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Analysis of electrolyte flow in localized electrochemical deposition

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Abstract

Localized electrochemical deposition (LECD) is a favorable technology for fabrication of the high-aspect ratio electrodes of various materials. This technology is found to be one of the simple and inexpensive ways to fabricate non-circular electrodes for micro-EDM. In order to fabricate non-circular electrodes a mask of non-conductive material is placed between the anode and cathode, which is immersed in a mixed electrolyte of copper sulfate, 1.0M sulfuric acid and as an additive agent 0.04 gm/liter of thiourea. The deposition of copper is localized on the cathode surface using a mask and applying ultra-short voltage pulses between the anode and cathode. In this set up the cathode is placed above the anode and mask, so that the deposited electrode can be used directly for EDM or any application without changing its orientation. In order to localize the deposited structure on the cathode surface, the electrolyte needs to flow through the mask and needs to touch the cathode and a constant flow rate of the electrolyte is maintained by using a pump. For this reason, micro holes of desired shapes are fabricated in the mask using micro milling. This study shows the effect of electrolyte flow through the micro holes of the mask and micro gap between the mask and anode on the microstructure of deposited electrode using FLUENT analysis. Moreover, an optimum range of electrolyte flow rate through the micro passages is also shown for the LECD process in order to fabricate high aspect ratio microstructures.

Keywords: Localized electrochemical deposition; LECD; electrolyte; micro holes; micro gap

1. Introduction

Currently new micro-fabrication processes are being been investigated worldwide to build micro electromechanical structure such as gears, springs, helices and columns and these are required for the apprehension of miniature micro machine that can access spaces never before explored by human beings. In order to handle this challenge fabrication techniques related to material deposition such as low-pressure chemical vapor deposition (LPCVD), laser-assisted chemical vapor deposition (LCVD), plasma-enhanced chemical vapor deposition (PECVD), ultraviolet stereo lithography, spinning, spraying and localized electrochemical deposition (LECD) are being used presently [1].

About a decade ago, as a practical technique for inexpensive free form micro-fabrication, the LECD process has a huge prospective to afford solutions to a variety of challenges [2]. Madden and Hunter are the first researchers to introduce the LECD process for microfabrication of the three dimensional metal structures [3]. Jansson et al. had tested the LECD process with different kinds of nickel plating solutions to deposit the nickel structures [4]. El-Giar et al. had used the same method to deposit the long thin micrometer-size copper columns, copper electrical inter-connects and tips for scanning probe

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microscopy applications [5,6]. Yeo et al. investigated the deposition phenomena of LECD for Ni micro column structure by using open-loop (without analog feedback) and closed loop (with analog feedback) systems [7]. Besides, the investigations have also done on the effect of rotational electrode on the growth of nickel micro column structure [8], and the effect of ultrasonic vibration on the rate of deposition, concentration and porosity of the nickel micro columns [9]. Most of the researches have used the copper as a substrate and the platinum as a counter electrode to fabricate a column structure in the LECD process. A new LECD process is implemented by Habib et al. [1, 10-11] to fabricate the complex cross-sectional shape of electrodes where the coppers are used for both substrate and counter electrode. The masks which are made from non-conductive materials and with different designs are used to provide the pre-shape for the deposition purpose. The substrate is located on the machine z-axis which is above the counter electrode because of it eases to proceed to EDM process directly just after the deposition. By applying this method, the electrode clamping error can be minimized and the production rate can be increased.

In order to increase the aspect ratio of the electrode, close loop control of the LECD process is required, where the effect of electrolyte flow plays a significant role. In this study, a detail electrolyte flow analysis is studied and a range of operational parameters are presented. It can be also seen that using these parameters a high aspect ratio micro electrode is fabricated and micro-EDM is also done by using that micro-electrode.

