however, may be constrained[87].

b) **Binder Jetting:** Using the additive manufacturing technique known as "binder jetting," layers of powdered materials are joined together to form solid objects. Layers of powder material are first deposited onto a build platform, and then a liquid binding agent is selectively deposited onto the powder layer to bind the particles together. Layer by layer, this process is repeated until the desired thing is constructed. The capacity to employ a variety of materials, such as metals, ceramics, and polymers, is one of the main benefits of binder jetting. Due to its adaptability, it is a great option for a variety of industries, including aerospace, automotive, and biomedicine. The rapidity of binder jetting is one of its key advantages. This method is perfect for industrial-scale production since it can swiftly produce big pieces. Additionally, because the procedure involves depositing powder materials, complex geometries that would be challenging or impossible to manufacture using conventional manufacturing techniques can be made. Binder jetting has several restrictions, though. The method requires joining layers of powder; therefore, the finished parts might not be as strong mechanically as those made with other AM technologies. Additionally, it can take time and result in additional material waste to remove extra powder material after the printing process[88].

c) **Direct Energy Deposition (DED):** It is an AM technique that includes melting and fusing materials together with the help of a concentrated energy source, such as an electron or laser beam. Feeding a wire or powder material into the energy source causes it to melt and deposit the material onto a substrate, where it solidifies to form the desired item. DED has several benefits over conventional manufacturing processes, including the capacity to create complicated geometries and the capacity to modify or add material to already manufactured items. In the aerospace and defence sectors, where the capacity to maintain and repair vital components is crucial, this technology is extremely helpful. The capacity of DED to quickly generate huge parts is one of its key advantages. It is feasible to create pieces in a single pass, cutting down on the amount of time needed for production, because the process includes melting and fusing materials together. In addition, a variety of materials, including as metals, ceramics, and polymers, can be employed with DED. DED is constrained in some ways, though. Materials are fused and melted together during the process, therefore the pieces that are produced may have residual stress or deformation that might alter their mechanical qualities. Furthermore, the process could generate a lot of heat, which could cause the part to warp or become distorted. Using a nozzle to deposit melted or semi-molten material onto a build platform to make the desired product is known as material extrusion. The procedure entails melting a thermoplastic material, extruding it through a nozzle, and layer-by-layer depositing it onto the build platform[89].

d) **Material Extrusion:** common AM technology is material extrusion since it is affordable and suitable for a variety of materials. Material extrusion, also known as Fused Filament Fabrication (FFF), is a type of additive manufacturing process that uses a filament of thermoplastic material to create three-dimensional objects. The filament is fed through a heated nozzle that melts the material, which is then deposited layer by layer to build up the object. The working principle of material extrusion involves the following steps: A spool of thermoplastic filament is loaded into the 3D printer. The filament is fed through a heated nozzle, which melts the material. The melted material is deposited layer by layer onto a build platform to create the object. Once a layer is complete, the build platform moves down by a small increment, and the process is repeated until the object is complete. Some of the benefits of material extrusion include Low cost compared to other 3D printing technologies, Easy to use and widely available, A wide variety of thermoplastic materials can be used, including ABS, PLA, PETG, and others, and can produce objects with good strength and durability[90].

e) **Powder Bed Fusion:** A powerful laser or electron beam is used in powder bed fusion, a type of additive manufacturing, to melt and fuse layers of powdered material together. The build platform is covered with a small layer of powder to start the process. The powder is then selectively melted by the laser or electron beam to form a solid layer. The process is then repeated as the build platform descends by one layer thickness. The design is entered into a computer software program, much like with other AM techniques, and this program directs the movement of the laser or electron beam. Complex metal pieces can be produced with great accuracy and resolution using powder bed fusion. Selective laser melting (SLM) or electron beam melting (EBM) are other names for this procedure[91].

f) **Sheet Lamination:** In the process of additive manufacturing (AM), sheets of material, such as paper, plastic, or metal, are bonded together. After being cut to the design's shape, the layers are joined together using heat, pressure, or an adhesive. Layer by layer, the process is continued until the desired thing is constructed. Prototyping and the creation of composite products, such fibre-reinforced composites, frequently involve sheet lamination[92].

g) **VAT Photopolymerization:** Vat photopolymerization is an additive manufacturing procedure that turns a liquid photopolymer into a solid item by curing it with a light source like a laser or projector. A build platform is lowered into a vat that contains the photopolymer. The photopolymer is then selectively cured by the light source to produce a solid coating. The process is then repeated after lifting the construct platform out of the tank by one layer thickness. Vat photopolymerization is frequently used to create extremely detailed, high-quality products with a smooth surface, such dental models and jewellery[93].

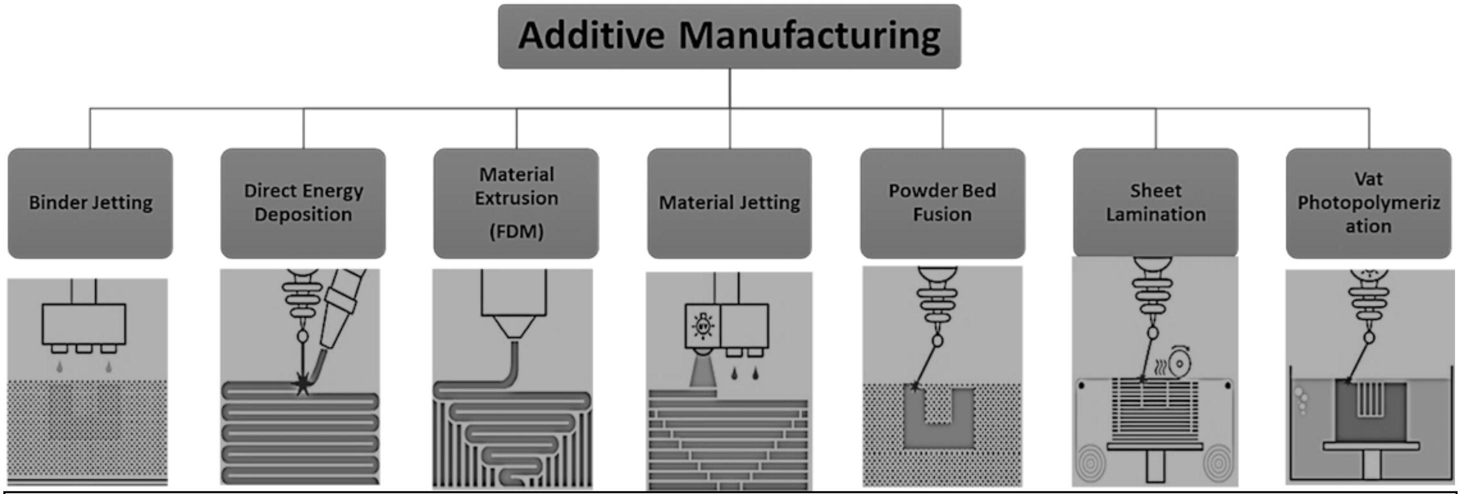


Figure 2.2: Types of Additive Manufacturing

The seven different AM technologies listed above offer a variety of additive manufacturing alternatives, each with unique advantages and disadvantages. Designers and manufacturers can select the optimal process for their unique demands and produce complicated parts with high precision and accuracy by being aware of the capabilities of each technology.

2.3.3 Advantages of Additive Manufacturing over conventional ceramic manufacturing

Additive manufacturing, also referred to as 3D printing, is a revolutionary technology that has transformed the product design and production processes. Due to its unique advantages over conventional ceramic manufacturing techniques, it has acquired popularity in recent years in the field of ceramics. In this paper, the advantages of additive manufacturing over conventional ceramic manufacturing techniques will be examined in depth. Using a digital model, additive manufacturing involves constructing three-dimensional objects layer by layer. The procedure entails dissecting a three-dimensional model into layers and then depositing material layer by layer to construct the object. Various materials, including ceramics, metals, plastics, and composites, are utilized. A computer program directs the printer to construct the object based on the digital model[82]. Following are the advantages of Additive Manufacturing over conventional ceramic manufacturing process:

a) **Design Flexibility:** One of the key advantages of additive manufacturing is its design flexibility. Unlike traditional ceramic manufacturing techniques, which require the use of moulds, additive manufacturing allows for the creation of complex geometries that cannot be produced using moulds. This allows for greater design freedom and enables the production of unique and customized ceramic products[94].

b) **Reduced Material Waste:** Another advantage of additive manufacturing is the reduced material waste. In traditional ceramic manufacturing techniques, excess material is often left over after the production process. This material is then discarded, resulting in significant waste. With additive manufacturing, the material is only used where it is needed, resulting in minimal waste[94].

c) **Reduced Lead Time:** Additive manufacturing also offers reduced lead time, as it eliminates the need for tooling and moulds. Traditional ceramic manufacturing techniques require the creation of moulds, which can be time-consuming and expensive. With additive manufacturing, the digital model can be produced quickly and easily, reducing the time needed to produce a finished ceramic product[5].

d) **Improved Quality Control:** Additive manufacturing also offers improved quality control. The process is highly automated and can be monitored in real-time using sensors and other monitoring tools. This allows for greater accuracy and consistency in the production process, resulting in higher-quality ceramic products[94].

e) **Reduced Cost:** Additive manufacturing can also be more cost-effective than traditional ceramic manufacturing techniques. Although the initial cost of the 3D printer may be high, the cost per part can be significantly lower than that of traditional manufacturing techniques, as there is no need for tooling or moulds. Additionally, additive manufacturing can be used to produce small batches of ceramic products, making it ideal for low-volume production runs[5].

2.4 Additive Manufacturing of Advance Ceramics

2.4.1 Overview of Additive Manufacturing Process of Ceramic Materials

AM provides an alternative to conventional formative processes, enabling the production of near-net-shape, three-dimensional ceramic components without the use of expensive tooling. Nonetheless, the implementation of AM technologies in the ceramic industry has been slower than in the polymer and metal industries due to the inferior resolution, surface quality, mechanical properties, and scalability of additively manufactured ceramic parts in comparison to conventional ceramic manufacturing processes. AM offers an alternative to conventional formative processes, enabling the production of near-net-shape 3D ceramic components without the use of expensive tooling[95].

Due to the inferior resolution, surface quality, mechanical properties, and scalability of additively manufactured ceramic parts compared to conventional ceramic manufacturing processes, the implementation of AM technologies in the ceramic industry has been significantly slower than in the polymer and metal industries. AM provides an alternative to conventional formative processes, enabling the production of near-net-shape, three-dimensional ceramic components without the use of expensive tooling. Large production volumes are typically required to amortize the high tooling costs; however, this is not necessarily the case for all conventional formative technologies, as the inexpensive plaster of Paris moulds used in slip casting can be used to circumvent this requirement[96].

Furthermore, design modifications and functional prototypes must be kept to a minimum because each design iteration necessitates the creation of a new mould, which is both time-consuming and expensive. Modifying the design of a component in the context of AM, on the other hand, is as simple as updating the corresponding digital design files, which may involve a change in build orientation and optimization of processing parameters but does not necessitate physical modifications to the machine or custom tooling. Since there are no fabrication expenses, the unit cost is no longer proportional to production volume. Therefore, the overall manufacturing cost of AM technologies is independent of design complexity and only relates to material use (i.e., material cost and construct size), machine power consumption, and labour cost. In contrast to conventional ceramic manufacturing processes, the overall manufacturing cost per part with AM technologies is completely independent of design complexity; rather, it is primarily related to material utilization and dependent on the number of parts to be produced. This factor is crucial to the case for ceramics AM. Numerous applications of ceramic components require significantly smaller production volumes than those of metals or polymers, which makes additive manufacturing a particularly attractive and cost-effective alternative to injection moulding for small production volumes, especially when parts are geometrically complex[97].

In addition to cost savings, the absence of custom tooling reduces prototyping and production lead times significantly. The inherent design freedom provided by layer-wise part formation, which enables the fabrication of complex geometries that would be difficult or impossible to produce using subtractive or formative manufacturing processes, is another significant benefit of additive manufacturing. This increased design flexibility afforded by AM allows for the reduction, and in some cases, elimination, of additional forming, cutting, and assembly processes, resulting in shorter lead times and lower manufacturing costs[83].

2.4.2 General additive manufacturing process and parameters for ceramic material

The General method of manufacturing the Ceramic products using the Additive Manufacturing is shown in the figure 2.3. This process starts from preparation of the ceramic powder of the desired particle size and composition. This step includes the calcination of the ceramic powder and the ball milling of the powder. In the calcination process the ceramic powder is heated or fired and this is done to remove the impurities of the ceramic powder including different sulphates, hydrates, and carbonates. The calcination of the powder also ensures that the plasticity is removed from the ceramic powder. It also removes the volatile impurities and can be termed as the purification process of the powder [82].

The second step is the fabrication of the ceramic slurry or ceramic ink or dry powder. In this step the powder prepared in the previous step is added with three other components which are: additives, binders, and the suspension media. The additives are the components which are added to enhance characteristics of the slurry and the final part. The suspension media and the binders are added to bind the ceramic powder particles and hold them in place so they can acquire the part geometry and support the layer wise additive manufacturing of the ceramic part. After the slurry or powder is prepared then the green body is fabricated which is transformation of slurry into a final geometry. The green body holds binders, and suspension media which is to be removed before sintering to avoid any chemical or physical hindrance in the growth of part microstructure. This is the reason that the green body is first fired at a high temperature ensuring that all the binder and suspension media has evaporated, and the part geometry left is only the ceramic powder and the additives added (if any). The process transforms the green body into brown body. The brown body is the part geometry which just requires to be fired at sintering temperatures to let the microstructure of the ceramic material grow and the ceramic part starts to attain a particular microstructure and properties that were planned. During the transformation of the green body into brown body and in final sintering it is ensured that the part geometry is isothermally heated at a certain temperature which prevents the material from thermal disruptions resulting from thermal shocks and ensures that the uniform heating or firing of the sample takes place. The sample after sintering is left to cool and retrieved when it cools. This step is the final step in Additive Manufacturing of the ceramic material. Further processing of the ceramic part includes machining if required, polishing or any other post manufacturing process as required [5].

