Electrochemical micromachining of nitinol by confined-etchant-layer technique

Xin-Zhou Ma\textsuperscript{a}, Li Zhang\textsuperscript{a}, Guo-Hui Cao\textsuperscript{b}, Yu Lin\textsuperscript{a}, Jing Tang\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a} Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, 361005 Xiamen, China
\textsuperscript{b} Harbin Institute of Technology, 150001 Harbin, China

Received 25 September 2006; received in revised form 21 November 2006; accepted 24 November 2006
Available online 4 January 2007

Abstract

The confined etchant layer technique has been applied to fabricate complex three-dimensional microstructures on nitinol for the first time. HF and HNO\textsubscript{3} were locally and simultaneously electrogenerated at the mold surface to etch a nitinol workpiece. NaOH was used as an efficient scavenger to confine the etchant close to the mold. Cyclic voltammetry was employed to study the electrochemical behavior of a Pt electrode in the etching solution in order to choose an appropriate potential for etchant generation on the mold. The thickness of the confined etchant layer was estimated to be several micrometers by inspecting the deviation of the sizes of the etched spots from the sizes of those on the microelectrode. Thus, the composition of the electrolyte could be optimized for better etching precision. By optimizing the composition of the electrolyte, complex microstructures on a Pt–Ir mold bearing the logo “XMU” of Xiamen University were successfully fabricated on nitinol. The etched patterns were approximately negative copies of the mold, and the precision of duplication could easily reach the micrometer scale.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Nitinol; Alloy; Micromachining; Etchant; Scavenger

1. Introduction

Nitinol is an alloy composed of near-equiaxial proportions of nickel and titanium. This alloy shows a very high elastic deformation and a shape memory effect, which are not shown by other types of conventional metallic alloys. These properties along with their superior ductility, fatigue strength and corrosion resistance have resulted in many applications in microelectromechanical systems (MEMS). Since the initial work of Walker and Gabriel that demonstrated the compatibility of NiTi with MEMS fabrication process \cite{[1]}, many research studies have been conducted on integrating the NiTi alloy into microdevices and the applications include microfluid control, optics, sensors, relays, and actuators \cite{[2–4]}. However the excellent mechanical properties of nitinol make its machining extremely difficult. TiNi alloys can be deformed under tensile stress in a ductile manner to about 50\% strain prior to fracture, but the machining process is complicated by severe strain hardening, high toughness and viscosity, and a unique superelastic property \cite{[5–7]}. Hence, it is difficult to use conventional machining processes, such as mechanical cutting, drilling, and shaping, to machine nitinol. To overcome this difficulty, special techniques, such as electro-discharge machining (EDM) \cite{[8]} and electrochemical micromachining (EMM) \cite{[9–11]}, may be used for this purpose. EDM can remove metals and ceramics by means of electric discharges between the workpiece and a tool electrode immersed in a liquid dielectric medium. These discharges melt and vaporize minute amounts of the workpiece, which are then ejected and flushed away by the dielectric. However, the machining speed of EDM is limited owing to its point-by-point fabrication process and it is time-consuming to make a complicated 3D microstructure. Landolt et al. \cite{[9,11]} and Chauvy et al. \cite{[9,11]} have applied the EMM technique to fabricate well-ordered hemispherical microstructures on a Ti-based alloy in a batch. In comparison with EDM, EMM is a suitable method for mass production, because its procedures are similar to those of photolithography. The complex procedures of EMM include exposure, developing, removal of resist, and electrochemical dissolution. Although the EMM permits the machining of chemically resistant metals such as superalloys, stainless steels, and titanium, the shape of the microstructures...
that can be produced to date is limited to a hemispherical form owing to diffusion of the electrolyte and the distribution of the electric field. Recently, Schuster and coworkers have invented an electrochemical technique [12–15], in which a microelectrode behaves as a milling cutter to engrave the workpiece electrode when an ultrashort voltage pulse is applied to it, and produces a 3D structure. This technique is based on the fact that local double-layer charging leads to the anodic dissolution of the metal workpiece when an ultrashort voltage is applied between the tool electrode and the workpiece. Although this technique has been applied successfully to metal workpieces [12,13], passivation by metal oxides inhibits further etching, and the quick removal of this oxide during micromachining is a critical problem for 3D micromachining.

