Studies in Pulsed Electrochemical Micro-Drilling on Titanium Alloy with an Addition of Complexing Agent to Electrolyte

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Abstract

Electrochemical Micro-Machining (ECMM) is an emerging technique for fabrication of micro and nano-features on difficult-to-machine materials for advanced engineering applications. With ECMM, it is possible to fabricate complex features with practically zero tool wear and no residual stresses on the machined surface. At IIT Bombay, we have developed an ECMM experimental set-up in-house in order to investigate the micromachining of high strength alloys. In this work, we present the effect of adding a complexing agent to the electrolytic solutions on the overcut during micro-drilling of Titanium alloy grade-5 (Ti6Al4V). The influence of different electrolytic concentration with and without the complexing agent on overcut during drilling on Ti6Al4V is studied. The formation of electrolysis precipitates, especially TiO_2 has been found to affect the accuracy of the fabricated micro holes. In order to address the issues, a complexing agent i.e., Ethylenediaminetetraacetic acid disodium salt (EDTA) is added in electrolytic mixture of NaCl and $NaNO_3$. EDTA is a non-toxic, non-corrosive, and environmental friendly complexing agent, when compared to the acids. The quality of micro-holes produced has been studied in the presence of the complexing agent and its effectiveness is assessed. It has been concluded that the micro holes produced in electrolyte with EDTA have better dimensional characteristics.

Keywords: Electrochemical Micro-Machining, micro-hole, complexing agent, overcut, titanium alloy

1. INTRODUCTION

Electrochemical Micro-Machining (ECMM) is a promising technique for fabricating Micro and Nano features on hard–to-cut materials as it dissolves (erodes) the material at atomic level through electrolysis reactions. In the past few decades, ECMM technique has attained notable importance because of its advantages such as no tool wear, no residual stress in work-piece and high material removal rates (MRR). It allows machining of materials such as copper alloys, super alloys, stainless steel and titanium and its alloys, irrespective of their physical and chemical properties [1]. Among metal alloys, titanium alloys have unique properties like excellent strength to weight ratio at high temperatures, biocompatibility and high corrosion resistance. Titanium based alloys have found wide applications in the fields of aircraft industry, bio-medical devices, MEMS, etc. [2][3]. However, excellent mechanical properties make processing of Titanium alloys very challenging. During ECMM of titanium in oxygen containing media such as air or water, a thin titanium oxide film forms on its surface. When Titanium and its alloys are dissolved in passive electrolytes, they form a film of TiO_2 on the surface, which is insoluble and hydrophilic in nature. This film adheres to the inside surface of drilled hole and blocks the electrolytic flow, thereby restricting further material dissolution [4]. For uniform dissolution of material, a proper electrolyte must be selected.

An ideal electrolyte should have high conductivity, non-corrosiveness, low viscosity and must be environmentally friendly. Aqueous solutions of $NaNO_3$, NaCl, NaBr, etc. are generally used as electrolytes for ECMM [5]. The electrolyte used in ECMM can be passive and non-passive electrolytes. $NaNO_3$ is a passive electrolyte having oxidizing anions and thus reduces the rate of dissolution due to formation of an oxide layer. NaCl is a non-passive electrolyte having aggressive anions and it removes material at faster rates than passive electrolytes [6]. In ECMM, accuracy will be affected due to formation of precipitates and stray current effects [7]. To dissolve precipitates, acids like Sulphuric acid are used as electrolytes but they are toxic and highly corrosive in nature [8]. Alternatively, a complexing agent is added to the electrolyte to avoid the formation of insoluble precipitates [9]. These complexing agents are non-toxic and non-corrosive compared to acids, and thus safe for the operator.

In this study, the effect of adding complexing agent to the electrolytic solution on radial overcut of micro-holes produced on Titanium grade-5 sheet is investigated. The electrolytic solution used is a mixture of NaCl and $NaNO_3$. Ethylenediaminetetraacetic acid disodium salt (EDTA) is selected as a complexing agent because it has the ability to form complex compound with most of the metal ions. Therefore, radial overcut with and without addition of EDTA in the electrolyte has been analyzed.

