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Threshold of laser-activated writing of metal using microbe metabolite

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ABSTRACT

A method of laser-activated deposition through the metabolite of *Acidithiobacillus ferrooxidans* is demonstrated. The experimental results indicate that the deposition process exhibits positive correlation to laser power and a negative correlation to scanning speed. The amount of deposition is related to the supplied energy per unit length of laser scanning. With respect to the thermal field on the substrate produced by a moving point source and a laser beam crossing a reference point, the temperature history and the accumulated energy are used to model the deposition process. The threshold temperature of the deposition is estimated 500 K, and the activation energy per unit volume of deposition of the process is about 120 pJ/μm^3.

1. Introduction

Laser-assisted deposition technology is a solid freeform fabrication (SFF) process, which is a technique for producing solid parts layer by layer by transferring energy to specific locations on a substrate. Techniques such as laser engineered net shaping (LENS®) [1], selective laser sintering [2] (SLS), stereolithography [3] and laser-assisted chemical vapor-phase deposition (LCVD) [4] are examples of layered and additive fabrication processes that use lasers as an energy source. However, the LCVD method requires a vacuum environment and toxic chemical reagents. In this study, a non-toxic, low-cost and low-environmental impact laser-assisted liquid-phase deposition method is proposed.

The proposed surface processing with laser, which enables local metal deposition of copper material through *Acidithiobacillus ferrooxidans* (*T. ferrooxidans*) metabolite, has the advantage of minimal environmental impact compared to other laser-assisted chemical vapor/liquid deposition techniques [5]. *T. ferrooxidans* is an autotrophic acidophilic bacterium, and its growth can be supported by the oxidation of inorganic ferrous to ferric ions [6]. The mechanism of displacement deposition is analogous to autocatalytic electroless deposition (AED), in that the reaction does not require any further chemical reducing agent other than ferric ions. This technique can be used to deposit a copper line on the same substrate at micrometer resolutions [5]. There are some concerns with controlling the beam parameters, the adhesion of copper and vapor confusion during the deposition process. The substrate uses copper as an ionic source to be oxidized by ferric ions of *T. ferrooxidans* metabolite with a positive electrode potential. The copper reduction is triggered by laser irradiation.

The use of this technique lies in two folds. The first is the repair of the micro-copper pattern when the continuity is broken during the service. The redeposition of the same copper metal on the original microstructure is applied as remedy. Such a laser-guided repair is time- and cost-effective and precise in practice compared to other lithography-based options or, in the worst case, discard of the component. The second is the construction of the three-dimensional microstructure by the continuous extraction into the medium the substrate copper, which is often coated on the lower substrate beforehand by industrial practice as a standard output material system, and the redeposition guided by laser, till the substrate copper is consumed and the new copper structure completed. The original thickness of copper coating can be readily calculated, specified and supplied for the required specific volume of deposition. Some difference of the volume between the to-deposit and the to-extract can be accommodated by adjusting the concentration of copper in the metabolite solution.

To predict the fabrication by laser-assisted liquid deposition, the correlation between the deposition results and processing parameters should first be investigated. In the processes, a laser beam is used as a heat source to provide energy to activate the chemical reaction within the illuminated spot. The amount of energy is sufficiently large to liberate electrons [7,8]. Previous studies have reported that various laser power and scanning

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speeds generate different temperature distributions and affect the deposition line width [5,9–12]. An earlier attempt of the fundamental investigation of the process proposed a threshold temperature on the sample surface caused by laser irradiation using a point thermal-source from a 1064 nm Nd:YAG laser through the metabolite [13]. Though the temperature is often pointed out for a chemical reaction, it alone cannot explain the process. The energy content is considered the substantial quantity to define the onset of such a process, while the history of the temperature profile over a certain period, rather than the temperature at a moment, contains the information of level of the accumulated required energy. In this paper, an analytical model of the threshold energy per unit volume further to the temperature distribution was developed for the laser-guided metal deposition process, which has not been reported before.

2. Experiment of deposition

The *T. ferrooxidans* metabolite can etch copper to copper ions. As laser energy is added, the copper ions are reduced and deposited. The reaction of the working medium is

$$2Fe^{3+} + Cu \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftarrows}} 2Fe^{2+} + Cu^{2+} \tag{1}$$

Fig. 1 shows the optical scheme in this study. A 1064 nm Nd:YAG was used. The laser beam travels through the VMU-L microscope unit, and is focused by long working distance objectives 100× on the substrate surface. A motorized *XY* and manual vertical translation *Z* linear stage was applied to move the specimen to obtain the path of the designed pattern. The substrate used in this study is a copper sheet of thickness of 0.5 mm. It was covered with a layer of protective film before it was cut. The substrate was cleaned with ethanol and (KIMWIPES) wiped and polished. Scotch tape was used to create a space of 60 μm for the working solutions. During the etching process, the pH value of *T. ferrooxidans* metabolite was maintained at 2.3. In this study, the parameters that were considered are shown in Table 1. A Wyko optical profiler (Model: NT1100) was used to measure the surface profile of the deposition area, as shown in Fig. 2. The line width of the copper line was calculated using a built-in function in the Wyko post-processing software. The deposition was found by the EDS that copper was the main constituent (above 95%) of the deposition.

