New development of combined electrochemical processes for mirror-like micro grooves

Jeong-Woo Park*, Eun-Sang Lee**, Young-Hun Moon***

* Graduate School of Mechanical Engineering Division, Pusan National University, Busan, Korea
** Mechanical Engineering Division, Inha University, Incheon, Korea
*** Mechanical Engineering Division, Pusan National University, Busan, Korea

Abstract

Pulse electrochemical machining process both with high current density and low current density may produce a non-lustrous surface on workpiece surface. The usual polishing process to remove a black layer from the surface has been hand polish the part. But the milli-to-micro meter scale structure formed by the electrochemical machining process may be destroyed while polishing process. The application of ultra short voltage pulses based on the analysis of electrical double layer charging process allows high resolution electrochemical machining and polishing. This technique was based on the specific polarization resistance from the comparison of ideal and experimental potential variation during short voltage pulses.

Key words: Pulse electrochemical machining/polishing, Electrical double layer, Specific polarization resistance

1. Introduction

Some investigators who have tried to achieve the highly smooth surface finish using electrochemical processes have reported that high current density produced lustrous surfaces while the opposite conditions produced a passive layer and had a tendency to produce a black surface. However, processing at a low current density may produce a non-lustrous surface but the improvement of dimensional accuracy of the surface is significant. It was found in previous study that the control of the machining depth with pulse electrical current is easier than continuous electrical current [1]. And it was also found that micro grooves within 20 micrometers in depth could be produced using electrochemical micro-machining (EMM) process with pulse current. The surface with pulse process was a bit more lustrous than with continuous current but the black passive layer still could be found at grooved surface. There are two ways to achieve highly smooth surface finish. One is brushing it with a brush, the other is electrochemical machining (ECM) with high current. The former method is the most common polishing practice, but not only may the surface obtained differ from operator to operator, but precision smooth surface on micro grooves are difficult to
obtain. The latter one recently has been used to produce a highly smooth surface after EDM process. However, the material removal rate in ECM with high current is relatively high. Hence the original shape of the micro grooves, which was formed by EMM process, may be destroyed.

In this study, an electrochemical polishing (ECP) process using pulse current is adopted as a possible alternative process when micro grooves, formed by EMM with pulse process, should be polished. This study will discuss the accurate control of physical and electrical conditions so as to achieve mirror-like micro grooves with lustrous and smooth surface without destroying the original shape of micro grooves.

2. Equivalent Electric Circuit Analysis in Electrochemical System

The concept of our method is based on a charging of electrical double layer (DL) where an electronic charge of electrode stands face to face with an ionic charge of solution. When an electrode is placed in an electrolyte solution, an equilibrium potential difference and the charging of DL usually become established between the electrode and solution. This potential difference arises from the transfer into solution of anodic metal ions and the simultaneous discharge of ions from the solution. Hence, these sequential charging and discharging of DL can be analyzed as a capacitor model when the short voltage pulses are applied. The electrical DL is composed of a compact DL (CDL), which covers from inner Helmholtz plane (IHP) to outer Helmholtz plane (OHP), and a diffuse DL (DDL), which covers the bulk electrolyte as shown in Fig. 1 [2].

From the capacitor analysis, a time constant \( \tau \) is defined as

\[
\tau = RC = \rho d c_{DL}
\]  

(1)

This time-constant of electrochemical system can be a criterion how fast the reaction occurs. The machining resolution \( d \) is proportional to the time constant \( \tau \), because the specific resistance \( \rho \), a factor defined by the electrolyte, and the electrical DL capacity \( c_{DL} \), defined by the summation of \( c_{CDL} \) and \( c_{DDL} \), are constant. Electrochemical system, where
electrodes are in close proximity, can be remodeled as a R-C equivalent electric system with capacitor behavior as shown in Fig. 2.

Two capacitors, \(c_{\text{CDL}}\) and \(c_{\text{DDL}}\), are connected in series circuit in the Helmholtz DL. The net capacitance has the value of 10~20\(\mu\)F/cm\(^2\), because the summation of different two capacitors with different capacitances approximates to the capacitor with small capacitance. The electrolyte resistance is classified into two independent resistances.

One is polarization resistance (\(R_p\)) connected to net capacitor in a parallel circuit in Helmholtz DL. If the \(R_p\) and \(c_{\text{DL}}\) are connected in series circuit, direct current cannot pass through the electrochemical system [3]. Hence the electrochemical reaction with direct current is impossible. The other is electrolyte solution resistance (\(R_s\)) connected to the \(R_p - c_{\text{DL}}\) system in series circuit. But the resistance to analyze the time-constant (equation 1) is the polarization resistance. However, the resistance measured by a resistance tester shows not the electrolyte resistance but the combined impedance including capacitances. Hence, it is inadequate that regarding the value measured by the resistance tester as a polarization resistance that is used in analyzing the electrochemical system related to capacitor. To obtain approximate polarization resistance in electrochemical polishing of the micro grooves, the new method of comparison of ideal and experimental potential variations, indicating charging and discharging of electrical DL, is applied in this study.

