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3D porous metal structure manufacturing using UV pulsed laser and copper formate solution

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Abstract

This paper demonstrates a simple fabrication method of porous metal structures using liquid phase solution (copper formate solution) based on UV pulse laser deposition. This process can produce arbitrary metal 3D structures at room temperature and atmosphere. Primary reactions are redox processes by photothermal effect. Local temperature elevation induced by laser exposure activates selective copper formation effects. It can be a method of 3D additive manufacturing processes, which has some advantages that no supporter and no shielding environment preventing the oxidation are required. Also, the density of porous copper structure could be predicted by concentration of solution. These experimental results showed that it was feasible to produce the metal foam-typed structures, and thus it would provide the potential possibilities of additive manufacturing by layering various metal structures. In the future, this process will be applicable to catalyst exchangers, electrodes, filters, and heat exchangers.

1 Introduction

Metals are one of the engineering materials commonly used in many fields because of their several useful properties such as high strength and conductivity. However, The metal-based additive manufacturing (AM) processes has given rise to problems like the rapid oxidation in air and the high melting temperature, but selective laser melting (SLM) was introduced with thin-walled circular tube of 316 L stainless steel to overcome these issues [1]. One of the issues is that it requires a printing space to prevent oxidation. Second, high-resolution printing cannot be achieved because of the high temperature condition and third, the price is substantially higher than other 3D printing using plastic materials [2]. Researche have recently been conducted on constructing electronic circuits by using the metal ink and then sintering them by laser. This approach offers a laser direct drawing technology with relatively precise electronic circuits. Generally the used Ag-based inks have low resistance to pure Ag and high redox potential, so they can be easily handled and reliable to Ag-powder based AM even when exposed to air [3–5]. Although copper has its own limitations due to its low oxidation resistance, the replacement with copper is motivated because the cost of preparation for Ag-based inks is high [5–9]. Moreover, inks with the metal-based decomposition which is activated with thermal reaction can be employed to mitigate this problem. Inks prepared in this method are less likely to cause critical problems such as the formation of undesirable copper oxide and/or precipitation since the compound has a copper atom in a monovalent or bivalent state [10–14].

In this paper, we fabricate metal structures in a desired shape by irradiating copper formate decomposition in a

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liquid with a laser. To demonstrate the possibilities of this proposed method, both the bulky hexahedron and cylinder structures can be deposited layer by layer. This process can selectively stack the metal structures at room temperature and under atmosphere. Throughout irradiating process with a 355-nm UV pulse laser, the copper formate compound is pretreated in the liquid phase and thus the copper is precipitated due to laser thermal reaction. The fabricated copper structure has been found to be a porous structure. Also, by controlling the concentration of the solution, the porosity of the structure can be predicted.

2 Experiment details

Copper(II) formate tetrahydrate (98%) was obtained from Alfa Aesar (USA) and used as received without further purification. Copper formate is a relatively stable material and is highly soluble in water. When heat is applied to a solution of copper formate dissolved in water, the copper is precipitated according to the following thermal reaction formula [15]:

$$Cu(HCOO)_2 \cdot 4H_2O \xrightarrow{\text{Thermal}} Cu(HCOO)_2 + 4H_2O \quad (1)$$

$$Cu(HCOO)_2 \xrightarrow{\text{Thermal}} Cu + H_2 + 2CO_2 \quad (2)$$

In order to obtain copper in such a manner, the copper was pre-heated at 200 °C or less. When this solution was directly irradiated with laser, some gas bubbling of H_2 CO_2 and a lot of wave patterns on the deposited copper surface occurred. The mechanism of gas generation was expressed from the above Eqs. (1) and (2). To resolve this problem, we used a concentration of the solution, prepared by dissolving 12.5 g of copper formate in 100 ml of deionized (DI) water at 20 °C. The solution was then heated to 90 °C for 1 to 8 h to obtain solutions with different viscosities. When the temperature exceeded 100 °C, there occurred a problem with the presence of bubbles in the solution of the high-viscosity samples. The obtained solutions were then irradiated with laser to obtain copper metal layer.

