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1	Title
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1 Abstract

A high speed and low-cost electrochemical additive manufacturing method for parallel microprinting of metals is proposed. Multicapillary 3D printed solution flow type microdroplet cells (Sf-MDC) with large capillary diameters (600 µm) are used to electrodeposit high-quality Ni microstructures. Three Ni lines each having a width of around 900 µm and a thickness of around 24.6 µm, 20.7 µm and 15.2 µm are simultaneously printed on Cu substrate. The influence of temperature and scanning speed on the height of printed Ni lines is studied. Independent control of solutions inside each capillary enables the simultaneous formation of Ni-Cu-Ni and Cu-Ni-Cu microdots without any cross-mixing of solutions. By replacing 3D printed inner capillaries (around 600 µm in diameter) with silica capillaries (around 100 µm in diameter) inside the Sf-MDC, free standing 3D structures such as Ni microrods are successfully fabricated. Localized electrodeposition using the Sf-MDC allows parallel process 3D printing of metal microstructures for a wide range of applications. Keywords: Electrodeposition; 3D printing; Droplet cell; Ni microrods; Electrochemistry

1 1. Introduction

2 Robust, reproducible and cost-effective fabrication of metals at micrometer scale would enable 3 rapid development of advance electronic devices, microelectromechanical systems (MEMS) 4 and biomedical devices [1–6]. Conventionally, mask-based lithography is the main standard of 5 industries to produce micro- or nano- scale patterns. However, production of expensive masks, 6 time-consuming pre- and post-processing steps and difficulty in fabricating freestanding 3D 7 structures are some limitations of this technique [7,8]. One-step fabrication techniques such as 8 focused ion beam-induced deposition (FIB-ID), electrohydrodynamic printing (EHD), direct 9 ink-writing (DIW), laser induced forward transfer (LIFT), local electrophoretic deposition 10 (EPD), and laser induced photoreduction (LIPR) have also been used to manufacture metal 11 microstructures for various applications [9–13]. Organic material contamination and high 12 carbon content in FIB-ID processes may hinder the properties of printed structures. EHD and 13 DIW methods often need sintering, and removal of binders and solvent, which may result in 14 porous structures and reduce the mechanical strength of the printed metals [14]. Besides the 15 above mentioned techniques, robocasting [15], hybrid metal additive manufacturing [16], 16 metal jetting [17] and laser engineering net shaping [18] techniques have also been utilized for 17 2D and 3D fabrication of metal microstructures. However, high equipment costs and risk 18 factors associated with the use of high-power lasers and heat treatments limit the use of these 19 techniques.

In recent years, additive manufacturing of metal microstructures using electrochemical microdroplet cells is gaining attention [19–30]. In this technique, micro- or nano-sized capillaries are used for localized electrodeposition of metal ions from the solution. Template free fabrication of complex structures without the use of thermal treatments makes this technique simpler, safer, and cost-effective as compared to previously mentioned techniques. Recently, Chen et al. has reported a low-cost electrochemical metal 3D printer capable of

1 printing highly conductive copper microstructures of 400 µm feature size [31]. Lei et al. has 2 reported a meniscus-confined electrodeposition approach for microprinting of copper lines on 3 gold, silicon and glass-substrates [32]. Lin et al. has also reported a nanopipette based metal 4 microprinting technique capable of fabricating high aspect ratio and high density 3D structures 5 with nanoscale precision [33]. Most of these techniques are limited to micro- or nano- scale 6 resolution and cannot be scaled up. Slow deposition rates (0.008 to 20.4 μ m³s⁻¹) and printing 7 speeds (100 to 180 nms⁻¹) are the major challenges to overcome [31]. Research on the 8 fabrication of metal microstructures using large sized nozzles or capillaries is still in its early 9 stages. Technological advances in terms material diversity, high-throughput and large spatial 10 resolution are required for the industrial implementation of electrochemical droplet cell based 11 additive manufacturing.

