Journal of Photopolymer Science and Technology
Volume23,Number3(2010)407－412©2010CPST

Production of A Magnetic Micro Capsule based on Photopolymerized Resin Mold and Its Motion in Viscous Liquid

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A magnetic micro machine was fabricated by using photopolymerized resin structure as the base, and its motion in viscous liquid was evaluated. The production method of two kinds using a positive-type mold and a negative-type mold was proposed. With ultrasonic vibration after the surface treatment using the ultra-fine particles of silica, electroless copper plating was realized to negative-type resin mold even inside the concave structure of 20 μm in width and 100 μm in depth. The magnetic micro capsule was produced by carrying out ferrite plating to positive-type resin mold, and the magnetic field guidance experiments were conducted in silicone oil. The sample of full length 800 μm swam by the guidance, always turning the head in the advance direction, and it rotated on the same spot.
Keywords: magnetic micro capsule, electroless plating, micro machine, micro molding, photopolymer

1. Introduction

Three-dimensional modeling technology using photopolymerized resin is expected as a new tool for manufacturing micro parts [1]. Based on the high resolution of polymerization as low as 30 nm [2], the application of the stereolithography has been considered in a wide range of fields, from the optical semiconductor field, e.g., a photonic crystal [3], to chemistry and bio field, e.g., Micro Total Analysis System (μ-TAS) [4].

If the minute structure made by photopolymerized resin can be transcribed to another materials, such as metal, the application range of the stereolithography will be expanded remarkably. Thus, the method of plating on modeled resin has been investigated. Based on this idea, production of meta-material structure, which can realize the negative refractive index of light by controlling a dielectric constant and amplitude permeability, has been examined [5]. Production of the magnetic micromachine, which moves in the living body by magnetic field guidance, has also been considered [6]. However, these productions hold resin inside. It is desirable to replace all resin from a viewpoint of the environment-proof nature to temperature, acid, alkali, etc..

We have proposed micro-molding method which transcribes completely the three-dimensional model produced using

Received March 31, 2010
Accepted May 7, 2010

photopolymerized resin to metal or metallic compound [7]. Our micro-molding process consists of four major steps. First, raw resin is polymerized by scanning with a focused laser beam to form the mold of microstructure. Next, the non-conductive polymer mold is coated by metal or metal compound through electroless plating [8 - 10]. In this step, not only the inner space but also the outer surface of the resin mold is coated. The outer coat is obstructive. So, the obstructive is removed by electrolytic grinding to expose the opening of the mold [11]. Since the electrolytic grinding stops by itself when the inner coat and outer coat are electrically isolated [12], a precise cut is attained at the opening of the mold. Finally, the metal or metal-compound microstructure in the mold is extracted by removing the resin by heat treatment or chemical processing.

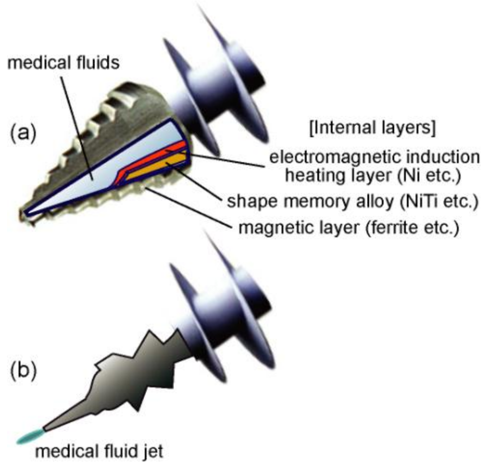

Fig. 1 Magnetic micro capsule for drug delivery system; (a) initial structure (with a part of sectional view), and (b) structure after transformation by heating.

If the micro-molding technology is completed, the magnetic micromachine for medical applications as shown in Fig. 1 will be realizable. It is a micro capsule for a drug delivery use. The inside is a cave, into which medical fluid can be put. The capsule has layer structure. It consists of the magnetic layer (ferrite etc.) to be guided by magnetic field, a shape memory layer (NiTi, FePd etc.) which changes form by heating, and an electrical resistance layer (nickel etc.) which takes charge of temperature by induction heating (IH) method. The magnetic micro capsule reaches the diseased part by magnetic field guidance, and changes its form by IH and discharges internal medical fluid. We have realized multi-plated structure on photopolymerized resin [10].

In this work, we produced the microcapsule of full length 800 µm and width 200 µm using the mold of photopolymerized resin. Two kinds of molds, a positive type and a negative type, were examined. The movement by the magnetic field guidance of the ferrite micro capsule made from the positive-type resin mold was evaluated in viscous liquid.