The laser used was Series 3500 UV, manufactured by DPSS Laser Inc. (USA). This laser consists of a source, a controller, a chiller, and a Galvano scanner and emits a pulse with a wavelength of 355 nm. The resonator of the laser uses a Nd:YVO4 and is pumped by a diode laser. The light with having a wavelength of about 1064 nm is frequency-doubled to a 532-nm wavelength in terms of a second harmonic generation, and this light is further oscillated by the third harmonic generation to a wavelength of 355 nm. It is switched to generate the pulse by the Q-switching method, and its full width at half maximum (FWHM) of the pulse is 25 nm and a repetition rate of 30 kHz. The use of the laser is motivated by its high absorption wavelength in the solution and copper. Because of the high repetition rate, the heat conduction area is small to be advantageous for fine structure. Copper was formed by varying the scanning speeds of the laser. The quality of copper pattern was evaluated by measuring its resistance.

After obtaining the conditions of the copper optimization above, 3D porous copper structures were fabricated by employing these optimal conditions. The internal porous structure of copper structures was evaluated by using Computer Tomography (CT) and in doing so in some applications for 3D metal printing.

3 Results and discussion

3.1 Pre-heated copper liquid solution

The viscosity of the solution was measured by observing the surface of the solution after the copper had precipitated by using a laser irradiation to understand the time step of the liquid phase change, which was divided into four categories according to the heating amount. The solution was crystallized and observed under a microscope. The experimental results showed that the surface formation of the solution was divided into four categories from (a) to (d) as follows. The ink gradually turned into blue as the process progressed from a to d. When extended a pre-processing period, the ink became dark (c) and became solid form (d). (a) and (e), (b) and (f), (c) and (g) are the surfaces of the copper obtained by laser processing in the pre-processed ink, respectively. In (d), no copper was produced despite the laser treatment. In the case of d, it was observed in liquid phase that the copper was precipitated because of the state changes occurred due to overheating. In the case of (g), it was also found that copper did not exist and the structures themselves come from the form of precipitated copper. Comparing (e) and (f), both of which were found to be good copper formation condition, we observed that (e) had a more porous than (f), (h) and (I) are 400-times magnified photomicrographs of (a) and (b), confirming that the crystal of the (h) is much larger than that of (i). Therefore, it was concluded to fabricate the copper metal structures by adjusting porosity under optimal process conditions between (a) and (b) (Fig. 1).

3.2 Copper line width according to laser irradiation

355 nm UV pulsed laser, a laser spot size of 200 µm, and laser power of 0.5–1.0 W were used to irradiate the liquid solution. Experiments were first conducted to stack lines by varying the speed from 1 to 20 mm/s to find minimum line width to build 3D shapes. Figure 2a–d shows the cut section views of result line width of copper at the speed of 1, 3, 5,

