Micromolding of Three-Dimensional Metal Structures

by Electroless Plating of Photopolymerized Resin

Kohki Mukai*, Toshiya Yoshimura, and Shoji Maruo

Department of Mechanical Engineering and Materials Science,

Yokohama National University,

79-5 Tokiwadai, Hodogaya, Yokohama 240-0197, Japan

*E-mail address: mukai@ynu.ac.jp

A novel microfabrication process for three-dimensional metal microstructures was proposed. The process consists of four steps: the fabrication of a resin mold by photopolymerization, the electroless plating of the mold, the electrolytic grinding to expose a metal inside the mold, and the extraction of the structure. We experimentally demonstrated the molding process. The epoxy resin suitable for polymerization via a two-photon absorption reaction was successfully plated using a nickel metal. The lattice distortion of the plated metal was found to be reduced by decreasing the pH of plate solution, which was revealed by X-ray diffraction measurement. We replicated the shape of a rice grain with nickel by immersing the plated polymer mold in acetone for extraction. X-ray fluorescence measurements indicated the high purity of the nickel replica.

KEYWORDS: electroless plating, electrolytic grinding, microstructure, molding, photopolymerization, nickel

1. Introduction

The three-dimensional microfabrication of photopolymerized resin aiming at micromachining has been achieved by accurate laser beam scanning [1]. Currently, the resolution of polymerization is as low as 100 nm with two-photon absorption [2]. To develop a photomicrofabrication technique, a combination of photopolymerization and electroless plating has been investigated in several studies. For example, Nishimura et al. studied the photopolymer micromachine coated with ferrite. By applying a rotational magnetic field, they succeeded in attaining the swimming of a millimeter-sized rod with a spiral ridge in water [3]. An application of the technique to a structure smaller than millimeter was studied by Formanek et al. [4]. They fabricated the silver-coated micrometer-sized photopolymer structure aligned periodically on a glass surface. This structure is useful in microphotonics as a three-dimensional metamaterial. These reported structures contain a polymer as a base. Therefore, the weakness of the polymer to heat or chemicals limits the use of the microstructures. The three-dimensional microstructure made of pure metal has various uses. In this viewpoint, a metal microfabrication technique using photochemical eduction was proposed [5]. However, the difficulty in controlling reaction volume results in a bumpy surface in a submicron order and limits the application of the three-dimensional structure.

In this paper, we propose a novel molding process for fabricating the three-dimensional metal microstructure. The process consists of four steps: the photopolymerization of a resin mold, electroless plating, electrolytic grinding, and extraction. We succeeded in plating the epoxy resin suitable for two-photon polymerization with nickel and molded the shape of a rice grain with nickel in the demonstration of the micromolding process.

2. Proposal of Microfabrication Process

The micromolding process we propose consists of four major steps, as shown in Fig. 1. As the first step, a raw resin is polymerized by scanning a focused laser beam in order to form a mold with a three-dimensional negative shape of a microstructure with small openings. This microfabrication technique is a type of stereolithography. In a conventional method, a three-dimensional structure is formed layer by layer on a stage that is gradually lowered [6]. A two-photon absorption method can omit such troublesome stage manipulation and achieve a high polymerization resolution [1]. As the next step, the nonconductive polymer mold is coated with a metal by electroless plating. In this step, the inner space of the negative shape of a microstructure is filled. The minute sticking of the metal to the polymer is required to fabricate a micro-order structure. In addition, a continuous uniform supply of metal ions to the surface is necessary to avoid a void in plating. This is due to the design of the mold for the sufficient circulation of plate solution, particularly the position and the number of openings. It was reported that the electroless plating of gold was successfully applied to the inner wall of a micrometer-scale capillary tube, where the inner diameter is 50 μm [7]. To fill the inner space of the mold, electroplating is useful once electroless metal coating is successfully performed. Hybrid plating also aids in fabricating a metal alloy microstructure with interdiffusion. As the third step, an obstructive metal is removed by electrolytic grinding to expose the opening of the mold. An electric field is applied between the outer coated metal and a grindstone in electrolytic solution. Electrolytic grinding differs from electrolytic machining. The metal is ionized by electrochemical reaction and the ionic metal is precipitated by chemical reaction. Then, precipitation is swept by the grindstone. The key point of this step is that electrolytic grinding stops by itself when the nonconductive resin is exposed since the inner metal and outer coating are electrically isolated [8]. Thus, a precise cut is attained at the opening of the mold, and a desirable shape is obtained even in the micrometer order. As the final step, the microstructure is extracted by removing the polymer. The removal is performed by burning or melting the polymer by heating, or solving the polymer chemically.

