

On the Simulation of Electrochemistry Aspect of Electrochemical Spark Micromachining Process

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Abstract: Electrochemical spark micromachining (ECSMM) process, an advanced machining process is investigated to understand process mechanism. The material removal mechanism in ECSMM is a complex phenomenon due to its multiphysics and transient nature. Experimental measurements of online current and voltage have been performed simultaneously. Different sequential operational stages in one single spark cycle have been identified in the light of the transient measurements. The Semiempirical electrical impedances during these identified operational stages have been formulated and compared with those derived by using measured online current and voltage data. Only the impedance results during electrochemical phase in a single spark cycle have been reported here. In case of ECS, considering the kinetics at the electrolyte and electrode interfaces, the effective equivalent circuit is derived. The charge transfer resistance in the equivalent circuit during the electrochemical phase is found by performing impedance spectroscopy using COMSOL multiphysics modeling software. For this 1-d model of the electrochemical process is developed using secondary current distribution. It is for the first time that COMSOL study has been attempted in analyzing the physics behind the material removal phenomenon mainly during the electrochemical operational phase of ECSMM. The modeled and measured impedances show close similarities.

1 INTRODUCTION

Electrochemical spark micromachining (ECSMM) process is an advanced machining process in which sparking is responsible for machining of wide variety of materials. The process is investigated in the holistic approach to understand process mechanisms. Material removal mechanism in particular is a complex phenomenon due to its multiphysics nature. The sparking during the machining process is not continuous as it is conventionally identified; rather it is a repetitively occurring discrete and complex phenomenon. Complexity arises primarily due to the presence of various physio-chemical phases involved in forming the discrete sparking. Moreover electrochemical systems are known to exhibit complex non-linear behavior. These nonlinearities arise due to electro hydro dynamism, ionic reactions, bubble generation, their growth and their breakdown phenomena, with material removal over a finite area as a final result. The spark formation cycle is a series of such activities. Also sparks are non-thermal in

nature as opposed to the theoretical assumption that spark is a heat source for material removal to take place. In the existent literature, spark energy is considered to be of thermal nature. Also the thermal analysis and material removal are considered to be due to this thermal source (Basak & Ghosh, 1992; Basak & Ghosh, 1996; Jain, Dixit & Pandey, 1999). But in a separate transient temperature study using pyrometer (Kulkarni, 2009), it has been found experimentally that the spark is a non thermal discharge. Through this study, it is established that the process is similar to a repeated sparking/discharge similar to that of the breakdown of the hydrogen gas bubble isolating the tool tip from the surrounding electrolyte. Consequent to this finding, electrical impedance in each sequential stage of a single spark cycle is modeled based on the physics of each stage respectively. This semiempirical impedance is compared against the impedance computed by taking the ratio of the measured online, transient and synchronized voltage and current data during single spark formation (Kulkarni, 2017). The modeled and

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measured impedances show close similarities. Findings of the impedance results during electrochemical phase during a single spark cycle have been reported here.

It is for the first time that COMSOL study has been attempted in analyzing the physics behind the mechanical removal phenomenon mainly during the electrochemical operational phase/stage in working of ECSMM. Hence no literature is available with the research findings with which comparison of results can be performed.

2 EXPERIMENTAL

The time varying online process current is measured in synchronization with the machining supply voltage using digital storage oscilloscope (DSO, Hameg 1008) by 'resistive shunt method'. For this, a 1 Ω resistance is connected in series with cathode (made up of copper wire of diameter 100 μm with its tip partially dipped in the NaOH electrolyte) and ground of the power supply to the ECS cell. The time varying voltage across this resistance is the direct measure of the time varying process current. These synchronized current and voltage waveforms are saved on the control PC via RS 232 connectivity module of the DSO. Each waveform contains 2000 samples of the voltage and current readings. The current waveform contains many spark cycles (Kulkarni, 2013; Kulkarni, 2015).

3 SEQUENTIAL OPERATIONAL PHASES OF ECSMM PROCESS IN THE LIGHT OF ONLINE, TRANSIENT CURRENT

The formation of spark happens through series of chemical and physical processes. When a voltage (enough to form spark) is applied across the electrolyte cell (containing electrolyte with cathode and electrode dipped partially in it with workpiece on which the micromachining is intended), mainly following series of events take place (Kulkarni, 2013; Kulkarni, 2015):

1. Electrochemical phase giving rise to oxidation and hydrogen gas generation.
2. Hydrogen and vapor bubbles formation, coalescence and bubble growth during pool boiling, slowly covering the tool tip.

