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Failure Mechanism Analysis of Silver Nanowires in Electrochemical Micromachining

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Abstract. Silver nanowires are an ideal type of nano-electrode for electrochemical micromachining due to their large aspect ratio and good conductivity. In this paper, self-assembled silver nanowires electrode are used as the tool electrode for electrochemical micromachining. It shows that the silver nanowires fail in electrochemical micromachining. The failure mechanism is researched by computer simulation and experimentation. And the results show that the silver nanowires dissolve on account of the temperature rise when the temperature exceed the melting point of Ga. In addition, the chemical reaction of the silver nanowire in dilute sulfuric acid solution accelerates, intensifying the dissolution of the silver nanowire. Results indicate that the silver nanowire electrode is not suitable for electrochemical micromachining directly. Then, some protective measures should be taken for silver nanowire when it is used as tool electrode in electrochemical micromachining.

1. Introduction

Micro/nano-structure is widely used in fields such as communication, medicinal apparatus, and the aerospace industry. Micro/nano-fabrication technologies such as electron beam lithography[1], focused ion beam[2–4], femtosecond laser techniques[5, 6], scanning probe techniques[7, 8] and electrochemical micromachining[9–11], among others, have become a primary focus in academia. Electrochemical micromachining is a special processing method for removing materials in the form of ions, which has great potential for application to micro/nano-machining. Various findings have been obtained and published from active research in the field of nano-electrochemical machining. Schuster et al.[12] fabricated a micro-triangular trough with width of less than 200 nm using a nano-tip that employed electrochemical micromachining.

A micro/nano-electrode is essential for electrochemical micromachining. The ideal size for the electrode has been shown to be as small as possible[13, 14]. Fabrication of the nano-electrode is not easy, especially for a large aspect ratio nano-electrode. Wang, Y. et al[15]. fabrication of a high-aspect-ratio cylindrical nano tool using liquid membrane ECM, in which a straight reciprocating motion is applied to the anodic electrode. Nano-electrodes with average diameters of several hundred nanometers and aspect ratios up to 70 are fabricated with this technique.

Metal nanowires is an ideal type of nano-electrode, being less than 100 nm in diameter and with typical aspect ratio greater than 1000, especially in the case of silver nanowires[16, 17]. The silver nanowire also has good conductivity and thermal properties. Silver nanowires cannot be used directly



for processing, must be connect the nanowires to electrodes and other devices by various means for clamping purposes. In this study, silver nanowires are directly assembled into the STM electrode tip by "pull" method.

In this paper, an investigation into electrochemical micromachining using silver nanowire electrode is carried out. The experiments show that the silver nanowires fail in electrochemical micromachining. The morphology change of the silver nanowire is studied. The failure mechanism are also researched by computer simulation and experimentation in the paper.

2. Failure phenomena

The electrochemical micromachining experimental setup is shown in Figure 1, which includes a motion control system, power supply system, silver nanowire electrode and workpiece. The workpiece (anode) and tool electrode are dipped in the electrolyte with an inter-electrode gap of several micrometres. With ultrashort voltage pulses of nanosecond pulse duration, the dissolution of the workpiece is localized very close to the tool electrode.

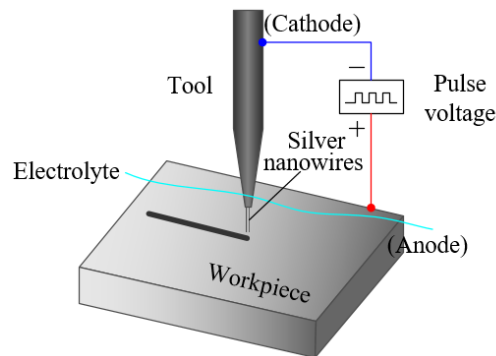


Figure 1. Schematic diagram of the electrochemical micromachining setup.

In this experiment, the silver nanowire electrode and Inconel 718 are employed as tool electrode and workpiece, respectively. The performance parameters of the silver nanowire electrode are listed in Table 1.

