Fabrication of LIGA mold insert using Ni-PTFE composite micro-electroforming

Yuhua Guo, Gang Liu, Ying Xiong, Xuelin Zhu, Wang Jun, Yangchao Tian*

National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui, 230029, P.R.China.

Email: ychtian@ustc.edu.cn

Abstract. The LIGA process, which combines deep X-ray lithography with electroforming and polymer molding, is a main fabrication method for producing MEMS. And hot embossing is one of the main processing techniques for polymer microfabrication, which helps the LIGA (UV-LIGA) technology to achieve low cost mass production. And electroforming of LIGA mold insert with lower surface energy and friction coefficient is required for demolding process during hot embossing to obtain better polymer replicas. In this paper, the Ni-PTFE compound material mold inserts is fabricated by special treated galvanic bath and operation conditions. And the results show that it is a robust Ni-PTFE composite micro-electroforming and basically changes the interaction property when demolding for producing high quality polymer replicas.

1. Introduction

The LIGA process, which combines deep X-ray lithography with electroforming and polymer molding, is a main fabrication method for producing MEMS [1]. And hot embossing is one of the main processing techniques for polymer microfabrication, which helps the LIGA (UV-LIGA) technology to achieve low cost mass production [2]. When hot embossing of high aspect ratio microstructures, the deformation of replicated polymer microstructures usually occurs due to the demolding forces between the sidewall of mold inserts and the thermoplastic. Ni electroforming has been fully developed for LIGA mold insert fabrication technology, but its surface energy is too high (1.7 J/m²) and the friction coefficient between nickel and polymer is big (about 0.45). In our previous work, it shows that interface adhesion between the mold insert and thermoplastic plays a key role in the demolding process [3]. So electroforming of mold insert with lower surface energy and friction coefficient is demanded for demolding process during hot embossing to obtain better polymer replicas.

The incorporation of polytetrafluoroethylene (PTFE) (Teflon) particles into nickel matrix can take advantage of the different properties of nickel and PTFE. PTFE is chemically very inert and has a relatively high melting point (325°C). Its coefficient of friction is lower than that of almost any other polymers and is steady in vacuum. Because of its extremely low surface energy (0.018 J/m²), PTFE has excellent non-stick properties. The resulting properties of the Ni-PTFE composite coatings, such as non-stick, non-galling, anti-adhesive, high dry lubricity, low friction, good wear, and good corrosion resistance, have been successfully used in many industries [4-6].

* Corresponding Author: Tel: +86-551-3601844, Fax: +86-551-5141087; Email: ychtian@ustc.edu.cn
The first composite coatings of electroless nickel-phosphorus and PTFE were introduced over 20 years ago which is widely used present in chemical, mechanical and electronic industries [7]. Contrast to Ni-(P)-PTFE electroless coating, the Ni-PTFE layers using composite electroforming have some advantages, such as steady chemical solution bath, easy temperature control and no adhesion problems. But the composite electroforming process still remains today a curiosity of the laboratory.

PTFE particles readily coagulate and precipitate in the electrolyte bath since PTFE is a water-repellent material. Due to this agglomerate formation it is difficult to obtain a uniform dispersion of PTFE particles in the electrolyte bath. This will not only reduce the PTFE content in the composites, but also influences the mechanical and tribological (surface energy, friction and lubrication) properties of the composites. And this is also main problem in both electroless Ni-P-PTFE coatings and Ni-PTFE composite electroforming. Zhao et al. [6] investigated the effect of the presence of cationic surfactants on the suspension of PTFE particles in electroless nickel plating solution and coating rate etc. Nishira et al. [8] studied the effects of agitation methods on the particle size distribution of PTFE aggregates in plating solution. One of their findings was that an ultrasonic homogenizer was more effective than mechanical agitation.

Something can be used for reference from electroless coating, but the process of composite micro-electroforming differs from electroless coating that electroforming usually costs a long time and its mass transfer is not only by convection and diffusion but also electro-migration. A continues uniform dispersion is not easy to realize. The difficulty in Ni-PTFE composite micro-electroforming is how to get a thicker uniform composite layer. As the PTFE particles incorporate into nickel matrix and the presence of cationic surfactant, the conductive area in cathode decreases which leads to increase of local current density. And the change of local current density will influence the deposition of nickel and PTFE particles. Electroforming process usually costs a long time and these effects are amplified. Where local current density exceeds the limitations, hydrogen pitting occurs (which are shown in Figure 1).

![Image of Figure 1](image.png)

**Figure 1.** Pitting defects occur during Ni-PTFE composite micro-electroforming where local current density exceeds the limitations due to the decrease of conductive area in cathode: (a) after 3 hours, (b) after 6 hours.

The purpose of this paper is to develop a robust process of Ni-PTFE composite micro-electroforming and obtain high quality composite LIGA mold insert.

2. **Experiment**

2.1. Sample preparation and exposure

In our experiments, Si wafers covered with Ti/Cu/Ti (30nm/100nm/30nm) layers and a layer of spin-on PMMA (1-2 μm) were used as substrate. And commercially available PMMA sheets were used as
resist layer. The thickness of the sheets is 1mm. Sheets were cut into pieces (35x35 mm) and annealed in oven (15°C/h up to 80°C, 1 h at 80°C and cool to room temperature). To glue the prefabricated PMMA foils, a resin (MMA) was applied to the substrate. After gluing, the samples were relaxed at room temperature for 24 h. Finally, the PMMA was filed cut to desired thickness. The used gold mask is thick enough for absorbing x-ray.

