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Investigation of Scanning Droplet Cell Technology for Electrochemical Deposition of Custom Three-Dimensional Alloys

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Disclaimer

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Corie Horwood

22-FS-031

Project Overview

The goal of this project was to assess the feasibility of a new method of electroplating, which we have termed "electroprinting", for fabricating millimeter to centimeter metal parts with full density, and eventually, with bespoke 3D internal density patterns. Alloys, gradients and varying density is beyond the scope of this work, and efforts were focused on developing the technology to be capable of printing solid parts, beyond the lines and columns previously reported in the literature. Enabling this technology would expand the design space possible for the WPD program, allowing for smooth and complex density gradients in parts rather than discrete density steps between multilayers.

We successfully designed and built an electroprinting apparatus, capable of printing copper in customizable 1-D patterns, which can be printed in stacked layers to form 3D parts. We successfully characterized the flat printed patterns, however, have encountered difficulty in characterizing multilayer prints. We have partially addressed the feasibility question, by developing the method for electroprinting 3D parts, however, some questions about the internal porosity and density of these parts still remain.

Mission Impact

This work expands on current capabilities in electroplating to form multilayer structures with discrete density layers. Current capabilities rely on a combination of electroplating and machining steps, whereas the electroprinting technology explored here would enable significantly more complex internal density structures, as well as complex gradients between different density regions. Expanding the design space for materials formed with varying density layers and gradients will strengthen the lab's mission for national security.

Publications, Presentations, and Patents

Presentations:

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Abstract

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Background and Research Objectives

The current state-of-the-art is often referred to as meniscus-confined electrodeposition and research efforts have largely focused on pushing to smaller and smaller deposited features. In this field, the goal is often to make the smallest dots, lines/interconnects and 3D structures possible.[1]–[4] The internal structure of the deposits is typically not examined, and there is no interest in overlapping/parallel deposits to make larger structures. Commercially made instruments, such as scanning-droplet cell microscopes, can be used for meniscus-confined electrodeposition. If the approach of using meniscus-confined electrodeposition is determined to be feasible for making complex 3D graded parts, a suitable commercial instrument should be used. However, for this study, a simplified in-house built setup is sufficient.

In this feasibility study, we investigated the feasibility of using the meniscus-confined electrodeposition approach to form larger scale solid parts with customizable internal composition/density profiles. Some key aspects to the feasibility of this approach include:

(1) Designing and building a simple electroprinting apparatus that allows continuous lines of copper to be electroplated.

(2) Evaluate the electroprinting parameters, such as print width/profile as a function of tip size, microstructure of printed lines, and height of lines as a function of printing parameters.

(3) Characterize electroprinted lines and objects (white light interferometry, tomography and/or cross-sectional SEM imaging to examine internal structure, density by Archimedes method).

(4) Demonstration of larger scale printed part (mm dimensions) and characterization of total density and internal porosity.

Scientific Approach and Accomplishments

A simple copper electroprinting setup was built in house, as shown in Figure 1, utilizing two motorized translation stages (Thorlabs MTS25-X8) which can be programmed and controlled through a USB computer interface. A silicon wafer, sputter coated with a thin layer of gold, comprised both the electroprinting substrate and the working electrode/cathode, and was positioned on two stacked translation stages, allowing the substrate to be moved in the X and Y directions. Experimentally, we determined that a gold-coated silicon wafer was critical to the success of the electroprinting process. The substrate is necessarily restricted to metals that are more noble than the metal to be printed; in the case of copper, this means gold, silver, iridium, palladium, ruthenium or platinum. Otherwise, a chemical redox reaction can occur wherever the plating solution contacts the substrate, plating a thin layer of copper and dissolving/oxidizing the less noble substrate metal in the absence of an applied potential.

A 10 mL Luer lock syringe contained the copper sulfate based electroplating solution (MacDermid/Enthone Microfab SC-40), and a copper wire (38 gauge, MSC Industrial Supply Company) was threaded through the syringe plunger and coiled inside the syringe barrel to form the anode (Figure 1). An electrical connection was formed between the anode copper wire and the gold coated wafer cathode using a potentiostat, and the circuit was completed when the meniscus from the syringe contacted the cathode wafer. The syringe assembly was held in a fixed position above the substrate, but was held within a fixture with a spring, allowing the syringe some freedom of motion in the Z direction. Between the substrate and the translational stages, we added a small balance (American Weigh Scales Digital Precision Pocket Weigh Scale) to measure the force loading on the substrate at the start of a print, and 10-20 g of force was found to be adequate.