12 High-throughput fabrication of metal microstructures can be achieved by combining multiple 13 capillaries in a parallel manner that are capable of simultaneous electrodeposition. The 14 deposition rate or printing speed can be increased by the use of large sized capillaries [34]. Few 15 studies have reported the applications of parallel, multi-capillary 3D printing for fast 16 fabrication of metal microstructures [29, 31–33]. These studies are limited to fabricating metal 17 microstructures in the range of 1-10 µm and offer slow deposition rates. The droplet cells are 18 fabricated manually using a series of complex processes. Problems such as capillary clogging 19 due to small diameter and the need to replace the cell after several hours of usage require 20 fabrication of new cells which consumes time. A single-step method to simultaneously 21 fabricate electrochemical droplet cells with multiple capillaries for high-throughput 22 electrodeposition would be important for a broad range of patterning applications [38].

Herein, a single step fabrication method is applied to fabricate a multicapillary 3D printed
solution flow type microdroplet cell (Sf-MDC) with capillary diameters of 600 µm. Unlike
manually made droplet cells, multiple Sf-MDC are fabricated at once with minimum resin

consumption and shorter fabrication time. An electrochemical additive manufacturing system is developed for the simultaneous electrodeposition of Ni microstrips on Cu substrate. The influence of temperature and scanning speed on the volume of deposit is studied. An attempt is made to simultaneously fabricate three separate Ni, Cu, Ni and Cu, Ni, Cu microdots on the specimen. Free standing Ni microrods are simultaneously fabricated using the Sf-MDC.

6 **2. Experimental**

7 Design and Fabrication of Sf-MDC

Fig. 1 depicts the design and fabrication of Sf-MDC used for simultaneous electrodeposition. 8 9 Blender 2.79 CAD software was used to design the Sf-MDC. Fig. 1 (a) shows the top view of 10 Sf-MDC. The Sf-MDC consists of three solution inlets capable of separately supplying the 11 solution to the inner capillaries. The type of solution, its flowrate and concentration inside each 12 capillary can be independently controlled. The outer capillaries are used for the continuous 13 removal of excess solution through a common solution outlet. The diameter of inner and outer 14 capillaries is 0.6 mm and 1.2 mm, respectively. Due to the complexity of the design and the 15 limited resolution of 3D printer (Formlabs, Form 2), further decrease in the diameter of 16 capillaries resulted in the blockage of capillary heads inside the Sf-MDC. A photopolymer resin (FLGPCL04, Formlabs Form 2) was used for fabricating the Sf-MDC. Fig. 1 (b) shows 17 18 the image of 3D printed cells attached to the build platform. Multiple cells can be printed at 19 once using a single-step fabrication method with minimum usage of polymer resin. The single cell consumes only about 5 mL of resin and can be used several times. An important aspect of 20 21 this technique is its simplicity, high-throughput capability and low-cost, especially when 22 compared with manually made droplet cells and micropipette-based techniques.

23 Materials

Cu sheets (0.1x10x30 mm) were used as a substrate (working electrode). The sheets were cleaned with ethanol and highly purified water. 0.31 M NiSO₄·6H₂O/ 0.4 M H₃BO₃ solution 1 was prepared for Ni electrodeposition. 1 M CuSO₄·5H₂O/ 0.9 M H₂SO₄ was prepared for Cu 2 electrodeposition. The chemicals were purchased from Kanto chemicals, Japan. Pt wires (50 3 μ m in diameter) were inserted inside the inner capillaries of Sf-MDC and connected with a 4 common Pt wire (500 μ m in diameter) to use as anode. Cu sheets and Pt wires were purchased 5 from Nilaco Corporation, Japan.