An alternative electrochemical micromachining method, named the confined-etchant-layer technique (abbreviated to CELT), has been proposed by Tian et al. [16–20]. This technique can be applied to fabricate 3D microstructures such as cones and trapezoids on metals. Its working principle can be described as follows. The etchant species is electrochemically generated on a mold (the working electrode) with a 3D pattern in the etching solution and diffuses into the bulk electrolyte. A scavenger is added to the electrolyte to quickly destroy the etchant so as to prevent it from diffusing away from the mold surface. Thus, the etchant layer is kept so thin that its profile reproduces approximately the contours of the microstructures of the mold. The key feature of CELT is distance-sensitive, and this characteristic has allowed arbitrary 3D microstructures to be replicated on metal or semiconductor substrates in a simple, maskless process.

In the work described here, CELT has been applied to fabricate complex microstructures on nitinol for the first time. We have demonstrated that nitrite can be used to generate protons on the mold surface [21], and then protons combine with F\(^−\) and NO\(_3\)\(^−\) to produce etchants on the surface of the mold. A base (NaOH) was used as an efficient scavenger to confine the etchants, namely HF + HNO\(_3\), close to the mold. Electrolytes with different concentrations of NaOH were tested in order to optimize the electrolyte composition to achieve the desired level of precision for 3D microfabrication.

2. Experiments

The experimental setup has been described elsewhere [17,18]. The workpieces to be etched were nitinol foils (Ni:Ti = 50:50) with a purity of 99.9% and a thickness of 0.5 mm. Alumina powder with diameters of 2 and 1 μm was used successively to polish the nitinol foils. The 3D mold, or microelectrode, generating the etchant was used as the working electrode in a three-electrode system. The counter electrode was a Pt wire ring surrounding the working electrode. The workpiece, consisting of the alloy, was left open-circuit in the solution. As contact between the mold and the workpiece would lead to anodic dissolution of the alloy, the distance between the mold and the substrate was kept constant at around 200 nm. The micromachining experiments were performed with the workpiece fixed at the bottom of a Teflon cell. The movement of the mold electrode towards the substrate was controlled precisely by an instrument composed of a stepping motor and a piezoelectric tube that could move the mold under computer control, through a distance of 50 nm to 50 μm in a single step.

Two kinds of molds were used in the etching experiments. One was a microcylindrical electrode made of Pt wires (Alfa, 99.99%) with a diameter of 250 μm. The wires were coated completely with epoxy resin and then polished with sandpaper until the top ends of the wires were exposed. They were further polished with a series of alumina powders of diameter 2, 1, and 0.05 μm successively. Finally, acetone was used to dissolve the top part of the epoxy resin on the wires, which were then rinsed in water in an ultrasonic bath. The second kind of mold was fabricated by an EDM technique. This Pt–Ir (80% Pt) mold included 3D microstructures made up of grooves tens of micrometers wide, forming the logo “XMU” of Xiamen University, and three hemispherical cavities with diameters of tens of micrometers.

Electrochemical measurements were performed with a single-compartment, three-electrode glass cell. A well-polished, 2 mm diameter polycrystalline Pt electrode was used as the working electrode, a saturated calomel electrode (SCE) was used as the reference electrode, and a Pt ring was used as the counter-electrode. All of the electrochemical measurements were made with a CHI 631B electrochemical workstation.

The chemicals used in the experiments were of analytical-reagent grade, and the solutions were prepared with ultrapure water. The microstructures of the mold and the etched NiTi workpieces were characterized with a confocal microscope (Olympus 2000) and an optical microscope (Leica Q550MW).