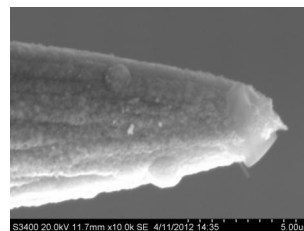
Table 1. Performance parameters of the silver nanowire electrode

Nanowire length	3–7 μm
Nanowire composition	70% Ag, 30% Ga
Substrate material	Tungsten
Substrate dimension	$20 \times 0.5 \text{ mm}$
Nanoprobe electrical resistivity	$1\text{--}1.01 \times 10^{-7} \Omega\text{m}$
Current tolerance	1–5 mA

The experiment is conducted with a voltage of 4 V, a pulse period of 50ns, a pulse width of 6ns, and 0.1 mol/L H_2SO_4 at room temperature. The silver nanowires electrode fail in electrochemical micromachining, and the morphology of the silver nanowires electrode is shown in Figure 2. The silver nanowires is “disappeared”.



(a) Before electrochemical micromachining



(b) After electrochemical micromachining

Figure 2. Change of the silver nanowire electrode during electrochemical micromachining.

3. Failure Mechanism Analysis

3.1. The temperature analysis of the silver nanowire electrode

As listed in Table 1, there is 30% content of the element Ga, which is used as binder, in the silver nanowire electrode. Ga has a melting point of 29.78°C. Generally, the heat generated by the passage of current and the electrochemical reaction of electrochemical micromachining will heat the electrolyte in the inter-electrode gap, which can result in temperature rise of the electrolyte around the electrode. When the temperature reaches the melting point of Ga, the silver nanowire electrode will be damaged. Hence, it is of critical importance to investigate the temperature change of the silver nanowire electrode in electrochemical micromachining.

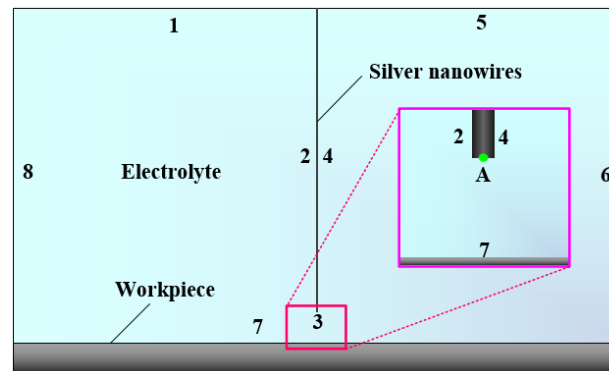


Figure 3. The mathematical model of electrochemical micromachining.

During the electrochemical micromachining process, it is difficult to detect the temperature around the electrode directly. In order to investigate the temperature change around the silver nanowire electrode during the electrochemical micromachining process, a physical model is built, as shown in Figure 3 with parameters as listed in Table 2. To simplify the proposed model, several assumptions are made:

- (1) The concentration polarization is negligible, because an ultrashort pulse current is employed.
- (2) The electric field in the inter-electrode gap is steady.
- (3) The electrode surface is an equipotential surface.

Table 2. Model parameters

Length of silver nanowire electrode, L	10 μm
Width of the region, W	20 μm
Diameter of silver nanowire electrode, d	100 nm
Inter-electrode gap, h	1 μm
Initial temperature of the electrolyte	25 C
Applied pulse voltage	4 V
Pulse period	50 ns
Pulse on-time	6 ns
Electrolyte conductivity	4.85 S/m

3.1.1. *Electrical model.* The electrical potential across the inter-electrode gap, ϕ , can be approximately described by Laplace's equations as follows:

$$\nabla^2 \phi = 0 \quad (1)$$

The corresponding boundary conditions are as follows:

$$\phi|_{\Gamma_7} = U \text{ (Anode)} \quad (2)$$

$$\phi|_{\Gamma_{2,3,4}} = 0 \text{ (Cathode)} \quad (3)$$

$$\frac{\partial \phi}{\partial n}|_{\Gamma_{1,5,6,8}} = 0 \quad (4)$$

3.1.2. Thermal model. The heat generate during electrochemical micromachining consists of Joule heat and electrochemical reaction heat. Compared with Joule heat, the electrochemical reaction heat is negligible. In the simulation, it is therefore assumed that the Joule heat is the only heat source.