Step Number	**Ceramic State**	**Processing Step**	**Objective of Processing**
1	Powder	Calcination of Powder and Ball Milling	To control the particle size and purity of ceramic powder
2.	Slurry or Ceramic Ink	Mixing of ceramic slurry components including ceramic powder, additives, and suspension media.	To prepare ceramic slurry capable enough to hold the geometric shapes and transform into a solid geometry
3	Green Body	Required part geometry formed using ceramic ink or slurry	To transform the ceramic slurry into part geometry.
4	Brown Body	Burning of additives, binders, and suspension media	To ensure that no ceramic slurry component hinders the microstructure transformation during sintering
5	Sintered Body	High temperature furnace sintering	To transform ceramic particles into part geometry by growth of microstructure using sintering process.
6	Final Part Geometry	Polishing, coloring, and deburring	To enhance the finish of final ceramic part

Table 2-1: General Ceramic Additive Manufacturing Process

Ceramic additive manufacturing, also known as ceramic 3D printing, requires a wide range of adjustable parameters to regulate the printing process and guarantee the delivery of flawless ceramic components. Some crucial factors to think about are as follows:

a) **Material selection:** One of the most important factors in the additive manufacturing of ceramics is the choice of the ceramic material. The great temperature resistance, hardness, and superior mechanical qualities of ceramic materials are well known. Not all ceramic materials, meanwhile, are appropriate for additive manufacturing. The choice of material should consider the material's physical and chemical characteristics, availability, pricing, and compatibility with the additive manufacturing process being utilized [98].

b) **Particle size:** This important variable has the potential to have a big impact on the finished part's printing quality and characteristics. The packing density, surface quality, and resolution of the printed object can all be enhanced by fine particles. However, excessively tiny particle sizes can affect the slurry's flow characteristics and clog the printing nozzle[98,99].

c) **Rheology and binder composition:** Binders are crucial elements in ceramic inks or slurries because they aid in the binding of ceramic powder particles during the printing process. The printability, stability, and strength of the green portion can be affected by the composition of the binder and its rheological characteristics, such as viscosity and yield stress. The ink or slurry's flow behaviour is determined by the binder's rheology, and the mechanical properties of the finished product are affected by the composition of the binder during sintering[98].

d) **Printing temperature:** During the printing process, the printing temperature has a significant impact on the bonding and adhesion of the ceramic layers. Additionally, it affects the final part's microstructure and properties. To achieve good layer adhesion and reduce warping or cracking during the sintering process, the temperature should be optimized based on the ceramic material and printing technology employed[76,100].

e) **Layer thickness:** The final part's resolution, precision, and surface quality are all strongly influenced by layer thickness. A smaller layer thickness can enhance the part's precision and resolution, but it also lengthens the printing process and raises the printing expense. A thicker layer might speed up printing and save money, but it might affect the part's accuracy and surface quality.

f) **Printing speed:** Printing speed is a crucial factor that influences both the length of time it takes to print a part and its quality. To ensure strong layer adhesion, reduce flaws, and avoid warping or cracking while printing, the printing speed needs to be optimized[76].

g) **Post-processing:** Sintering the printed item to give it the necessary mechanical characteristics is a crucial post-processing parameter. To improve the qualities of the finished item, any further post-processing operations, such as polishing, glazing, or coating, should be taken into consideration. The sintering temperature and time should be tuned based on the specific ceramic material employed[83].

The parameters for ceramic additive manufacturing are crucial elements that affect the quality, characteristics, and cost of the finished product. Manufacturers can achieve the desired mechanical characteristics, surface finish, and accuracy of the finished product by optimizing these parameters. Understanding the ceramic material's physical and chemical characteristics, the printing process being utilized, and the desired mechanical attributes of the finished product are essential for parameter optimization[98].

2.4.3 Single Step Additive Manufacturing vs Multistep Additive Manufacturing Process for Ceramics

Ceramic AM processes can be divided into "single step" and "multi-step" categories. Multi-step AM processes result in the formation of a green body, which requires subsequent de-binding and sintering thermal treatments to obtain the final advanced ceramic component. The Single Step AM consisting of 4 Steps whereas the Multi Step AM consisting of 8 Steps as shown in figure 2.4. The first three steps are common amount both the AM process. The process of single step AM starts by the preparation of the ceramic feedstock. This typically includes four components: Ceramic Powder, Binders, Additives, and Suspension media[101].

The ceramic powder is added with additives to impart any special desired property or characteristic to the final part. The binders are used to keep the feedstock bound in the desired shape or geometry. The suspension media supports binder in holding the particles and particularly used in hydro slurry ceramic feedstocks and inks. Usually, the aqueous based ceramic slurries use Deionized Water as suspension media. The Ceramic Feedstock is then additively manufactured. The single step AM of ceramics is commonly conducted by applying the Direct Energy Deposition or Direst Laser Sintering process. The Slurry is made to flow through a nozzle in this case and the laser heats and sinters the slurry at the same time converting the ceramic slurry directly into the final product bypassing the green body and brown body stages. Afterwards the ceramic part is retrieved, and this marks the completion of the single step AM of ceramic Parts[5].

In contrast to this method the Multi Step AM of Ceramic Parts involves an extra four step processing of the ceramic slurry before the final ceramic part is manufactured. After the slurry or feedstock is manufactured and additively manufactured, it is converted into a green body by forming the slurry to acquire the part geometry. Afterwards the green body is heated to burn the suspension media, binder and additives present which transform the green body into brown body. Later the brown body is sintered in the furnace to get the desired growth of microstructure in the sample. This completes the Multistep AM for ceramics and the part is retrieved for any further processing.[5]

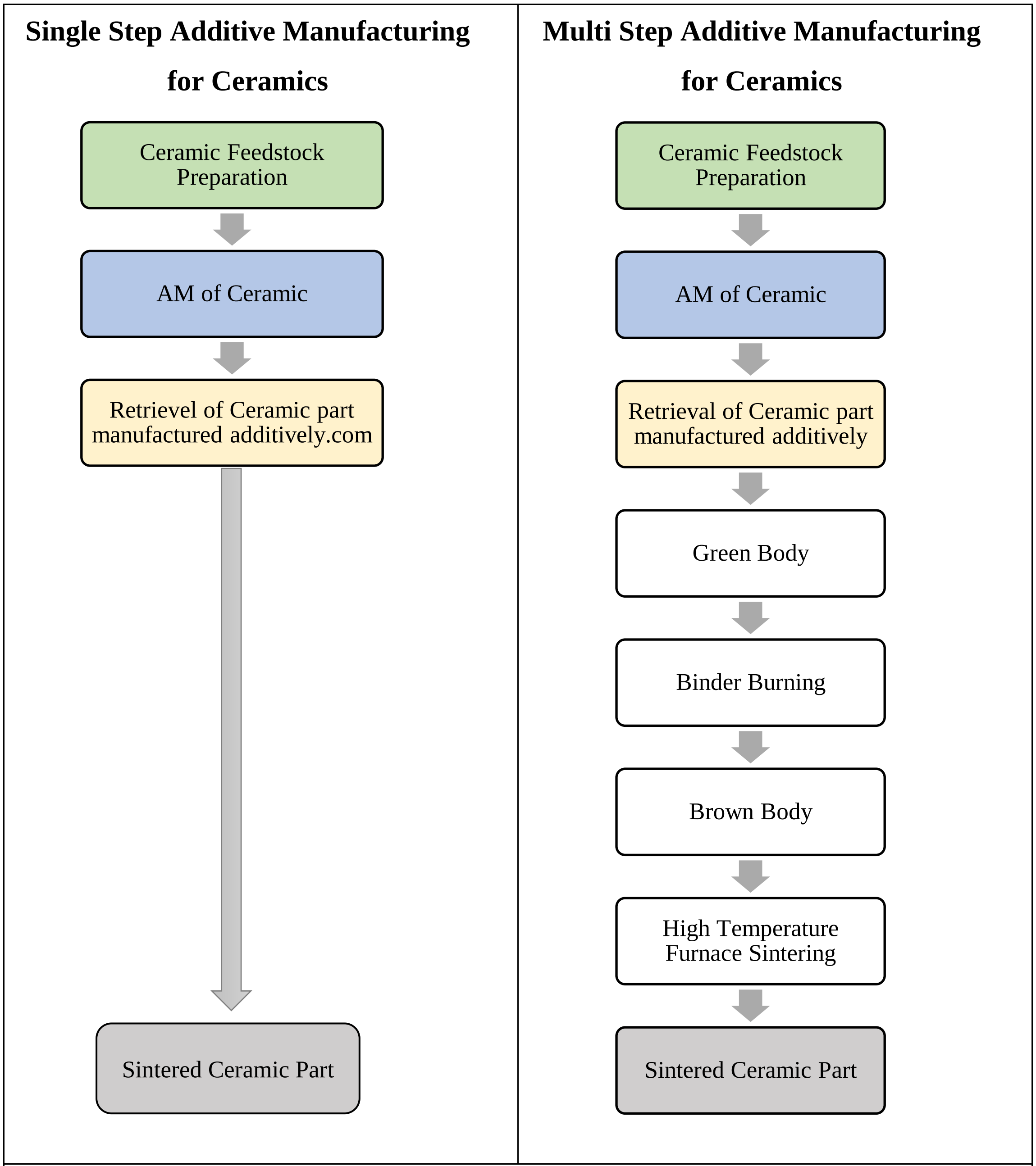


Figure 2.3: Comparison of Multi Step AM vs Single Step AM for Ceramics

These are the two general category Additive Manufacturing techniques are used to manufacture the ceramics. From the seven mentioned AM Processes, the Direct Energy Deposition, and Powder Bed Fusion are the AM Method that categorized as Single Step AM for Ceramics. Most of the AM methods for ceramics belong to the Multi Step AM which including Sheet Lamination, Vat Polymerisation, Material Extrusion, Material Jetting, Binder Jetting, and the Powder Bed Fusion. The powder bed fusion is categorized as single and multistep AM process when ceramic materials are considered[5].

2.4.4 Ceramic and metallic powders used in ceramic manufacturing.

Ceramic powders are finely ground materials that are made up of various minerals and oxides, such as aluminium oxide, silicon carbide, and zirconium oxide. These powders are used to make ceramics, which are materials that are created by heating a mixture of ceramic powders at high temperatures until they fuse together. Ceramic powders are also used in the production of ceramic coatings, which can provide protection from heat, wear, and corrosion. Metallic powders are made up of small particles of metal that are used in a variety of applications, including the production of metal parts and components. These powders are commonly used in the manufacturing of ceramics as they can improve the properties of the ceramic material, such as its strength, wear resistance, and thermal conductivity. In ceramic manufacturing, both ceramic and metallic powders are used to create slurries or pastes that are applied to a surface to form a ceramic coating or to create a ceramic object. Ceramic slurries are typically made by mixing ceramic powders with a liquid, such as water or a solvent, to create a paste-like substance that can be applied to a surface. Metallic powders can be added to ceramic slurries to improve the properties of the final ceramic material. In ceramic ink production, ceramic powders are mixed with a liquid medium and other additives to create a fluid ink that can be applied to a surface using various printing techniques. These inks are commonly used for printing images and patterns onto ceramic surfaces, such as tiles, mugs, and plates[102].

2.4.5 Agglomeration of metallic powders

Agglomeration of metallic powders occurs when small particles of metal combine or stick together to form larger aggregates. This phenomenon can arise due to several factors such as electrostatic forces, surface tension, and van der Waals forces. Copper powder is susceptible to agglomeration due to its high surface area, reactivity, and the presence of surface oxides. The surface oxides on copper particles can cause them to clump together, making it challenging to disperse them in a liquid medium. Additionally, the high surface area and reactivity of copper powder can promote the oxidation of the particles, leading to further agglomeration. When copper powder is ball-milled, the milling process can induce mechanical and thermal stresses on the particles, leading to the formation of defects and dislocations. These defects can function as sites for oxidation, further promoting the agglomeration of the particles. The oxidation of copper powder during ball milling is also facilitated by the high surface area of the particles and the exposure of fresh surfaces that are susceptible to oxidation[103].

To prevent or reduce the agglomeration of copper powder, various strategies can be employed, such as surface treatments, coatings, dispersants, or surfactants. These methods can help to reduce the reactivity of the particles and prevent the formation of surface oxides. Proper storage and handling of the powder can also help to minimize the impact of environmental factors such as moisture, which can further promote agglomeration[104].

2.4.6 Ceramic Slurry

Ceramic inks and slurries are essential components in the manufacturing of ceramic products. They are used in a variety of applications such as creating decorative designs, lettering, and logos on ceramic surfaces, and as a coating material for different types of ceramic products. In this article, we will explore the world of ceramic inks and slurries, their properties, and their applications. Ceramic inks are liquid materials that contain ceramic particles, pigments, and other additives. They are used to create decorative designs on ceramic products by printing or painting on the surface. Ceramic inks are composed of different types of pigments, binders, and solvents. Pigments are responsible for the colour of the ink and can be organic or inorganic. Binders are used to hold the pigment particles together and provide adhesion to the surface. Solvents are added to the ink to make it flow more easily and evaporate quickly.

There are two main types of ceramic inks: organic and inorganic. Organic inks are made from carbon-based compounds and are used for decorating ceramics. They are more environmentally friendly than inorganic inks because they contain fewer toxic chemicals. Inorganic inks, on the other hand, are made from metal oxides and are used for creating conductive patterns on ceramics, such as electronic components. Ceramic slurries, on the other hand, are mixtures of ceramic particles and liquid. They are used for coating ceramic products, such as tiles and sanitaryware, to improve their physical and chemical properties. Ceramic slurries are composed of different types of ceramic particles, binders, and solvents. The ceramic particles used in slurries are usually finer and more homogeneous than those used in ceramic inks[105].

Ceramic slurries can be classified into two types: aqueous and non-aqueous. Aqueous slurries are made with water-based solvents and are used for coating ceramic tiles. Non-aqueous slurries are made with organic solvents and are used for coating ceramic products that require high-quality finishes, such as sanitaryware. The properties of ceramic inks and slurries are critical in determining their suitability for specific applications. The most important properties of ceramic inks are viscosity, adhesion, and colour intensity. Viscosity refers to the thickness of the ink, which affects how easily it can be applied to the surface. Adhesion is the ability of the ink to stick to the surface, and colour intensity refers to the strength of the colour of the ink[106].