2. EXPERIMENTAL SETUP

An ECMM setup has been developed at IIT Bombay for the electrochemical system consists of Tool Positioning System, DC Power Supply, Pulse Generation System and Electrolytic Supply System. An Arduino micro-controller system is used to control and operate these systems. The tool positioning system consists of a stepper motor controlled by the Micro-controller, which moves the tool along the Z-Axis with variable feed. A DC Power Source is utilized which has a 0-60V Voltage range and 0-5A Current rating. The MOSFET (IRF530N) and the current sensor are connected to the circuit as shown in Fig. 1 to generate pulses at frequencies up to 60 KHz and measure the current respectively. The tool is connected to the negative terminal while workpiece is connected to positive terminal. The electrolyte system consists of a tank and a submersible pump

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which pumps electrolyte on the machining surface through a nozzle. The electrolyte then returns to the tank through a filter which filters the precipitates. The Inter-electrode gap is maintained via real time feedback from the electrolysis zone.

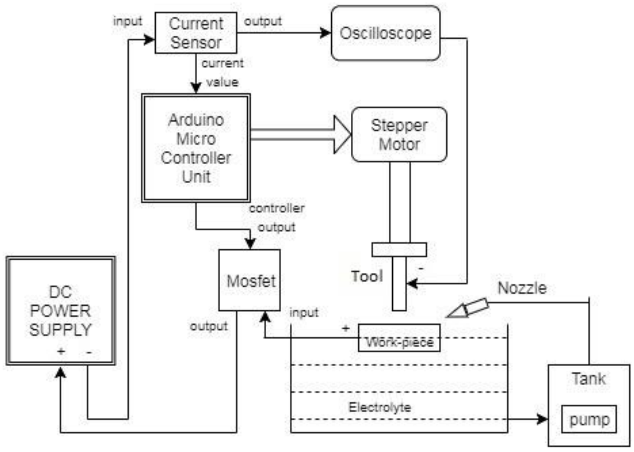

Fig. 1 Schematic diagram of Experimental Setup

3. EXPERIMENTAL PLANNING:

Tungsten Carbide straight wire of diameter 300µm has been used during the experiments as the tool. The length of the wire was reduced using wire-cut EDM, following which the tip of the wire was polished using grit paper. Titanium grade 5 sheet of thickness 400µm was used as a workpiece. Composition of grade 5 Titanium alloy is tabulated in Table 1.

Trial experiments were conducted to determine the range of process parameters: machining voltage, feed of tool, pulse frequency, duty cycle and electrolyte concentration. During the course of the trial experiments, it was seen that no hole is drilled when the voltage is less than 8.5V. At 9.0V, pitting was seen on the surface, but no hole was formed. When the voltage was set to 10V, formation of holes was not consistent and only a few holes were obtained. Thus the voltage range 11V-13V is selected for further experimentation. Since the in-house ECMM system has a capacity to produce pulses with a maximum frequency of 60 KHz, which corresponds to a time of 16.6µs per cycle, it was chosen as the pulse frequency during experimentation. It was further observed that the size of the hole reduces as the duty cycle of the pulse is varied due to better flushing of precipitates formed during machining. For this reason, a duty cycle of 20% at the above frequency was selected.

During machining, 10% wt. NaCl solution was first used. It was observed that the overcut was large and reddish brown precipitate was seen in the solution. To reduce the overcut, $NaNO_3$ was added to the solution. However, a TiO_2 film formed at the surface of the workpiece. TiO_2 film is less conductive and while the formation of a small layer reduces the overcut, a thick layer severely restricts the formation of holes and even the shapes of the holes formed is irregular. To reduce the formation of TiO_2, EDTA was added to the solution as a complexing agent. EDTA reacts with metals ions and forms a dissolvable complex. This can reduce the formation of TiO_2 films. A total of 18 experiments with 6 electrolytes at 3 different voltages have been conducted with 3 repetitions each. The machining parameters chosen for experimentations are as shown in Table 2.

