Machining of Molybdenum by EDM-EP and EDC Processes

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Abstract. Molybdenum metal (Mo) can be machined with conventional tools and equipment, however, its refractory property tends to chip when being machined. In this study, the nonconventional processes of electrical discharge machining (EDM) and electro-polishing (EP) have been conducted to investigate the machining of Mo metal and fabrication of Mo grid. Satisfactory surface quality was obtained using appropriate EDM parameters of \( I_p \leq 3 \text{A} \) and \( T_{on}< 80 \mu \text{s} \) at a constant pulse interval of 100\( \mu \text{s} \). The finished Mo metal has accomplished by selecting appropriate EP parameters such as electrolyte flow rate of 0.42m/s under EP voltage of 50V and flush time of 20 sec to remove the recast layer and craters on the surface of Mo metal. The surface roughness of machined Mo metal can be improved from \( R_a \) of 0.93\( \mu \text{m} \) (\( R_{max} = 8.51\mu \text{m} \)) to 0.23\( \mu \text{m} \) (\( R_{max} = 1.48\mu \text{m} \)). Machined Mo metal surface, when used as grid component in electron gun, needs to be modified by coating materials with high work function, such as silicon carbide (SiC). The main purpose of this study is to explore the electrical discharge coating (EDC) process for coating the SiC layer on EDMed Mo metal. Experimental results proved that the appropriate parameters of \( I_p = 5 \text{A} \) and \( T_{on}=50 \mu \text{s} \) at \( T_{off}=10 \mu \text{s} \) can obtain the deposit with about 60\( \mu \text{m} \) thickness. The major phase of deposit on machined Mo surface was SiC ceramic, while the minor phases included MoSi₂ and/or SiO₂ with the presence of free Si due to improper discharging parameters and the use of silicone oil as the dielectric fluid.

1. Introduction
Molybdenum (Mo) metal is a refractory metal with characteristics of high melting point, great strength, good thermal/electrical conductivity and low thermal expansion coefficient. It has been widely applied in electrical and electronic devices, material processing, glass manufacturing, high-temperature furnaces, aerospace and defence applications. Although Mo metal and its alloys can be machined by common metal removal processes, its superior mechanical properties pose difficulty to high-quality surface polishing due to the very high temperature reached by the cutting edges of machining tool during processing.

Electrical discharge machining (EDM) is an electro-thermal process which removes materials by melting and vaporization without direct contact with the workpiece surface. Hence, EDM can be employed to process difficult-to-machine materials, high-strength temperature-resistant alloys with complicated geometrics [1-3]. However, care must be taken when EDMing molybdenum and its alloys
because the surface zone frequently contains a recast layer. This structure is susceptible to micro-
 cracking and needs improving by mechanical or chemical polishing prior to placing the part in service
 [4]. A technique of electro-chemical machining (ECM) named electro-polishing Electro-polishing (EP)
 is one of the surface treatment processes which can be employed to finish the machined Mo metal.

The EP process involves an anodic dissolution or electrochemical reaction between workpiece and
 electrode. It improves the machined surface to microscale or nanoscale smoothness through leveling
 and brightening. The proposed mechanisms include mass transfer mechanism, current distribution,
 shape control, and passive oxide film behaviours [5]. According to the partial inter-granular corrosion
 theory, Lee et al. investigated the corrosion resistance properties of 316L stainless steel and proved
 that EP can enhance corrosion resistance significantly [6]. Hocheng et al. examined EP parameters
 using different electrode feeding rates, rotating electrodes and disks of various shapes, and explored
 new applications of EP [7-8]. For decades, machined Mo metal has been applied in vacuum devices
 [9]. It can lead to hot electron emission from the Mo grid and destroy the grid cut-off characteristics
 of the advanced microwave tube, rendering it unstable [10]. To alleviate this undesirable effect, the
 Mo grid needs to be coated with materials of high work function, such as silicon carbide (SiC)
 \( \varphi = 4.4eV \) [11-12]. The objective of this study is to investigate the surface quality of Mo metal by
 using EDM, EP and EDC process separately and to obtain the appropriate combination of their
 working parameters.

2. Experimental setup and procedure
The EDM/EDC processes were carried out using the conventional Die-EDM equipment shown in
 Figure 1(a). In EDM, a pure copper electrode was employed to machine 99.9% Mo metal in kerosene;
 while in EDC, an artificial graphite electrode (IG-11, Toyo Tanso, Japan) was utilized to coat the Mo
 metal surface in silicone oil.