6 **Procedures**

7 Fig. 2 schematically depicts the procedure of simultaneous electrodeposition using the Sf-MDC. 8 The substrate is placed on a computer controlled XYZ moving stage. The inlets of the Sf-MDC 9 are connected with three peristaltic pumps. The solution was supplied to the inner capillaries at a flowrate of 1.5 µm³ to form droplets at the three capillary tips. The solution droplets were 10 11 allowed to come in contact with the specimen. Separation distance of around 50 µm was 12 maintained between the specimen and the inner capillary tips. A vacuum pressure of 85 KPa 13 was set to remove the solution from a common outlet with a vacuum pump. Continuous 14 removal of the used solution ensured uniform solution composition at the electrode-electrolyte 15 interface and gave Sf-MDC the ability to control the droplet size by controlling the vacuum 16 pressure. By following these parameters, reproducible meniscus could be formed under each 17 capillary during the metal microprinting process. A constant current of 500 µA is applied to 18 print Ni microstrips and Ni-Cu-Ni microdots on the Cu substrate. The moving speed and 19 temperature of the XYZ stage were varied to examine the influence of these parameters on 20 volume and height of the deposit. Free-standing Ni microrods were simultaneously fabricated 21 by inserting silica capillaries (diameter = 0.1 mm) instead of using 3D printed inner capillaries 22 (diameter = 0.6 mm) to better control the structure of the deposit and prevent the capillary 23 blockage issues. A constant current of 300 µA was applied and the stage was kept stationary 24 for first 30 min of electrodeposition process. The stage was then moved along z-axis at constant 25 speed (0.25 μ ms⁻¹) to fabricate the microrods.

1 **Observations**

2 The surfaces and cross-sections of the specimens were observed with an optical microscope 3 (Wraycam, NOA630, Tokyo, Japan) and a scanning electron microscope equipped with an 4 energy-dispersive X-ray spectroscopy (EDS) analyzer (SEM, JEOL, JSL6510-LA, Tokyo, 5 Japan). For cross-sectional measurements, the specimens were cut using a cutting machine 6 (RC-120, Ritoku Co. Ltd., Japan) and ultrasonically cleaned with ethanol. The cross-sections 7 of the specimen were embedded inside the epoxy resin and allowed to cure for two days. The 8 exposed surface of the specimens was mechanically abraded with a series of SiC abrasive 9 papers under running water. The abraded specimens were washed with ethanol and highly 10 purified water before SEM observations.

11 **3. Results and discussions**

As the electrodeposition process is initiated with Sf-MDC, metal microprinting simultaneously takes place under the droplets-confined microcapillaries. Precise movement of stage in X-, Yand Z- directions results in fabrication of desired microstructures. This process is similar to fused deposition modeling (FDM) printing process, except the hot end of the extruder filled with melted resin is replaced with droplet-confined microcapillaries, capable of simultaneous electrodeposition. The electrochemical cell (Sf-MDC) enables the control of electrochemical parameters such as current or voltage during the printing process.

Fig. 3 shows the optical, SEM and EDS elemental mapping images of Ni microstrips printed on Cu substrate. The optical microscope image of the specimen (Fig. 3 (a)) shows three uniformly sized Ni lines simultaneously printed on Cu substrate at two different scanning speeds ($2 \mu m s^{-1}$ and $4 \mu m s^{-1}$). A slight decrease in the width of lines is observed as the scanning speed is increased from $2 \mu m s^{-1}$ and $4 \mu m s^{-1}$. This may be attributed to the stability in the movement of droplets at higher scanning speeds which allows the droplets to maintain the surface tension equilibrium. The size of the droplets also depends on the wettability and contact

