

Investigation of pulsed electrochemical micro-drilling on titanium alloy in the presence of complexing agent in electrolyte

Journal of Micromanufacturing

1(2) 142–153

© The Author(s) 2018

Reprints and permissions:

in.sagepub.com/journals-permissions-india

DOI: 10.1177/2516598418784682

journals.sagepub.com/home/jmf



Mukesh Tak¹, Vedanth Reddy S², Abhijeet Mishra³ and Rakesh G. Mote¹

Abstract

Titanium and its alloys have excellent mechanical and chemical properties; however, these properties make the processing of titanium alloys more challenging compared with other engineering materials. Electrochemical micromachining (ECMM) is a non-conventional machining process, which removes material through anodic dissolution regardless of the material's hardness. However, during the electrochemical machining of titanium, the formation of a passive oxide layer inhibits further material removal and deteriorates the machined surface quality. In addition, the accuracy of micromachining of titanium alloys is especially affected by the formation of electrolysis precipitates such as TiO_2 and stray current dissolution. In this study, the effect of the addition of the complexing agent to different electrolytic solutions on the radial overcut during micro-drilling of titanium alloy grade 5 (Ti6Al4V) has been experimentally studied using the in-house developed ECMM set-up. The influence of parameters such as applied voltage and different electrolytic concentration with and without the complexing agent on overcut during ECMM on Ti6Al4V of micro-holes has been studied. It has been safely concluded that the quality of micro-holes fabricated in the presence of EDTA in the electrolyte while machining is responsible for better dimensional characteristics.

Keywords

Electrochemical micromachining, micro-hole, complexing agent, overcut, titanium alloy

Introduction

Electrochemical micromachining (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. Advantages such as practically no tool wear, no residual stresses in workpiece and high material removal rates (MRRs) are responsible for ECMM gaining notable importance in the past few decades. Machining of materials such as copper alloys, super alloys, stainless steel and titanium and its alloys are possible with ECMM, irrespective of their physical and chemical properties.¹ Among metal alloys, titanium alloys have unique properties such as excellent strength-to-weight ratio at high temperatures, biocompatibility and high corrosion resistance. Titanium-based alloys have found wide applications in the aircraft industry, bio-medical devices, MEMS, etc.^{2,3} However, processing of titanium alloys is very challenging due to its excellent mechanical properties. During the ECMM of titanium, in oxygen containing media such as air or water, a thin titanium oxide film forms on its surface. When tita-

nium and its alloys are dissolved in passive electrolytes, they form a film of titanium oxide (TiO_2) on the surface, which is insoluble and hydrophilic in nature. This film adheres to the inside surface of a drilled hole and blocks the electrolytic flow, thereby restricting further material dissolution.⁴ For uniform dissolution of material, a proper electrolyte selection is a critical criterion.

An ideal electrolyte possesses 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 Passive

¹ Department of Mechanical Engineering, Indian Institute of Technology Bombay, Mumbai, India

² National Institute of Technology Karnataka, Surathkal, India

³ Sinhgad College of Engineering, Pune, India

Corresponding author:

Rakesh G. Mote, Department of Mechanical Engineering, Indian Institute of Technology Bombay, Mumbai, India.

Email: rakesh.mote@iitb.ac.in

as well as non-passive electrolytes can be used for ECMM. NaNO_3 is a passive electrolyte having oxidizing anions and thus reduces the rate of dissolution due to the formation of an oxide layer, while NaCl is a non-passive electrolyte having aggressive anions which remove material at rates faster than those of passive electrolytes.⁶ Formation of precipitates and stray current effects affect the accuracy of micro-holes in ECMM.⁷ The stray current effect has been reduced by providing low vibration to the micro-tool which improves the current density as well as current efficiency which further increases the accuracy of micro-features.⁸ Stray current dissolution has been also reduced by controlling the conductive area along the length of the micro-micro-electrode by helically wrapping metal.⁹ A novel micro-electrode has been fabricated with retracted tip structure to concentrate the electric field distribution to a narrow region, which results in reducing stray effect.¹⁰ Localized material dissolution is a necessary condition for high precision micromachining. To gain the accuracy and precision of micro-manufacturing, ultra-short voltage pulse showed a remarkable improvement in the replica of the micro-features.¹¹ Acids like sulphuric acid are used as electrolytes to dissolve precipitates, but they are toxic and highly corrosive in nature.¹² Acidified NaNO_3 electrolyte has been found to produce higher MRR and lower overcut when compared to NaNO_3 alone.¹³ The overcut is also found to be reduced by using non-aqueous solvents like ethylene glycol as compared to the aqueous solvents. However, the toxicity of non-aqueous solutions being more

than the aqueous solutions pose a limitation to their extensive usage.¹⁴ Alternatively, the addition of a complexing agent to the aqueous electrolytes reduces the formation of the insoluble precipitates.¹⁵ These complexing agents are non-toxic and non-corrosive compared to acids, and thus safe to use in ECMM.¹⁶ In short, the stray current effect and the removal of the insoluble TiO_2 layer formed on the surface of titanium alloys are the major issues in the ECMM of titanium alloys. In this work, an attempt has been made to overcome the challenges in machining of titanium alloys during ECMM, by mixing complexing agent to the electrolyte solution.