3. Results and discussion

3.1. Solution for nitinol micromachining

According to the principle of CELT, the etching solution should normally include a precursor of an etchant, and a scavenger. The selection of an effective etchant and a suitable scavenger is a very important issue concerning the application of CELT to the micromachining of NiTi alloys. When a suitable potential of the electrode (mold) is set, the precursor can be oxidized or reduced to an etchant on the electrode and then it can chemically etch the workpiece when the confined etchant layer (CEL) touches the workpiece. For example, Br\(^−\) has been explored as a precursor to generate bromine, which can etch GaAs and Si workpieces in micromachining experiments [18]. Similarly, an attempt was made here to generate HNO\(_3\) and HF simultaneously on the mold surface, because NiTi alloys can be chemically dissolved by a mixture of HF and HNO\(_3\) with an etch rate from 0.1 to 0.5 μm/s with the use of different volume ratios [22]. Therefore, the precursor was chosen to be NO\(_3\)\(^−\), since this has been applied to generate protons (H\(^+\)) and NO\(_3\)\(^−\) on an electrode for the micromachining of Ni, as shown in our earlier paper [20]. When fluoride is added to the etching solution, the protons produced on the electrode can combine with F\(^−\) ions to form the weak acid HF, which can etch the Ti component of nitinol. Meanwhile, Ni\(^{2+}\) is generated when HNO\(_3\) etches the Ni component; tartrate (Na\(_2\)C\(_4\)H\(_4\)O\(_6\)) must also be added.
to the electrolyte to produce $\text{C}_4\text{H}_4\text{O}_6^{2-}$, which functions as a complex-forming ligand in the solution in order to prevent the formation of Ni(OH)$_2$ precipitates in the basic solution [20,21]. Since the etchant is composed of HF and HNO$_3$, a basic solution containing sufficient OH$^-$ was added to react with HF or HNO$_3$ in order to obtain a very thin CEL. Thus, the etching solution contained NaNO$_2$, KF, Na$_2$C$_4$H$_4$O$_6$, and NaOH. The electrochemical and chemical reactions that take place during the etching can be expressed as follows:

**Generation reaction at tip**:

$$\text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + 2\text{H}^+ \quad (1)$$

**Heterogeneous surface etching reaction**:

$$\text{Ti} + 6\text{HF} \rightarrow \text{H}_2\text{TiF}_6 + 2\text{H}_2 \quad (2)$$

$$3\text{Ni} + 8\text{HNO}_3 \rightarrow 3\text{Ni(NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O} \quad (3)$$

**Homogeneous scavenging reaction**:

$$\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \quad (4)$$

Fig. 1 shows cyclic voltammograms of a polycrystalline Pt electrode obtained in solutions with various concentrations of NaOH. The concentrations of NaNO$_2$ and KF were fixed at 1.5 and 0.5 M, respectively. The increase in current density appearing at 0.9 V in curve a corresponds to the irreversible oxidation of NO$_2^-$, with a current density of 0.06 A/cm$^2$. Curves b–d show that the current density of NO$_2^-$ oxidation decreases gradually with increasing concentration of added NaOH. When the concentration of NaOH is 0.6 M (curve d), a low anodic current density of 0.02 A/cm$^2$ is observed at 0.9 V. Comparing curve d with curve a, we observe that the peak current density decreases by a factor of three when the concentration of NaOH increases from 0.2 to 0.6 M. Meanwhile, the starting potential of electrooxidation moves in the positive direction, which means that electrooxidation proceeds with more difficulty at higher concentrations of NaOH. This phenomenon indicates that the concentration of NaOH and the pH value of the solution strongly influence the electron transfer process of NO$_2^-$ oxidation on the Pt electrode. In addition, the reductive curve in Fig. 1 shows a decrease in the wave current density when the pH value increases. This can be explained by the competitive diffusion of HNO$_2$, H$^+$, and NO$_2^-$. The reductive wave is caused by the reduction of HNO$_2$ to NO$_2$OH, which cannot be observed in the first negative scan, with a starting potential at 0 V, and appears only after the generation of protons on the electrode. When the concentration of OH$^-$ is low on the surface of the Pt electrode, the redundant protons can combine with NO$_2^-$, which increases the concentration of HNO$_2$ near the electrode. After addition of enough NaOH, the protons quickly react with OH$^-$ and thus cannot be reduced on the electrode. Another reductive current at ca. $-500$ mV is attributed to the reduction of nitrate in the presence of NO$_2^-$ in the acidic surrounding [23]. Curves b–d in Fig. 1 show that the concentration of NaOH affects the reductive process of nitrate strongly because OH$^-$ can react with H$^+$ quickly and then change the pH value nearby the electrode. On the basis of these electrochemical measurements, the potential of the working electrode (the mold) in the micromachining experiments was set at 1 V.