In the case of ceramic slurries, the most important properties are viscosity, thixotropy, and green strength. Viscosity is the thickness of the slurry, which affects how easily it can be applied to the surface. Thixotropy is the ability of the slurry to become less viscous when agitated, which allows it to flow more easily. Green strength refers to the strength of the coating when it is still wet and has not been fired. The applications of ceramic inks and slurries are vast and varied. They are used in the manufacturing of a wide range of ceramic products, including tiles, sanitaryware, and electronic components. In the case of ceramic inks, they are used to create decorative designs, lettering, and logos on ceramic surfaces. They are also used for printing barcodes, serial numbers, and other identification markings on ceramic products[107].

Ceramic inks are widely used in the production of tiles. They are applied to the surface of the tile using a printing process, and then the tile is fired in a kiln to fix the design onto the surface. The use of ceramic inks has revolutionized the tile industry, allowing for the creation of highly intricate and detailed designs on tiles. Ceramic slurries are used to improve the physical and chemical properties of ceramic products. They are used for coating ceramic products, such as tiles and sanitaryware, to improve their strength, abrasion resistance, and chemical resistance. Ceramic slurries can also be used for creating special effects, such as a metallic finish or a textured surface. In the case of ceramic tiles, slurries are used to coat the surface of the tile to improve its physical and chemical properties. The coating can provide the tile with increased strength, abrasion resistance, and chemical resistance. Ceramic slurries can also be used to create special effects, such as a metallic finish or a textured surface. The use of ceramic slurries has led to the development of new tile products with unique properties and finishes[108].

Ceramic slurries are also used in the production of sanitaryware. Sanitaryware is a term used to describe a range of ceramic products used in bathrooms and kitchens, such as toilets, sinks, and shower trays. Ceramic slurries are used to coat the surface of these products to improve their strength, durability, and chemical resistance. The use of ceramic slurries has led to the development of new sanitaryware products with improved properties and finishes. In the electronics industry, ceramic slurries are used to create conductive patterns on ceramic components, such as circuit boards. The slurries are used to coat the surface of the ceramic component with a conductive material, such as silver or copper. This allows for the creation of electronic components with intricate and precise conductive patterns[109].

2.4.7 Ceramic Slurries and Inks used in Additive Manufacturing

Ceramic slurries and inks are critical components in the additive manufacturing process of ceramics. The properties of the slurries and inks, such as viscosity, thixotropy, and rheology, have a significant impact on the deposition rate, layer thickness, and quality of the final product[110]. The properties and their impact on ceramic AM are described below:

a) **Viscosity** is a measure of the resistance of a fluid to deformation or flow. In ceramic AM, the viscosity of the slurry or ink affects the extrusion process, i.e., how easily the material flows out of the print head, and how quickly the material can be deposited. A slurry or ink with low viscosity will flow easily, while a slurry or ink with high viscosity will flow slowly. The viscosity of ceramic slurries and inks can be affected by several factors, such as the particle size distribution, solids loading, binder type, and processing conditions. In general, slurries and inks with lower solids loading tend to have lower viscosity, while those with higher solids loading tend to have higher viscosity[111].

b) **Thixotropy** is a property of some materials that exhibit a decrease in viscosity when they are subjected to shear stress or agitation. In ceramic AM, thixotropy can be beneficial for improving the flow behaviour of the slurry or ink during printing. When the slurry or ink is sheared by the print head, the viscosity decreases, allowing the material to flow more easily. After the shear stress is removed, the material gradually returns to its original viscosity. Thixotropy can be influenced by several factors, such as the particle size distribution, solids loading, and binder type. Slurries and inks with smaller particle sizes tend to exhibit higher thixotropy, while those with larger particle sizes tend to exhibit lower thixotropy[112].

c) **Rheology** is the study of the deformation and flow of materials. In ceramic AM, rheology is a crucial property that affects the deposition rate, layer thickness, and quality of the final product. Rheology is determined by the viscosity and elasticity of the material, and the ratio between the two is called the viscoelasticity. The rheology of the slurry or ink must be carefully controlled to ensure optimal printing conditions. If the slurry or ink is too viscous, the deposition rate may be too slow, and the printed layers may be too thick, leading to poor surface quality and accuracy. On the other hand, if the slurry or ink is too thin, it may not hold its shape after deposition, leading to deformation or collapse. The rheological properties of ceramic slurries and inks can be affected by several factors, such as the solids loading, particle size distribution, binder type, and processing conditions. In general, slurries and inks with higher solids loading tend to exhibit higher viscoelasticity, while those with lower solids loading tend to exhibit lower viscoelasticity[113].

d) **Deposition rate** is the rate at which the ceramic material is deposited during the AM process, and it is influenced by several factors, such as the nozzle diameter, printing speed, and material properties. In general, a higher deposition rate can lead to faster printing speeds and shorter build times. However, a high deposition rate can also result in lower accuracy and surface quality, especially in complex geometries. In ceramic AM, the deposition rate can be controlled by adjusting the extrusion parameters, such as the nozzle diameter, printing speed, and layer thickness. A larger nozzle diameter can increase the deposition rate, while a smaller nozzle diameter can improve the accuracy and resolution of the printed part. Similarly, a higher printing speed can increase the deposition rate, while a lower printing speed can improve the surface quality and accuracy of the printed part[114].

e) **Layer thickness** is the height of each layer that is deposited during the AM process, and it is a critical parameter that can affect the surface quality, accuracy, and mechanical properties of the final ceramic part. In general, thinner layers can lead to higher accuracy and surface quality, but they can also increase the build time and reduce the deposition rate. In ceramic AM, the layer thickness can be controlled by adjusting the extrusion parameters, such as the nozzle diameter, printing speed, and layer height. A smaller nozzle diameter and slower printing speed can help to achieve thinner layers, while a larger nozzle diameter and faster printing speed can result in thicker layers[115].

It is important to note that the deposition rate and layer thickness are interrelated parameters, and their optimal values may depend on the specific application and material properties. For example, a high deposition rate may be desirable for large parts or bulk production, while a low deposition rate may be preferable for small parts or high-precision applications.

The success of additive manufacturing (AM) of ceramics heavily relies on the properties of ceramic slurries and inks, including viscosity, thixotropy, and rheology. These properties dictate the flow behaviour of the material during the AM process, which affects the deposition rate, layer thickness, and quality of the final product. Therefore, it is crucial to carefully control these properties during the formulation of the slurry or ink to achieve optimal printing conditions and high-quality ceramic parts. The deposition rate, which is the rate of ceramic material deposition during the AM process, can be controlled by adjusting extrusion parameters such as nozzle diameter, printing speed, and layer thickness. A high deposition rate can lead to faster printing speeds and shorter build times, but it may compromise accuracy and surface quality in complex geometries. On the other hand, thinner layers can lead to higher accuracy and surface quality, but they can also increase build time and reduce the deposition rate. Therefore, finding the optimal balance between deposition rate and layer thickness is important and may depend on the specific application and material properties. Careful control of the properties of ceramic slurries and inks, along with extrusion parameters, can lead to successful AM of ceramics with high quality and desired properties. The significance of ceramic slurry or ink lies in its ability to facilitate the production of complex and intricate ceramic parts with high accuracy and precision. The use of slurry or ink in ceramic manufacturing enables the production of parts with fine details and tight tolerances that may be difficult or impossible to achieve through traditional ceramic manufacturing methods. It is commonly used in additive manufacturing techniques such as material extrusion and binder jetting. The composition of ceramic slurry or ink can vary depending on the specific application and manufacturing process being used. Ceramic slurry or ink is composed of ceramic particles and a liquid medium, which can include a binder, a solvent, and other additives[115].

2.4.8 Components of Ceramic Slurry and their significance

Ceramic slurry or ink is typically made by mixing ceramic powder, a liquid solvent, and various additives to create a homogeneous mixture that can be used for 3D printing or other additive manufacturing processes[116]. Here is a breakdown of the components of ceramic slurry or ink and their roles:

Component	Function	Examples
Ceramic Powder	Provides material for part formation	Alumina, zirconia, silicon carbide
Solvent	Controls viscosity and enables flow	Water, ethanol, propylene glycol
Binder	Promotes adhesion between particles and prevents cracking	Polyvinyl alcohol, carboxymethyl cellulose
Surfactant	Controls particle dispersion and improves rheology	Sodium dodecyl sulphate, Triton X-100
Plasticizer	Controls ink flexibility and reduces shrinkage	Glycerol, ethylene glycol
Rheology modifier	Adjusts ink viscosity for printing	Xanthan gum, hydroxyethyl cellulose
Crosslinker	Enhances strength and durability	Bismaleimide, melamine formaldehyde

Table 2-2: Ceramic slurry components, their functions, and examples

The exact composition of a ceramic ink can vary depending on the specific application and the materials being used. Ceramic inks can contain a range of elements and components, including:

a) **Ceramic powders:** These are the primary materials used in the ink and are typically fine powders of ceramic materials such as alumina, zirconia, or silicon carbide. The particle size and shape can affect the ink's viscosity, flowability, and printability[107].

b) **Solvents:** These are liquids used to dissolve or suspend the ceramic particles, control the ink’s viscosity, and flow properties. Common solvents include water, ethanol, and propylene glycol[106].

c) **Binders:** These are materials that promote adhesion between the ceramic particles and prevent cracking or deformation of the printed part. Binders can be organic or inorganic and include materials such as polyvinyl alcohol and carboxymethyl cellulose[117].

d) **Surfactants:** These are chemicals that control the dispersion of ceramic particles in the ink and improve the ink's rheology. Surfactants can include materials such as sodium dodecyl sulphate and Triton X-100[118] .

e) **Plasticizers:** These are materials that are added to the ink to control its flexibility and reduce shrinkage during drying or firing. Common plasticizers include glycerol and ethylene glycol[114].

f) **Rheology modifiers**: These are materials that adjust the ink's viscosity and flow properties for printing. Rheology modifiers can include materials such as xanthan gum and hydroxyethyl cellulose[114].

g) **Crosslinkers**: These are materials that enhance the strength and durability of the printed part. Crosslinkers can include materials such as bismaleimide and melamine formaldehyde[119].

Overall, the composition of ceramic ink can be customized based on the specific application and desired properties of the printed part. The combination of ceramic powders, solvents, binders, surfactants, plasticizers, rheology modifiers, and crosslinkers allows for a wide range of ink formulations that can be optimized for different printing methods, ceramic materials, and part geometries. If these components are not added in the required amount, it can affect the properties of the printed part. The element may be brittle or fragile if there is an excess of binder. If there is insufficient plasticizer, the component may contract or fracture during curing or firing. If the particulate size of the ceramic powder is too large, it can interfere with the printability of the ink and produce a rough or porous surface. If the ink's viscosity is too high or too low, it can impair the flowability and quality of the printed piece [98].

2.4.9 Carboxymethyl Cellulose (CMC) Binder

CMC, or carboxymethyl cellulose, is a typical binder used to increase the viscosity and flowability of ceramic slurry. It is a water-soluble polymer formed from cellulose, which is found naturally in plants. CMC is utilized as a binder in ceramic inks because it dries to form a robust and flexible film. It works as a thickening and binder in ceramic slurry, keeping the ceramic particles suspended and preventing them from settling out. It also acts as a lubricant and aids in the dispersion of ceramic particles. The amount of CMC used in the slurry might vary based on the application and the desired slurry qualities[120].

CMC is not reactive with the components of ceramic inks. It is chemically inert and does not react with the ceramic particles or other ink components. CMC, on the other hand, can be sensitive to variations in pH, temperature, and other external conditions, which can have an impact on its characteristics and performance. The CMC binder generates a coating that holds the ceramic particles together when the ceramic slurry is applied to a substrate and dries. The CMC binder decomposes and burns away during firing, leaving behind a porous ceramic structure. The CMC binder is commonly evaporated by heating, which causes the water in the slurry to evaporate and the CMC to dry out and disintegrate[121].

CMC, in general, is not reactive with DCM, or dichloromethane, a typical solvent in ceramic ink formulations. However, because the specific properties of CMC might vary based on the production process and other conditions, it is always recommended to evaluate the compatibility of CMC with other components in a ceramic ink formulation before usage[120].

In conclusion, CMC is a key binder used in ceramic slurry to improve its properties and make the fabrication of high-quality ceramic components easier. It is not commonly thought to be reactive with ceramic ink components or DCM. When developing ceramic inks or building ceramic components, it is critical to carefully address the unique features and behaviour of CMC. CMC is a common binder used in a variety of industries, including food, pharmaceuticals, and personal care goods. Its capacity to produce gels, thicken liquids, and stabilize emulsions is well known. CMC is utilized in a variety of applications in the ceramic industry, including the manufacturing of green bodies, as a binder for ceramic powders, and as a thickening for ceramic glazes. CMC has several essential qualities that make it a useful component in ceramic slurries in addition to its duty as a binder. CMC improves a slurry rheology, making it more flowable and easier to manage. It can also strengthen the ceramic body, which is useful for handling and processing[122].

The evaporation of CMC from a green body during the firing process can also influence the final ceramic product's characteristics. Evaporation rate and temperature can have an impact on the porosity, density, and other physical properties of a ceramic material. Controlling these characteristics carefully can be critical for getting the desired attributes in the final product. The likelihood of contamination is one potential difficulty with utilizing CMC in ceramic slurries. CMC is a flexible and frequently used binder in the ceramic sector, offering significant advantages in terms of rheology, green strength, and other qualities. While CMC is thought to be stable and non-reactive with other components in ceramic inks, it is vital to evaluate its specific qualities and evaluate its compatibility with other materials before usage. Overall, CMC is a significant component in the manufacture of high-quality ceramic components, and its use is anticipated to be an important feature of ceramic manufacturing in the future[5,120,123,124].

2.4.10 Water as Suspension Media in Ceramic Slurry

Water is a common suspension medium in the ceramic industry for both inks and slurries due to its polar nature and high surface tension, which make it an excellent dispersion for ceramic particles. Water is also advantageous due to its inexpensive cost, abundant availability, and non-toxic nature. Water as a suspension medium for ceramic inks and slurries presents certain issues. One of the key difficulties is the possibility for water to react with the ceramic particles or other components in the ink or slurry, causing corrosion or degradation and resulting in diminished performance or quality issues in the final product[125].

