

Introduction

In the ever-evolving landscape of modern technology, there is an increasing demand for smaller, more functional components. This drive towards miniaturization has resulted in an increase in demand for microsystems technologies, which are capable of providing innovative solutions to meet the changing needs of a wide range of industries. Microsystems play a crucial role in various technological applications, and the development of microstructures and microcomponents is pivotal for their advancement. Various cutting-edge techniques, including 3D printing, electrical discharge machining (EDM), electrochemical machining (ECM), lithography, severe plastic deformation, chemical vapor deposition (CVD), physical vapor deposition (PVD), and electrochemical assisted technique have been devised to facilitate the production of these microsystems (Kufner et al., 1993; X. Li et al., 2022). While these techniques offer numerous advantages, it's important to acknowledge that they also come with certain drawbacks and limitations.

Mechanical and laser machining techniques are a subtractive type of technique that involve the removal of material using mechanical tools (e.g., milling, turning) or lasers to get the required features. Mechanical machining offers high precision and accuracy but can be time-consuming and expensive, especially for complex geometries. Laser machining, on the other hand, utilizes laser beams to precisely remove material, offering high-speed processing with minimal tool wear (Kumar et al., 2020; H. S. Li et al., 2015; Z.). However, both techniques may face challenges when manufacturing microstructures with intricate geometries due to limitations in achieving fine details and intricate shapes. EDM and ECM are non-traditional machining processes with unique mechanisms. EDM utilizes electrical discharges to erode material from a workpiece, making it suitable for machining hardened materials but less optimal for complex microstructures (Li et al., 2018a). ECM, on the other hand, relies on electrochemical dissolution to remove material, offering high precision but limited capability for intricate geometries (Tsai et al., 2004). Lithography may be used to manufacture very small structures, but it needs a clean atmosphere and has material limitations. Extreme plastic deformation may produce fine-grain structures, but the resultant microstructure may be challenging to regulate. Contrarily, PVD and CVD techniques have drawbacks such as expensive and sophisticated equipment, limited film thickness capabilities, substrate compatibility challenges, potential concerns with establishing uniform film deposition, and relatively lower deposition speeds (Endo et al., 2019; Quinto, 1996).

In recent years, additive manufacturing (AM) technology has played a pivotal role in this transformative journey. With its remarkable capability to produce precise designs and geometries at a small scale, 3D printing, and other AM techniques have revolutionized microsystem production, rendering it more accessible, cost-effective, and precise than ever before (Hassanin et al., 2021). With the ability to rapidly develop designs and produce smaller batches, AM has created new opportunities for customized and individualized microsystems. This novel approach to manufacturing has been extensively studied, highlighting both the benefits and drawbacks of using such methods and techniques. This strategy is expected to benefit "low volume/high value" industries such as aerospace, marine, and energy. There could be a reduction in industrial and economic waste, lowering operating costs and reducing environmental impacts. 3D printing is restricted by material possibilities and has issues in obtaining surface smoothness, precision, scalability, and cost-efficiency, particularly for large components, with its best possible precision now in the millimeter range (Aghili et al., 2023; Gargava et al., 2019).

All the procedures are well-documented from a research standpoint, particularly in the microelectromechanical system (MEMS) fabrication industry. However, electrochemical-assisted manufacturing (EAM) offers a non-thermal additive technique that utilizes electrical energy to deposit thin or thick layers in a controlled manner, enabling the creation of complex and miniaturized systems with ease. By adding material atom by atom, EAM results in superior microstructural qualities that can be adjusted during the manufacturing process. Moreover, the EAM technique is capable of depositing a wide range of conductive materials, including metals, alloys, and semiconductors.

Three renowned metal AM techniques, such as rapid plasma deposition (RPD), electron beam melting (EBM), and EAM, are illustrated in Figure 1.1, along with their roles in the AM process design. RPD employs the melting of mm-sized wires through a plasma arc, with a robotic arm utilized for local material transport to the melt pool to shape it accordingly (Martina et al., 2012). EBM employs a focused electron beam to selectively melt a powder layer, with the beam directed across the powder bed to determine the shape of each layer individually (Heinl et al., 2008). EAM, on the other hand, enhances the electrochemically reduced metal pattern generated through electropolishing by electroplating it according to a predetermined sacrificial material template pattern. In this present thesis work we will be discussing the EAM technique in more detail.