Table 1. Composition of Titanium grade-5

Constituents	Ti	O	Al	V	Si	C
Weight %	77.8	14.3	4.8	3.1	0.1	< 0.1

Table 2. Machining parameters

Parameters	Values
Electrolytes*	5% NaCl + 5% $NaNO_3$ 5% NaCl + 5% $NaNO_3$ + EDTA 10% NaCl + 5% $NaNO_3$ 10% NaCl + 5% $NaNO_3$ + EDTA 10% NaCl 10% NaCl + EDTA
Voltage	11 V, 12 V, 13 V
Pulse Frequency	60 KHz
Duty Cycle	20%
Inter electrode gap	50 µm
Feed	2.4 µ/s

*All values of electrolyte are in weight percent

4. RESULTS AND DISCUSSION

Investigation into the radial overcut obtained when holes are machined in mixtures of NaCl and $NaNO_3$ with different concentration has been carried out. The graphs of percentage overcuts in the dimension of holes observed in each mixture with and without EDTA and at different voltages have been plotted as shown in Fig. 3 and their results are discussed as follows:

4.1 Effect of salt concentration

When concentration of $NaNO_3$ is decreased from 5% to 0% in 10% NaCl solution, the oxygen percentage at the hole's inside surface decreases from 45.3% to 25.3% as seen in Fig. 2. This means that the TiO_2 film at the surface is also decreasing. When EDTA is added to the above solutions, the oxygen percentage further reduces in each solution by an average of approximately 33% which indicates that TiO_2 film layer has also decreased and thus it is responsible for lesser overcut values at entry and exit. Replacing part of the NaCl concentration in a solution with $NaNO_3$ also leads to reduction of overcut.

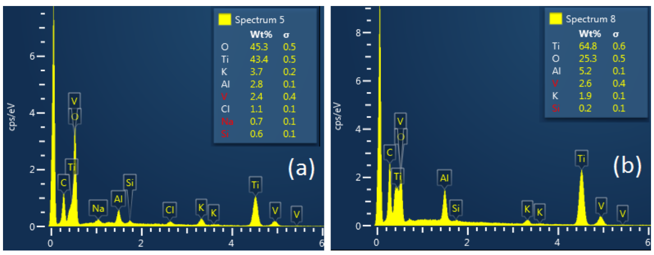

Fig. 2 EDS spectrum of TiO_2 layer in: (a) 10% NaCl+ 5% $NaNO_3$ (b) 10% NaCl

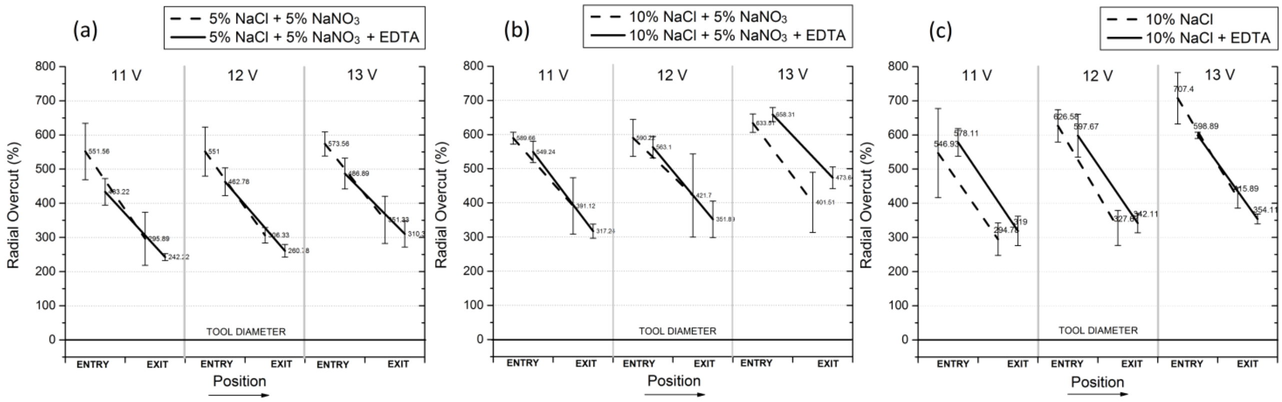

Fig. 3 Comparison of Mean Radial Overcut at the Entry and Exit of micro-holes drilled at 11V, 12V and 13V (a) 5%NaCl + 5%$NaNO_3$ with and without EDTA (b) 10%NaCl + 5%$NaNO_3$ with and without EDTA (c) 10%NaCl with and without EDTA