Another issue with employing water as a suspension medium is the risk of it evaporating too quickly during the drying process. This can result in cracking, shrinkage, or other problems in the final ceramic product. To circumvent this problem, ceramic manufacturers may need to add other additives to the ink or slurry, such as surfactants or plasticizers, to slow down the rate of water evaporation. To solve these issues, ceramic manufacturers frequently employ deionized or distilled water in their ink or slurry formulations, which have been processed to remove impurities and pollutants, minimizing the likelihood for interactions with other components in the ink or slurry. Additionally, ceramic manufacturers may utilize additives or other treatments to modify the qualities of the water, such as modifying the pH or adding dispersants, to maximize its performance in the ink or slurry[126].

The elimination of water from the green body during the sintering process is a vital step in the creation of ceramic components. The pace and temperature of evaporation can impact the porosity, density, and other physical parameters of the ceramic material. To get the desired qualities in the finished product, these parameters must be carefully controlled[127].

Water is a popular suspension medium in the ceramic industry for both inks and slurries due to its inexpensive cost, extensive availability, and desired qualities as a polar solvent with high surface tension. However, there are drawbacks to employing water, such as the possibility of interactions with other components in the ink or slurry and quick evaporation during the drying process. To address these issues, ceramic manufacturers may utilize purified water, add additives or treatments to affect the qualities of the water, or tweak other parts of their ink or slurry formulations. Despite these problems, water remains a critical component in the production of high-quality ceramic components, and controlling water evaporation is critical to achieving the appropriate characteristics in the final part geometry[128].

2.4.11 DCM as Demoulding Agent for Polylactic acid (PLA)

DCM, also known as dichloromethane, is a colourless, volatile liquid used as a solvent and dissolving agent in numerous industrial applications, such as 3D printing. One of its primary applications in 3D printing is as a polylactic acid (PLA) dissolver. Commonly used in 3D printing, PLA is a biodegradable and environmentally benign thermoplastic material. To construct complex or intricate shapes, often removable supports are printed alongside the main part. Nevertheless, removing the supports can be a time-consuming and challenging process, particularly in the case of intricate or fragile structures. This is where DCM enters the picture. DCM has a high affinity for PLA, allowing it to selectively dissolve PLA supports without affecting the integrity of the primary part or object. The printed object is submerged in a bath of DCM, which dissolves the PLA supports over a period, typically a few minutes[120].

As a dissolving agent for PLA, DCM has several advantages. First, it enables the creation of intricate and complex 3D prints that would otherwise be difficult or impossible to create. Second, it can save time and effort during the post-processing of 3D-printed objects by eradicating the need for manual support removal. Finally, it can reduce waste by enabling the reuse of excess or refuse PLA material[129].

DCM may react with certain varieties of ceramic or metallic powders, depending on their chemical composition, in terms of its compatibility with other substances. In general, DCM is not recommended for use with metal powders due to the potential for corrosion or degradation of the metal. Ceramic powders may be more compatible with DCM, but this will depend on the specific type of ceramic and its chemical composition. To eliminate DCM from a printed part, the part can be subjected to sintering. Sintering involves heating the part to a high temperature, which causes the particles to bond together and form a solid mass. During the sintering process, any remaining DCM will evaporate and be removed from the part, leaving behind a solid ceramic or metal object[130].

DCM is a solvent and dissolving agent frequently used in industrial applications, including 3D printing. Its high affinity for PLA makes it an effective dissolving agent for supports in 3D printing, and it can be removed from parts by subjecting them to a sintering process. However, DCM may react with certain types of powders, so it is important to carefully consider its compatibility with different materials before using it. Additionally, proper handling and disposal procedures must be followed to[120].

2.4.12 Sintering Process of Ceramic Slurry

Sintering ceramic inks and slurries normally consists of many phases. First, using a printing or deposition technique such as screen printing, inkjet printing, or extrusion, the ink or slurry is placed onto a substrate or mould. The ink or slurry contains a carefully selected mixture of ceramic particles, binders, and solvents to achieve the appropriate characteristics and rheology for the ink or slurry.

After depositing the ink or slurry onto the substrate or mould, it is dried to eliminate the solvent and form a green body. The green body is a delicate, unfired ceramic component that contains ceramic powder and binder but has yet to be sintered. The sintering process includes heating the green body to a high temperature for an extended period, in a furnace or kiln. The heating process fuses the ceramic granules in the green body to form a solid, dense ceramic portion. The sintering process is normally conducted in phases, each with its own temperature, time, and environment[83].

The heating rate is an important aspect in the sintering process. The heating rate controls how quickly the green body reaches sintering temperature. A rapid heating rate might cause cracking or distortion of the green body, whereas a slow heating rate can lengthen the sintering time and raise the overall cost of the operation. To obtain the appropriate sintering results, the heating rate is carefully controlled. Another aspect influencing the sintering process is whether it is isothermal or not. Isothermal sintering is the process of keeping the green body at a steady temperature for an extended period. This can help with homogeneous densification and shortening the overall sintering time.

Because it provides strong adherence and durability to ceramic particles, CMC binder is often employed in ceramic inks and slurries. During the sintering process, the CMC binder is burnt away, leaving behind a solid, dense ceramic component. The temperature at which the CMC binder is burned off varies depending on the ink or slurry formulation, although it normally occurs during the earliest stages of the sintering process. DCM is evaporated from the green body using a high-temperature sintering technique. The isothermal sintering method removes the DCM and any impurities, including the PLA dissolved in DCM, from the green body. Water is another commonly utilized solvent in ceramic inks and slurries, and it must be evaporated from the green body during the sintering process. This is commonly accomplished by gradually raising the temperature of the green body, allowing the water in the pores of the ceramic powder to evaporate[131].

The green body is sintered and then turned into the final ceramic portion. Additional post-processing procedures, such as grinding, polishing, or coating, may be required. Diffusion is the process by which the ceramic powders in the green body migrate and fuse together to produce a solid, dense ceramic component, and it is the primary sintering activity for ceramic slurries. The high temperature and pressure of the sintering environment drive the diffusion process, causing ceramic particles to form necks and bridges as they come into touch with one another. These necks and bridges develop and consolidate over time, resulting in the formation of a solid, dense ceramic part. Several physical and chemical changes occur in the green body throughout the sintering process. Shrinkage, densification, grain expansion, and phase changes are examples of these. The green body shrinks as it loses moisture and other volatile components, causing it to shrink in size. Densification happens when the ceramic granules in the green body combine to produce a solid, thick ceramic portion. As the ceramic powders recrystallize and create larger grains, grain growth occurs. Phase transformations occur when the crystal structure of ceramic powders changes because of the sintering environment's high temperature and pressure[131,132].

Sintering is a complicated and important phase in the manufacturing of ceramic items from ceramic inks and slurries. To get the required sintering results, the heating rate, temperature, duration, and environment must be carefully controlled. The use of CMC binder, water, and other solvents in ceramic inks and slurries must be carefully controlled to ensure that they are burnt off or evaporated effectively during the sintering process. Manufacturers may make high-quality, dense ceramic pieces with the necessary qualities and shapes by knowing the principles and procedures involved in the sintering of ceramic inks and slurries[133].

2.4.13 Defects in ceramic parts and their cause in context of additive manufacturing

Defects in ceramic parts produced by additive manufacturing can arise from various sources and can negatively impact the functionality and performance of the final product. Common defects that occur in ceramic parts produced by additive manufacturing, their causes, and some strategies to prevent them are:

a) **Warpage** is a common defect in ceramic parts produced by additive manufacturing, especially for large or complex parts. Warpage occurs when the part distorts or deforms during the printing process or cooling stage. The primary cause of warpage is uneven cooling rates, which can occur due to a temperature gradient within the part, resulting in internal stresses[134].

b) **Cracking:** Cracking is another common defect in ceramic parts produced by additive manufacturing. Cracks can occur during printing or post-processing stages, such as drying or sintering. The main causes of cracking include thermal shock, residual stress, or poor bonding between layers[135,136].

c) **Porosity:** Porosity is the presence of small voids or pores in the ceramic material. Porosity can occur due to various factors, including inadequate powder packing, insufficient sintering, or the presence of gas or air pockets in the material. Porosity can negatively impact the mechanical properties, strength, and durability of the part[135].

d) **Delamination:** Delamination is a defect that occurs when the layers of the printed part separate or peel apart. Delamination can occur due to poor bonding between layers, insufficient drying or sintering, or inadequate adhesion between the printed material and the build platform[134].

e) **Shrinkage:** Shrinkage is the reduction in size of the part during sintering. Shrinkage can occur due to the densification of the material during sintering, which results in a decrease in porosity and an increase in density. However, excessive shrinkage can result in dimensional inaccuracies, warping, or cracking[135].

f) **Rough Surfaces:** Rough surfaces refer to ceramic parts with an uneven or rough surface finish. Rough surfaces can occur due to inadequate powder spreading, poor layer adhesion, or insufficient smoothing or polishing of the final part[100].

To prevent these defects in the final ceramic part, following strategies shall be used:

a) **Optimization of printing parameters:** Optimizing printing parameters, such as temperature, speed, and layer thickness, can help to prevent warpage, cracking, and delamination[137].

b) **Powder quality control:** Controlling the quality of the ceramic powder, such as particle size and shape, can help to prevent porosity and improve the mechanical properties of the final part[134].

c) **Post-processing techniques:** post-processing techniques, such as sintering, polishing, and surface treatment, can help to improve the accuracy, strength, and surface finish of the final part.

d) **Process monitoring and control:** Monitoring and controlling the printing process using sensors and software can help to detect defects in real-time and prevent them from occurring.

e) **Design optimization**: Optimizing the design of the part, such as reducing overhangs or adding support structures, can help to prevent warpage, cracking, and delamination[131].

f) **Compensation for Shrinkage:** Designing the part with a larger size to account for the expected shrinkage can help to prevent dimensional inaccuracies or warping[134].

g) **Pre-treatment of powder:** Pre-treating the ceramic powder, such as surface modification or chemical treatment, can help to improve its flowability, dispersion, and adhesion[83].

h) **Post-processing heat treatment:** Applying a heat treatment after printing can help to reduce residual stress and improve bonding between layers, preventing cracking and delamination[135,138].

i) **Quality control testing**: Performing quality control testing, such as X-ray diffraction or scanning electron microscopy, can help to detect defects and ensure the quality of the final part[135].

j) **Material selection:** Selecting the appropriate ceramic material for the intended application, with suitable mechanical, thermal, and chemical properties, can help to prevent defects and improve the functionality and performance of the final part[135].

Defects in ceramic parts produced by additive manufacturing can arise from various sources, including uneven cooling rates, thermal shock, porosity, and poor bonding between layers. Strategies to prevent defects include optimizing printing parameters, controlling powder quality, using post-processing techniques, monitoring, and controlling the printing process, compensating for shrinkage, pre-treating the powder, applying post-processing heat treatment, performing quality control testing, and selecting the appropriate ceramic material for the intended application. By implementing these strategies, it is possible to produce high-quality ceramic parts with improved accuracy, strength, and functionality.

2.5 Additive Manufacturing of Cupric Oxide material in research literature

2.5.1 Overview of Additive Manufacturing of Cupric Oxide material in research literature

According In recent years, pure cupric oxide (CuO) ceramic additive manufacturing (AM) has attracted attention, especially for uses in gas sensing, photocatalysis, and energy storage. However, there is not as much research on AM of pure CuO ceramic as there is on other ceramic materials. Due to its high melting temperature and poor heat conductivity, CuO presents difficulties when printed, which could be one explanation. To overcome these difficulties and successfully print CuO ceramic, researchers have investigated a variety of AM processes, but focused on fused deposition modelling. CuO ceramic printing parameter optimization and post-processing treatments, however, are still active research areas.

Despite a lack of literature on AM of pure CuO ceramic, the few research experiments that have been conducted have yielded good results and highlight the material's adaptability. More research is needed to completely understand the spectrum of properties and applications of CuO ceramic, as well as to enhance printing conditions and post-processing techniques.

2.5.2 FDM Method Additive Manufacturing of Cupric Oxide Composite

According to the research literature, the cupric oxide composite was manufactured using FDM. Two research articles confirmed the production of a porous CuO composite. Copper powder was combined with PLA to produce cupric oxide, which was then extruded in the form of a filament. This filament was utilized to print composite material. This printed CuO composite was utilized as an ammonia gas sensor, and it was determined that as the copper loading increased, the composite's gas sensing characteristic improved. The research also confirmed that the FDM-produced CuO was sensitive to temperature, pressure, and light. Only these two articles were discovered during a search of the scientific literature concerning the additive manufacturing of purified cupric oxide[139,140].

2.6 Negative Additive Manufacturing

2.6.1 Overview of Negative Additive Manufacturing

Negative Ceramic Additive Manufacturing (NCAM) or Negative Additive Manufacturing is a novel ceramic additive manufacturing technique that allows the production of intricate, complex shapes of ceramics. Unlike conventional additive manufacturing techniques, which build up structures layer-by-layer, NAM uses a subtractive approach to create a negative mould or shell, which is then filled with ceramic slurry or powder to form the final object[5].

The working principle of NAM involves three main steps: mould creation, mould filling, and mould removal. In the first step, a negative mould or shell is created using a variety of techniques, including 3D printing, CNC machining, or casting. The mould can be made from various materials, such as plastic, wax, or metal. In the second step, the negative mould is filled with ceramic slurry or powder. The ceramic ink, which is a suspension of ceramic particles in a liquid binder, is used to create the slurry. The slurry is then poured or injected into the mould, where it fills the voids and takes the shape of the mould. The third step involves the removal of the mould to reveal the final ceramic object. The mould can be removed using a variety of techniques, including thermal decomposition, dissolution, or mechanical means. The ceramic ink used in NAM is an important component of the process. The rheology of the ink, which refers to its flow behaviour, is critical to achieving the desired properties of the final ceramic object. The ink should have a controlled viscosity and thixotropy to ensure uniform filling of the mould and prevent settling of the ceramic particles. The ink should also have good adhesion to the mould and good stability during storage and transportation. It is a novel technique that allows the production of intricate, complex shapes of ceramics[120].