3. Tool tip isolation, momentary 'virtual switch off' phase.
4. Instantaneous generation of high electric field which causes sparking due to hydrogen breakdown.
5. Drifting of energetic electrons towards the workpiece due to potential gradient and subsequent material removal from the workpiece kept near the tool tip due to this 'electron gun'.
6. Reestablishment of tool-electrolyte contact leading to a 'virtual switch on' phase.
7. steps 1-6 begin all over again.

Following section establishes the theoretical background behind electrochemical phase operation. It also identifies major electrical parameters responsible for the instantaneous current contribution in that phase of operation during the single spark formation.

3.1 Electrochemical Phase

When the machining supply to the electrolyte cell is applied in the proper polarity, (i.e. positive terminal connected to graphite anode and negative terminal to copper cathode) electrochemical action starts. Electrochemical reactions that occur at the electrode-electrolyte interface continuously supply electrons from cathode to solution and solution to anode. This is called as the 'migration' state of the ECSMM process and causes the electronic current. The anodic and cathodic reactions occur together with reduction in electrolyte. These liberated positive ions move towards cathode and negative ions move towards anode and causes the ionic current. Ionic and electronic current together form the **average current** and it is of the order of 100 – 200 mA as is measured. Major other (transient) current contributing circuit elements during this phase are investigated in the next section.

3.2 Current Contributing Elements during Electrochemical Phase

Electrolyte resistance, double layer capacitance, polarization resistance, and charge transfer resistance are the elements those contribute to the overall electrochemical reactions during electrochemical phase and hence the **instantaneous current**, as described below.

3.2.1 Electrolyte Resistance

In an electrochemical cell, bulk solution resistance is a significant factor. In this experimental situation, estimation of NaOH solution resistance is estimated by taking the inverse of the conductivity. But in real situations, it depends on the geometry of the solution (container), its temperature, etc. It is found that the effect of electrolyte resistance is dominant during electrochemical and bubble growth phases only.

3.2.2 Double Layer Capacitance

An electrical double layer exists on the interface between an electrode and its surrounding electrolyte. This double layer is formed as ions from the solution 'stick on' the electrode surface. The charged electrode is separated from the charged ions. The separation is very small, of the order of angstroms. Charges separated by an insulator form a capacitor. Practically the capacitance such formed is of the order of 20 to 60 μF per cm^2 area of the electrode. Figure 1 shows the process of double layer formation. All the electrolyte processes take place at the electrode-electrolyte interface. The structure of the double layer is similar to an electrical capacitor formed by a dielectric of thickness of about an ionic radius, i.e. 50 nm. Figure 1 A shows the formation of inner Helmholtz plane (IHP), outer Helmholtz plane (OHP) and the electrode with an excess of negative charge. Figure 1 B shows the localization of the excess charges and Figure 1 C shows the potential gradient formed.

3.2.3 Polarization Resistance

Whenever the potential of an electrode is forced away from its value at 'open-circuit', it is referred to as polarizing the electrode. When an electrode is polarized, it causes current to flow through electrochemical reactions that occur at the electrode surface. The amount of current is controlled by the kinetics of the reactions and the diffusion of reactants both towards and away from the electrode. In the case of ECS cell, the diffusion of reactants is absent. Hence only the kinetics of the reactions plays the major role.

3.2.4 Charge Transfer Resistance

Another resistance is formed by a single kinetically controlled electrochemical reaction. In the case of ECS, the reactions occurring at the cathode-electrolyte interface are of concern and form the basis

of the analysis. The kinetics of the charge transfer depends on the kind of reaction, the concentration of reactants, the potential, and many other factors.

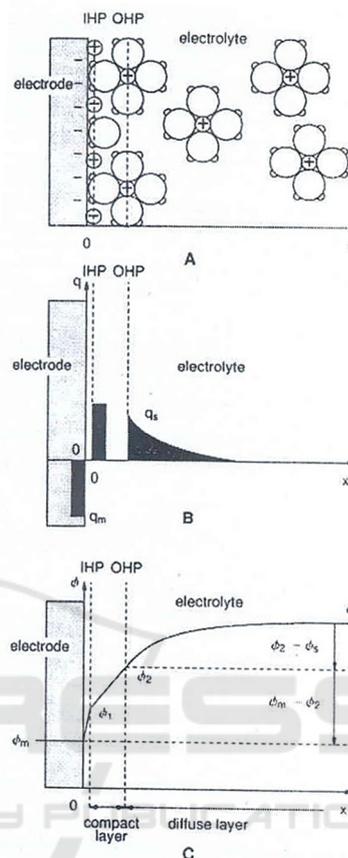


Figure 1: This Process of the double layer formation (Kulkarni, 2013).