Table 1 lists the properties of the materials used in this study. The material removal rate (MRR) of
 the Mo metal and the tool wear rate (TWR) of electrodes before and after processing were measured
 using a fine balance (accuracy:0.0001g). A mixed signal oscilloscope (DL-1200A, Yokogawa, Japan)
captured the discharge waveforms during the EDM process. The EP treatment was operated in a
 commercial machine (LectroPol-5, Struers™, Denmark) as shown in Figure 1(b). The commercial
electrolyte (A3, Struers™) made up of methanol (60.36vol%), 2-butoxyethanol (55.49vol%), perchloric acid (4.51 vol%) and H₂O (3.00 vol%) was used. During polishing, the electrolyte is pumped onto the surface of the workpiece at a specific flow rate and voltage. The anodic polarization (V-I) curve was monitored by a potentiostat (Parstat 2263). The morphologies and elemental distributions of the machined surfaces were examined by SEM/EDS (JSM-6360LV, Hitachi, Japan). The deposit on Mo metal was analyzed by an X-ray diffractometer (XRD-6000 Shimadzu, Japan) to verify the phases under various treatment conditions. The surface roughness (Ra) of machined surface was measured by using a contact type stylus based surface roughness tester, 2D Surfcooder (E35A, Tokyo Seimitsu, Japan).

**Table 1** Properties of materials used in EDM/EDC processes.

| Material   | Density (g/cm³) | Melting Point (°C) | Boiling Point (°C) | Thermal Conductivity (W/mK) | Specific Heat (J/kgK) | Tensile Strength (MPa) | Young's Modulus (GPa) |
|------------|----------------|--------------------|--------------------|----------------------------|-----------------------|------------------------|-----------------------|
| Mo         | 10.22          | 2617               | 4612               | 138                        | 255                   | 415                    | 330                   |
| Cu         | 8.96           | 1083               | 2567               | 391                        | 385                   | 215                    | 110                   |
| Graphite   | 1.90           | 3852               | 4250               | 139                        | 713                   | 29.4                   | 12                    |

| Dielectric Fluid | Molecular Formula | Density (g/cm³) | Flash Point (°C) | Thermal Conductivity (W/mK) | Dielectric Breakdown (MV/m) | Viscosity (mm²/s) | Surface Tension (mN/m) |
|------------------|-------------------|----------------|------------------|-----------------------------|---------------------------|--------------------|------------------------|
| Kerosene         | C₁₀H₂₆             | 0.78–0.81      | 101              | 0.15                        | 20                        | 2.4                | 28                     |
| Silicone Oil     | (C₂H₆O₂Si)₃       | 0.96           | 316              | 0.10                        | 10–15                    | 1000               | 21.2                  |

3. Result and discussion

3.1. EDM of Mo metal

The electrode polarity, discharge current (I₀) and pulse duration (T_on) of EDM parameters affect the machining quality soundly. Figure 2 displays the effect of polarity of electrode on MRR and TWR of Mo metal under constant I₀=0.4A and T_on=100μs. As seen in Figure 2(a), the copper electrode with positive polarity (i.e., acathodicworkpiece) achieved high MRR while maintaining low TWR. In other words, when using an anodic electrode, the discharge energy can be effectively employed for removal of Mo metal, while the carbon coating on the electrode surface offers protection against rapid electrode wear [4]. However, the opposite was observed when using an electrode with negative polarity. As seen in Figure 2(b), the MRR of workpiece was much reduced as a result of the carbon layer protection, while the TWR of electrode increased more than three folds as compared with that for an anodic electrode, shown in Figure 2(a). Sufficient discharge energy favored the dissociation of kerosene to produce cathodic carbon ions. Thus, anodic workpiece would attract the carbon ion to form carbon layer on the surface of workpiece during the electrical discharge. Figure 3 compares surface roughness on EDMed Mo metal obtained using electrodes of positive and negative polarity. As can be seen, lower surface roughness of machined Mo metal was obtained by a negative electrode (i.e., an anodic workpiece) while a coarse machined Mo surface was obtained by a positive electrode (i.e., a cathodicworkpiece).
Figure 2 Effect of (a) positive and (b) negative polarity of electrode on MRR/TWR of Mo metal.

Figure 3 Effect of electrode polarity on surface roughness of machined Mo metal.