4.2 Effect of Applied Voltage

As the voltage increases, the overcut and hence the size of the hole increases. In Table 3 and 4, the variation in entry and exit dimensions of micro-hole is due to the stray current attack from side wall of the tool. This is expected since a higher voltage corresponds directly to denser electric field lines which are responsible for high material removal rate. Secondly, as the voltage increases, TiO_2 layer decreases. As observed in the EDS analysis shown in Fig. 4, the oxygen levels reduced from 51.3% to 39.4%. This suggests that formation of TiO_2 decreases leading to reduction in overcut. In Table 4 especially at 13V, the effect of voltage dominates as the overcut is greater in solution with EDTA, while it is lesser at 11V and 12V. These results are more pronounced because this solution has a greater concentration of salt which increases conductivity. In summary, even though the addition of EDTA reduces TiO_2 layer formation, the higher voltage leads to increase in overcut.

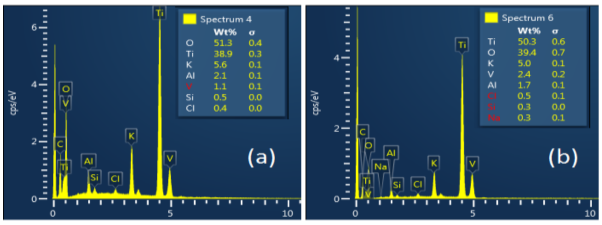

Fig. 4 EDS spectrum of TiO_2 layer in 5% NaCl + 5% $NaNO_3$ + EDTA at (a) 11 V (b) 13 V.

4.3 Effect of adding EDTA

$NaNO_3$ is a passive electrolyte and reduces the rate of machining. However, a layer of TiO_2 is also formed when $NaNO_3$ salt is added. While a thin layer of TiO_2 is required to reduce and focus electric fields, a thick layer severely hampers machining along the axial direction and causes large radial overcuts. It is thus imperative to maintain only a thin layer of TiO_2. EDTA is a chelating agent which forms soluble complexes with Ti^{+4} ions, thereby reducing the formation of TiO_2 oxides. EDS results shown in Fig. 5 depict that the oxygen content without EDTA is 45.3% and with EDTA 29.1%. This leads to only a thin layer of titanium oxide being formed with EDTA solution and thus we achieve micro-holes with lesser overcuts. Fig. 6 shows the micro-holes drilled at 11 V in 5% NaCl + 5% $NaNO_3$ solution with and without EDTA. The size of the micro-holes with electrolytes having EDTA is also lesser than those without EDTA. A trend clearly observed in Fig.3 is that the 95% confidence intervals, which represent the range in which the mean of the population is estimated to lie, are much smaller for solutions with EDTA when compared to solutions without EDTA. This implies that we can predict the mean overcut of the holes in solutions containing EDTA with greater accuracy than in solutions without EDTA.

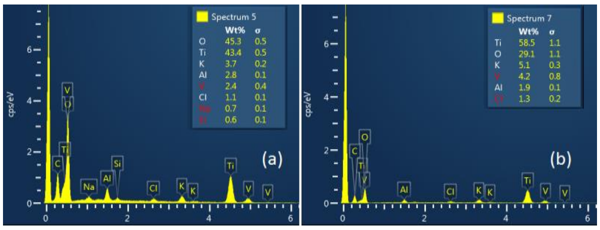

Fig. 5 EDS spectrum of TiO_2 layer in: (a) 10% + 5%$NaNO_3$ (b) 10% + 5%$NaNO_3$ + EDTA