2. Production procedure

The production procedure of the magnetic micro capsule which used a positive-type mold and a negative-type mold is shown in Figs. 2(a) and 2(b).

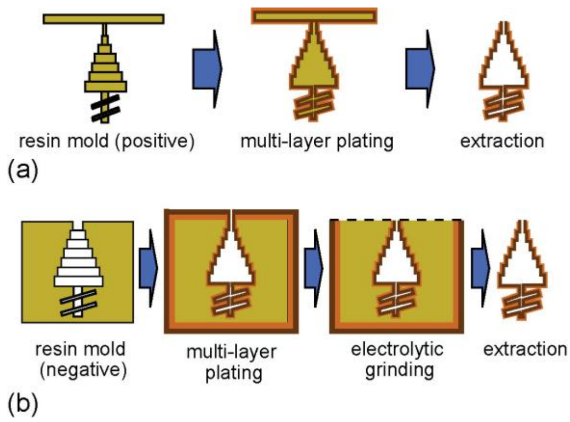

Fig. 2 Micromolding processes for micro capsule using (a) a positive-type resin mold, and (b) a negative-type resin mold.

Figure 2(a) shows the case where a positive-type mold is used. After multilayer plating is performed, the capsule is removed from a substrate, and is heated up to sublime resin. In the case of acrylic resin, the temperature of about 600°C is required for the sublimation. The cave where resin escapes becomes a capsule into which a medical fluid is put. Since plated layers determine the outside shape of a capsule, the difficulty of this production method is that an outside changes from a prototype a lot when plated layers become thick.

On the other hand, the outside is precisely controllable if the capsule is manufactured based on negative-type mold. Figure 2(b) is a production procedure using a negative-type mold. By performing multi-layer plating in a reverse order, the same structure as a positive-type case is formed. In negative-type case, the cave in mold becomes a cave of product for a medical fluid. Therefore, the capacity of a cave is decided by the thickness of plating. In order to take out an internal structure from plated mold with sufficient accuracy, electrolytic grinding is desirable to be used. Copper can be used as the stop layer of electrolytic grinding by using the ground of multi-plated film [11]. After performing separation of the inside and the exterior of negative-type mold, an internal capsule structure can be taken out by heat treatment or chemical processing.

3. Mold of micro capsule

Figure 3(a) shows the design of our micro capsule in this work. Full length is 800 μm and the maximum diameter is 200 μm. A front half is a capsule whose shape is piled disks having various diameters. There is a small slot in the direction of shaft. A rear half is a shaft of diameter of 60 μm, and has the 20-μm-thick spiral wing. The rear half is attached in order to make the head of micro capsule turn to the advance direction owing to viscous resistance. We also expected the torque of the spiral stream by the wing that may rotate the capsule around the shaft. The rotation will stabilize swim of the capsule.

Figures 3(b) and 3(c) show negative-type resin molds used in this work. On a resin flat substrate of about 1 cm around, the total of eight arrays was modeled. Figure 3(c) is enlargement of a part of one array. Five micro capsules are seen in the inside of a 800-μm-wide array. In the molds, upper and lower sides are opened, i.e., the hole has penetrated, so that it might be easy to circulate through for plating liquid.

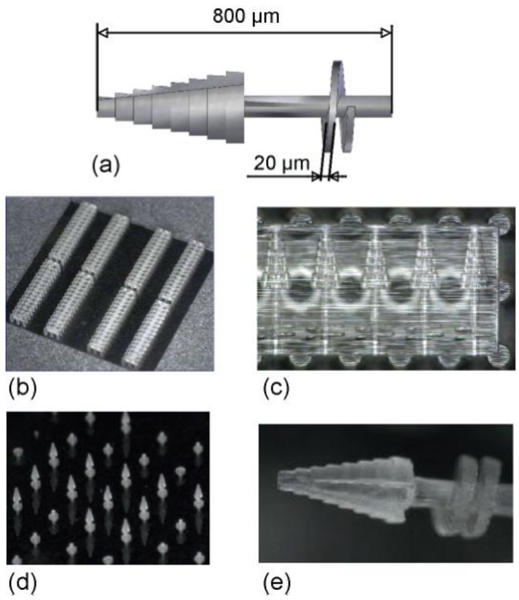

Fig. 3 Micro capsule in this study; (a) basic design, (b) arrays of negative-type molds, (c) part of one negative-type array, (d) arrays of positive-type molds, and (e) one of the positive-type molds.