1 time, diameter of inner and outer capillaries and the distance between the specimen and the 2 capillary tips. The height of the printed Ni lines was estimated from the cross-sectional SEM 3 images. The specimen was cut from the middle of fabricated Ni lines. Fig. 3 (b) shows the EDS 4 mapping images of the printed Ni fabricated at 4 µms⁻¹. The deposition rate in the central region 5 is higher than at the edges, resulting in convex shaped cross-sections of the printed Ni lines. 6 This may happen due to higher current density in the central region of the droplets as compared 7 to the edges. The presence of capillary forces and surface tension at the electrode-electrolyte interface allow the droplets to minimize their surface area. Maximum volume of the droplets 8 9 is thus confined in the central region, resulting in low solution resistance and higher current 10 density. However, very thin layer of droplets spreads outside the diameter of inner capillaries 11 (Fig. S1) and results in high solution resistance. Similar results have been obtained in previous 12 studies [28,32,39]. The shape and height of the simultaneously printed lines are different. 13 Several factors were taken into consideration to investigate the reason of this difference after 14 repeated experiments gave similar results. Since the Sf-MDC is fabricated by stereolithography 15 type 3D printer having a minimum resolution of 100 µm, a slight variation in the dimensional 16 accuracy of capillaries could lead to difference in the IR drop inside each capillary. The use of 17 high-resolution 3D printers capable of accurately fabricating complex designs having multiple 18 micro- or nano-meter sized capillaries may solve this problem. Factors such as variation in 19 solution removal from each inner capillary through a common outer capillary, unequal distance 20 of droplets from the working electrode and irregular distribution of current through the inner 21 capillaries may also lead to a difference in the height of each printed line. In this study, a single 22 power supply was used to supply the current to the three inner capillaries through a common counter electrode as shown in Fig. 2. The use of separate power supplies for each inner 23 24 capillary may result in uniform supply of current but with added cost. Fig. 3 (c) shows the 25 cross-sectional SEM images of the specimen. The height of the printed lines is around 24.6 µm,

1 20.7 µm and 15.2 µm, respectively. The volume of each printed line can be calculated by 2 considering the shape of deposit as a trapezium (Fig. S2). The total volume of simultaneously printed lines is around 0.133 mm³ ($1.3 \times 10^8 \,\mu\text{m}^3$). The-deposition rate (printing speed) using 3 this method is around 800 µm³s⁻¹, and width of deposit ranges from 800 µm to 1100 µm. 4 Simultaneous use of three capillaries with large capillary diameters (600 µm) significantly 5 6 enhanced the printing speed. It is worth mentioning that the highest printing speed previously 7 achieved using the droplet cell or meniscus confined electrodeposition technique ranges from 10^{-3} to $10^2 \,\mu\text{m}^3\text{s}^{-1}$ at feature size of 10^{-1} to $10^2 \,\mu\text{m}$, respectively [5,7]. 8

9 The influence of temperature and scanning speed on the height of deposit and volume of 10 deposition is shown in Fig. 4. For simplicity, a single capillary is used to deposit Ni line on the 11 substrate. As the temperature of the specimen is varied from 20 °C to 65 °C, the height of 12 deposit increases from 16.5 µm to 27 µm (Fig. 4 (a)). Although the height of deposit is mainly 13 influenced by the applied current (or voltage), increase in temperature may slightly increase 14 the coating thickness due shift in the activation energy of the reaction. This increases the overall 15 reaction kinetics, and more Ni ions are deposited at the cathode [40–42]. However, the quality 16 of electrodeposited lines may start to degrade at higher temperatures due to thermal stresses. 17 Fig. S3 shows the cross-sectional SEM of the electrodeposited lines fabricated at different 18 temperatures. Fig. 4 (b) shows the influence of moving speed on the volume of deposition. As the scanning speed is increased from $2 \,\mu\text{ms}^{-1}$ to $8 \,\mu\text{ms}^{-1}$, the deposition volume decreases from 19 around 4.8 x 10^{-3} mm³ to 0.9 x 10^{-3} mm³. Higher scanning speed leads to a decrease in the 20 21 volume of deposit due to less contact time between the droplet and the specimen. Fig. 5 shows 22 the ability of Sf-MDC to simultaneously use different electrodeposition solutions during the 23 metal microprinting process. Fig. 5 (a) shows the schematic of Sf-MDC during the Ni-Cu-Ni 24 electrodeposition process. Due to the use of separate pumps for each inner capillary of Sf-MDC, 25 the composition of electrodeposition solution and flowrate can be independently controlled.