The formulation of ceramic ink is crucial to the success of the NAM process. The ink must have a high viscosity to maintain its shape and form as it is printed onto the substrate, but it must also be able to flow smoothly through the print head nozzle. The ink must also be able to dry or cure quickly and must be compatible with the substrate material and firing conditions. Rheology is an important factor in the formulation of ceramic inks for NAM. Rheology refers to the flow behaviour of the ink, and includes factors such as viscosity, shear rate, and thixotropy. The rheological properties of the ink can affect the print quality, resolution, and stability of the printed pattern[141]. NAM offers several advantages over conventional ceramic manufacturing techniques, including:

a) **Speed and Efficiency**: NAM is a fast and efficient process that allows to produce high-resolution ceramic parts in a fraction of the time it takes using conventional manufacturing techniques[142].

b) **Design Flexibility:** NAM allows for the creation of complex and intricate ceramic parts that would be difficult or impossible to produce using conventional manufacturing techniques[120].

c) **Reduced Waste:** NAM produces less waste than conventional manufacturing techniques, as only the ink is used to create the final part[83].

d) **Cost-Effective:** NAM is a cost-effective process, as it reduces the need for expensive moulds, tooling, and other equipment required for conventional manufacturing techniques[142].

e) **Improved Quality**: NAM allows to produce high-quality ceramic parts with uniform properties and precise dimensions[99].

NAM is a new additive manufacturing process involves the creation of a negative mould, filling the mould with ceramic slurry or powder, and the removal of the mould to reveal the final object. The ceramic ink used in NAM is critical to achieving the desired properties of the final ceramic object, and its rheology plays a significant role in the success of the process. This process involves the use of a ceramic ink, which is printed onto a substrate in a specific pattern using a print head, and then fired in a kiln to produce a solid ceramic object[83,120].

2.6.2 Identification of research gaps in the literature regarding negative additive manufacturing of cupric oxide

It was determined after examining the literature review that no researchers have attempted to manufacture cupric oxide ceramic in a negative additive way. It was noted that there were just two research publications published that covered cupric oxide additive manufacturing. These studies examined the production of cupric oxide using the additive manufacturing technique known as FDM. More investigation and concentrated research are needed on the cupric oxide material produced using additive manufacturing technologies. The author has attempted to address a methodology-based research gap on negative additive manufacturing utilizing the research trials described in this thesis, and these results have proven that deficit. The development of new sensors, electronics, and other materials, such as different medical grade textiles, will be made possible by the negative additive manufacture of cupric oxide ceramic.

2.6.3 3 Step Novel Negative Additive Manufacturing of Cupric Oxide

A porous, copper oxide ceramic was manufactured in the lab using copper powder loaded in an aqueous solution of CMC binder. The CMC binder holds copper particles in the aqueous binder solution. The slurry was injected in a 3d-printed mould fabricated in a local lab. Afterwards, the slurry was left in the mould to dry naturally at STP. The green body was manufactured by dissolving the slurry-filled mould using DCM. The green body underwent two-step isothermal sintering. This novel method produced a sintered porous cupric oxide ceramic, turning the slurry-prepared green body into a monoclinic CuO ceramic sample. The 3 Step process is shown in the figure below:

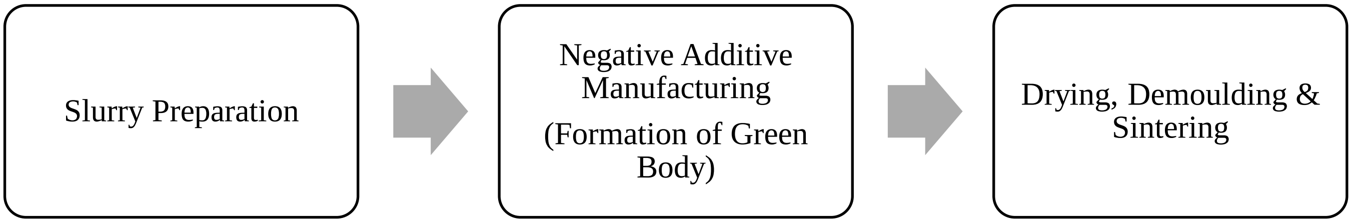


Figure 2.4: Novel Negative Additive Manufacturing Process

CHAPTER 3: MATERIALS AND METHODS

3.1 Materials used in the research experiment

This research experiment used five materials, including copper powder, deionized water, and a Carboxymethyl Cellulose binder. The research experiment was completed in three steps, and the details of materials used in each step are:

3.1.1 Materials used in Slurry Preparation

Three materials were used in the slurry preparation: Copper Powder, De-Ionized Water, and CMC Binder. Vanuatu was the source of the 10µm sized copper particles. The copper powder underwent agglomeration, as confirmed by SEM images. To prevent oxidation, the copper powder was not ball-milled before slurry preparation. This experiment utilized DI water to exclude the possibility of any contamination or chemical reaction that could alter the slurry's chemical composition during production. We obtained CMC binder with the CAS number 9000-11-7 from Purge Chemical Industries in Karachi, Pakistan.

3.1.2 Materials used in Negative Additive Manufacturing

PLA filament was used to create the 3D-printed mould for slurry casting. The PLA material was available in the local 3D Printing Lab and was not purchased.

3.1.3 Materials used in Demoulding of ceramic slurry filled mould

The DCM Chemical reagent was used to demould the slurry-filled mould. For this purpose, the Dichloromethane (DCM) chemical reagent was purchased from a nearby chemical supplier. Chemical Abstracts Service assigned the identifiers 32222-M-1 and 75-09-2 to the product manufactured by Sigma-Aldrich. The copper powder underwent agglomeration, as confirmed by SEM images. To prevent oxidation, the copper powder was not ball-milled before slurry preparation. This experiment utilized DI water to exclude the possibility of any contamination or chemical reaction that could alter the slurry's chemical composition during production. We obtained CMC binder with the CAS number 9000-11-7 from Purge Chemical Industries in Karachi, Pakistan.

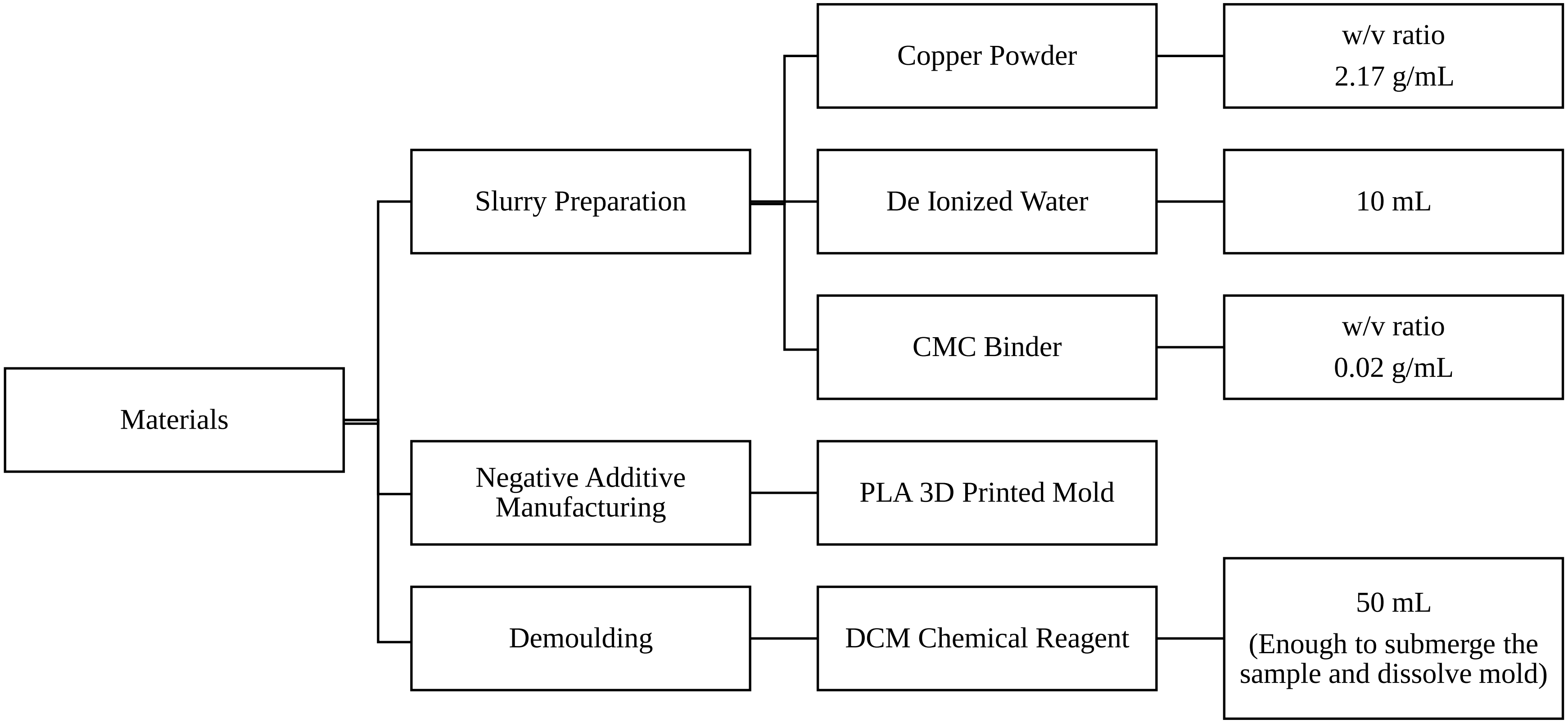


Figure 3.1: Materials used in the research experiment

3.2 Experimental Setup and Procedure

3.2.1 Equipment and Resources

The equipment and resources used in this research experiment included:

a) 3D printer in the local additive manufacturing lab. (Manufacturer: Voxelab)

b) The weighing scale available in the materials lab

c) The sintering furnace available in the heat treatment lab (Manufacturer: Nabetherm)

d) SEM Microscope (Materials lab at PAF Base Faisal)

e) XRD Equipment (NUST H-12)

f) XRF Equipment (Jewellery Lab Lahore)

g) Density Calculations (Quality Lab at Pakistan Cables Limited)

h) 4 Point Resistivity (using the personal 4-point probe of Dr.Shehryar and performed at local electronics lab.

3.2.2 Details of the experimental setup and parameters

The details of the experimental parameters are:

1. 3D Mould printing parameters were set to:
   a) Nozzle Temperature: 200℃
   b) Printing Bed Temperature: 60℃
   c) Infill: 100%
2. Sintering Parameters: The sintering process was completed in two-step isothermal heating stages, as shown in the figure 3.3.
   a) The first isothermal heating stage was completed by programming the sintering cycle to achieve 400℃ in 75 minutes and holding at the 400℃ for 45 minutes.
   b) The second isothermal heating stage was completed by programming the sintering cycle to achieve 900℃ in 80 minutes and holding the sample at 900℃ for 180 minutes.

3.3 Negative Additive Manufacturing

3.3.1 Slurry Preparation

The study slurry was a copper particle-laden aqueous binder solution. The aqueous binder solution was prepared by dissolving 0.2g CMC Binder in 10 ml DI water. After adding the CMC Binder to the DI water, the solution was manually stirred for 3 minutes to establish homogeneity. 21.7g copper was loaded in this aqueous binder slurry. 2g of copper powder was initially dissolved in the aqueous binder solution, followed by 1-minute continuous manual stirring until all the weighted 21.7g copper powder was loaded in the aqueous binder solution. The manual stirring ensured that the payload was distributed uniformly in the aqueous solution. The w/v ratios for CMC binder and copper powder in DI water were 0.02 g/mL and 2.17 g/mL, respectively. Slurries with a copper to DI water w/v ratio of less than 2.17 g/mL showed significant shrinkage, resulting in poor shape retention.

3.3.2 Negative Additive Manufacturing of Cupric Oxide Ceramic

Figure 3.2 below shows the part geometry chosen for copper oxide ceramic manufacturing using the innovative negative additive manufacturing process. A local 3D printer produced the PLA mould for the desired part geometry. A 30 ml Syringe injected the copper-loaded aqueous binder slurry into the mould. The mould was filled in steps and lightly tapped during pouring to verify that the slurry filled all cavity spaces and voids. The mould was filled in five steps until the slurry could not penetrate within the mould cavity due to the slurry filling all the mould cavities.

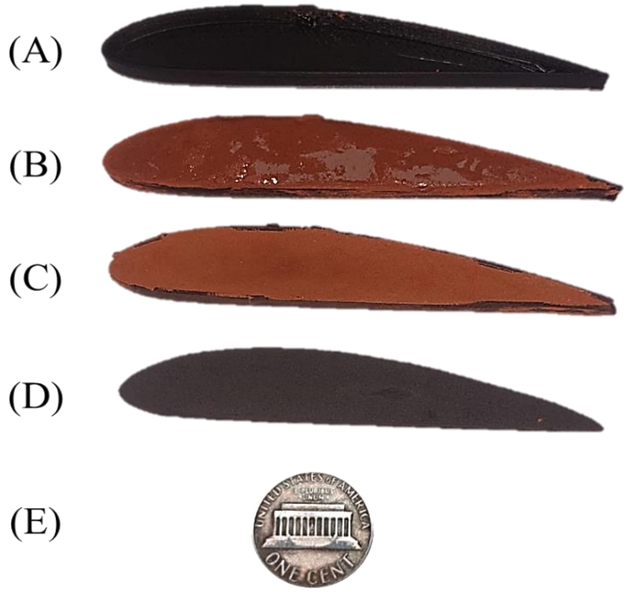


Figure 3.2

(A) 3D Printed Mould of Aero foil

(B) Mould filled with aqueous binder copper loaded slurry

(C) Green Body containing moisture traced

(D) Final Sintered Cupric Oxide Aerofoil

(E) One Cent coin for relative scaling

3.3.3 Drying, Demoulding and Sintering

The Green Body was naturally dried by keeping the casted mould at STP inside the lab for 24 hours. The same filled mould was then immersed in a beaker of DCM Chemical for 2 hours to ensure that the PLA mould was completely dissolved. The demoulding step was finished with this action. The Green body was then naturally dried for 24 hours before sintering. It was done to ensure the complete evaporation of DCM Vapours. The sample was placed in a furnace for a 2 Step Isothermal Sintering process. In this process, the furnace was powered on, and a shooting time was set for 75 minutes to achieve 400°C Temperature (T1). The sample was heated at 400°C (T1) in the furnace for 45 minutes. Later the shooting time was changed to 80 minutes, and the temperature was set to 900°C (T2). The sample was fired at 900°C (T2) to ensure complete sintering for 180 minutes. 6.5 hours of two steps isothermal sintering process was performed to turn the green body into a ceramic body.