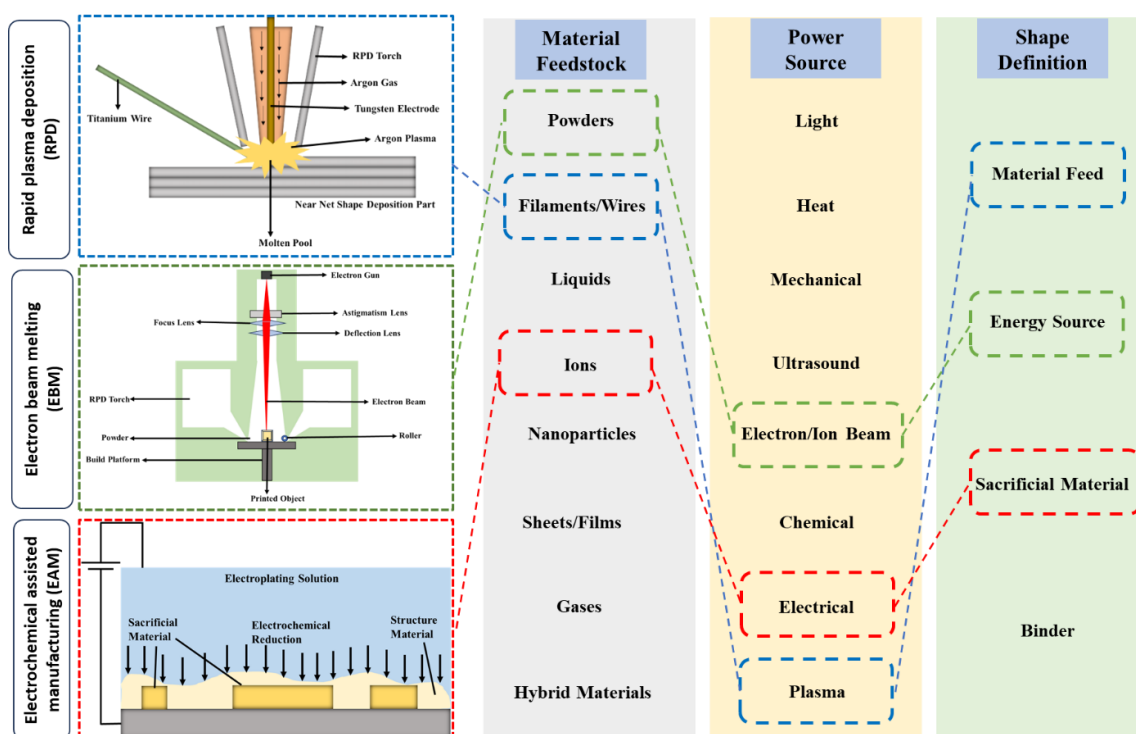


Figure 1.1 : Comparison of three metal AM techniques RPD, EBM, and EAM

1.1 ELECTROCHEMICAL ASSISTED MANUFACTURING

EAM stands as a noteworthy advancement in the realm of metal microstructure production. It employs electroforming, a prevalent technique, alongside additive manufacturing principles to fabricate intricate metal structures with precision and efficiency. It has a range of advantages, including a higher reproduction ability, dimensional accuracy, room temperature operating condition, greater flexibility, and less material and energy consumption (B. yan Jiang et al., 2016). The American Electroplaters and Surface Finishers Society (AESF) describes electroforming as "Electroforming is the fabrication or replication of products by electrodeposition upon a mandrel or mold that is subsequently removed from the deposit" (Chiba et al., 2003). The fact that electroformed products have a higher surface finish, narrower dimensional tolerances, and better metallurgical properties has ensured that electroforming is a trivial method in advanced manufacturing. Its applications range from common household items

to highly specialized aerospace components. Electroforming, although versatile and accurate, has significant limitations, including a sluggish deposition rate that impedes the quick manufacturing of complicated shapes, particularly thicker sections. It is best suited for thin-walled components, making it impracticable for larger ones. Material limits emerge because of the reliance on the substrate's electrical conductivity during electroplating, as well as the demand for conductive models on their active surfaces (Biswal, Vundavilli, et al., 2021).