The exposure was performed at the LIGA station of National Synchrotron Radiation Laboratory (NSRL) of the University of Science and Technology of China (USTC) working at 800MeV (magnetic field: 6T; the e-beam current: 150–200 mA). A 200-µm thick beryllium window separates the vacuum of the beam line and the working chamber. The distance source-sample is 12.3 m. The scanning speed is 8 mm s⁻¹. In all experiments, we have used several 100 µm -KAPTON polyimide films to obtain the desired dose profile. The exposure was performed in a 10 kPa Helium gas condition.

After the exposure, we use GG-developer for development. At last plasma cleaning is applied before micro-electroforming.

2.2. Electrolyte make-up and operation conditions

To get a healthy Ni-PTFE composite micro-electroforming, the process is investigated. Many experiments were performed and they show that the content of PTFE particles and cationic FC surfactant in the bath is very important. Initially if too much content was added into electrolyte bath, it is easy to cover the surface of cathode. Contrast to electroless coating, the mass transfer in electroforming process is not only by convection and diffusion, but also electro-migration. In the electrolyte bath, the PTFE particles and cationic surfactant is recommended to add gradually. To improve the composite electroforming, a gradient composite electroforming was developed by gradually add the PTFE and cationic surfactant into in the electrolyte bath. Thus a robust composite electroforming process can proceed. The bath compositions and operating conditions are listed in the table 1 below.

| Ni(SO₃NH₂)₂ 4H₂O: 330g/L | C₂₁F₁₇H₂₉O₃N₂SІ : (0.05%) 1ml/L initially |
|--------------------------|------------------------------------------|
| NiCl₂ 6H₂O: 40 g/L       | pH : 4.2-4.5                              |
| H₃BO₃ : 50 g/L           | Temperature : 38 °C                       |
| PTFE particle:( 2um) 5g/L initially | Additive agent: adjusted with pH value |

The PTFE particles and cationic surfactant is to add for three times entire electroforming process, until PTFE particle in bath reaches 15 g/L and cationic surfactant (C₂₁F₁₇H₂₉O₃N₂SІ) reaches 3 ml/L.

3. Results

3.1. Morphology

Traditional optical microscopy and electronic scanning microscopy are used to realize the various stereotypes.

Micrographs presented allow comparison between a pure nickel electroforming (see figure 2) and Ni-PTFE composite electroforming (see figure 3). The pure nickel deposit has a rather regular surface, whereas the composite electroforming develops in a nodular way as the PTFE particles are introduced into electrolyte bath. And SEM image of Ni-PTFE composite is also presented in figure 4.
3.2. PTFE content in composite

PTFE particles are distributed throughout the entire nickel matrix and the following two equations are obtained:

\[ \rho_{Ni} V_{Ni} + \rho_{PTFE} V_{PTFE} = \rho V = W_{Ni-PTFE} \quad (1) \]

\[ V_{Ni} + V_{PTFE} = V \quad (2) \]

Where \( \rho_{Ni} \), \( \rho_{PTFE} \) and \( \rho \) are the densities of nickel matrix, PTFE and Ni-PTFE composite respectively. \( V_{Ni} \), \( V_{PTFE} \) and \( V \) are the corresponding volumes of nickel, PTFE and overall Ni-PTFE composite respectively. \( W_{Ni-PTFE} \) presents the weight of Ni-PTFE electroforming composite which can be measured by balance. And \( \rho \) (or \( V \)) can also be measured by Archimedes method. The corresponding density of nickel is approximately 8.9 g/cm\(^3\). So the PTFE content in composite can be calculated by equation (3):

\[ \frac{V_{PTFE}}{V} = \frac{\rho_{Ni} - \rho}{\rho_{Ni} - \rho_{PTFE}} \quad (3) \]
In this way, PTFE content in our electroforming composite is calculated about 20% with total 15 g/L PTFE.

3.3. Hot embossing of PMMA replica
In our previous work, it shows that interface adhesion between the mold insert and thermoplastic plays a key role in the demolding process. The Ni-PTFE compound material mold inserts use special treated galvanic bath but basically change the interaction property when demolding. And the fabricated Ni-PTFE compound mold insert is used to testify for hot embossing of PMMA replicas. And the results show that the deformation defects can be greatly reduced. SEM image of PMMA replica without pull-up or pull-off defects is presented in figure 5 below.

Figure 5. SEM image of hot embossing of PMMA replica using Ni-PTFE compound mold insert.[5]

4. Conclusion
In this paper, the Ni-PTFE compound material mold inserts is fabricated by special treated galvanic bath and operation conditions. And the results show that it is a robust Ni-PTFE composite micro-electroforming and basically changes the interaction property when demolding for producing high quality polymer replicas.

Acknowledgement:
This work is supported by National Natural Science Foundation of China (No.10375058)

References
[1] Becker E W, Ehrfeld W, Maner A, and Munchmeyer D 1986 Microelectronics 4 35-36
[2] Heckele M, Bacher W, Muller K D 1998 Microsystem Technologies 4 122-124
[3] Guo Y H, Liu G, Zhu X L and Tian Y C June 2005 The High Aspect Ratio Micro Structure Technology Workshop (HARMST 2005) Gyeongju Korea 238-239
[4] Zhang P, Liu G, Tian Y C and Tian X H 2005 Sensors and Actuators A 118 338-341
[5] Tian Y C, Zhang P, Liu G and Tian X 2005 Microsystem technologies 11 261-264.
[6] Zhao Q, Liu Y, MullerSteinhagen H and Liu H 2002 Surface and coating technology 155 279-284
[7] Tulsi S S 1983 Finishing 7(11) 14
[8] Nishira M, Yamagishi K, Matsuda H, Suzuki M and Takano O 1996 Trans.Inst.Metal Finishing 74 62