In order to obtain an acceptable surface quality of Mo metal via EDM process, assigned the polarity of electrode as negative. However, in such case, the discharge parameters need to be modulated to reduce electrode wear. Figure 4 displays the MRR and TWR obtained under various discharge currents ($I_p=0.4-9A$) and pulse durations ($T_{on}=1-240\mu s$). As can be seen, when $I_p<6A$, MRR was always lower than TWR (cf. Figure 4 (a) and (b)), revealing that low discharge energy yielded poor material efficiency but caused rapid wearing of the electrode. It was ascribed to the high melting point of Mo metal protected by carbon layer. When $I_p\geq 6A$ and in the case of $T_{on}\leq 80\mu s$, MRR and TWR showed identical trend of increase. In this stage, each discharge column continued expanding and exploding periodically between electrode and workpiece. The weak bonding protective carbon layer on anodic workpiece was easily destroyed as a result of severe electron bombardment and thus resulted in the similar weight loss. On the other hand, when $T_{on}>80\mu s$, MRR declined slowly while TWR remained unchanged. Such changes can be attributed to the lower discharge energy density under long pulse duration which caused inefficient machining of Mo metal.
Figure 4 Effects of discharge current and pulse duration on MRR and TWR of Mo metal.

Figure 5 presents the variations of surface roughness of EDMed Mo metal under different discharge currents (Ip) and pulse durations (Ton). Although Ra at Ip = 0.4A was kept small for all Ton, the material removal efficiency was also low. On the other hand, high Ip (> 0.4A) yielded rough surface and long Ton (> 20 μs) deteriorated the surface quality. Considering the machining time of refractory Mo metal with an acceptable surface quality, the EDM parameters combination of Ip ≤ 3A and Ton = 20 μs was adopted in the subsequent experiments.

Figure 6 displays the SEM images of Mo metal surface before and after EDM processes (Ip = 3A, Ton = 20 μs). As can be seen, the surface roughness after EDM increased from Ra = 0.17 μm to Ra = 0.93 μm due to formation of the recast layer, craters and micro-cracks on the EDMed Mo metal, thus necessitating surface finishing.
3.2. **EP of EDMed Mo metal**

Figure 7 shows how surface roughness variations of machined Mo metal by EP voltage. As can be seen, surface roughness of Mo metal EDMed was apparently improved from $Ra = 0.93 \mu m$ to a minimum value of $0.36 \mu m$ when EP voltage = 50V. Meanwhile, it showed that $R_{max}$ on EPed Mo metal dropped rapidly from $8.5 \mu m$ to $5.3 \mu m$ when EP voltage = 10V. During EP, discharging will occur at the sharpest point of crater on the EDMed surface, which results in a levelling effect. As a result, the rugged surface then becomes smooth and the dissociation of material will slow down. Therefore, the minimum $Ra$ of EDMed Mo metal under flush time of 10 sec and electrolyte flow rate of 0.42 m/s can be obtained when EP voltage = 50V. During EP process, bubbles formed at the anode due to dissociation, which increased the resistance of electrolyte, resulting in pitting on the workpiece surface. The stagnant electrolyte will further accelerate this phenomenon. Therefore, flowing of electrolyte is essential for achieving a good-quality EP surface. In this study, the flowing rate of electrolyte ranged from 0.42 to 1.05 m/s.

![Figure 7](image7.png) **Figure 7** Effect of EP voltage on EDMed Mo metal surface roughness.

![Figure 8](image8.png) **Figure 8** Effect of EP flush time on surface roughness of EDMed Mo metal.

Figure 8 illustrates the improvement in surface roughness under EP with different flush durations. As can be seen, the average surface roughness was reduced to $0.46 \mu m$ ($R_{max} = 3.04 \mu m$) after 5sec and approached the minimum value of $0.29 \mu m$ ($R_{max} = 1.70 \mu m$) when flush time reached 20sec. As the EDC process would further modify the EPed Mo, the interactive influences of EP voltage, flush time and electrolyte flow rate were ignored in this stage and hence chose flush time of 20sec under EP voltage = 50V and electrolyte flow rate = 0.42 m/s for further investigation.

3.3. **EDC of Mo metal**

The graphite and silicone oil adopted instead of copper and kerosene, respectively because their ion sources of carbon and silicon can confer a SiC coating on the EDMed Mo metal surface. In addition, during the EDM/EDC process, the higher the discharge current, the larger the discharge energy and explosive force will be, thus yielding a coarse machined surface. Hence, to explore the effect of discharge current and pulse duration, surface roughness of the coated Mo metal obtained under EDC parameters $I_p=1-13A$, $T_{on}=1-200\mu s$, $T_{off}=10$ and 50\mu s were examined.