3. Machining Resolution Analysis in Pulse Electrochemical Machining

The electrochemical reaction can occur with sufficient electrical charge in DL, when the pulse duration over time-constant is applied. This is understandable only for the static condition of electrolyte solution. As mentioned equation (1), \(\tau\) is dependent on the \(\rho\), \(d\) and \(c_{\text{DL}}\). To specify this relation, Fig. 3 is plotted. In Fig. 3, the experimental machining resolution [(final width-tool width)/2-electrode distance], resulting after machining time of 1 min, is plotted for different pulse durations and 3.5M NaNO\(_3\) with specific electrolyte resistance of 62.5\(\Omega\cdot\)cm and DL capacitance of 18\(\mu\)F/cm\(^2\). Especially, the electrolyte solution is circulated with 1m/s velocity to flush the generated heat and gas away. Even though Rolf Schuster and Viola Kirchner showed the experimental results
are in agreement with the prediction in static HClO$_4$ and CuSO$_4$ solution [4], the experimental resolution has a tendency to be lower, according to the increment of the pulse duration, than the prediction in this study. When the pulse voltage is applied between the electrodes, the charging in the electrolyte and the starting of current flow occur through the movement of ion charge. Hence, the lower experimental resolution than prediction in this study is owing to the disturbance of the movement of ion charge by the forced electrolyte circulation.

Fig. 4 shows the anode surface micrograph resulting after EMM. In pulse width below 13μsec, the width of grooves is smaller than the pattern width of cathode tool about 100μm for lack of charging ions between the electrodes, the boundaries between treated and untreated metal are nevertheless distinct. In pulse width within 13μsec ~ 20μsec, the width of grooves is in agreement with the pattern width of cathode tool and the boundaries are distinct.

In pulse width over 20μsec, the width of grooves is bigger than the pattern width of cathode tool about 100μm ~ 200μm for excessive charging ions, the boundaries between treated and untreated metal are vague compared to above conditions.

4. Pulse Electrochemical Polishing

Upon a single potential pulse voltage is applied the electrodes, the charging current is generated between electrolyte solution and electrode because of the abrupt potential difference. The charging current is equal to the capacity of DL by differential rate of voltage, $I = C dE/dt$, so the high differential rate of voltage brings about high current charging. If the charge of capacitor is zero at $t = 0$, the potential variation of charging and discharging of DL capacity is defined as

$$E = E_0(1 - e^{-\frac{t}{RC}}), \text{ for charging DL capacity} \quad (2)$$

$$E = E_0e^{-\frac{t}{RC}}, \text{ for discharging DL capacity} \quad (3)$$
From above equations (2) and (3), the instantaneous potential variations of charging and discharging of DL capacity are plotted in Fig. 5 (a) according to various specific polarization resistances ($\rho_p$). In Fig. 5, A, B, C and D are simulations of potential variations of single pulse voltage (a) for $\rho_p=74.0, 35.0, 14.8$ and $3.7 \, \Omega \cdot \text{cm}$ respectively. The specific polarization resistance, $\rho_p$ and net capacitance, $c_{DL}$ are constant, when a certain electrolyte solution is chosen. The pulse width is plotted to 200\,\mu\text{sec} to compare with the experimental results.

Fig. 4 Groove Patterns with Various Pulse Durations. Bright part shows electrochemically-machined groove and dark part shows untreated metal surface. In 3.5M NaNO₃ solution with 4.0V for 1 min.

![Groove Patterns with Various Pulse Durations](image)

In case of A, if the voltage pulse of 200\,\mu\text{sec}-pulse width is applied, this pulse width is close to the time-constant. From experimental result, resulting after a polishing time of 10min, there is no polishing effect on metal surface even though the potential variation signal represents the charging and discharging of DL capacity. Hence, the experimental application of pulse width of the same as the time-constant is found to be inadequate. For more sufficient electrochemical reaction, series of pulse width over time-constant should be applied like B, C and D as shown in Fig. 5. Fig. 5 (b)
shows the experimental potential variation for 2.4M H$_2$SO$_4$ and 5.9M H$_3$PO$_4$ electrolyte, and 1cm$^2$ of electrode area. The result is in agreement with the simulation, but does not represent the ‘ideal’ charging and discharging of DL capacity. From comparison Fig. 5 (a) with (b), $\rho_p$, representing the closest charging and discharging variation, can be obtained. A value of 14.8$\Omega$·cm is the closest $\rho_p$ for this electrolyte, so the time-constant is defined as 50$\mu$sec. Therefore the pulse width over 50$\mu$sec should be applied for more electrochemical reaction.

5. Conclusion

From the machining resolution analysis, the experimental resolution becomes lower than prediction owing to the disturbance of the movement of ion charge by the forced electrolyte circulation. To obtain approximate polarization resistance in electrochemical polishing of micro grooves, the new method of comparison of ideal and experimental potential variations, indicating charging and discharging of electrical DL, is applied in this study. The experimental potential variation for 2.4M H$_2$SO$_4$ and 5.9M H$_3$PO$_4$ electrolyte is in close agreement with the simulation with $\rho_p$ of 14.8$\Omega$·cm, so the time-constant is defined as 50$\mu$sec. Therefore the pulse width over 50$\mu$sec should be applied for more electrochemical reaction. From this result, some applications with pulse electrochemical process are shown in Fig. 6.

Fig. 6 Some Applications of Pulse Electrochemical Process. A Hole with over charged DL capacity (a), Comparison of EMM with rough groove surface and ECP with smooth groove surface (b), 250$\mu$m-diameter hole with various pulse width in DHF solution (c)

References