Positive-type resin molds used are shown in Figs. 3(d) and 3(e). Top and bottom are contrary to the illustration of Fig. 2(a) in this work. The 800-μm-long micro capsule has aligned for the square periodically on a resin flat substrate. During modeling, some shafts were broken and hence some micro capsules have disconnected themselves from the substrate. In addition to the 800-μm-long molds, we prepared four kinds of samples whose sizes are the integral multiples of basic design, i.e., the full length was 1600, 2400, 3200, and 4000 μm. Some variations described later were given to the samples about the form of wing. In consideration of the durability of 800-μm-long sample, the diameter of shaft was changed to 80 μm, and thickness of spiral wing was changed to 30 μm. Figure 3(e) shows one of the 800-μm-long molds.

4. Plating inside negative-type micro mold

Electroless plating was carried out using our conventional conditions to the negative-type mold. After degreasing the sample with acetone and carrying out catalyst processing, electroless plating of copper was performed. The catalytic solution was composed of 0.8 g/L $PdCl_2$, 15 g/L $SnCl_2$, and 150 mL/L HCl (35 %). The plate solution was composed of 15.3 g/L $CuSO_4.5H_2O$, 53.3 mg/L CH_2O (37 %), 40 g/L $C_4H_4KNaO_6.4H_2O$ (Rochelle salt), and 25 g/L H_2NCH_2COOH. Temperature of plate solution was 25°C, and pH was adjusted to 12.5 - 13.0 by NaOH. The air bubbles inside the mold immersed in the solutions were removed with the vacuum pump.

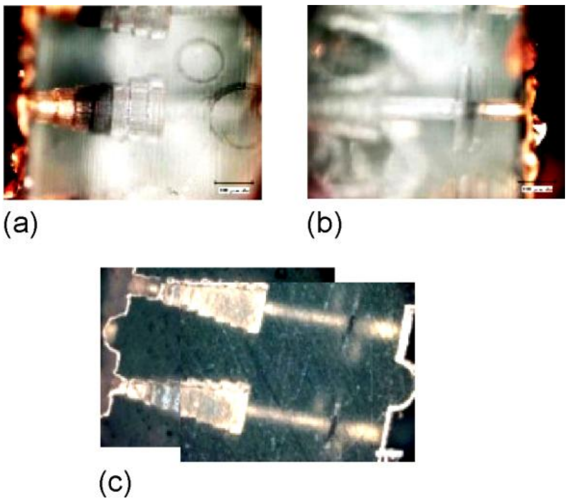

Fig. 4 Optical microscope images of electroless copper plating to negative-type mold; (a) initial result at the front, (b) initial result at the rear, and (c) result with ultrasonic vibration and surface treatment.

The results of initial plating experiments are shown in Figs. 4(a) and 4(b). For the observation, the plated film on the surface of mold was removed mechanically. Both images indicate that plating had adhered only near an opening part of the negative-type mold. We considered that the reasons of the partial plating were that the plate solution did not fully circulate into the hole and that the reactivity on the surface of resin was low.

Based on the above considerations, electroless copper plating was performed with ultrasonic vibration, after processing the surface by 4-methyl-2-pentanone in which the ultra fine particles of silica were dissolved. The result is shown in Fig. 4(c). We saw that whole inside of the mold was plated. It should be noted that the plating was realized even inside the wing of 20 µm in width and 100 µm in depth. We are now conducting the experiments for sublimating resin by heat treatment to take out the micro capsule. The result will be reported elsewhere.

5. Production of magnetic micro capsule using positive-type mold and its motion

Ferrite plating was given to positive-type mold. By our conventional plating conditions [11], plating was adhered satisfactorily to the mold surface. The plate solution of 11.9 g/L $FeCl_2.4H_2O$ + 9.5 g/L $CoCl_2.6H_2O$ and the oxidizing solution of 7.7 g/L $NaNO_2$ + 0.7 g/L CH_3COONH_4 were injected into the bath, and the mixed solution was homogenized using a temperature-controlled hot plate stirrer. pH of the oxidizing solution was adjusted between 7 and 8 using NH_3.

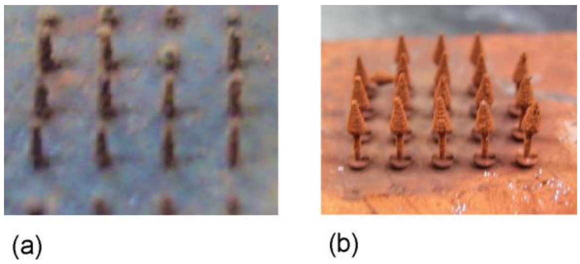

Fig. 5 Optical microscope images of plated positive-type molds, the full length of which is (a) 800 µm and (b) 2400 µm.