The temperature distribution in this cell is calculated[18] as follows:

$$\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + P_{bulk} \quad (5)$$

Where, C_p is the electrolyte specific heat capacity, and k is the electrolyte thermal conductivity. P_{bulk} denotes the Joule heating in the electrolyte and can be obtained by Joule's law as follows:

$$P_{bulk} = Ui \quad (6)$$

Due to its good conductivity, the heat exchange between the silver nanowires and outside air is rapid. The temperature of the interface between the electrode and electrolyte is equal to ambient temperature. The boundary conditions are given as follows:

$$T|_{\Gamma_{2,3,4}} = T_0 \quad (7)$$

$$\frac{\partial T}{\partial n}|_{\Gamma_{1,5,6,7,8}} = 0 \quad (8)$$

All models are coupled and analyzed using COMSOL software version 3.5a.

3.1.3. Simulation results. Figure 4 shows the temperature field distribution of the inter-electrode gap simulated by COMSOL Multiphysics software.

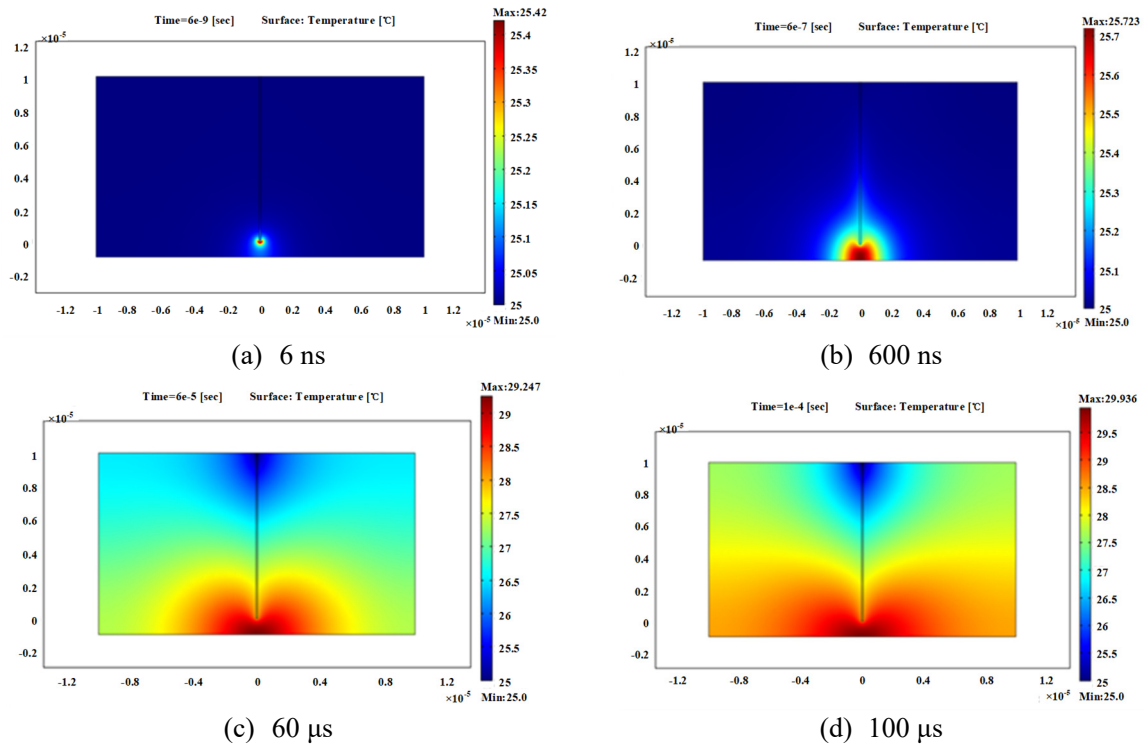


Figure 4. Temperature field change of the inter-electrode gap.