Figure 9 shows the MRR of Mo workpiece and TWR of graphite electrode under EDC with different discharge currents and pulse durations. When $I_p > 1A$ and $T_{on} > 10\mu s$, the MRR and TWR were negative, indicating that both workpiece and electrode gained, instead of lost, weight when discharge energy increased. The increase in their net weights is not only due to the polarity effect
(TWR>MRR), but also contributed by the layer of surface deposit made up of ions from graphite, silicone oil and Mo metal during electrical discharge.

Figure 9 Effects of Ip and Ton on MRR and TWR under EDC.

Figure 10 shows the surface roughness of various EDCed Mo metal. As can be seen, surface roughness on EDCed Mo varied with discharge current and pulse duration. The higher the Ip and Ton of EDC process, the coarser the EDCed Mo metal. Between 50μs and 100 μs, the Ra reached the maximum for different discharge currents. Thereafter, Ra declined with further increase in energy density. According to these results, appropriate EDC parameters should be low Ip and long Ton.

Figure 11 displays the SEM images of Mo surface after EDC process (Ip=5A, Ton=200μs, Toff=10μs). As can be seen, the EDCed Mo metal surface has a fine grain texture with average surface roughness of 3.17 μm (Rmax=4.16μm). XRD proves that the layer is SiC phase with minor silica. Figure 12 demonstrates the cross-sectional view of EDCed Mo metal. The thickness was approximately 60μm as shown in Figure 12(a). Results of EDS analyses on the elemental distribution of the coating deposited on Mo metal, as indicated in Figure 12(b), confirmed that the coating comprised mainly Si and C with few oxygen ion originated from graphite and silicone oil, respectively. Nevertheless, Mo did not found on the surface of the coating layer.
Figure 12 (a) SEM image of cross-sectional view of EDCed Mo metal and 
(b) elemental distribution by EDS analyses

4. Conclusions
The present study demonstrates that the refractory Mo metal has successfully machined by EDM, finished by EP and surface modified by EDC processes. According to the results obtained, the following conclusions include as follows:

1) Machining of Mo requires high energy density due to its high melting point. However, the polarity of electrode and workpiece can alter the quality of machining. For better-machined surface roughness and lower electrode wear rate, workpiece of positive polarity (+) and low discharge current should be used.

2) The appropriate EDM discharge current (I_p) and pulse duration (T_on) for machining anodic Mo metal should be $\leq 3$ A and $< 80\mu s$, respectively at $T_{off}=100\mu s$.

3) EP of EDMed Mo metal undervoltage=50V, flush time=20sec and electrolyte flowing rate=0.42m/s improved surface roughness from $Ra =0.93\mu m$ ($R_{max}= 8.51\mu m$) to $Ra = 0.23\mu m$ ($R_{max}= 1.48\mu m$), evidencing the effectiveness of EP in enhancing surface quality.

4) The EDMed Mo metal surface has successfully modified by EDC process using graphite as electrode and silicone oil as dielectric fluid. The appropriate parameters are $I_p =5A$ and $T_{on}=50\mu s$ at $T_{off}=10\mu s$. The deposit on the EDCed surface comprised mainly the SiC ceramic phase.

References
[1] SortinoM, TotisG andProsperiF2013 *J. Mater. Process. Technol.* 2131179
[2] OjhaK, GargRK and SinghKK2010 *J. Miner. Mater.Charact.Eng.* 9(8)709
[3] AbbasMM, SolomonD Gand BahariMF 2007 *Int. J. Mach.Tool. Manuf.* 47 (7-8)1214
[4] Demellayer R and RichardJ2013 *Procedia CIRP* 689
[5] Rokicki R and Hryniewicz T 2012 *Trans. Inst. Met. Finish.* 90(4)188
[6] Lee SJ andLaiJJ2003 *J. Mater. Process. Technol.* 140206
[7] Hocheng H andPaPS2003*J. Mater. Process. Technol.*120 6
[8] Hocheng Hand PaPS.2003*J. Mater. Process. Technol.* 142 203
[9] Lawrence R. 2004*IEEE Trans. Plasma Sci.*32(3)1277
[10] JiangJ, JiangB, Ren C, Zhang F, Feng T and Wang X 2006*Vac.*80537
[11] Tang H Tan S, Huang Z, Dong S and Jiang D2005Surf. Coat. Technol. 197161
[12] Wang J, Wu XM and Zhuge LJ 2007*Vac.*81890