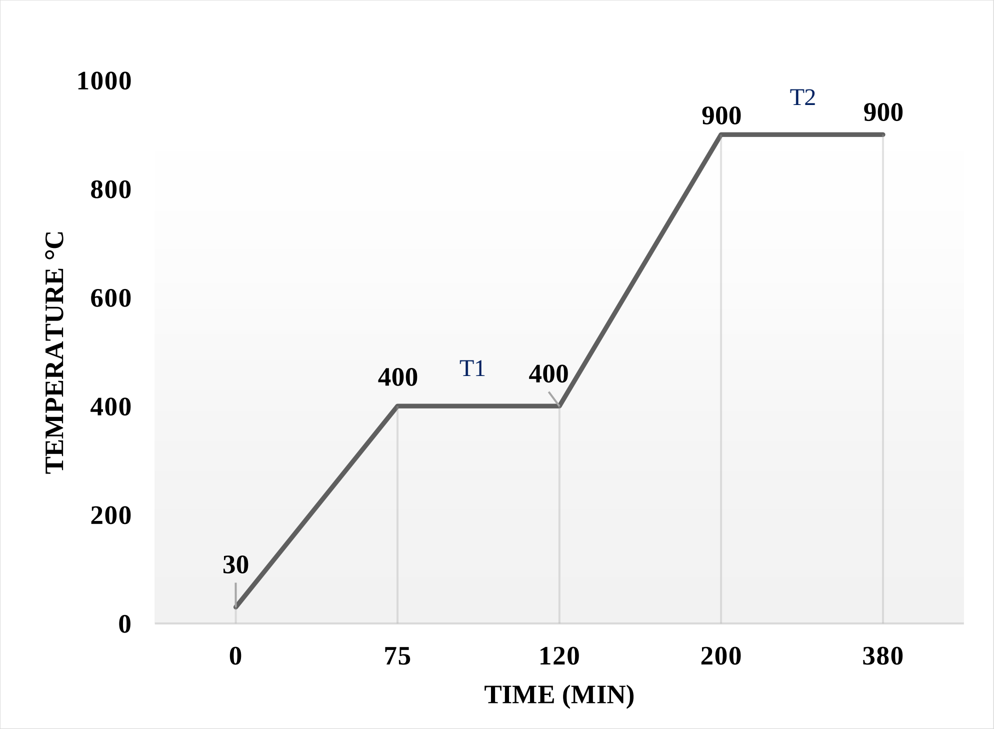


Figure 3.3: 2 Step Isothermal Sintering Process

Figure 3.4: The final Cupric Oxide ceramic part resting on firebrick after sintering process.

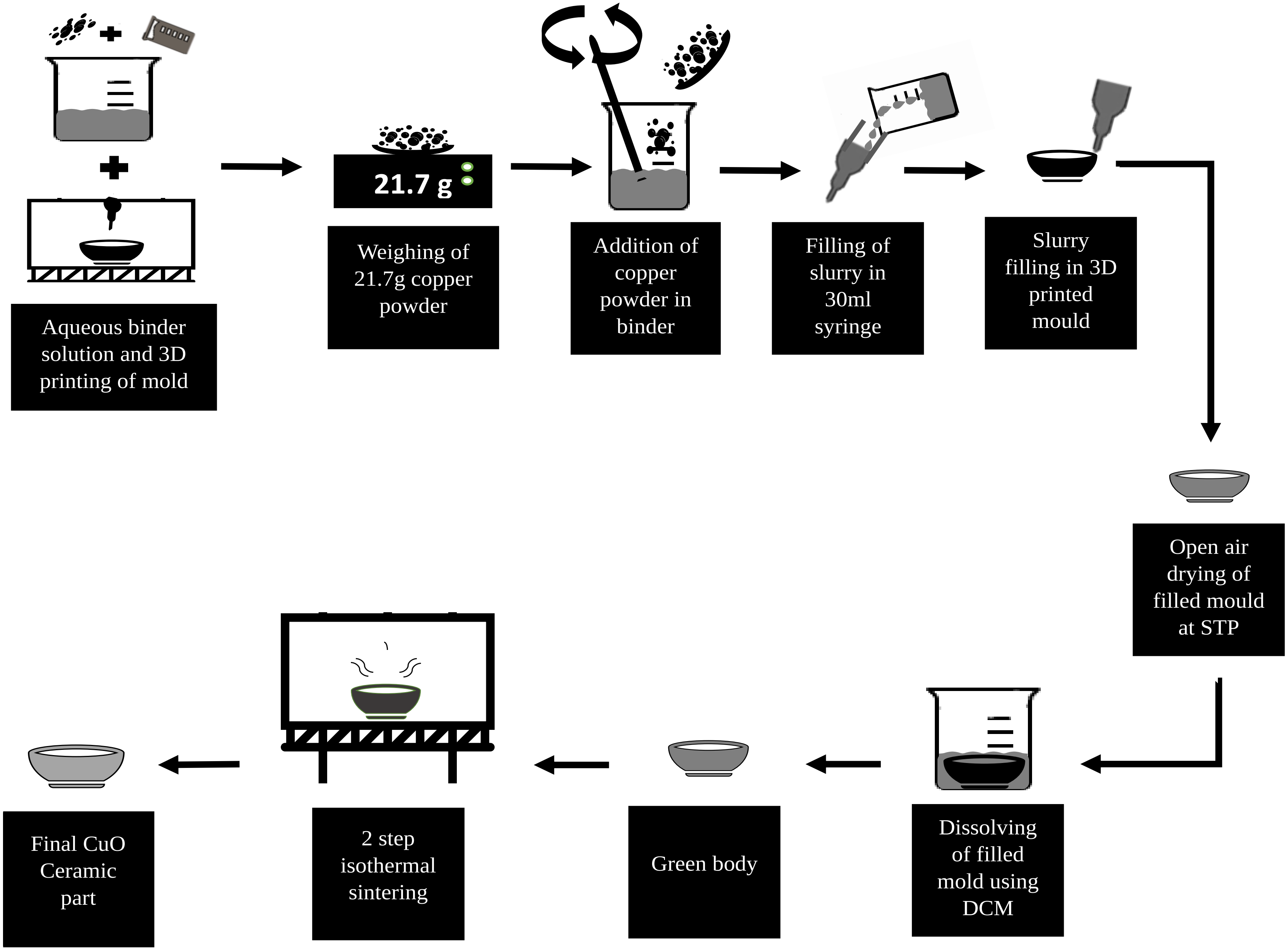


Figure 3.5: Novel Negative Additive Manufacturing of CuO ceramic

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Characterization of additively manufactured cupric oxide sample

Six different methodologies were used to characterize the manufactured copper oxide ceramic. The density of the fabricated sample was determined using the Archimedes principle. The water saturation test was performed to measure the porosity of the ceramic structure. The ceramic's resistivity was calculated using the 4-point resistivity formula. Furthermore, SEM and XRD were performed on the manufactured cupric oxide sample to investigate its microstructure.

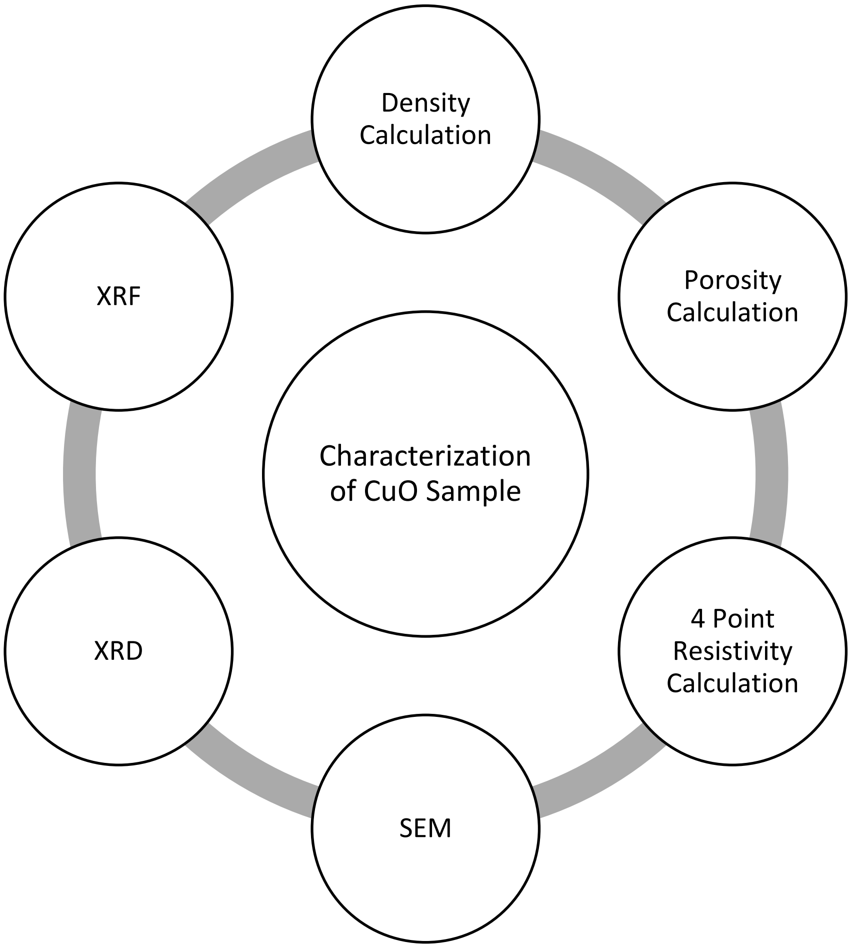


Figure 4.1: Six material characterization techniques used in the research.

4.2 Density Calculation

The Archimedes principle was used to compute the density of the fabricated sample, following the ATM C830–00 standard procedure[143]. A graduated beaker was filled with alcohol for rapid and exact volume measurement. The sample of mass 1.36 grams, determined using the weighing scale available in the local lab, was used in this density calculation. The manufactured copper oxide sample was suspended inside the graduated beaker. There was a volume change for alcohol before and after the sample was dipped. This volume was later used to compute the sample density, which was discovered to be **3.556 g/cm3**. This was the sample's solid density since the pores were filled with alcohol. However, because it was sintered under air circumstances and no graphite coating was put on the top and bottom of the sample to minimize porosity, the created sample was porous. This solid density was further used to calculate the % Porosity of the CuO Sample.

4.3 Porosity Calculation

A water saturation test using standard ATM C830–00 was used to validate and determine the porosity of the current sample[143]. For this test, the material was dried in the furnace for 40 minutes before being weighed to 2.8541 g. It was then immersed in de-ionized water for 1 hour to properly hydrate the sample's pores. The sample was then carefully removed and weighed right away. The wet weight of the sample was 3.2348 g. The difference between dry and wet weights was found to be 0.3807 g. Porosity was determined to be 42% in the sample. The actual density of the porous sample was determined to be 2.4187 g/cm3.

<u>Calculations for Porosity</u>

Data:

- Density of sample: 3.556 g/cm^3
- Wet Weight of Sample: 3.2348 g
- Dry Weight of Sample: 2.8541 g

Formulae:

1. Volume of Pores = Volume of Wet Sample – Volume of Dry Sample
2. Density = $\frac{Mass}{Volume}$
3. % Porosity = $\frac{Volume\ of\ Open\ Pores}{Volume\ of\ dry\ sample + Volume\ of\ Pores}\ x\ 100$

Calculations:

Volume of Wet Sample = $\frac{\text{Mass of Wet Sample}}{\text{Density of Sample}} = \frac{3.2348}{3.556}$ = 0.90 cm^3

Mass of Pores = Wet Weight of Sample - Dry Weight of Sample = 3.2348 – 2.8541

Mass of Pores = 0.3807 g

Density of Pores = Density of Water, as the pores are filled with Distilled Water = 1 g/cm3

$$\text{Volume of Pores} = \frac{\text{Mass of Pores}}{\text{Density of Pores}} = \frac{0.3807}{1} = 0.3807\ \text{cm}^3$$

$$\%\ \text{Porosity} = \frac{\text{Volume of Pores}}{\text{Volume of Wet Sample}}\ \text{x}\ 100 = \frac{0.3807}{0.9}\ \text{x}\ 100 = 42.3\%$$

$$\text{Actual Density} = \frac{\text{Mass of Dry Sample}}{\text{Volume of Wet Sample}} = \frac{2.8541}{0.9} = 3.1712\ \text{g/cm}^3$$

Results:

- The sample porosity was calculated to be 42.3%
- The actual density of the sample was computed to be 3.1712 g/cm^3

4.3 Resistivity calculation using the 4-point resistivity method

The CuO Sample's resistivity and conductivity were determined using the 4-point resistivity technique[144]. The 4-point probe was utilized in this procedure. Figure 4.2 shows a probe with a spacing of -= 2.54 mm = d between the two subsequent probes. The voltage was measured using the two inner probes while the current was delivered to the two external probes. The computations were carried out using the resistivity formula for the bulk material:

$$\rho = \frac{V}{I} x \frac{\pi x t}{\ln(\frac{\sinh(\frac{t}{s})}{\sinh(\frac{t}{2s})})}$$

Calculations for Resistivity

Data:

- Probe spacing = d = 2.54 mm
- Average thickness of sample = t = 2.8 mm
- Voltage = V = 1 V
- Current = I = 1 mA

Calculations:

$$\boldsymbol{\rho} = \frac{V}{I} x \frac{\pi x t}{\ln(\frac{\sinh(\frac{t}{s})}{\sinh(\frac{t}{2s})})}$$

$$\boldsymbol{\rho} = \frac{1}{0.001} x \frac{\pi x 0.0028}{\ln(\frac{\sinh(\frac{0.0028}{0.00254})}{\sinh(\frac{0.0028}{2 x 0.00254})})}$$

$\boldsymbol{\rho}$ = 10.5 Ωm

Results:

- The resistivity of the Cupric Oxide Ceramic sample was computed to be 10.5 $\Omega\,m$.