Figure 4(a) shows that the temperature around the nanowire tip rose by 0.42 °C in a single pulse width (6 ns) in. As time progress to 600 ns, the area of temperature increase in the electrolyte is expanded, with the peak temperature in the inter-electrode gap close to the nanowire tip rising to 27.723 °C. As time passes, the area of temperature rise continues to expand, with the peak temperature reaching 29.936 °C after 100 μs is shown as in Figure 4(d).

The temperature change curve of a nanowire tip at point “A”(Figure 3) for 100 μs is shown in Figure 5. It can be seen that within a single pulse cycle, the temperature rose during the pulse on-time, and fell

during the pulse off-time. The magnitude of the temperature fall is lower than that of the rise, hence the temperature at the nanowire tip appears to continually increase. By employing polynomial fitting, the temperature change curve over time can be described by Eq (9), where we see the temperature increasing with time. Presumably, the temperature around the electrode continue to rise, as the temperature increases, the silver nanowire would be damaged due to the low melting point of Ga.

$$T = 26.62931 + 39713.6948t - 2.82206E8t^2 + 8.3963E11t^3 \quad (9)$$

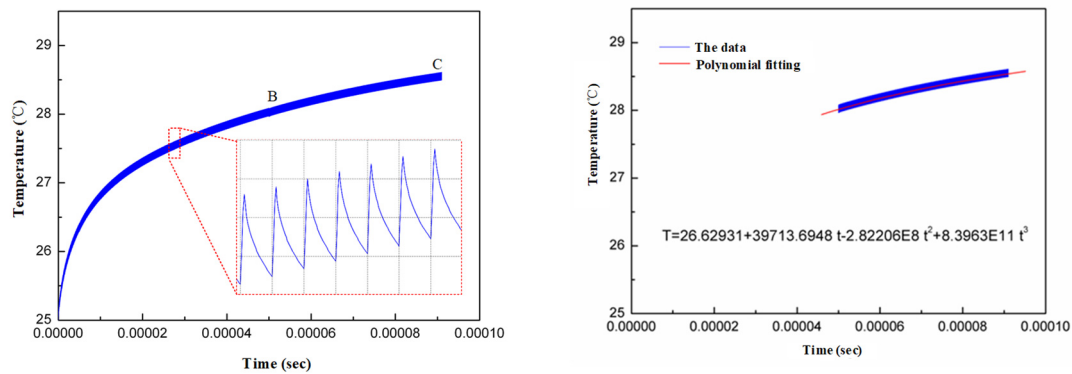


Figure 5. Temperature change curve over 100 μ s.

3.2. The corrosion analysis of silver nanowire in experiment

3.2.1. Corrosion experiment. In order to investigate the influence of the chemical reaction on the silver nanowire, a comparative corrosion experiment is performed with the parameters listed in Table 3.

Table 3. Parameters of comparative experiment.

Experiment No.	Electrolyte	Temperature	Power	Time
1	Dilute sulfuric acid	25°C	Off	30 min
2	Dilute sulfuric acid	30°C	Off	30 min

3.2.2. Experiment results. At room temperature, Ag is very stable, but Ga can react slightly in dilute sulfuric acid solution, with the following reaction equations:

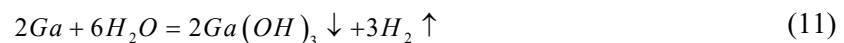
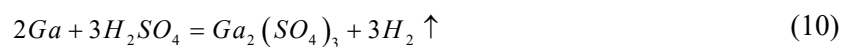


Figure 6 shows the change in the silver nanowire for different electrolyte temperatures with the power off. It can be seen that at 25°C, the silver nanowire has had little reaction in the electrolyte. With the temperature increased to 30°C, the silver nanowire dissolves, and the length reduces. This indicates that as the temperature increases, the silver nanowire would be damaged due to the low melting point and chemical reaction of Ga.