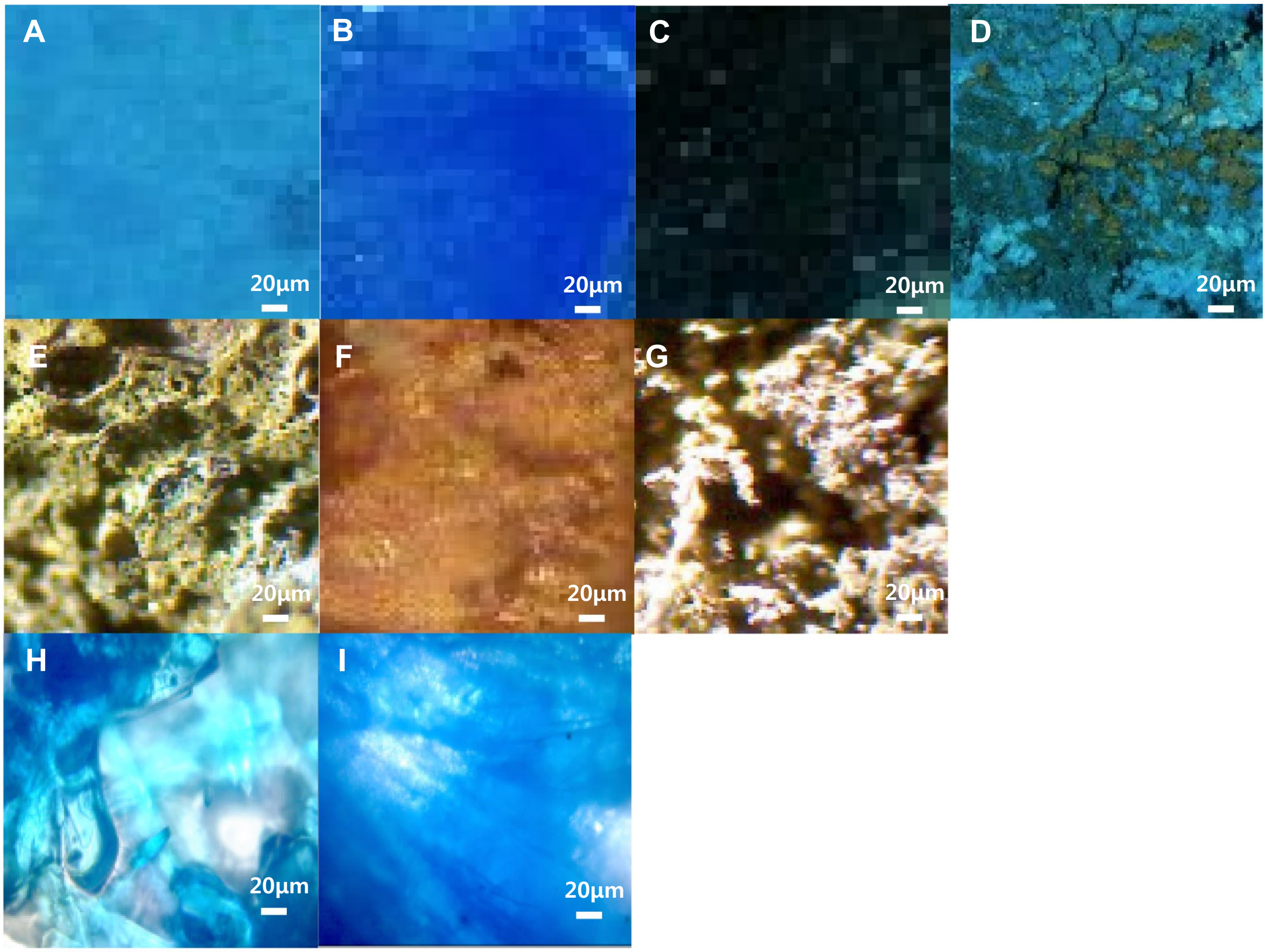

Fig. 1 Inner crystal structures of copper formate solution and copper surfaces prepared by pretreatment of copper formate solution. **a–d** Copper formate solution pretreated under different experimental conditions. **e–g** Copper generated by the laser irradiation on the solution of the **a–d** and **h, i** internal crystal structure of each of the copper solution **a**, **b**

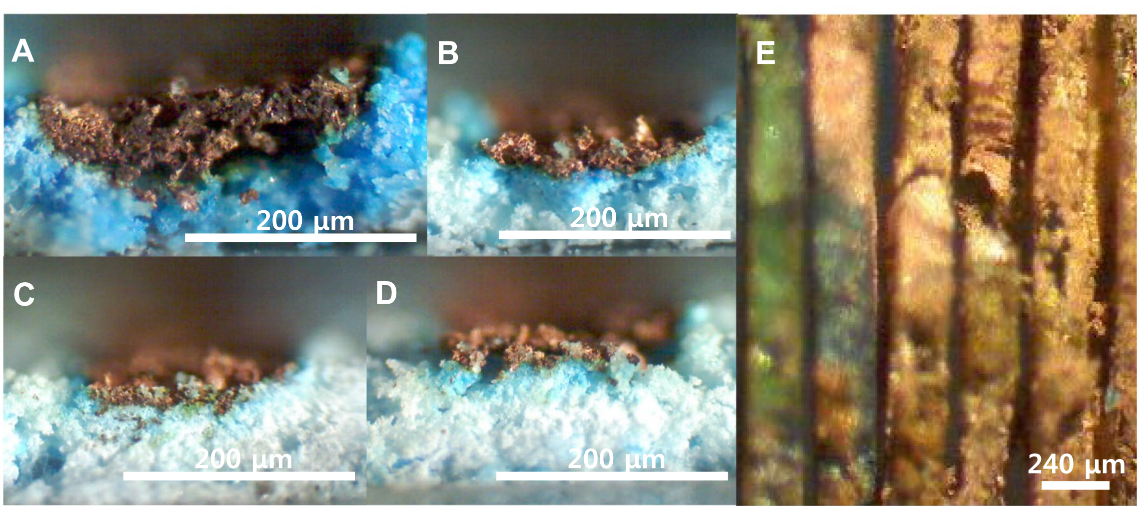

Fig. 2 Copper line width according to different laser scan speed at **a** 1 mm/s, **b** 3 mm/s, **c** 5 mm/s, **d** 7 mm/s, and **e** at 20 mm/s, respectively