3. Experimental Demonstration

We investigated the plating of epoxy resin with nickel. Nickel is very popular in electroless plating, and the alloy of which is widely used as a structural material, a magnetic material, an electricity conductor, and a memory alloy. The epoxy resin we used has been utilized for two-photon polymerization. A cup made of silicone was first prepared, and the resin was polymerized in the cup using an ultraviolet (UV) lamp. The appearance of the sample during the experiments is shown in Fig. 2. The sample has a shape of the pellet founded on the cup. At the beginning of the plating process, the contaminants on the resin surface were rinsed out with pure water and acetone with ultrasonic waves. Then the sample was immersed in catalytic solution composed of $PdCl_2$, $SnCl_2$, and HCl at 30°C for 5 min.. Subsequently, the sample was immersed in plate solution composed of $NiSO_4$, $C_2H_5O_2N$, PbO, and NaH_2PO_2. The temperature was 45 ˚C and the pH was controlled between 7 and 9 using HCl. The growth rate of the plated film was about 2.5 μm/h. The maximum fluctuation of the thickness was ± 6.8 % during the growth of the film. In the typical electroless plating of nickel, etching and neutralization are often performed before immersing the sample in catalytic solution. Also, acceleration is performed before immersing the sample in plate solution. However, for the epoxy resin, we found that these three processes are not only ineffective but also obstructive to the formation of a nickel film. For example, etching with the solution composed of H_2CrO_4 and H_2SO_4 blackened the metal-resin interface.

Figure 3 shows a high-resolution optical microscopy image of the cross section of the plated film, which was stuck to another plastic under cool condition for microscopy observation. We observed that the surface of the photopolymerized resin has many small pits of 2-5 μm depth. This is due to the surface of the resin replicating the surface of the silicone cup. We also observed that the small pits are completely filled with the plated metal. This result suggests that the micrometer-sized mold is filled with the metal by electroless plating.

The lattice distortion of the plated metal was evaluated by X-ray diffraction (XRD) measurement. Figure 4 shows the XRD rocking curve around a Ni(111) peak. The measurement was performed using "JDX-3530 (JOEL Inc.)" with a tube current of 40 mA at a tube voltage of 40 kV. The broadening of the full width at half maximum (FWHM) of the diffraction peak indicates the residual crystal stress. The inset shows the FWHM of the Ni(111) peak as a function of the pH of plate solution. This result indicates that the crystal stress decreases with pH. Since the growth rate of the plated film increases with pH, impurities and dislocations are introduced into the metal with an increase in pH. We found that a glossy metal with a low lattice distortion is obtained without etching.

As a primary demonstration of molding, we replicated the shape of rice grain with nickel. To fabricate the polymer mold, we dipped half of rice grain in the raw resin in the silicone cup and polymerized it with the UV lamp as the rice grain was dipped. After polymerization, the rice grain was removed and the negative shape of half of rice grain was left in the polymer. Figure 5(a) represents the polymer mold.

The mold plated with nickel is shown in Fig. 5(b), where the inside bottom of the mold is found to be completely plated with glossy nickel.

We then extracted the replica of rice grain from the mold by deteriorating the polymer chemically. The sidewall of the plated pellet was cut horizontally and the pellet was immersed in acetone for 2 days. Probably because the polymer absorbed acetone and expanded during immersion, nickel peeled off from the polymer. Figure 5(c) indicates the extracted nickel shape. We observed that metal gloss was obtained at almost the entire surface of the replica. On the other hand, the surface touching the rice grain blackened at the replica. We evaluated the component elements of the plated nickel by x-ray fluorescence measurement, which was performed using "RIX-2100 (RIGAKU Inc.)" with a tube current of 50 mA at a tube voltage of 50 kV. The results are shown in Table I. We compared the component elements at the glossy and black surfaces, and found that the nickel of high purity was obtained at the glossy surface. The black metal was oxide. The other impurities are attributed to catalytic solution or plating solution. We suppose that the carbohydrate of rice grain bran was left after the rice grain was removed and that the residue was not rinsed out completely in the negative shape of rice grain and caused surface oxidation in plating. If the mold is fabricated by laser scanning, such oxidation will not occur and a pure-metal microstructure will be produced.