### 3.2. Optimization of the electrolyte composition for micromachining with a Pt microcylindrical electrode

Since the micromachining process on nitinol is an irreversible electrochemical reaction followed by a homogeneous chemical reaction, it is very complicated to quantitatively calculate the theoretical value of the thickness of the CEL. In previous studies, Jiang et al. etched Ni using a mold with gear-like microstructure fabricated by a bulk-Si etching technique [20] and the CEL thickness ($\mu$) is theoretically calculated to be around 1 nm according to the equation of $\mu = (D/k)^{1/2}$, assuming the value of the rate of the scavenging reaction ($k$) is around $1.4 \times 10^9$ s$^{-1}$ (high). In comparison with those results, micromachining on nitinol is more complex, since the etchant consists of both HF and HNO$_3$ and an accurate concentration of both etchants on the surface of mold needs to be determined. Furthermore, this ratio between HF and HNO$_3$ will affect the components of the residue and the etching rate of the Ni or Ti component. The best ratio is reported to be HF:HNO$_3$:H$_2$O = 1:4:5 [22]. However, it is very difficult to know the concentration ratio of the generated HF and HNO$_3$ in the very thin CEL. Therefore, it is a critical problem to choose appropriate concentrations for the various components of the etching solution.

One simple method to determine the concentrations of the components of the etching solution was applied here. A well-defined, polished Pt microcylindrical electrode was used as a kind of mold for micromachining. The method was based on inspecting the deviation of the sizes of the etched spots from the real diameter of the microelectrode (250 μm). During the micromachining experiments, the distance between the microelectrode and the workpiece was kept constantly at a fixed distance of 200 nm. When the distance between the alloy and the mold was much less than the thickness of the CEL, the substrate was etched by the CEL and a negative copy of the Pt
microelectrode could be replicated on the workpiece. The thickness of the CEL could be estimated and thus the composition of the electrolyte, especially the concentration of NaOH, could be optimized for the best etching precision. The laterally diffused etchant needed only to etch a very thin layer of the workpiece so that it made the etched surface rougher, and then the diffusion length would be very near to the value of the CEL thickness. However, the depth of an etched hole cannot be equal to the CEL thickness, since this is closely related to several other factors, including the total amount of etchant in the very thin CEL, the distance between the substrate and the mold, and the reaction of the etchant with the substrate. Therefore, despite the close relation between the depth and the CEL thickness, it is not necessary to measure the depth in order to obtain information about the thickness of the CEL.

In Fig. 2, all the etched spots shown were fabricated by keeping the Pt microcylindrical electrode at a fixed distance of ~200 nm above the Ni–Ti alloy surface. As shown in this figure, several different spots, with sizes ranging from 249 to 641 µm, were etched on the substrate. The diameter of a spot fabricated in a solution without the addition of NaOH (Fig. 3(b)) was 641 µm, which is due to the fact that H+ electro-generated on the mold diffuses quickly into the solution and generates etchants. Afterwards, the etchants diffuse laterally and react with the nitinol workpiece. This leads to widening of the etched spot, and the size of the etched spot here was the largest for all the fabricated structures. Assuming that the etching precision is $P = (\Phi_{etched} - \Phi_{electrode})/2$ and the machining error is $E = P/\Phi_{electrode} \times 100\%$, where $\Phi_{etched}$ and $\Phi_{electrode}$ are the diameters of the etched pattern and the microelectrode, respectively, $P$ for spot b is $(641 - 250)/2 = 195.5$ µm and $E$ is $(195.5/250) \times 100\% = 78.2\%$. In the case of spot c, the micromachining was done in a solution with 0.2 M NaOH, and here $P$ is 67.5 µm and $E$ is 27%. When the concentration of NaOH
is increased to 0.4 M and 0.6 M, the values of $P$ for the corresponding spots d and e are 36.5 and 1 μm, respectively, and the values of $E$ are 14.6% and 0.4%.