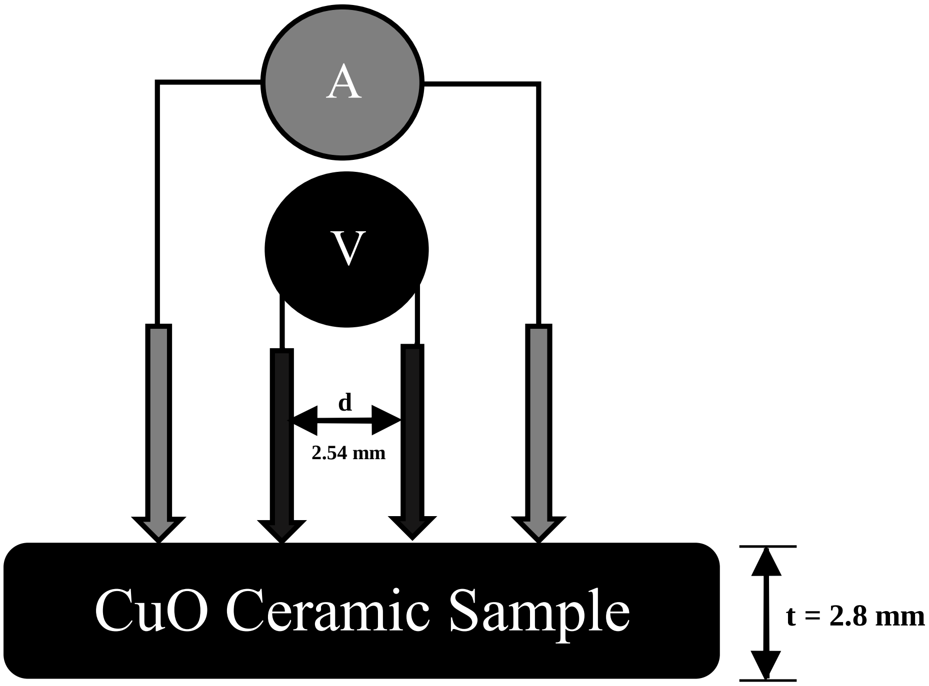


Figure 4.2: 4 Point Probe

4.5 Scanning Electron Microscopy (SEM) of Cupric Oxide Sample

SEM micrographs of copper powder and the sintered CuO ceramic were studied for morphology and porosity. SEM micrographs of copper powder in Figure 4.3 depict the powder having an average size of 10μm. The SEM micrographs confirm the agglomeration of the copper powder. The copper powder was not subjected to ball milling to prevent it from early oxidation. Figure 4.4 shows the SEM images of the CuO Sample manufactured using negative additive manufacturing. The micrographs confirm CuO's porous sintered ceramic structure, confirming the earlier porosity calculations using the ATM C830–00 standard test. The SEM Images also confirm the XRD analysis findings regarding the CuO ceramic sample's crystallinity.

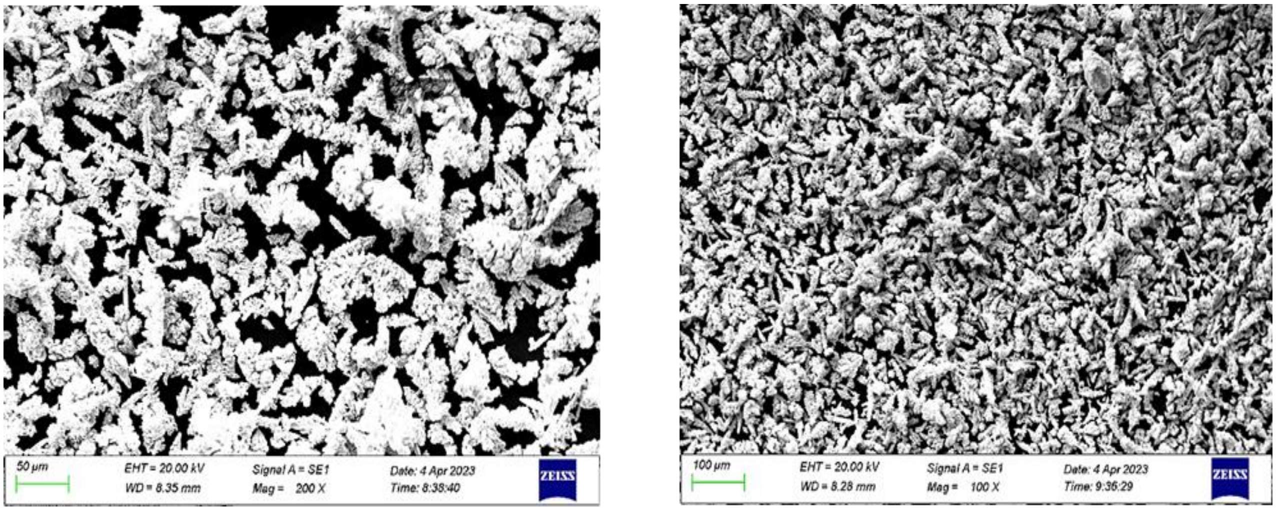


Figure 4.3: **SEM Images of copper powder**

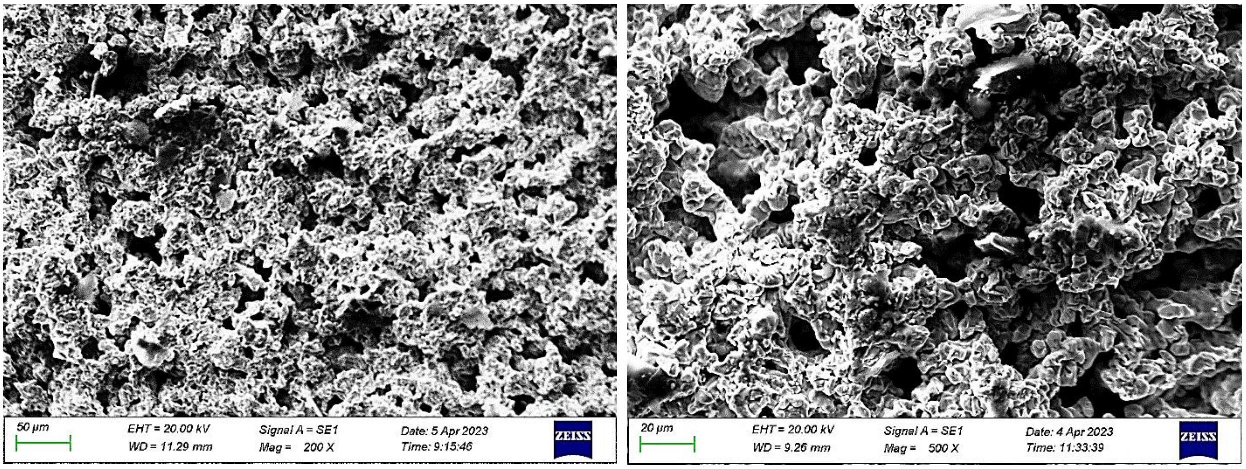


Figure 4.4: SEM Images of CuO ceramic sample manufactured in Lab

4.5 X-Ray Diffraction (XRD) Analysis

COD (Crystallography Open Database) was used for matching the obtained XRD patterns[145]. Besides the qualitative analysis, a quantitative analysis by Rietveld refinement using FullProf software (by J. Rodriguez-Carvajal) was preformed to identify the ratio of the phase.

Peak List

No.	***2theta [º]***	***d [Å]***	***I/I0***	***FWHM***	***Matched***
1	32.54	2.7497	76.01	0.0818	A
2	35.47	2.5285	302	0.1228	A
3	35.55	2.5232	1000	0.1228	A
4	38.74	2.3223	973.55	0.1228	A
5	38.97	2.3091	234	0.1228	A
6	46.27	1.9607	17.29	0.1228	A
7	48.74	1.8667	234.08	0.1228	A
8	51.37	1.7772	8.93	0.1228	A
9	53.48	1.7119	55.94	0.1637	A
10	58.32	1.581	89.04	0.1637	A
11	61.54	1.5056	143.74	0.1228	A
12	61.54	1.5056	143.74	0.1228	A
13	65.81	1.4179	81.68	0.2046	A
14	66.25	1.4096	113.93	0.1228	A

15	66.43	1.4062	60.42	0.1637	A
16	67.95	1.3784	60.93	0.2046	A
17	68.1	1.3757	116.99	0.1637	A
18	71.73	1.3148	30	0.1228	A
19	72.43	1.3038	39.47	0.2046	A
20	75.01	1.2652	40.17	0.1228	A
21	75.24	1.262	55.23	0.1228	A
22	79.79	1.201	30	0.1228	A

Table 4-1: XRD Peak List of CuO Sample

XRD pattern

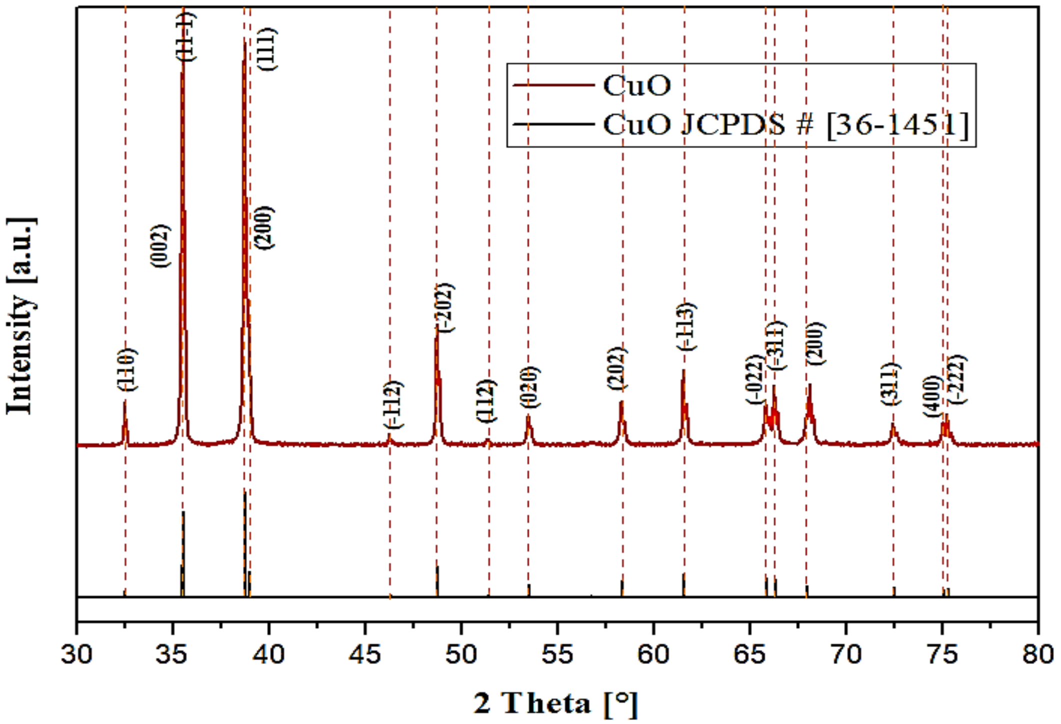


Figure 4.5: XRD Peak Pattern of CuO Sample matched with CuO JCPDS 36-1451

Figure 4.5 shows the XRD pattern of the Cupric Oxide sample and of CuO with a monoclinic crystal system (Space group C 1 2/c 1 (15), a= 4.68300 Å b= 3.42030 Å c= 5.12450 Å β= 99.707 º) according to the JCDPS card number [36-1451][146]

The degree of Crystallinity

The crystalline fraction can be determined by integrating the area under the crystalline (A_c) and amorphous (A_a) diffraction patterns.

$$X_c = \frac{A_c}{A_c + A_a}$$

The XRD pattern peaks were integrated using origin lab software and the peak analyser tool, and the XRD patterns' crystallinity degree were listed below.

Sample	A_c	Total area ($A_c + A_a$)	Crystallinity degree [%]
CuO	12583.8701	18842.0316	65.78

Table 4-2: Crystallinity Degree calculation for CuO Sample

The Crystallite Size

The crystallite size of the XRD patterns, was estimated using the Scherrer's equation:

$$D = \frac{k\,\lambda}{\beta \cos\theta} \tag{1}$$

Where D is the crystallite size, k is the so-called shape factor (0.9), λ is the wavelength (0.15418 nm, Cu$K\alpha$), β is the Full Width at Half Maximum (FWHM), and θ is the diffraction angle [147].

Peak position 2θ (°)	FWHM B_{size} (°)	Dp (nm)
32.54	0.0818	105.75
35.47	0.1228	70.99

35.55	0.1228	71.01
38.74	0.1228	71.68
38.9 7	0.1228	71.73
46.27	0.1228	73.53
48.74	0.1228	74.23
51.37	0.1228	75.03
53.48	0.1637	56.80
58.32	0.1637	58.09
61.54	0.1228	78.70
61.54	0.1228	78.70
65.81	0.2046	48.34
66.25	0.1228	80.74
66.43	0.1637	60.63
67.95	0.2046	48.94
68.1	0.1637	61.22
71.73	0.1228	83.44
72.43	0.2046	50.30
75.01	0.1228	85.24
75.24	0.1228	85.37

79.79	0.1228	88.14

Table 4-3: Crystalline Sizes of CuO Sample crystals

Exploiting the previous table allowed determine an average crystallite size of **71.75 nm.**

Crystal structure

Crystal system	monoclinic
Cell parameters	a= 4.68370 Å b= 3.42260 Å c= 5.12880 Å α= 90 ° β=99.54 ° γ = 90°