1 Fig. 5 (b) shows the optical microscope image of the Ni-Cu-Ni microdots simultaneously 2 printed on Cu substrate. The diameter of Ni microdots is about 800 µm while the diameter of 3 Cu microdot is about 1000 μ m, although all the inner capillaries have same diameter (600 μ m). 4 Similar results were obtained in case of Cu-Ni-Cu microprinting (Fig. S4). This may happen 5 because the current efficiency of Cu is higher than the current efficiency of Ni. Since the Cu 6 substrate was used to deposit Cu from CuSO₄·H₂SO₄ solution, some dissolution may happen 7 due to the presence of H₂SO₄ in the solution. Fig. 5 (c) shows the EDS elemental mapping 8 images of Ni-Cu-Ni microdots. Pure Ni and Cu microdots are obtained without any 9 contamination or cross-mixing of solutions. Cu substrate and printed Cu microdot could not be 10 distinguished from the EDS image. The printability of Cu microdot was exlamined from the 11 CSLM image and height profile of Cu deposit (Fig. S5). The microstructure of deposited Cu is 12 very different from the Cu substrate (Fig. S4). The surface SEM images of simultaneously 13 printed Ni and Cu microdots are shown in Fig. 5 (d). The Ni deposit consists of coarse structure 14 while Cu deposit consists of fine structure. The surface roughness and crystallite size increase 15 by raising the current density [41]. Using Sf-MDC, the optimum applied current is 50-100 µA 16 for Ni electrodeposition and 300 µA for Cu electrodeposition [28]. Since a single power supply 17 was used to supply current to multiple capillaries in this study, a current of 300 µA was set for 18 simultaneous electrodeposition. This resulted in higher surface roughness of Ni. Simultaneous 19 electrodeposition using different solutions can be applied for fabrication of resistance-20 controlled metal micropatterns for electronics applications.

An attempt was made to fabricate freestanding 3D structures such as Ni microrods by Sf-MDC based parallel metal microprinting process. Fig. 6 illustrates the possibility of fabricating Ni microrods on Cu substrate using 3D printed Sf-MDC and conventional Sf-MDC. Fig. 6 (a) shows that three microrods having different aspect ratios are simultaneously fabricated on the specimen. Large capillary diameters (600 µm) and variation in the dimensional accuracy of

1 capillaries is one reason behind non-uniform fabrication of microrods. The use of high-2 resolution 3D printers capable of accurately fabricating micro- or nano-meter sized capillaries 3 may solve this problem. Maintaining level build-up of materials under each capillary is another 4 important issue to be addressed. Use of separate power supplies for each capillary may also 5 solve this issue but with increased cost. Synchronizing the withdrawal speed of Sf-MDC with 6 the growth rate of deposit is critical in maintaining the level build-up of materials under the 7 capillaries. Higher withdrawal speed results in a decrease in the diameter of microrods. As the 8 withdrawal speed is increased further, the deposit breaks its contact with the droplet. On the 9 other hand, too slow withdrawal speed results in capillary clogging. Fig. 6 (b) shows that high 10 aspect ratio and high-quality Ni microrod can be fabricated by using conventional Sf-MDC. 11 Use of silica capillaries (diameter = $100 \mu m$) instead of 3D printed capillaries (diameter = 60012 µm) results in uniform fabrication of Ni microrod. Optimized withdrawal speed and smaller 13 capillary diameters result in smooth fabrication of 3D structures as compared to large sized 14 capillaries.