2. Concept and structural construction of LECD and EDM combine setup

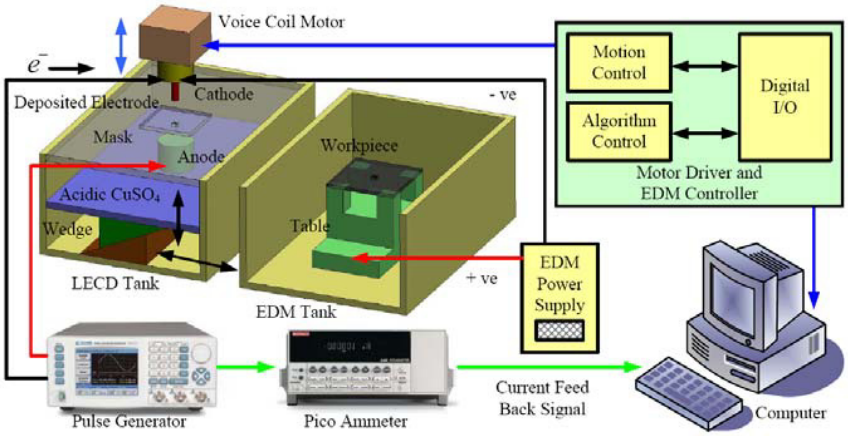


Fig. 1. Schematic diagram of LECD and EDM combine setup

In the experimental setup, two separate sub-setups are used one for LECD and another for EDM operation. Both of them are mounted on a 3-axes multi-process machine and figure 1 and 2 show the structure of desktop machine.

The LECD sub-setup consists of two main parts: a cathode electrode holder and a deposition tank. In this process the metallic ion can become solid metal and deposited on the cathode surface if sufficient amount of electric current pass through an electrolyte or plating solution. Solution that contains charged ions known as electrolyte or plating solution. These positively charged ions can be achieved by dissolving metallic salt into water. The acidic supper sulfate is used as an electrolyte and an anode is immersed in this electrolyte. Cathode is placed above the anode and between the anode and cathode a non-conductive mask is located to create the non-circular shape of the deposition. The mask is made from a non-conductive material like PMMA (Poly methyl methacrylate). A small constant gap is maintained between the anode and mask during deposition time using a micrometer screw. When both of the electrodes are conducted electrically, current will pass through the plating solution. The positively charges metal ions get (Cu^{2+}) deposited as solid metal on the cathode through the non-conductive mask. The through hole of different shape (X shape, Y shape, O shape etc.) of the mask is prepared by micro-milling operation. A more realistic equation is

$$Cu^{2+} + 2e^- \rightarrow Cu \downarrow \text{ (Cathode)} \qquad H_2O \rightarrow 2H^+ + 2e^- + \frac{1}{2}O_2 \uparrow \text{ (Anode)}$$

For electrode deposition pure copper is used for both the base material where the metal will be deposited and anode material. For electrode surface finish it is required to polish surface by the successive grade of 600, 1200, 1500 and 2000 silicon carbide papers. Finally, to obtain a smooth and mirror surface a final fine polishing was done by 1.0μm diamond paste on nylon cloth. In the EDM sub-setup a workpiece fixing table is used to fix the workpiece which is kept inside an

EDM tank and the dielectric is supplied in the working area with the help of a nozzle. Finally, the deposited electrode which is attached with the voice coil motor can do the EDM without changing the tool position.

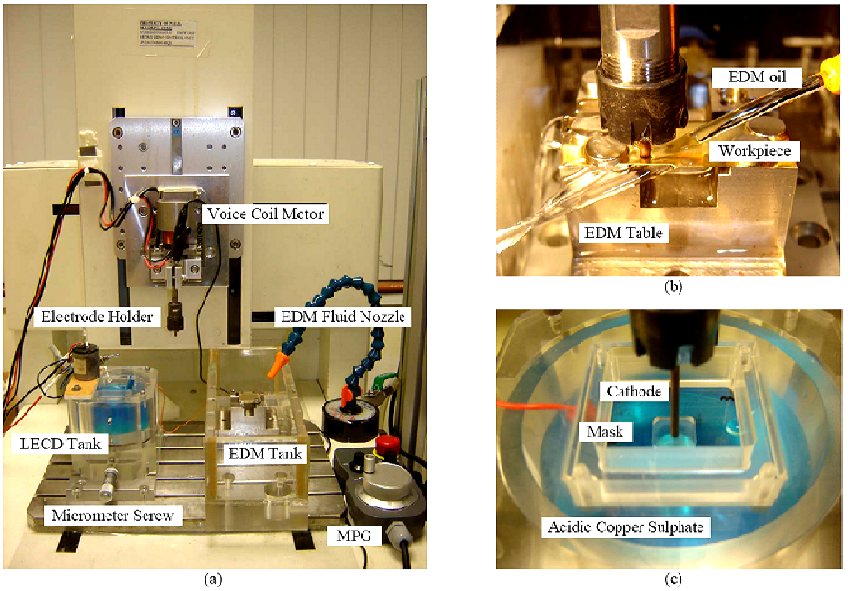


Fig. 2. (a) LECD and EDM setup (b) LECD operation running (c) EDM operation running