1.2 HISTORY AND BACKGROUND OF ELECTROCHEMICAL ASSISTED MANUFACTURING

EAM has existed for several centuries, which makes it difficult to ascribe its development to a single individual. The history of EAM is intertwined with the groundbreaking work of numerous famous scientists. Michael Faraday, in the 1830s, set the essential framework for electroforming by developing the concepts of electrochemistry and the electroplating process. Jacobi invented electroforming in Russia in 1838 (McGeough, 2014). During his galvanic cell research, he employed an engraved copper printing plate as a cathode using a copper sulfate solution and electrodeposited copper onto it. Since then, various scientists and engineers have contributed to the improvement of the electroforming procedure, and it has become a crucial technology for the creation of microstructures and microcomponents.

In the early 20th century, when electroplating was acknowledged as a science as compared to a trade secret, the electroforming sector underwent a major transformation. In 1913, the American Electrochemical Society recognized electroplating as a genuine branch of scientific study, resulting in a research and development explosion in the area (W. X. Yu & Zhou, 2014). In the 1940s, the expansion of the electronics sector caused significant demand for gold electroplating, which was highly regarded for its excellent conductivity and corrosion resistance. This need prompted scientists to invent new and improved electroplating processes, such as electroforming, which was utilized to generate minuscule individual pieces that traditional machining was difficult to produce.

Late in the 20th century, electrodeposition research concentrated mostly on basic research, whereas micro-scale electroforming was a relatively new and less-discussed field of study. In addition, the concepts of alloy and composite electroforming have not yet been extensively investigated. Until now, there was a growing interest in micro-scale electroforming and MEMS production towards the turn of the 21st century. Together with UV and X-ray, the LIGA process gained growing importance in the high-accuracy manufacturing of large aspect-ratio microstructures, especially in the electronics industry. Although X-ray LIGA has shown significant potential in manufacturing structures with a high aspect ratio, it has not yet been embraced by large-scale businesses. UV light had been utilized since the late 20th century, but important advancements in UV-LIGA came with the creation of SU-8, a UV-sensitive epoxy-based substance that was first intended as a mask for reactive ion etching (Genolet & Lorenz, 2014). In 2010, an ultrasonic-assisted technology was incorporated into the electroforming process, leading to a nanoscale reduction in the grain size of the electroformed structures. This technology also produced electroformed coatings with higher surface tensile properties compared to other existing technologies. By altering the strength of the magnetic field used during the electroforming process, another researcher showed that the size of grains of a deposit could be altered. In addition, the combination of UV lithography and pulse electroforming has been researched further to produce complex geometric shapes while simultaneously decreasing deposition time. UV LIGA has also been utilized widely in the manufacture of a vast array of industrial goods, including moulds used for microfluidics, with favorable results compared to traditional micro-machining processes. The overview of the evolution and development of EAM technology is depicted in Figure 1.2.