15 Fig. 7 shows the simultaneous fabrication of Ni microrods with modified Sf-MDC. In this case, 16 silica capillaries are used as inner capillaries. The optical microscope image (Fig. 7 (a)) shows 17 the formation of two Ni microrods with different sizes. The formed micro-rods have sufficient 18 strength to support their own weight. Due to the instabilities that occur during the process, one 19 droplet breaks its contact with the microrod while other continues to grow. Fig. 7 (b) shows 20 the SEM images of the fabricated microrods. The microrod-1 has a non-uniform diameter and 21 breaks its contact with the droplet after 2 h. The microrod-2 has a uniform diameter and 22 continues to grow after microrod-1 breaks its contact with the droplet. The magnified view of 23 SEM images shows that the microrods have different morphologies. Because of the variation 24 in solution removal from each inner capillary through a common outer capillary and irregular 25 distribution of current through the inner capillaries, uniform fabrication of equally sized microrods using this technique is still a challenge. This study provides a step forward towards the development of high speed and low-cost metal 3D printers. By properly optimizing the Sf-MDC and changing the designs of capillaries, an array of more complicated 3D metal microstructures than those presented in Fig. 6 and Fig. 7 can be produced with this parallel printing process to significantly multiply the production.

6 4. Conclusions

7 3D printed multicapillary solution flow type microdroplet cells are used to successfully develop 8 a parallel, high speed and low-cost electrochemical metal microprinting system. Three Ni lines 9 having uniform width (around 900 µm) and different thickness (around 24.6 µm, 20.7 µm and 10 15.2 µm, respectively) are simultaneously printed on Cu substrate. The deposition rate or 11 printing speed achieved using this technique is around 800 µm³s⁻¹, and feature size ranges from 12 800 µm to 1100 µm. An increase in deposition rate is observed at higher temperatures while a 13 decrease in deposition volume is observed at higher scanning speeds. Simultaneous printing of 14 multiple materials (Ni-Cu-Ni and Cu-Ni-Cu microdots) became possible with the Sf-MDC. By 15 using silica capillaries (diameter = $100 \mu m$) as inner capillaries inside the Sf-MDC, two 16 freestanding and straight Ni microrods of different sizes were fabricated. This method can be 17 applied for simultaneous microprinting of resistance-controlled metal microstructures for 18 electronic applications.

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1	Captions
2	Fig.1 Top view of Sf-MDC obtained from CAD software, (a), and image showing multiple Sf-MDC
3	printed at once (b).
4	
5	Fig.2 Schematic illustration of Ni microprinting using the Sf-MDC.
6	
7	Fig. 3 Optical microscope image of Ni lines fabricated on Cu substrate, (a), EDS elemental mapping
8	images of the specimen cross-sections showing the size of printed Ni lines, (b), and cross-sectional
9	SEM image of the specimen showing thicknesses of the printed Ni lines, (c).
10	
11	Fig. 4 Influence of temperature on the height of deposition, (a), and influence of moving speed on
12	volume of deposition, (b).
13	
14	Fig. 5 Schematic of simultaneous electrodeposition using different solutions, (a), and corresponding
15	optical microscope image, (b), EDS elemental mapping, (c), and SEM images, (d).
16	
17	Fig. 6 Fabrication of Ni microrods with 3D printed Sf-MDC, (a), and conventional Sf-MDC, (b).
18	
19	Fig. 7 Electrodeposition with Sf-MDC and the corresponding optical microscope image of specimen,
20	(a), and SEM images of the Ni microrods (b).

Figures



Fig.1 Top view of Sf-MDC obtained from CAD software, (a), and the image showing multiple Sf-MDC printed at once (b).



Fig.2 Schematic illustration of Ni microprinting using the Sf-MDC.



Fig. 3 Optical microscope image of Ni lines fabricated on Cu substrate, (a), EDS elemental mapping images of the specimen cross-sections showing the size of printed Ni lines, (b), and cross-sectional SEM image of the specimen showing thicknesses of the printed Ni lines, (c).



Fig. 4 Influence of temperature on the height of deposit, (a), and influence of moving speed on volume of deposition, (b).



Fig. 5 Schematic of simultaneous electrodeposition using different solutions, (a), and corresponding optical microscope image, (b), EDS elemental mapping, (c), and SEM images, (d).



Fig. 6 Fabrication of Ni microrods with 3D printed Sf-MDC, (a), and conventional Sf-MDC, (b).



Fig. 7 Electrodeposition with Sf-MDC and the corresponding optical microscope image of specimen, (a), and SEM images of the Ni microrods (b).