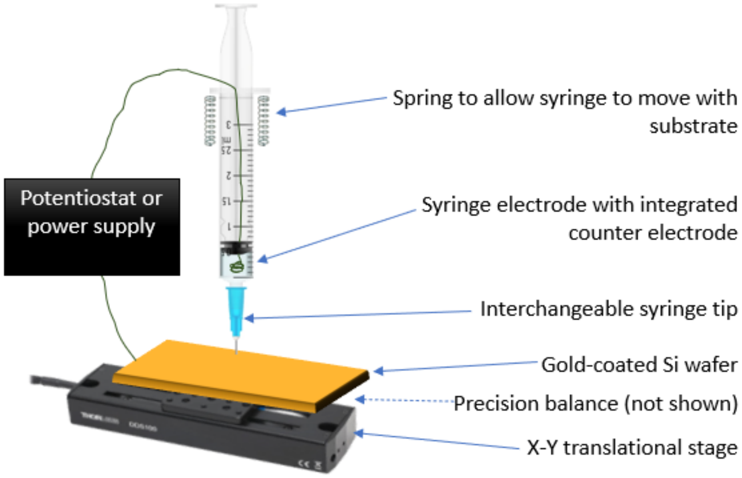

Figure 1. In-house built electroprinting setup used for printing copper.

Early prints using the in-house-built setup had frequent issues with bubbles or copper plugs forming in the syringe tip, both of which stop the electroprinting process. The formation of bubbles in the syringe tip was remedied by switching to conical rather than straight-walled tips, leveling both the substrate and the syringe, and applying the appropriate amount of force/spring loading on the tip (10-20 g). Copper plugs forming in the syringe tip was mitigated by applying potential rather than constant current, and by keeping the reduction potential applied < 700 mV vs. copper wire combined counter/reference electrode. The appropriate force loading on the printing tip also helped to achieve straighter printed lines, whereas too much force on the tip results in bending tips and curved lines, as shown in Figure 2.

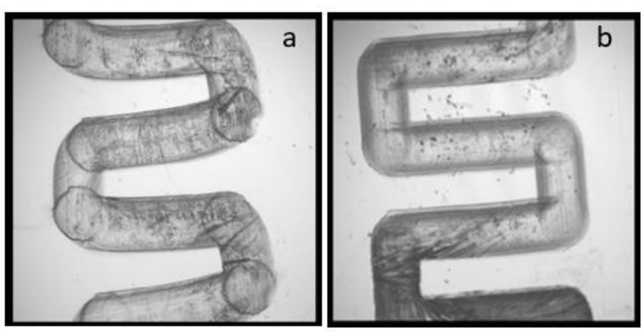

Figure 2. Optical microscope images of copper lines printed (a) with too much force on the tip, causing tip bending and (b) the same print program after adding a balance under the substrate to allow 10-20 g of force applied to the printing tip.

After refining the printing process, single layer metal prints were able to be made reproducibly, allowing for the determination of print parameters as shown in Figures 3 & 4 (line width/cross-sectional profile vs. tip size, line height vs. applied potential and linear translation speed, etc.). Characterization was performed using white light interferometry as a surface height mapping tool.

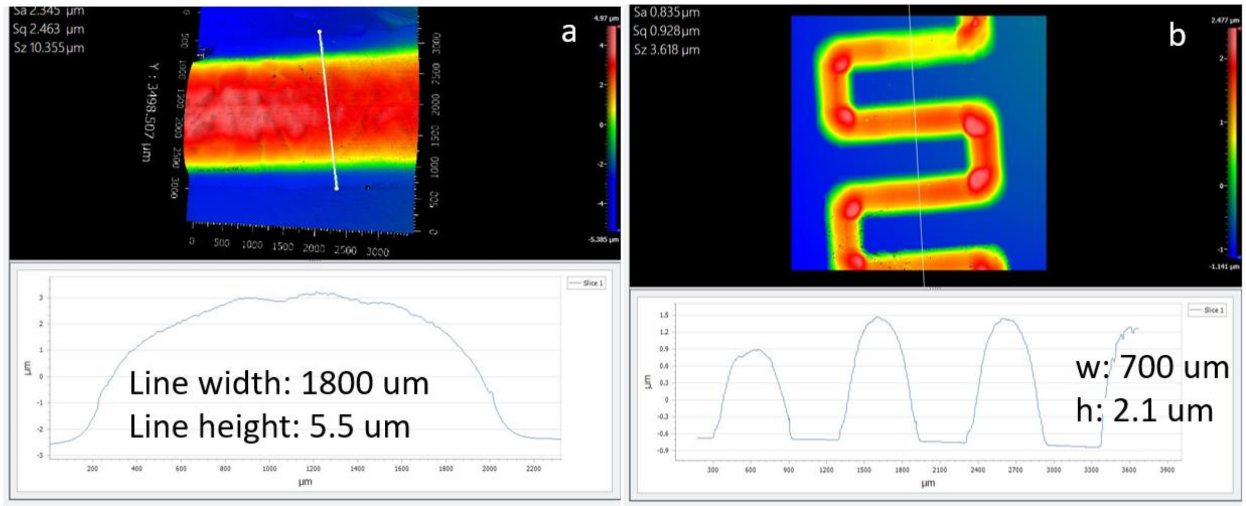

Figure 3. White light interferometry surface maps of lines printed with (a) a large tip with an inner diameter of approximately 1600 micron and (b) with a 610 micron inner diameter tip.