The optical microscope images of samples after plating are shown in Figs. 5(a) and 5(b). Figure 5(a) shows the sample of full length of 800 µm. Micro capsules on a base plate are fully covered with ferrite. The reason for ambiguous form is that the fine deposits had adhered under plating. When ultrasonic washing was carried out with water, the micro capsule form appeared as shown later. The optical microscope image after plating of mold of 2400 µm in full length is also shown in Fig. 5(b). These plated samples were physically and carefully folded to remove from the base plate.

In dimethyl silicone oil (viscosity is 50 cSt), the magnetic field guidance experiment was conducted using a neodymium magnet. The sample was dipped in the silicone oil in a metal can, and the magnet was applied and slid from the reverse side of the can to guide the sample. The motion by the guidance was taken by the substance microscope as a movie. We evaluated the sample motion from three viewpoints shown in Fig. 6. [A] When a magnet is slid, does the head of a sample turn to a direction of movement or not? [B] When rotating a magnet on the same spot, does a sample follow to a magnet and rotate or not? [C] When a sample goes straight on, does it rotate around the shaft or not? In item C, we expected the torque of spiral stream produced by the spiral wing at the rear half.

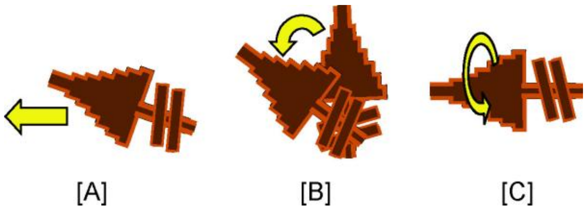

Fig. 6 Examined three motions of magnetic micro capsule; [A] head turn to the direction of movement, [B] rotation on the same spot, and [C] rotation around the shaft.

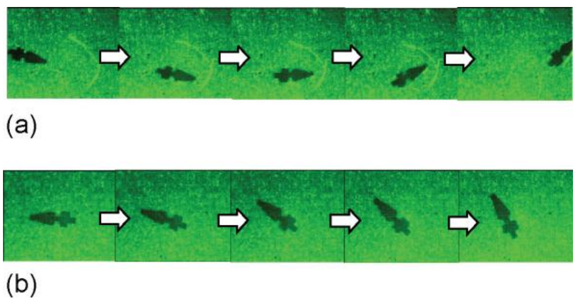

Fig. 7 Motion of magnetic guided 800-μm-long capsule: (a) head turn to the direction of movement, and (b) rotation on the same spot.

Figure 7 shows the sequential photographs at the magnetic field guidance of sample whose full length is 800 μm. Head turn to the direction of movement is shown in Fig. 7(a), and rotation on the same spot is shown in Fig. 7(b). Thus, the good performance of motion as a magnetic micromachine was confirmed with the sample whose full length is 800 μm.

In order to check the conditions which opt for motion of magnetic micromachine, we prepared samples which have various wings as shown in Table I and compared their motion. We can see that the spiral wing has very important influence on the motion. Without wing, we cannot control the direction of head at all. When wing is one thick lump, motion control was inferior compared with the case of spiral wing. We think that the reason the head did not turn to the direction of movement is that the difference in the viscous resistance in oil was lost between the front part and the rear part of sample. As for rotation on the spot, the thick lump raised the viscous resistance to prevent sharp head turn. In all samples, rotation around the shaft was not observed. This suggests that the torque of spiral stream by the spiral wing was not sufficiently strong. The micro capsule may rotate around the shaft by making the form of head spiral instead of the shape of stacked disks.

Table I Dependence of the motion of magnetic micro capsules on the structure.

length (μm)	wing	motion		
		[A]	[B]	[C]
800	spiral	very good	very good	impossible
1600	(lack)	impossible	impossible	impossible
2400	thick lump	good	impossible	impossible
3200	thick lump	good	good	impossible
4000	spiral	very good	very good	impossible

6. Conclusion

Production and evaluation of the motion of magnetic micro capsule which was based on photopolymerized resin mold were performed. Two kinds of production methods using positive-type and negative-type mold were proposed. By ultrasonic treatment and surface processing using silica ultra-fine particles, electroless copper plating was realized inside the cave of 20 μm in width and 100 μm in depth. Ferrite plating was carried out to the positive-type mold to produce magnetic micro machine, and the magnetic field guidance experiments were conducted. The sample of full length of 800 μm swam in silicone oil, always turning head in the advance direction, and rotated on the same spot. It was shown that the ability of magnetic field guidance was greatly dependent on the form of wing at the rear half of micro capsule.

Acknowledgements

We would like to thank "Laser Micro-Fabrication Open Laboratory" of Sony Corporation for the preparation of resin sample.

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