Figure 2 shows the various potential drops formed during a general electrochemical cell with an applied supply voltage. The supply voltage overcomes the following potentials:

- The electrode potential,
- The activation over potential,
- Ohmic potential drop,
- Concentration over potential (not of much relevance in ECS) and
- The potential due to resistance of electrolyte.

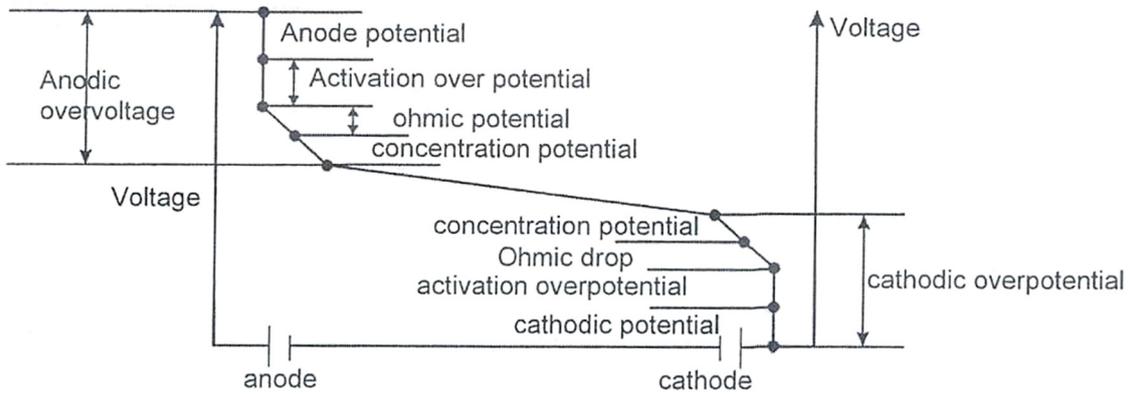


Figure 2: Various potential drops during a general electrochemical cell (Kulkarni, 2013).

4 EQUIVALENT CIRCUIT DURING ELECTROCHEMICAL PHASE

Figure 3 shows the circuit parameters for a general electrochemical cell. In the case of ECS, the kinetics at the anode electrode is neglected due to the non consuming electrode material.

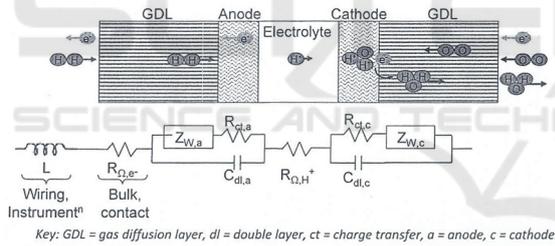


Figure 3: Circuit parameters for a general electrochemical cell (Kulkarni, 2013).

4.1 Time Varying Impedance during Electrochemical Phase

Neglecting the wiring inductance, bulk contact resistance, Z_w , the effective equivalent circuit during electrochemical phase is as shown in Figure 4.

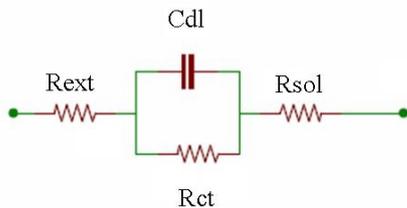


Figure 4: Electrical equivalent circuit in the electrochemical stage of ECS process.

The time varying impedance $Z(t)$ during electrochemical phase (neglecting R_{ext}) is shown by equation (1) below, where, R_{sol} is Electrolyte resistance, C_{dl} is Double layer capacitance, and R_{ct} is Charge transfer resistance

$$Z(t) = R_{sol} + \frac{R_{ct}}{1 + j\omega R_{ct} C_{dl}} \quad (1)$$

Butler-Volmer and Tafel (an equation in electrochemical kinetics relating the rate of an electrochemical reaction to the overpotential) expressions (<https://www.gamry.com/application-notes/EIS/basics-of-electrochemical-impedance-spectroscopy/>, retrieved 26 May 2012) are used to derive electrode kinetics for the charge transfer reactions.

In the Secondary Current Distribution interface, the electrochemical reactions are described as a function of the overpotential. The interface uses several relations for the charge transfer current density and the overpotential. The most general expression is of Butler-Volmer type:

$$i_{loc,m} = i_0 \left(\exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(\frac{-\alpha_c F \eta}{RT}\right) \right) \quad (2)$$

where $i_{loc,m}$ denotes the local charge transfer current density for reaction m , i_0 the exchange current density, α_a the anodic transfer coefficient, α_c the cathodic charge transfer coefficient, F the Faraday constant, and R the universal gas constant. On a single electrode the Tafel equation can be stated as:

$$\eta = \pm A \times \log_{10}(i/i_0) \quad (3)$$

where the plus sign under the exponent refers to an anodic reaction, and a minus sign to a cathodic reaction, and η is overpotential (V), A is "Tafel slope", (V), i is current density (A/m^2) and I_0 is "exchange current density" (A/m^2).