and 7 mm/s and the top section view of that 20 mm/s under constant laser power of 1.0 W, respectively. The width of the copper line shown in Fig. 2b–d did not change even when the laser speed increased. The copper structures in Fig. 2e are three-dimensional copper structures made up from the laser speed at which the width of the copper line does not increase. The copper structures in Fig. 2e are made at different laser speeds, and the copper structures on the right have faster laser speeds. The faster the laser speed, the more defects you see.

Figure 2 showed that the copper line width does not tend to become smaller than the spot size of the laser even though the scanning speed increases. Therefore, when the copper will be practically stacked by using these optimal process conditions, arbitrary three-dimensional structures will be automatically built up layers from *.*stl* file format which is commonly used in one of standard formats of 3D printing. It is necessary to increase the laser scanning speed without broadening the copper line width as compared with the laser spot size. However, when the copper resistance is measured, it can be seen that when the line width is thick enough, the copper resistance remains as low as 8.6×10^{-7} Ω m or less. When the scanning speed is increased as the line width is fixed, the resistance is increased more than 10 times compared to the previous one. This problem can be reduced by adding a co-complexing agent to the liquid phase and a sintering promoter [16]. When copper structure was three-dimensionally stacked at a critical speed of 20 mm/s, some cracks on the surface of copper metal line were observed without continuously stacking lines, as shown in Fig. 2e, and the cracks become wider and propagated faster.

3.3 Evaluation of copper structures

3D copper structures such as hexahedron and cylinder structures were modeled and stacked layer by layer. The length, width, and height of hexahedron are 6, 6, and 6 mm, respectively. The diameter and height of cylinder are also 5 and 3 mm, respectively, as shown in Fig. 3.

In addition, it could be observed that the internal porous structure was well fabricated. Furthermore, the boundary of each layer could be found, and the height of the layer and the shape of the structure between the layers could clearly be observed as shown in Fig. 3c. As shown in Fig. 4, CT images of hexahedron model have offered the internal structure to be porous and laminated. From these results, the copper structures have been stacked with the well-defined internal porosity. The calculated porosity was easily theoretically obtained by comparing the structure volume to the pore volume. The calculated porosity in this experiment was then classified in terms of shapes. The calculated porosity of hexahedron structure according to volume was from 68 to 31%. However, measured porosity of hexahedron structure, by using the actual CT, was found to be from 42.5 to 16% lower than the calculated. It is found that the porosity measured by the actual experiment is always smaller than that calculated based on the CAD model of its shape, and thus the internal porosity is reduced.

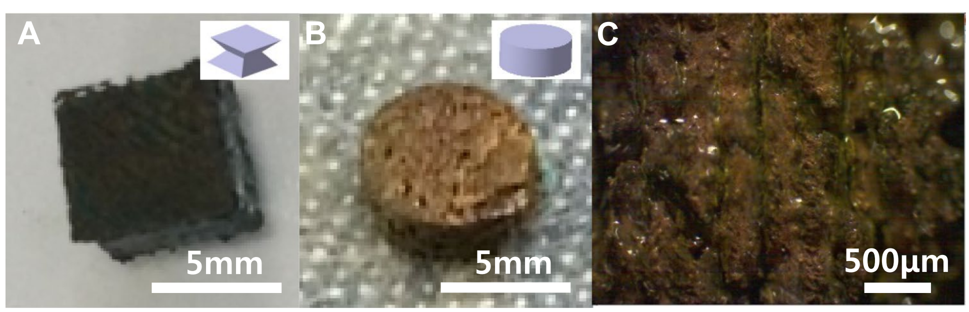

Fig. 3 Additive manufactured copper structures, **a** hexahedron, **b** cylinder, and **c** surface image