4. Conclusions

A novel three-dimensional microfabrication process for metal was proposed. This process involves the photopolymerization of a resin mold, electroless plating, electrolytic grinding and extraction. We succeeded in plating the photopolymerized mold of an epoxy resin with nickel and extracted the plated metal having the shape of rice grain by immersing the mold in acetone. XRD measurements revealed that the lattice distortion of the metal was reduced by decreasing the pH of plate solution. X-ray fluorescence measurements indicated that high-purity nickel was obtained after the replication.

Acknowledgements

This work is supported by the Electro Mechanic Technology Advancing Foundation.

References

[1] S. Maruo, and S. Kawata, J. Microelectromech. Syst. **7** (1998) 411.

[2] S. Kawata, H.-B. Sun, T. Tanaka, and K. Takada, Nature **412** (2001) 697.

[3] K. Nishimura, H. Uchida, M. Inoue, M. Sendoh, K. Ishiyama, and K. I. Arai, J. Appl. Phys., **93** (2003) 6712.

[4] F. Formanek, N. Takeyasu, T. Tanaka, K. Chiyoda, A. Ishikawa, and S. Kawata, Appl. Phys. Lett., **88** (2006) 083110.

[5] T. Tanaka, A. Ishikawa, and S. Kawata, Appl. Phys. Lett. **88** (2006) 081107.

[6] K. Ikuta, and K. Hirowatari, proc. IEEE Int. Workshop on Micro Electro Mechanical Syst. (MEMS 1993), p.290.

[7] N. Takeyasu, T. Tanaka, and S. Kawata, Jpn. J. Appl. Phys. **44** (2005) L1134.

[8] Toshikazu Sato: Denkaikako to Kagakukako (Electrolytic Processing and Chemical Processing) (Asakura Shoten, Tokyo, 1970) [in Japanese].

Figure captions

Figure 1 Proposed micromolding process.

Figure 2 Pellet of resin (a) as polymerized, (b) after catalytic process, and (c) after plating.

Figure 3 Cross-sectional optical microscopy image of plated film. The film was supported by another plastic for observation.

Figure 4 XRD curve of nickel plated with plate solution with pH of 8.3 without etching. The inset shows the FWHM of a Ni(111) peak as a function of the pH of plate solution.

Figure 5 Top views of polymer mold (a) before and (b) after plating. (c) Replica of rice grain made of nickel via optimized process.

Table I. Components of plated nickel at glossy and black surfaces.