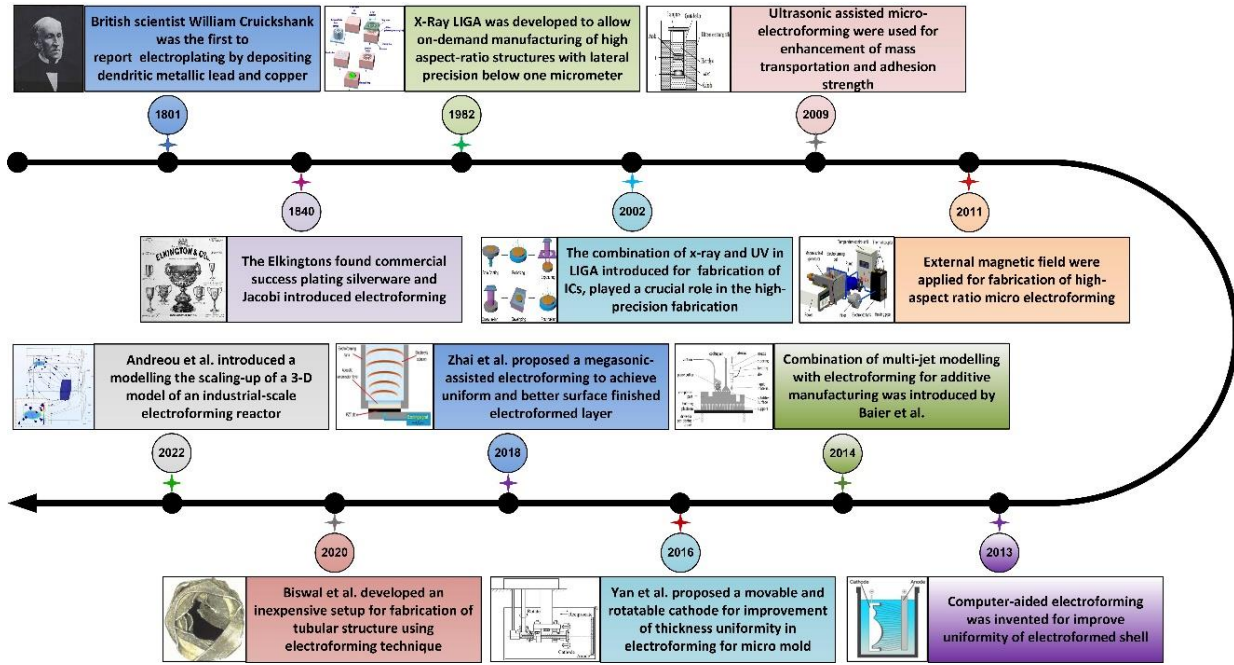


Figure 1.2 : Evolution and development of EAM technology

1.3 FUNDAMENTALS AND GOVERNING EQUATIONS

EAM is a process involving electrodeposition to manufacture a precise and accurate metal part or component. The procedure entails producing a mold or mandrel of the appropriate shape and then electrolytically depositing metal onto the surface of the mold. The electrolytic bath is a solution composed of metallic salts and other chemicals that aid in controlling the deposition process. The principle of electrochemistry, which includes the transmission of electrons between two electrodes in an electrolytic solution, underlies the electrodeposition procedure. The principle of electrodeposition is based on Faraday's law of electrolysis, which states that the quantity of metal deposited at the cathode is directly proportional to the number of electrons transferred in the reaction (Hannavy, 2013). This relationship can be represented by Eq. (1.1):

$$\nabla n = \frac{It}{ZF} \quad (1.1)$$

The formula relates the current (I), time (t), charge on metal ion (Z), and the Faraday constant (F) to the change in the Number of moles of metal (Δn) that is deposited. To regulate the thickness of the electrodeposited layer, one can adjust the current, time, and electrolyte concentration. The Nernst equation in electrodeposition predicts the cell potential required to deposit a specific metal under given conditions. It is represented by Eq. (1.2) (Biswal et al., 2022):

$$E_{cell} = E_0 - \frac{RT}{nF} \ln \frac{M}{M^+} \quad (1.2)$$

Where E_{cell} is the cell potential, and standard potential (E_0), Gas constant (R), temperature (T), number of electrons (n) and M and M^+ are the concentrations of the metal ion at the cathode and anode, respectively. The Nernst equation provides a measure of the thermodynamic feasibility of a reaction.