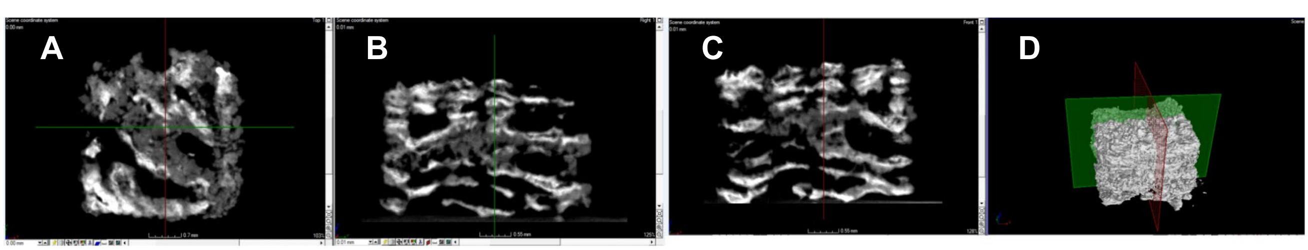

Fig. 4 Measured results of CT images of hexahedron structure, **a**–**c** Sectional CT images of copper structure, **d** CT Image of 3D hexahedron copper structure

4 Conclusion

A simple process for fabricating copper metal structures with a relatively low energy by using a liquid-based copper solution has been experimentally demonstrated. Some porous structure also has been successfully fabricated layer by layer. According to experiment, the optimum process conditions for obtaining porous copper structures were found to be the mixing ratio of copper formate to liquid solution which was 0.125 g/ml and pretreat temperature of 90 °C to increase the viscosity. Subsequently, the copper is precipitated by the laser energy that does not increase the copper line width. The copper structures produced in the liquid phase have generally been obtained to have the higher resistance than pure solid state. 3D metal structures comprised of copper as well as similar types of a lot of metal formate can be fabricated using this simple method, which would be very promising to be applicable to arbitrary shaped catalyst exchangers, electrodes, filters, and heat exchangers having pore metal structures in the future.

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References

1. J.S. Mohammed, Methods Oceanogr. **17**, 97 (2016)
2. Z. Yang, Y. Yu, Y. Wei, C. Huang, Thin–Walled Struct. **1**, 111 (2017)
3. J. Perelaer, P.J. Smith, D. Mager, D. Soltman, S.K. Volkman, V. Subramanian, J.G. Korvink, U.S. Schubert, J. Mater. Chem. **20**, 8466 (2010)
4. K. Woo, Y. Kim, B. Lee, J. Kim, J. Moon, ACS Appl. Mater. Interfaces **3**, 2377 (2011)
5. Y. Lee, J. Choi, K.J. Lee, N.E. Stott, D. Kim, Nanotechnology, **19**, 415604 (2008)
6. B.K. Park, D. Kim, S. Jeong, J. Moon, J.S. Kim, Thin Solid Films, **515**, 7706 (2007)
7. S. Jeong, H.C. Song, W.W. Lee, S.S. Lee, Y. Choi, W. Son, E.D. Kim, C.H. Paik, S.H. Oh, B.-H. Ryu, Langmuir, **27**, 3144 (2011)
8. S. Jeong, K. Woo, D. Kim, S. Lim, J.S. Kim, H. Shin, Y. Xia, J. Moon, Adv. Funct. Mater. **18**, 679 (2008)
9. M. Abdulla-Al-Mamun, Y. Kusumoto, M. Muruganandham, Mater. Lett. **63, 2007** (2009)
10. C.S. Choi, Y.H. Jo, M.G. Kim, H.M. Lee, Nanotechnology, **23**, 065601 (2012)
11. S.J. Kim, J. Lee, Y.-H. Choi, D.-H. Yeon, Y. Byun, Thin Solid Films **520**, 2731, (2012)
12. B. Lee, Y. Kim, S. Yang, I. Jeong, J. Moon, Curr. Appl. Phys. **9**, E157, (2009)
13. Y.I. Lee, K.J. Lee, Y.S. Goo, N.-W. Kim, Y. Byun, J.-D. Kim, B. Yoo, Y.-H. Choa, Jpn. J. Appl. Phys. **49**, 086501 (2010)
14. A. Yabuki, N. Arriffin, M. Yanase, Thin Solid Films **519**, 6530 (2011)
15. V.M. Yosi Shacham-Diamand, Dubin, Microelectr. Eng. **33**, 47 (1997)
16. V.A. Kochemirovsky, E.M. Khairullina, S.V. Safonov, L.S. Logunov, I.I. Tumkin, L.G. Menchikov, Appl. Surface Sci. **280**, 494 (2013)