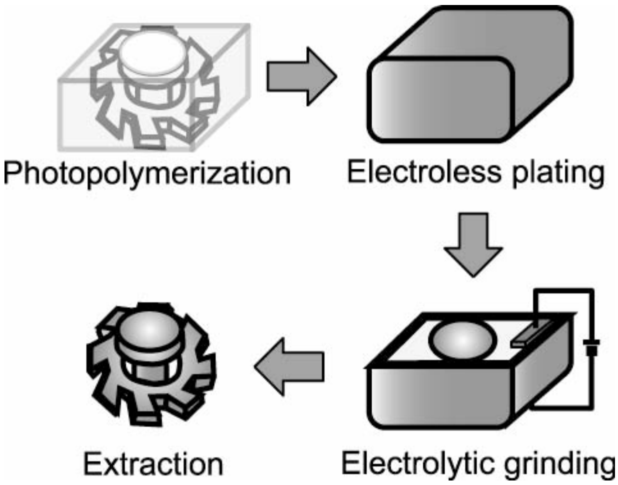


Fig. 1

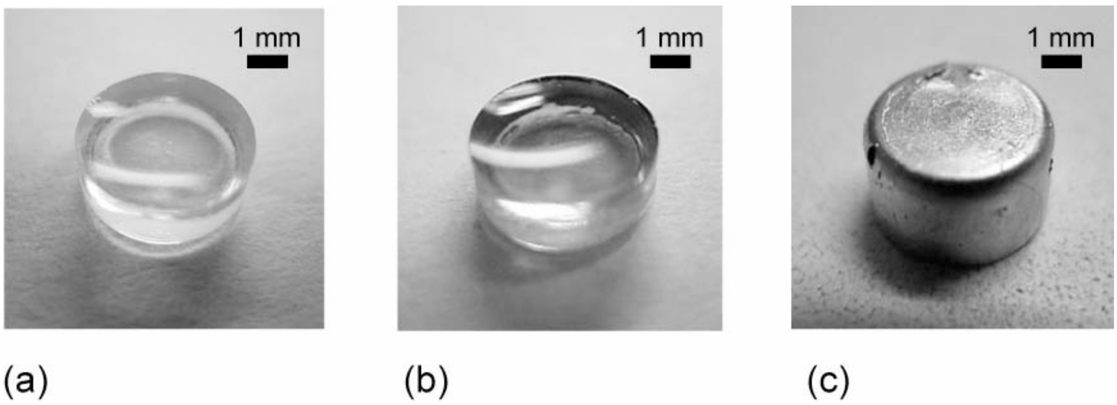


Fig. 2

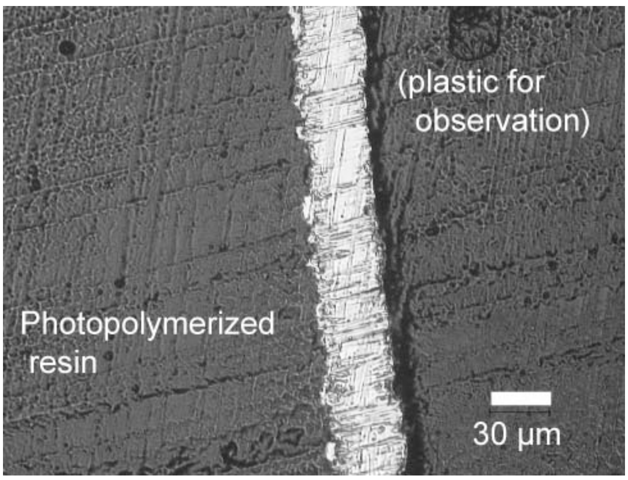


Fig. 3

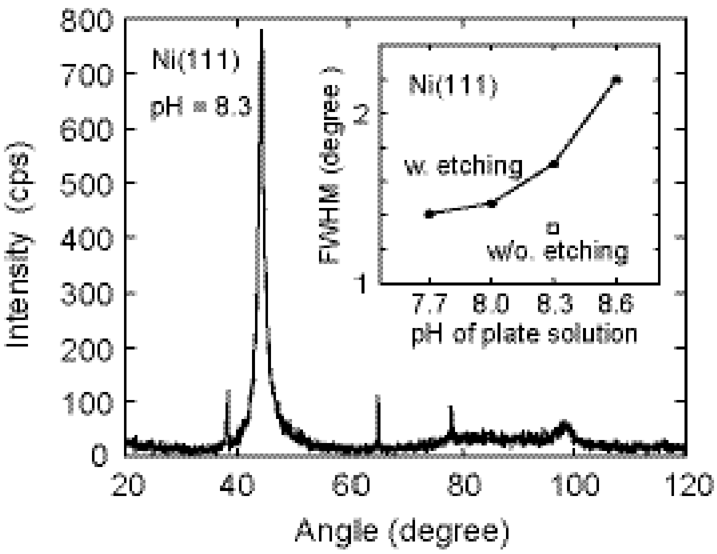
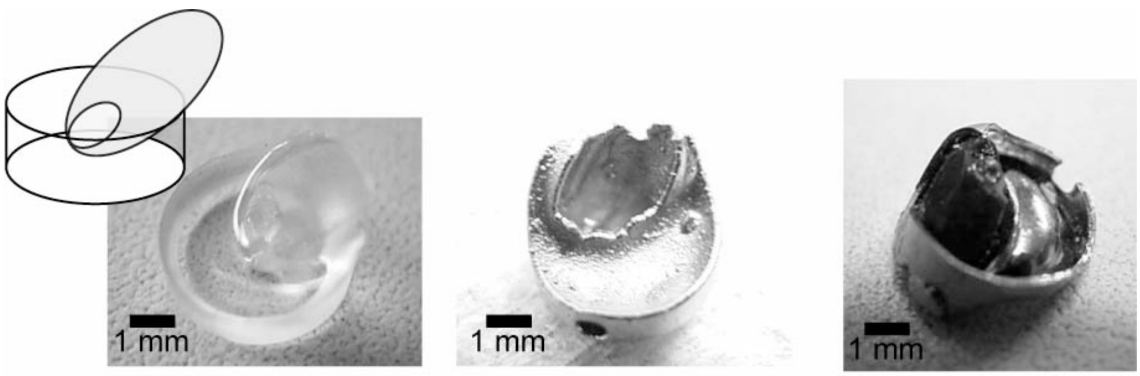


Fig. 4



(a) (b) (c)

Fig. 5

Table 1

	Glossy surface (mass%)	Black surface (mass%)
Ni	92.8	51.6
O	-	25.3
Cl	0.29	9.86
P	4.3	8.79
Na	1.98	2.58