3. Results and discussions

3.1. Process modeling and simulation

When a cathode and an anode are immersed in a solution, an interface consists of two equal and opposite layers of charge, one on the metal and other in solution is created. This pair of charged layers, called the double layer, is equivalent to a parallel plate capacitor. The variation of potential in the double layer with the distance from the electrode is linear. On both the electrode surface the electro chemical double layer forms a capacitor. This double layer is charged when a potential is applied between the two electrodes. The charging time constant (τ_c) for the double layer is the product of resistance (R) and capacitance (c_{DL}). The charging current has to flow through the electrolyte, whose resistance is proportional to the length of the current path; that is, the distance between the electrodes (d_{gap}). Therefore, resistance is the product of the gap distance between the electrodes (d_{gap}) and the specific electrolyte resistivity (ρ). Finally, the time constant:

$$\tau_C = R \times C = \rho . c_{DL} . d_{gap} \tag{1}$$

The charged potential of a double layer at any time (t):

$$\varphi_C = \varphi_0 \left(1 - e^{-\frac{t}{\tau_C}} \right) \approx \varphi_0 \frac{t}{\tau_C} \tag{2}$$

When plus voltage is applied, there is no electrochemical reaction or metal deposition during the pulse off time and pulse off time voltage is comparatively less than pulse on time voltage. This is why, charged potential (φ_C) can be judged as overpotential *(η)*. From the Butler-Volmer equation, during the pulse on-time, reaction current density *(i)* is:

$$i = i_0 \exp\left(\frac{\alpha n F}{RT} \varphi_C \right) \approx i_0 \exp\left(\frac{\alpha n F}{RT} \varphi_0 \frac{t}{\tau_C} \right) \tag{3}$$

Here, i_0 exchange current density, α leakage factor, F Faraday constant, R gas constant, T temperature, n the number of electrons taking part in the reduction, φ_0 potential. Since the reaction rate is proportional to the reaction current density, i.e. $\zeta(t) \infty i$. This can be represents as

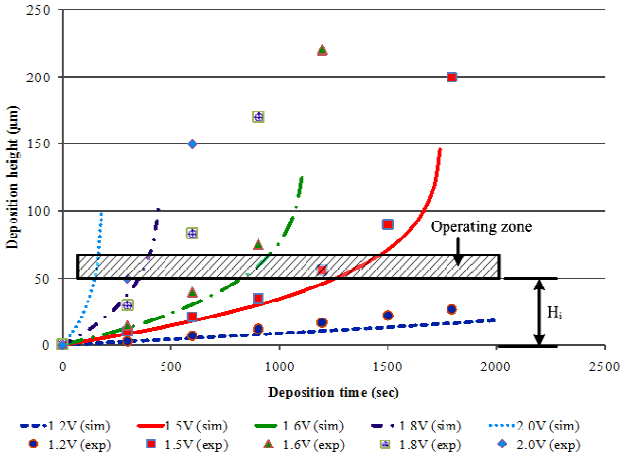
$$\zeta(t) = \frac{i}{nF} = \frac{i_0}{nF}\exp\left(\frac{\alpha F}{RT}\varphi_0\frac{t}{\tau_C}\right) = \frac{i_0}{nF}\exp\left(\frac{\alpha F}{RT\rho c_{DL}}\frac{\varphi_0 t}{d_{gap}}\right) \tag{4}$$

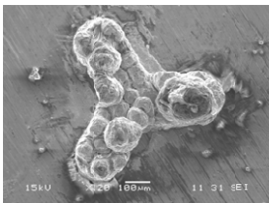
The electrochemical reaction or deposition occurs only during on time of pulse. For this reason the deposition rate can be calculated by integrating the reaction rate during pulse on time. Therefore, localized electrochemical deposition rate, Z:

$$\begin{aligned} Z\left(\varphi_0, t_{on}, t_{period}, d_{gap}\right) &= \frac{1}{t_{period}}\int_0^{t_{on}} \zeta(t)\,dt \\ &= \frac{d_{gap} f}{\varphi_0}\frac{i_0 RT\rho c_{DL}}{\alpha z F^2}\left[\exp\left(\frac{\alpha F}{RT\rho c_{DL}}\frac{\varphi_0 D}{d_{gap} f}\right) - 1\right] \end{aligned} \tag{5}$$

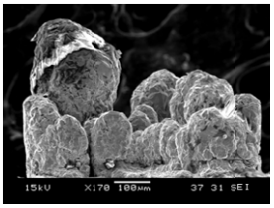
Here, frequency $f = \frac{1}{t_{period}}$ and duty ratio $D = \frac{t_{on}}{t_{on}+t_{off}} = \frac{t_{on}}{t_{period}} = t_{on}\times f \;\Rightarrow t_{on} = \frac{D}{f}$