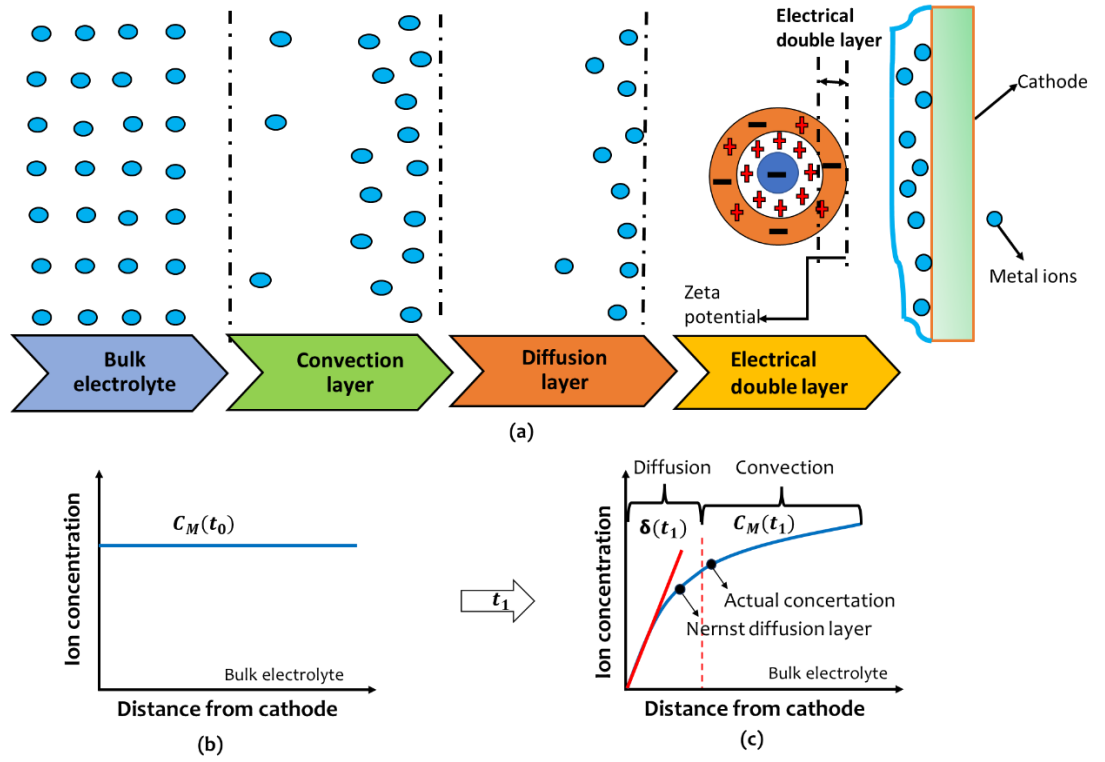


Figure 1.3 : (a) Schematic of mass transfer in the electrochemical manufacturing process, (b) Variation in diffusion-layer thickness at t_0 , (c) Variation in diffusion-layer thickness at t_1 (H. Zhang et al., 2021)

The process of electrodeposition entails several sequential steps as shown in Figure 1.3 (a) the transportation of ions from the bulk electrolyte to the cathode, their absorption on the cathode surface, the electrochemical reduction process, and the subsequent growth and nucleation of crystals. Mass transfer during this process can be delineated into three distinct mechanisms: migration, convection, and diffusion. Migration is governed by the electric field, convection by the external flow field, and diffusion by the concentration gradient within the electrolyte. Given the low imposed current in electroforming, migration-induced mass transfer is considered negligible. Figure 1.3 (b) and (c) illustrates the relationship between the thickness of the diffusion (δ) layer and electrodeposition time. Initially, the ion concentration on the cathode surface decreases over a certain electrodeposition time (t_1), with this decline becoming more pronounced as the electrodeposition time continues to increase (t_2), resulting in the formation of a δ .

1.4 EFFECTS OF PROCESS PARAMETERS

Achieving precise electroforming with high dimensional accuracy and outstanding surface polish necessitates a comprehensive understanding of the factors that influence the process as illustrated in Figure 1.4. The EAM process is governed by a variety of characteristics, the most significant of which is electric potential or overpotential. However, various other electrolyte-related parameters, including temperature, agitation, concentration, and pH, are also important in influencing the quality of the electroformed components. High precision, dimensional accuracy, and exceptional surface quality in the electroforming process need a thorough grasp of these elements. The electroforming process begins with interactions between the substrate and the seed deposition layer, which are followed by nucleation and growth processes that establish the geometrical and metallurgical structure of the electroformed portion. These processes are affected by variables such as current density, current waveform, temperature, electrolyte pH, bath agitation, and the application of additives and surfactants. To accomplish efficient electroforming of microfeatures, a detailed understanding of these influencing variables is required.