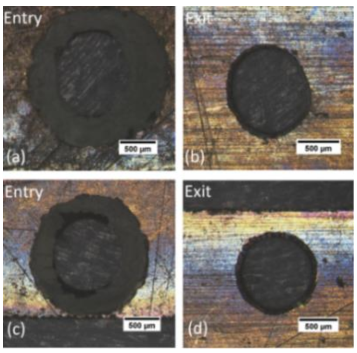

Fig. 6. Optical images of micro hole with 5%NaCl + 5%$NaNO_3$ at 11V at (a) Entry (b) Exit without EDTA; at (c) Entry (d) Exit with EDTA

Table 3. Mean radial overcut in 5% NaCl + 5% $NaNO_3$ with and without EDTA

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Voltage	5%NaCl + 5%$NaNO_3$		5%NaCl + 5%$NaNO_3$ + EDTA		% Reduction in Overcut	
	Entry	Exit	Entry	Exit	Entry	Exit
11V	826	443	650	363	21.5	18.1
12V	827	459	624	391	16.0	14.8
13V	860	527	730	465	15.1	11.7

Table 4. Mean radial overcut in 10% NaCl + 5% $NaNO_3$ with and without EDTA

Voltage	10%NaCl + 5%$NaNO_3$		10%NaCl + 5%$NaNO_3$ + EDTA		% Reduction in Overcut	
	Entry	Exit	Entry	Exit	Entry	Exit
11V	884	586	824	475	6.8	18.9
12V	885	632	844	527	4.6	16.6
13V	950	602	987	710	-3.8	-17.9

*All dimensions in µm.

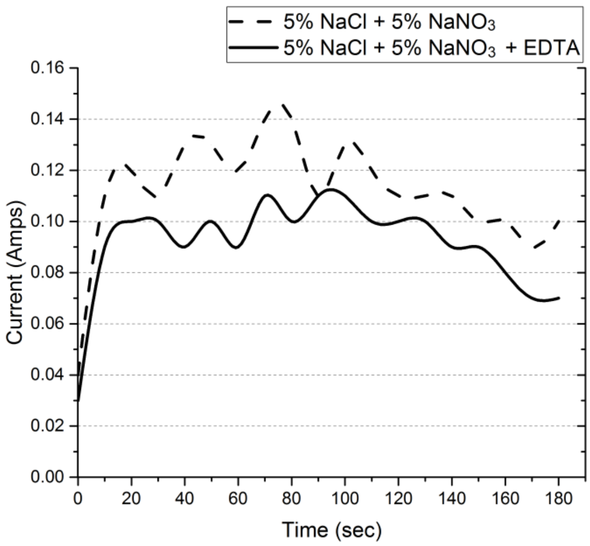

Fig.7. Current profile at 11 V in solution with and without EDTA

Fig. 7 depicts the profile of current recorded every 10 seconds while machining the micro-holes in 5%NaCl + 5%$NaNO_3$ solution with and without EDTA. It shows that the value of the current is less in solution with EDTA which results in less metal removal rate in lateral directions. This further reduces the overcut.

5. CONCLUSIONS

This research work mainly consists of how the percentage radial overcut is affected by the applied voltage, concentration of salt and the addition of EDTA as a complexing agent to electrolyte. The following conclusions can be summarized.

(i) When complexing agent, EDTA is added to the 5%NaCl + 5%$NaNO_3$ solution, the percentage radial overcut reduces by 21.5%, 16.0%, 15.1% at Entry and 18.1%, 14.8%, 11.7% at Exit at 11V, 12V, 13V respectively. It is also concluded that the effect of EDTA reduces as the voltage increases.

(ii) Addition of EDTA to the electrolyte solutions results in reduction of TiO_2 layer on the surface of the micro hole.

(iii) As applied voltage increases, the percentage overcut also increases because the stronger electric field is generated.

It is observed that the addition of EDTA to a solution during Pulse-ECM of titanium sheets reduces the formation of titanium oxides on the machining surface of the holes which in turn tends to reduction of stray currents. This leads to better machining of titanium and the holes obtained have smaller overcuts and exhibit a smaller layer of oxides on the surface. Thus, the addition of EDTA to electrolyte solutions improves the characteristics of micro holes obtained in pulse-ECM.

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