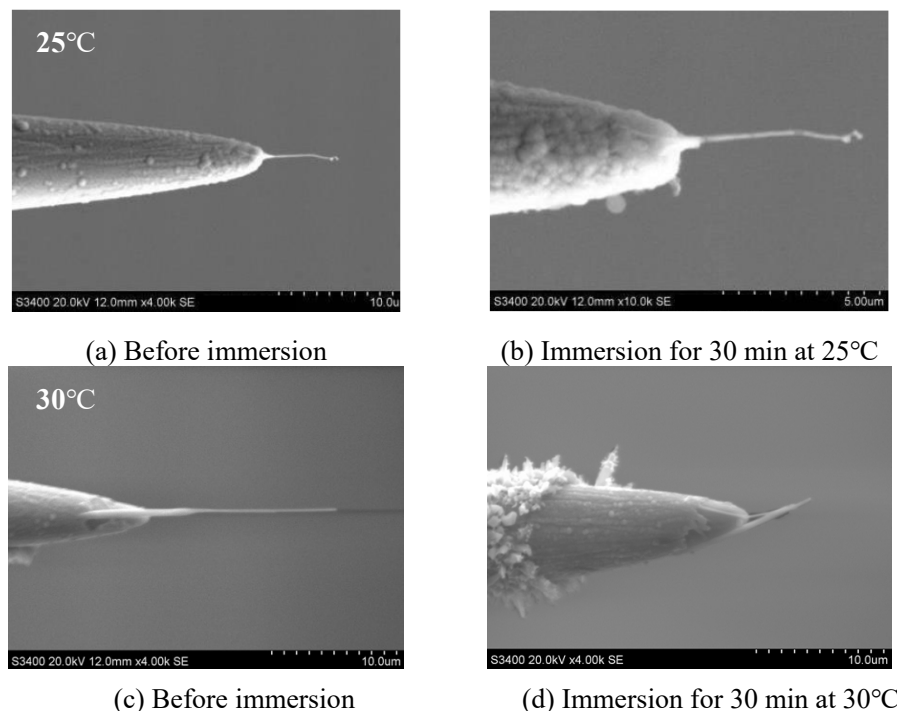


Figure 6. Change of silver nanowire electrode in electrolyte with power off.

Computer simulation (Section 3.1) indicates that the temperature of the electrolyte rises around the electrode during electrochemical micromachining. According to Eq (9), the temperature may rise to 30°C in 20 ms, as the process time extends, the temperature continues to rise, exceeding the melting point of Ga. Hence, the disappearance of silver nanowire electrode can be attributed to the temperature rise of the electrolyte around the electrode. As the temperature increases, the silver nanowire dissolves.

In addition, the chemical reaction of the silver nanowire in dilute sulfuric acid solution accelerates with the temperature rise of the electrolyte. According to the electrode reaction equation, H_2 generate on the cathode tool (silver nanowire electrode), which intensifying the dissolution of the silver nanowire.

4. Conclusions

In this paper, a silver nanowire is introduced as the tool electrode for electrochemical micromachining. The failure mechanism analysis of silver nanowire in electrochemical micromachining is investigated. Based on the simulation and experimental results, the following conclusions can be drawn:

- During electrochemical micromachining, the temperature around the electrode continues to rise. As the temperature increases, the silver nanowire would be damaged due to the low melting point of Ga.
- Temperature rise of the electrolyte accelerates the chemical reaction of the silver nanowire in dilute sulfuric acid solution, which leads to the dissolution of the silver nanowire.
- The silver nanowire electrode is not suitable for electrochemical micromachining directly, some protective measures should be taken for silver nanowire if it is used as tool electrode in electrochemical micromachining.

Acknowledgements

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