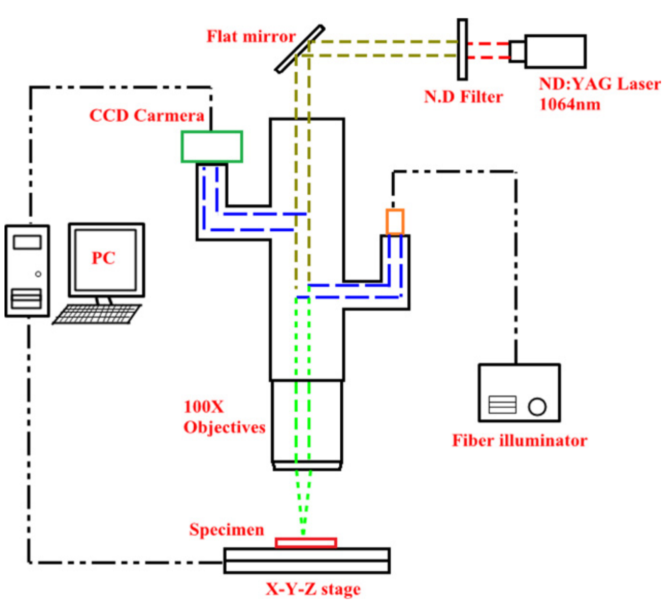

Fig. 1. Schematic of the optical setup.

Table 1
Processing parameters in the current analysis.

Conductivity (W/m K)	401
Specific heat (J/kg K)	385
Density (kg/m^3)	8920
Laser power (mW)	160/180/200/220/250
Scanning speed (μm/s)	10/15/20
Absorption coefficient (1/cm) (Cu, 1064 nm)	91
Beam spot radius (μm)	3.85

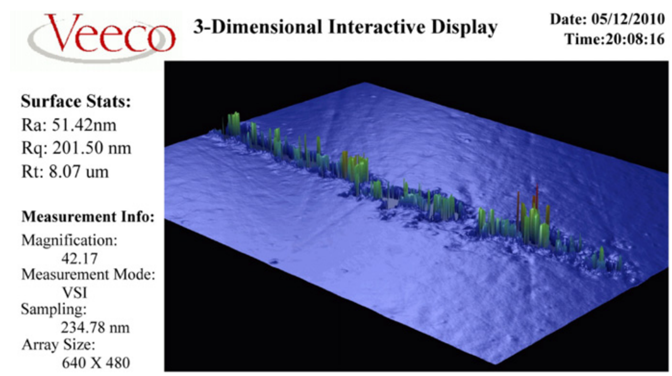

Fig. 2. Wyko image of the sample at laser power = 160 mW and scanning speed = 15 μm/s.

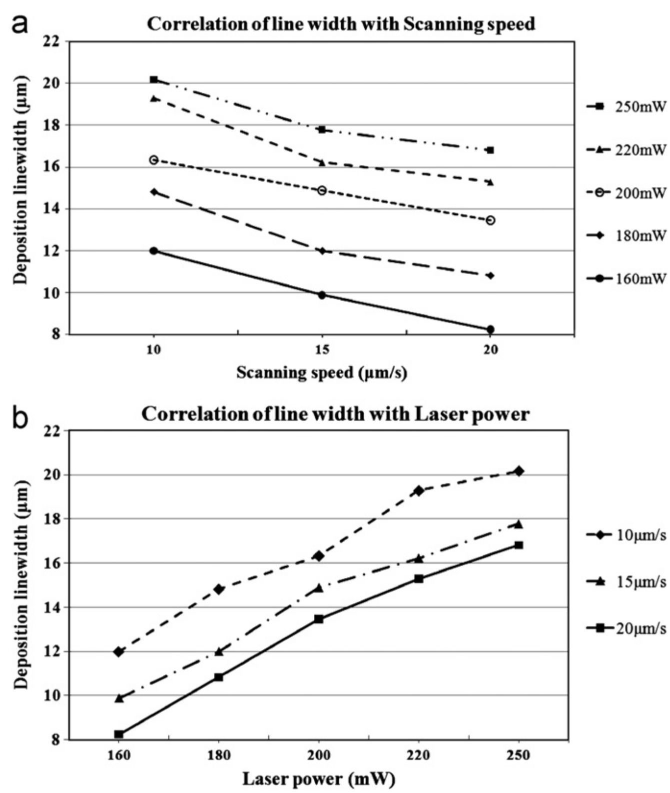

Fig. 3. Correlation between line width and (a) scanning speed and (b) laser power.

In this experiment, five different laser power levels were used. The copper line width was positively correlated to the laser power as shown in Fig. 3. An increase in the laser power resulted in an increase in the amount of deposition; and thus an increase in the line width. The process parameter is related to the deposition line