Although the above experiments were done with a simple Pt microelectrode used as the mold, they provide a semiquantitative basis for the fabrication of more complicated patterns. These experiments on micromachining by CELT demonstrate that the thickness of the CEL and the micromachining resolution can reach the micrometer range when the concentration of NaOH in the etching solution is increased.

### 3.3. Micromachining with a 3D complex mold

In our study of micromachining with a complex mold, a Pt–Ir mold bearing the logo “XMU” was fabricated by EDM and employed as a 3D mold. Following the results of the micromachining experiments using a Pt microcylindrical electrode, the composition of the etching solution for an etching precision of around 1 μm should be 1.5 M NaNO$_2$, 0.5 M KF, 0.6 M NaOH, and 0.1 M C$_6$H$_5$O$_6$Na$_2$. However, when this same solution was applied to 3D complex molds as shown in Fig. 3(a), the micromachining process did not work very well. This might be because the change of the solution underneath a 3D mold is different with that under a microcylindrical electrode during the etching process. Therefore, the concentration of NaOH was chosen to be 0.4 M for micromachining with the 3D complex mold. The distance between the mold and the nitinol was kept constant at ca. 200 nm. The potential applied to the mold was constant at 1.0 V, and the etching time was 200 s.

Before the experiment, the mold was observed with a microscope. Fig. 3(a) shows that there were three letters “XMU” and three hemispherical microholes on this 3D mold. After etching with CELT, micropatterns complementary to the corresponding patterns on the mold were observed to have been fabricated on the substrate. On careful analysis of the micropatterns shown in Fig. 3(b), we observed that the microstructure “U” fabricated on the NiTi alloy had a better resolution than the other two letters “X” and “M”. The line widths are 21 and 23 μm for the two sides of the microfabricated “U” in Fig. 3(b), which are near to those of the corresponding microstructures on the Pt–Ir mold (23 and 24 μm). The diameters of the microholes (A–C) were 67, 100, and 68 μm. The diameters of the convex microstructures (A1–C1) were 46, 84, and 63 μm. Therefore, the etching precision for the fabricated microstructures corresponding to A, B, and C can be calculated to be 15.6%, 8%, and 3.6%. This can be explained by a tilted mold and a lack of parallelism between the mold and the workpiece. It can be observed that the microstructure labeled “C” is on the same side as the letter ‘U’, and both of them have a very good machining precision, since the distance between them and the substrate was smaller than on the other side. These results demonstrate again that CELT is a distance-sensitive technique.

In the experiment, the parallelism was adjusted by use only of the naked eye and a gradieter, the initial distance between the mold and the substrate varied over the area of the mold, and hence the precision of the fabricated structure was not uniform over the workpiece. The fabricated microstructures were convex features with a height of less than 1 μm measured with an atomic force microscope, but the cavities in the mold (A–C) were hemispherical with a depth of tens of micrometers. To achieve a complete negative copy of the mold, it would be essential for the mold to approach the substrate stepwise until the whole of the microstructures on the mold had been replicated on the workpiece. A study of this is under way in our laboratory.

### 4. Conclusion

We have demonstrated that CELT has been successfully applied to the micromachining of nitinol with appropriate etching solutions containing F$^-$ and NO$_2^-$ groups. The micromachining process depends on the concentration of OH$^-$ in the etching solution. Our micromachining experiments show that OH$^-$ is an effective scavenger for electrogenerated HF and HNO$_3$. The etched patterns on the nitinol match approximately the size of the patterns on the mold and retain the complex shape of the mold. The major advantages of CELT have been demonstrated, and can be summarized as follows. (1) The technique can be used to fabricate complex three-dimensional micropatterns or nanopatterns. (2) It can be used in a batch process with fewer steps than in photolithography.

### Acknowledgments

Support for this research by the National Science Foundation of China (20503024) and by the Natural Science Foundation of Fujian Province (E0520001) is gratefully acknowledged. The Pt–Ir mold prepared by the EDM technique was provided by Dr. Guo H. Cao of the Harbin Institute of Technology, China. All the authors acknowledge helpful discussions with Professor Zhao W. Tian and Professor Zhong Q. Tian.

### References