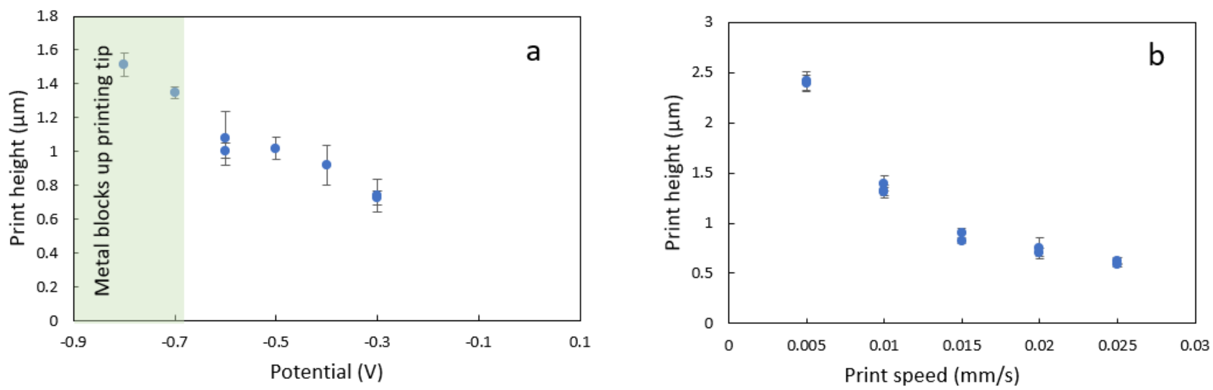

Figure 4. Print height, measured by white light interferometry, for multiple lines printed over two separate days at (a) linear translation speed of 0.1 mm/s and varying applied potential and (b) a constant potential of 0.5 V and varying print speed.

Prints were made with concentric square spirals to demonstrate lines printed adjacent to one another with no gap in between. It was found that lines can be printed partially overlapping a previously printed line, indicating that the height variation tolerance for the tip/substrate was at least ~2 microns. Prints were made with multiple printed layers on top of one another. Despite the smooth gold coated wafer substrate used, the roughness of the print increases with each subsequent layer. Typically, a print with two layers was too rough to be measured by white light interferometry, i.e., too much light was scattered from the copper surface, which while smooth was no longer mirror-like, and characterization could not be performed.

Mission Impact

This work expands on current capabilities in electroplating to form multilayer structures with discrete density layers. Current capabilities rely on a combination of electroplating and machining steps, whereas the electroprinting technology explored here would enable significantly more complex internal density structures, as well as complex gradients between different density regions. Expanding the design space for materials formed with varying density layers and gradients will strengthen the lab's mission for national security.

Conclusion

The realization of this work to form a full prototype of a bespoke graded metal object has numerous challenges remaining. The most critical of these challenges, and one that this project was unfortunately not successful in solving, is the challenge of metrology, detecting and hopefully minimizing internal voids in larger electroprinted structures. Careful cross-sectioning, polishing and analysis with SEM, or ideally, FIB-SEM are expected to be the best methods of detecting nanometer sized voids in electroprinted 3D parts.

Electroplated metals naturally have a tendency to be preferentially deposited on outside corners, edges, ridges and bumps, and less metal is deposited on inside corners, groves, divots and pits. If voids in the 3D structure are found to be unacceptable, minimizing these voids may be aided by using a smaller current or potential for the print, thus slowing down the printing speed. Alternatively, an increase in pressure for the electroplating solution (generally achieved by using a larger syringe containing more solution) could be helpful in encouraging solution to flow into voids and pores.

A third challenge, which is well beyond the scope of this project, is in combined electroprinting of two or more metals to form alloys and gradients. This will likely be best achieved using a pumped flow system, where the ratio of the metals in the plating solution (pumped separately from two reservoirs and mixed in the syringe/print head) is the primary means of control of the alloy being printed.

This project investigates a niche of materials science that does not have broad applicability in other industries. Electroplating of metals, alloys and gradients has a large range of applications, however, by electroprinting solid structures in a voxel-by-voxel fashion, fabrication time and process complexity are greatly increased. This is a trade-off for the custom, 3D control of metal densities that the approach will allow, but that complex and intricate architecture must be an integral part of any application of this approach.

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[2] D. Eliyahu, E. Gileadi, E. Galun, and N. Eliaz, "Atomic Force Microscope-Based Meniscus-Confined Three-Dimensional Electrodeposition," *Adv. Mater. Technol.*, vol. 5, no. 2, pp. 1–9, 2020.

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metallic microstructures with in-process monitoring of surface qualities,” *Precis. Eng.*, vol. 70, pp. 34–43, 2021.

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