(a)





(b)



(c)

Fig. 3. (a) Deposition height and Operating zone for LECD process (b) Tree structure of deposited electrode side view (c) top view

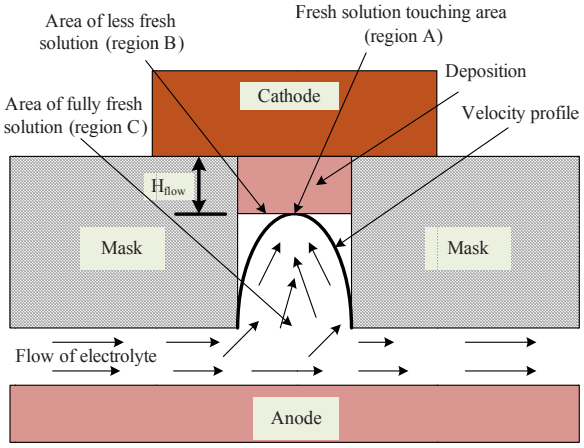


Fig. 4. Concept of FLUENT simulation

Figure 3(a) shows the simulation and experimental results of equation (5) where the value of $\varphi_0$is 1.2V, 1.5V, 1.6V, 1.8V and 2.0V. However, the value of f, D and d_{gap} are kept constant on 100 kHz, 0.33 and 350 µm. The simulation and experimental results both indicate that at the beginning of the depositing height the deposition rate is very low, as the deposition height increases the rate is becoming high. This is because, with the increase of deposition height the gap between the anode and cathode will decrease, cause the increase of the deposition rate. Fig. 3 (b) and (c) show the improper

deposited electrode under the condition of φ_0, f, D and d_{gap} are 1.5V, 100 kHz, 0.33 and 350 µm. It can be seen from the fig. 3 that when the deposition height reaches around the mask height (250 µm) the deposition starts become tree type. This is because, after 250 µm there is no mask to guide the deposition structure. For this, in order to increase the aspect ratio of the deposited structure it is needed to lift up the z axis with a close lope control system. If we apply the control algorithm at the beginning of the deposition then it will take long time to reach the desire height, because the deposition rate is very low at the beginning. This is why; the control zone is selected after deposition structure reaches up to certain height. The electrolyte flow region plays a significant role in metal deposition. Depending on the flow pattern, the initial growth height is needed to select. This is why FLUENT analysis is conducted in the mask hole and the gap between anode and mask, in order to fine the actual scenario.

3.2. Determination of limit of the initial growth by FLUENT analysis

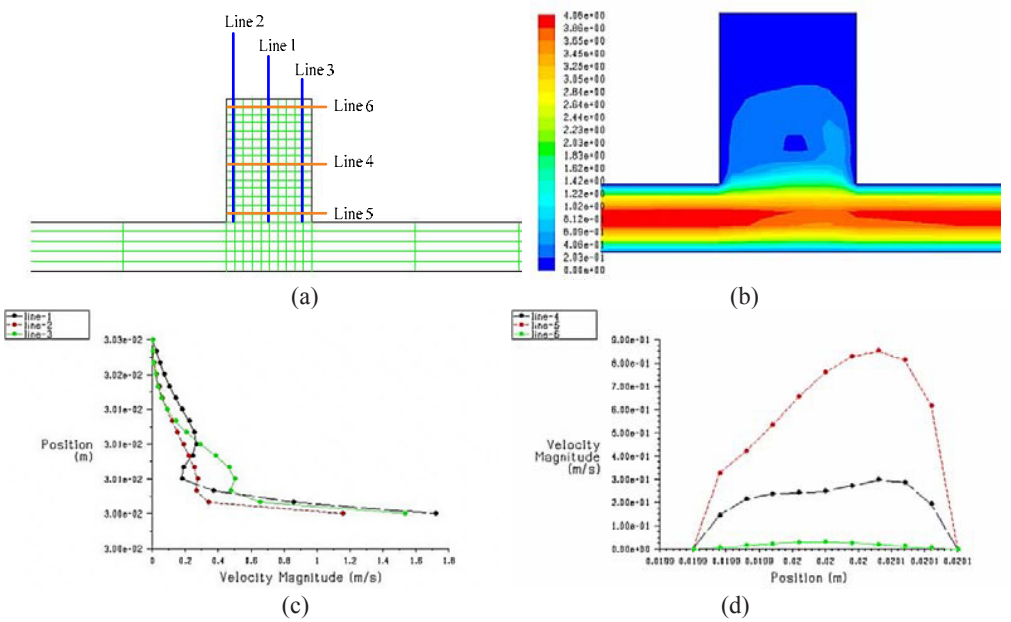


Fig. 5. (a) Grid inside the mask area (b) Flow analysis (c) Velocity for vertical grid line (d) Velocity for the horizontal grid line