Table 4-4: Crystal Structure of CuO Sample

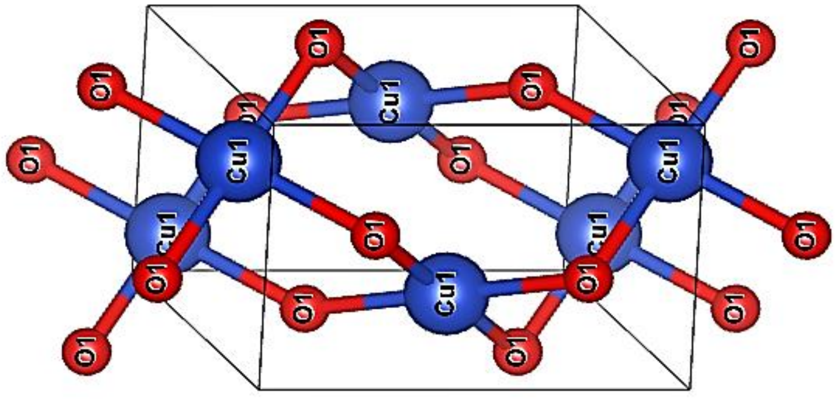
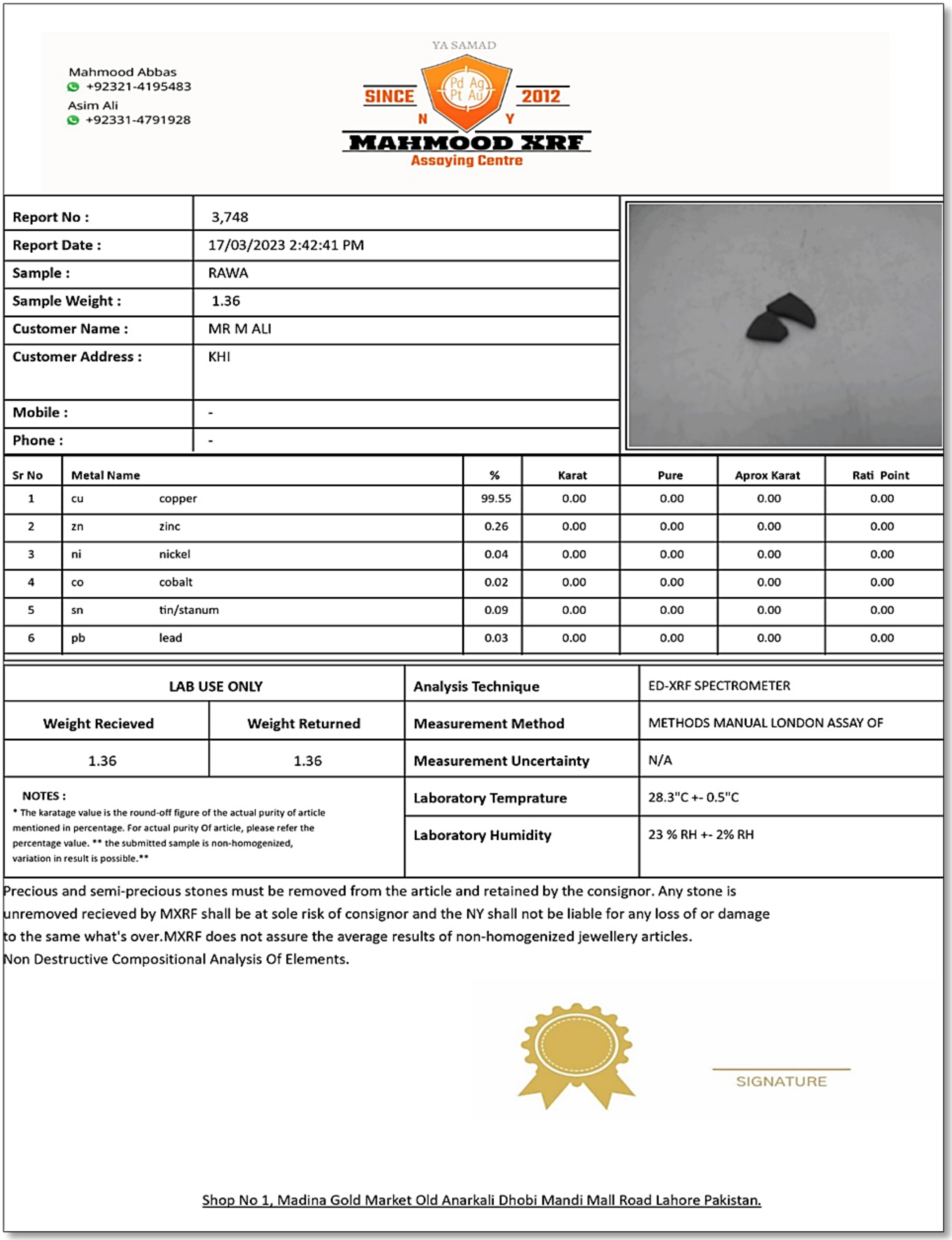


Figure 4.6: Atomic Coordinates of CuO sample

4.6 X-ray Fluorescence Analysis (XRF)

X-ray fluorescence (XRF) analysis was performed on a sample of the manufactured CuO ceramic. Consequently, we contacted numerous XRF analysis facilities across the nation. At the time, only one facility could perform XRF analysis. An Element X-Ray Fluorescence Analysis was performed on the sample to aid the investigation. This analysis determines the integrity of precious metals and jewellery by identifying the metals present in the sample. It aids in determining the specimen's composition despite the need for additional computation. A local logistics company conveyed the sample material to an XRF analysis laboratory in Lahore. The X-ray fluorescence analysis revealed that 99.5% of the sample was copper, with the remaining 0.5% consisting of extremely low concentrations of titanium, zinc, nickel, cobalt, and lead. CuO was identified as copper by the XRF analysis due to its limitation of identification of metals only. So, identifying the Copper metal in the sample was crucial to the success of the research experiment. This XRF analysis was limited to determining oxygen and oxides. This result proved beyond a reasonable doubt that the CuO produced in the lab is indeed 99.95 percent pure CuO, as shown in the XRF Report below.



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SINCE 2012
MAHMOOD XRF
Assaying Centre

Report No :	3,748
Report Date :	17/03/2023 2:42:41 PM
Sample :	RAWA
Sample Weight :	1.36
Customer Name :	MR M ALI
Customer Address :	KHI
Mobile :	-
Phone :	-

Sr No	Metal Name		%	Karat	Pure	Aprox Karat	Rati Point
1	cu	copper	99.55	0.00	0.00	0.00	0.00
2	zn	zinc	0.26	0.00	0.00	0.00	0.00
3	ni	nickel	0.04	0.00	0.00	0.00	0.00
4	co	cobalt	0.02	0.00	0.00	0.00	0.00
5	sn	tin/stanum	0.09	0.00	0.00	0.00	0.00
6	pb	lead	0.03	0.00	0.00	0.00	0.00

LAB USE ONLY

Weight Recieved	Weight Returned
1.36	1.36

Analysis Technique	ED-XRF SPECTROMETER
Measurement Method	METHODS MANUAL LONDON ASSAY OF
Measurement Uncertainty	N/A
Laboratory Temprature	28.3"C +- 0.5"C
Laboratory Humidity	23 % RH +- 2% RH

NOTES :
* The karatage value is the round-off figure of the actual purity of article mentioned in percentage. For actual purity Of article, please refer the percentage value. ** the submitted sample is non-homogenized, variation in result is possible.**

Precious and semi-precious stones must be removed from the article and retained by the consignor. Any stone is unremoved recieved by MXRF shall be at sole risk of consignor and the NY shall not be liable for any loss of or damage to the same what's over.MXRF does not assure the average results of non-homogenized jewellery articles.
Non Destructive Compositional Analysis Of Elements.

SIGNATURE

Shop No 1, Madina Gold Market Old Anarkali Dhobi Mandi Mall Road Lahore Pakistan.

Figure 4.7: XRF Report of CuO Sample

CHAPTER 5: CONCLUSION

5.1 Summary of findings

The research experiment successfully manufactured the cupric oxide ceramic sample using a novel negative additive manufacturing process.

5.1.1 Recap of the key findings of the Study

A monoclinic, 42% porous CuO ceramic sample was successfully manufactured using the negative additive manufacturing process in the laboratory. The sample's analysis revealed that 65.78 percent of it was crystallized. The density and resistivity of the CuO sample were determined to be $2.4187\,\frac{g}{cm^3}$ and $10.5\Omega\, m$, respectively. It has been proven that negative additive manufacturing can manufacture pure CuO ceramic samples.

5.1.2 Recap of the research questions and answers to the research questions in context with this research experiment

Three research questions were formulated at the beginning of the thesis to conduct research experiments with these questions in mind. These are the answers to the following three research questions:

Research Question 1: Can Pure Cupric Oxide Ceramic be Negatively Additively Manufactured?

Answer 1: Yes, Pure Cupric Oxide Ceramic can be manufactured by Negative Additive Manufacturing process.

Research Question 2: What will be the porosity of the manufactured Cupric Oxide Sample fabricated using NAM?

Answer 2: The manufactured Cupric Oxide sample is 42% porous.

Research Question 3: Is it possible to manufacture a functional Cupric Oxide ceramic part in Local Lab using?

Answer 3: Yes, aero foil was manufactured using Negative Additive Manufacturing. We can manufacture different electrode geometries, filters, antibacterial door handle covers, gas sensor tips and several antibacterial devices using this manufacturing method.

5.2 Comparison of Results to previous research

In this study, a PLA-printed mould was used with a copper-loaded aqueous binder slurry. The binder concentration remained unchanged throughout the trial, while the copper concentration changed from 1 g/mL to 2.17 g/mL. The optimum concentrations of the binder and copper powder in the DI water were determined to be 0.02 g/mL and 2.17 g/mL, respectively. These concentrations allowed the slurry's components to remain in equilibrium while the flow was sustained. Due to the CMC binder's compressive effect, the geometry shrank for copper concentrations below 2.17 g/mL. The ideal concentration was determined based on two fixed criteria: (1) shape retention and (2) slurry flow from the 30 ml syringe tip. Both conditions were met by the optimal concentrations proposed in this research. The green body had traces of CMC binder, PLA, and moisture. The green body was heated to 400 ℃ for 45 minutes to eliminate these traces. This brown body was sintered to grow microstructure into a CuO ceramic sample. To achieve this result, the brown body was sintered at 900℃ for 180 minutes. This sintering process also ensured that the brown body was oxidized entirely and transformed into CuO ceramic.

The manufactured sample was examined using six distinct characterization methods to verify its characteristics. Using the standard ATM C830-00 method and Archimedes' principle, we determined that the density of the CuO ceramic sample is 3.556 g/cm3. The porosity of the sample was determined using the same standard method and was found to be 42%. The porosity of the sample is essential for its use as a gas-sensing probe or device. The sintered CuO ceramic's porous nature was validated by SEM images, which also supported the 65.78% structural crystallinity calculated by XRD analysis.

Compared to the CuO Film gas sensor for hydrogen, which has a porosity ranging from 39.4% to 95.2%[148], the CuO ceramic produced using this innovative technique has a porosity of 42%. This substantial change in porosity is due to the increased pressure applied during manufacturing. In this study, the resistivity value for CuO ceramic manufactured is 10.5 $\Omega\, m.$. Copper powder is wet ball milled to produce a CuO ceramic with a resistance of 5 $\Omega\, m$ [29]. The resistivity of a CuO ceramic manufactured using negative additive manufacturing is double that of a ceramic made using wet ball milling. Other materials can be doped into the slurry in powder form to change the resistivity value and porosity of cupric oxide ceramic[29].

5.3 Implications and Contributions to the Field

The research experiment fills the methodology gap in the additive manufacturing of pure cupric oxide ceramic, which adds significance to the current research.

- This novel additive manufacturing method for cupric oxide ceramics will enable us to manufacture cupric oxide ceramic in three steps, directly from copper powder. It does not require complex chemical reactions or any complex green synthesis.

- Complex geometries can be easily fabricated through this method without the requirement of special ceramic ink printers.

- This research experiment can also easily manufacture the doped cupric oxide ceramic, which can be achieved by adding powders of different metals and ceramics in the slurry. This doping is of great importance as it enhances the properties of the cupric oxide ceramics, including its gas sensing ability, conductivity, and other such properties.

- This method can be altered easily to control porosity, crystallinity, and other features by changing the simple process parameters, which include Slurry Loading & Concentration, Drying Time, and Sintering Cycle

- We can manufacture complex cupric oxide products using this method very quickly. Such products include:

    1. Cupric Oxide Filters for masks

    2. Cupric Oxide door handle covers

    3. Cupric Oxide holding devices for use in medical labs and hospitals to apply their anti-bacterial and anti-viral properties.

    4. Cupric Oxide Ceramic can be crushed after manufacturing to produce powder additives which can be used in fuels, drugs, and different chemical reactions as catalysts and can be added to textile fibres to manufacture antibacterial and antiviral cloth.

- All these aspects of the current research show how significant this research is and the contribution that this research can make to the field. This will take some time as any researcher is not studying this novel manufacturing method and will revolutionize the manufacturing of cupric oxide in the future.

5.4 Limitations and future research directions

5.4.1 Research Limitations

The research presented in this document focuses on the additive manufacturing of pure Cupric Oxide Ceramic. No literature review claimed to manufacture pure Cupric Oxide Ceramic using Negative Additive Manufacturing. This research study focused on only one parameter of Negative Additive Manufacturing, which is Part Shrinkage. With this precise aim, the slurry prepared for this experiment:

1. was optimal to produce the lowest shrinkage in the ceramic part.
2. had such rheology, making it flow through the nozzle without choking it.
3. had optimal copper loading to support the material so every layer can support its upper layer enabling slurry to be formed as part geometry.
4. had optimal drying time so the part could be easily moulded.

The scope of the research was limited because:

1. All materials used in the research were of scientific grade and imported.
2. The import and acquisition of the materials were time-consuming.
3. The analysis techniques, including SEM, XRD, and XRF, were unavailable in-house and were conducted by sending the samples to other research facilities.

5.4.2 Recommendations for future research

Some recommendations for future research based on the current research experimentation are:

1. Study of optimal printing parameters for the negative additive manufacturing of cupric oxide ceramic.
2. Printing of scaffolds using negative additive manufacturing of cupric oxide ceramics

3. Fabrication of different devices, including gas sensors, blood glucose sensors, photo sensors, solar panels, electrodes, and other such devices by manufacturing the cupric oxide ceramic electrode

.

4. Achieving the superconductivity for cupric oxide by manufacturing doped cupric oxide ceramic using negative additive manufacturing.

5. Comparison of manufacturing time and cost for manufacturing cupric oxide powder additives by comparison of negative additive manufacturing and other chemical manufacturing methods.

6. Recycling the discarded copper into ceramic using negative additive manufacturing.

5.5 Conclusion

A monoclinic structured, 42% Porous CuO ceramic sample was successfully manufactured using the negative additive manufacturing process in the lab. The sample analysis confirmed the crystallinity of the sample to be 65.78%. The CuO sample's density and resistivity value was calculated to be 2.4187 g/cm3 and $10.5\Omega\, m$, respectively. It is confirmed that negative additive manufacturing can manufacture pure CuO ceramic samples. Crystallinity and other properties of the CuO sample can be further refined by exploiting the parameters of the process. These parameters include the amount of copper loading in the slurry, CMC concentration, dehydration time, sintering temperature, and sintering steps. This novel technique can manufacture complex geometry parts for electrodes and sensing surfaces for gas and particle sensors. This technique can also manufacture filters for medical devices and containers containing viruses and bacteria. It can be used to manufacture the push keys of different devices installed at public locations to minimize the transmission of viruses by touch.

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