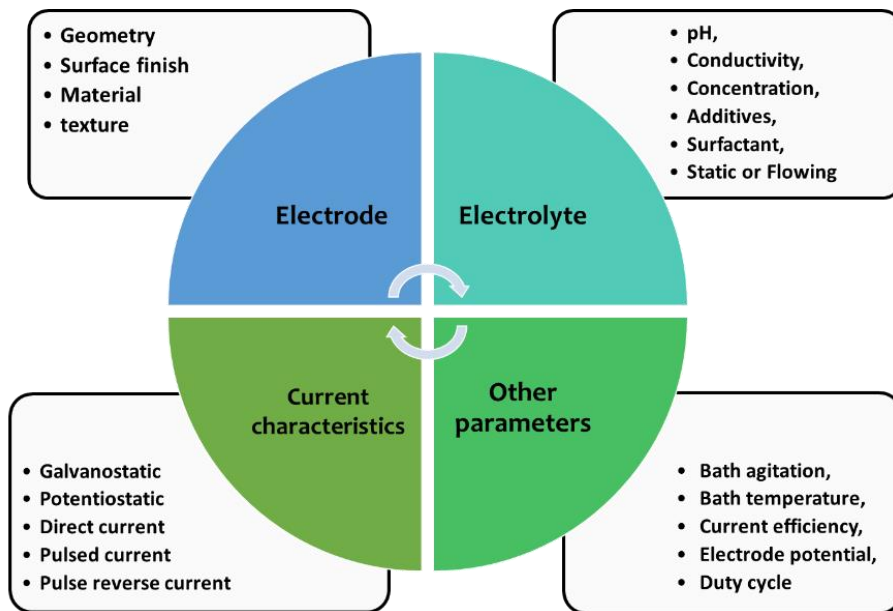


Figure 1.4 : Factors affecting the electrochemical assisted manufacturing process

Achieving uniform coating thickness in EAM relies on precise current distribution. Differences in current density affect how coatings form: sharp edges get thicker coatings, while recesses get thinner ones due to how electricity flows. Too much current can harm coating quality, while too little can introduce impurities. Finding the right current density involves looking at things like salt concentration and electrode shape. Electroforming can employ direct current (DC), pulse current (PC), or pulse reverse current (PRC). Whereas PC and PRC methods offer advantages such as higher deposition rates, uniform coatings, improved material properties, and increased efficiency compared to traditional DC-EAM.

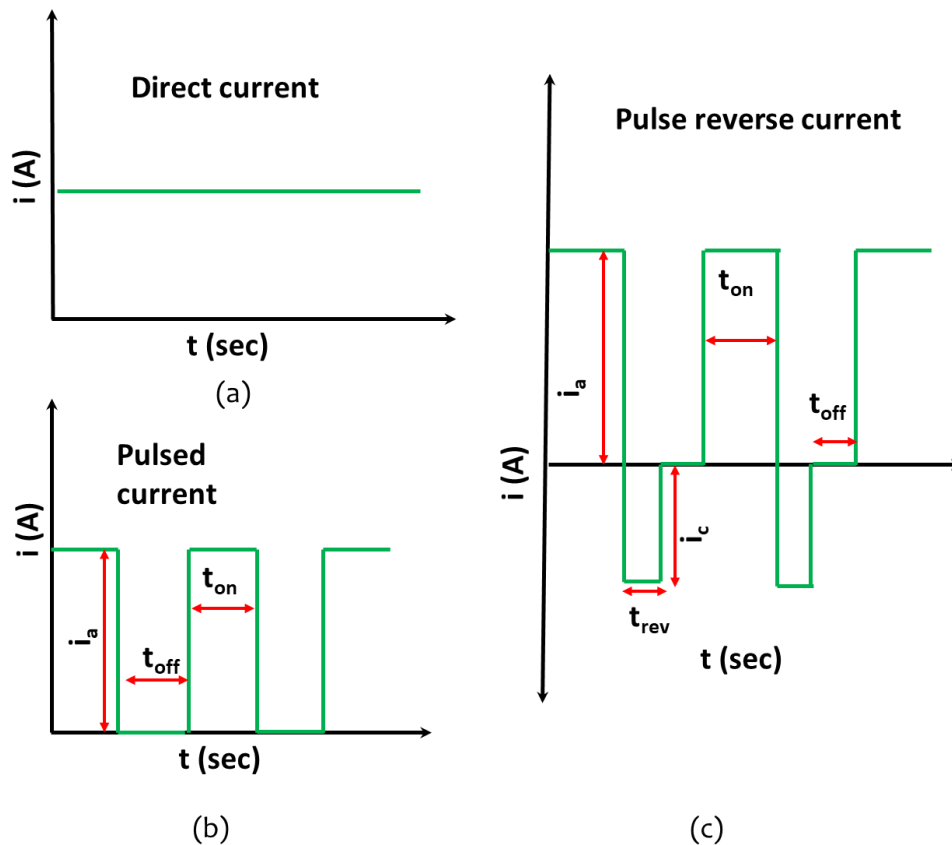


Figure 1.5: Different type of current source (a) Direct current (b) Pulsed current, (c) Pulse reverse current