Butler-Volmer (B-V) equation has been used to estimate the charge transfer resistance with appropriate boundary conditions. The interfaces define two dependent variables of potentials. The conduction of current in the electrolyte is assumed to take place through transport of ions while electrons conduct the current in the electrode.

4.2 Impedance Spectroscopy using COMSOL 4.2 Multiphysics

The ‘electrochemical model’ in COMSOL 4.2 software is used to solve 1-d simulation of the electrode kinematics in the ECS cell using the ‘secondary current distribution’ physics built-in in COMSOL (<https://doc.comsol.com/5.3/doc/com.comsol.help.echem/ElectrochemistryModuleUsersGuide.pdf>, retrieved on 26 May 2012). Figure 5 shows the simulated electrolyte potential distribution in the cell. The electrolyte voltage in the cell is seen around 75×10^{-6} V at a distance of $22 \mu\text{m}$ away from the cathode.

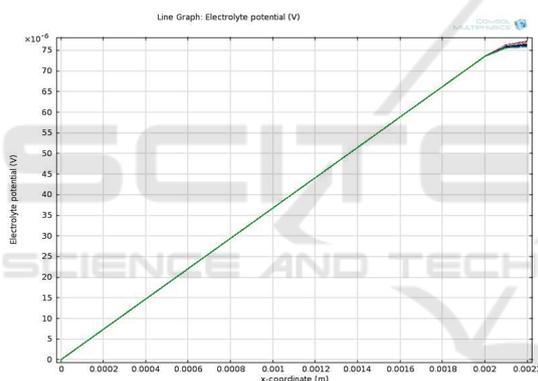


Figure 5: Electrolyte potential distribution in the cell (Kulkarni, 2013).

Figure 6 gives the Nyquist plot generated by COMSOL software by using the perturbation current of 5 mA. It gives R_{ct} around $14.8 \times 10^{-6} \Omega$. The $R_{ct} \times C_{dl}$ time constant is very small and is of the order of few hundreds of ns. That means the electrochemical reactions are very fast. The hydrogen bubble growth due to pool boiling phenomenon soon takes over (which is not the scope of this paper).

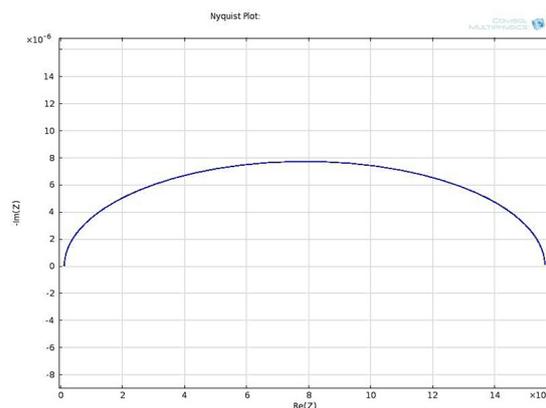


Figure 6: Nyquist plot generated by the COMSOL 4.2 software (Kulkarni, 2013).

5 CONCLUSIONS

- The important intermittent sequential phases of the process have been identified and analyzed. Repeated formations of spark happen through series of chemical and physical processes in phases. These are: electrochemical action, bubble formation, coalescence and growth of bubble during pool boiling slowly covering the tool tip, tool tip isolation leading to a momentary ‘virtual switch off’ situation, instantaneous application of high electric field causes sparking of hydrogen breakdown, reestablishment of tool-electrolyte contact leading to ‘virtual switch on’ situation, drifting of energetic electrons towards the workpiece due to potential gradient.
- The instantaneous process current comprises of current due to these sequential events. The electrical impedance during each phase of operation varies. Of these phases, the electrochemical action phase is the fastest process.
- Charge transfer kinetics at anode electrode is neglected. This is minimized by the design of the anode electrode.
- The charge transfer resistance in the equivalent circuit during the electrochemical phase is found by performing the impedance spectroscopy. It is done using COMSOL Multiphysics modeling software. For this 1-d model of the electrochemical process is developed using secondary current distribution. The time constant due to the parallel combination of the double layer capacitor and the charge transfer resistance is of the order of thousands of ns. That means the formation of the double layer capacitance and

charge transfer resistance happens within thousands of ns time.

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