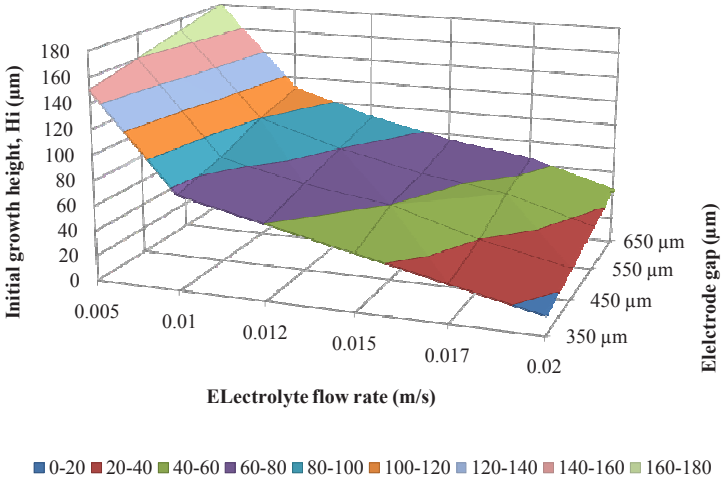
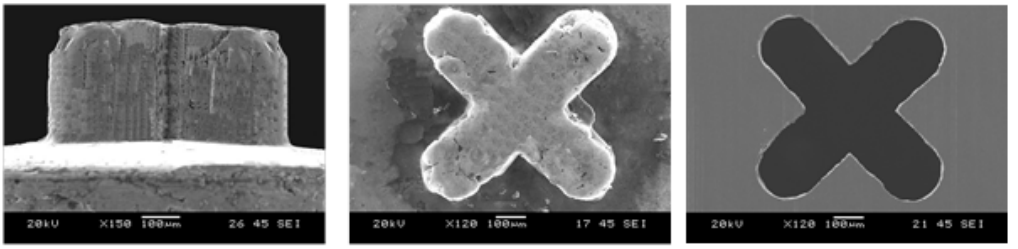


Fig. 6. Surface plot for initial growth height for different flow rate and electrode gap.

It can be seen from Fig. 4, when the electrolyte is flowing through the narrow passage between the mask and the anode, a flow region is created inside the mask. In that flow region, fresh copper ion is always available. Outside the flow region, the

copper ion is reached by diffusion process. If the deposition structure reaches and touches the flow region, then in region A the deposition growth will be higher than the region B. In region B, the fresh copper ion is lesser because ions are reaching there through diffusion and in region A, fresh ions are coming by force convection. If the deposition reaches this zone, then the deposited structure will become tree type. On the other hand, if the deposition reaches up to region C, then there is a chance of become powdery structure. This is why, the initial growth height should not cross the flow region and the initial growth height should be $H_i < H_{flow}$.

Figure 5 shows the FLUENT simulation for the electrolyte flow 0.01 m/s and 250µm mask height and 100µm gap between the mask and anode. From the above condition, it can be concluded that the safer initial growth height can be 50µm or less than this. For different flow rate condition and different electrode gap, a surface plot was done in Fig. 6. In order to get a high aspect ratio electrode the initial growth height can be selected from the Fig. 6 surface plot. Fig. 7 (a) and (b) show the LECD structure under above operating conditions and using close loop control algorithm within the operating zone. Fig. 7 (c) shows that the micro-EDM hole using the deposited electrode on stainless steel.



(a) (b) (c)

Fig. 7. LECD electrode (a) side view (b) top view (c) EDM hole on stainless steel using LECD electrode

4. Conclusions

Localized electrochemical deposition is a simple and attractive method for making complex cross sectional electrode. These studies give an idea of the operating parameters range of the electrolyte flow as well as the gap between the anode and mask. By this, it is easy to control the deposition growth. The limiting value is decided from FLUENT analysis, on various electrolyte flow rate and various electrode gap. If the parameters are maintained within these parameters range it is possible to fabricate high aspect ratio micro structure. Finally, the deposited copper electrodes are used as a micro EDM electrode. Micro-holes with good surface quality with rim free of burr-like recast layer are fabricated with the LECD electrode by die-sinking EDM with RC circuit.

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