1.5 CHALLENGES ASSOCIATED WITH EAM

While offering numerous advantages, the EAM technique encounters certain technical limitations that could impact the reliability and quality of the deposited layers. Achieving thickness homogeneity poses a significant challenge, as the precise deposition of metal layers is critical in EAM, deviation from the specified thickness could lead to diminished performance or potential equipment failures (Hernández et al., 2015). Current distribution is a critical aspect in micro electroforming. When metal is formed by electroforming, the thickness and quality of the metal layer might vary due to differences in the existing patterns of current density allocation across the substrate's surface. The size and form of the substrate, the positioning of the electrodes, and the conductivity of the electrolyte solution are some of the variables that affect the current distribution (Z. Li et al., 2018b). During traditional electroforming of large-aspect-ratio nanostructures, high current density tends to concentrate at the top and bottom edges, resulting in accelerated formation of the electroformed layer. This phenomenon leads to the development of nanovoids, diminishing the performance of electroformed material.

Another significant issue in micro electroforming is the presence of residual stress, which can significantly affect the effectiveness and quality of the deposited metal layer (Jeong et al., 2016). Residual stress arises from the mismatch in thermal expansion coefficients between the deposited metal and the substrate. Such stress can cause distortion, breakage, or delamination of the deposited layer, ultimately impairing the product's performance (Qiang et al., 2023). Throughout the electroforming process, severe bending deformation occurred in cantilever-based microstructures due to residual stresses. Additionally, poor adhesion between the electroformed layer and the base metal may result in flaking or delamination, which can be attributed to insufficient cleaning, inadequate substrate surface activation, or excessive current density during plating.

In my thesis work, we had taken these limitations into consideration and aimed to mitigate their impact during our experimental procedures. To address these challenges, we made modifications to our experimental setup and optimized the process parameters accordingly.

1.6 ORGANIZATION OF THESIS

The present thesis focuses on utilizing electrochemical manufacturing techniques for fabricating components with applications in various fields such as microfluidics, catalysts, sensing, dye degradation, and wastewater treatment. Our objective was to introduce a novel, cost-effective method for producing metallic as well as composite tubular structures. We conducted a study on metallization over complex 3D printed architectures. Additionally, considering the significant pollution caused by various textile industries in India, we explored a new approach for treating real industrial textile wastewater.

Chapter 1 provides a historical overview and background of AM and EAM fabrication techniques, presented advantages and limitations of the electroforming process. It focuses on presenting a comprehensive understanding of electroforming, including fundamental equations and the impact of influencing factors on the process.

Chapter 2 comprises a comprehensive literature review that addresses various topics, including traditional AM processes and their limitations, as well as EAM. It also encompasses literature concerning the fabrication of microtubes using traditional techniques and their dimensional constraints. Additionally, the chapter includes a review of literature focusing on applications such as creating superhydrophobic surfaces, photocatalytic assisted wastewater treatment.

Chapter 3 explains theoretical and experimental investigations aimed at fabricating metallic and composite microtubes. The chapter is organized into four parts, covering the design and development of the experimental setup, the fabrication process of tubular structures,

optimization of process parameters, and exploration of various applications for the fabricated microtubes.

Chapter 4 explores the electrochemical manufacturing technique for producing metallization on 3D printed cubic lattice architecture and producing nanoporous Cu electrodes by chemically dealloying a less noble element (Zn) after depositing Cu-Zn alloy onto a Cu wire. Machine learning (ML) algorithms such as adaptive neuro-fuzzy inference systems (ANFIS), artificial neural networks (ANN), and response surface methodology-box behnken design (RSM-BBD) have been implemented.

Chapter 5 elaborates on the electrochemical-assisted treatment of industrial textile wastewater, divided into two parts. Initially, integrating electrochemical and photocatalytic methods effectively removes contaminants and color from the effluent. Later, the chapter focuses on optimizing process parameters and incorporating ultrasound to enhance removal efficiency of color, organic and inorganic contaminants, and turbidity through statistical analysis.

Chapter 6 concludes the dissertation by summarizing the presented results and proposing future work.

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