In this study, investigation of the effect of adding a complexing agent to the electrolytic solution on radial overcut of micro-holes produced on titanium grade 5 sheet is undertaken. A mixture of NaCl and NaNO_3 is selected as an electrolyte. The ability to form a complex compound with most of the metal ions is one of the main factors why Ethylenediaminetetraacetic acid (EDTA) disodium salt is selected as a complexing agent. Therefore, the radial overcut during micro-drilling of titanium alloy with and without the addition of EDTA in the electrolyte has been analysed.

Development of experimental set-up

An ECMM set-up was developed in-house for the machining and experimentation. It consists of a micro-electrode positioning system, a DC power supply, a pulse generation system

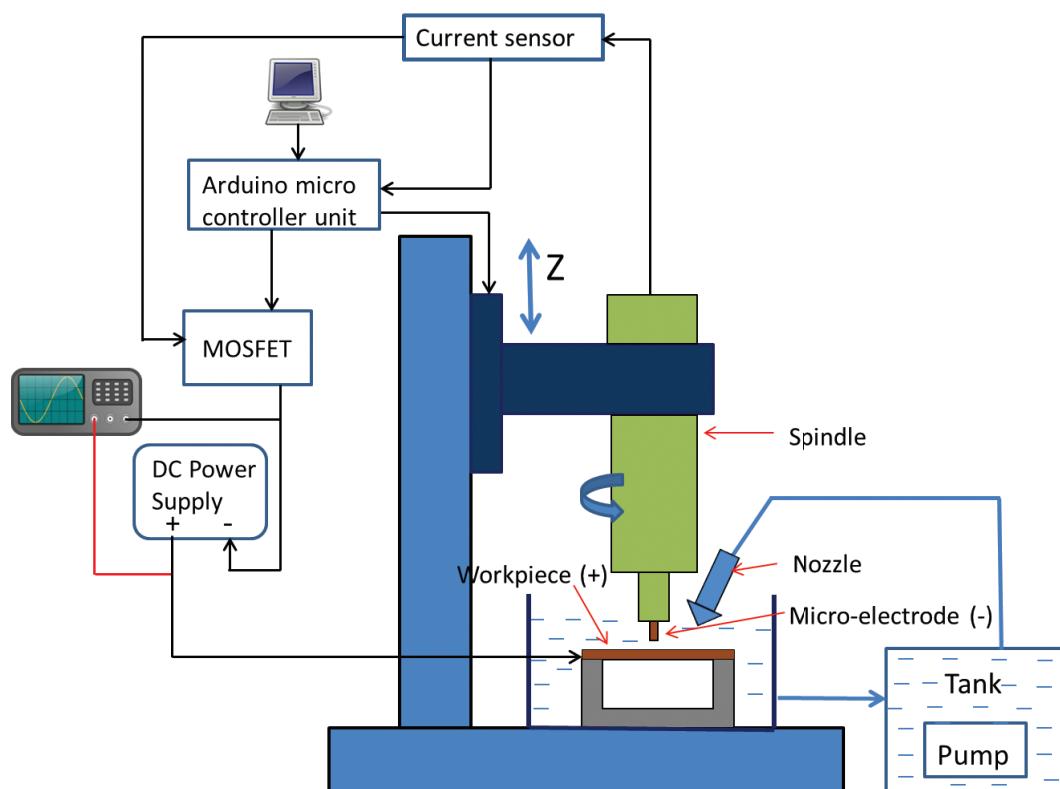


Figure 1. Schematic diagram of ECMM experimental set-up.

and an electrolytic supply system. An Arduino micro-controller unit is used to control and operate these systems. The micro-electrode positioning system consists of a stepper motor controlled by the micro-controller, which moves the micro-electrode with a resolution of $0.6\text{ }\mu\text{m}$ along the tool feed direction, that is, Z-Axis. A DC power source of $0\text{--}60\text{ V}$ at $0\text{--}5\text{ A}$ current rating was used. Generation of pulses at frequencies up to 60 KHz and measurement of current are handled by the MOSFET and the current sensor respectively, as shown in Figure 1. The negative terminal is connected to the micro-electrode, while the positive terminal is connected to the workpiece. The electrolyte system consists of a tank and a submersible pump which pumps electrolyte on the machining surface through a nozzle. The electrolyte then returns to the tank through a filter to remove the precipitates of the electrochemical reaction. The inter-electrode gap (IEG) is maintained via real-time feedback from the electrolysis zone.

Inter-electrode gap control system

A micro-controller unit is used for controlling the IEG. During the initial IEG setting, the micro-electrode starts

moving down during which the current is measured using a Hall-effect sensor and the feedback is sensed after each step. While setting the initial IEG, a voltage of 4 V is applied between the micro-electrode and the workpiece, which is smaller than the machining voltage. During the downward movement of the micro-electrode, a sudden jump-up in current is detected, which is pre-cursor to the short circuit between the micro-electrode and the workpiece. Therefore, when the short circuit is detected, a ‘contact’ condition has been assumed between the micro-electrode and the workpiece. When the ‘contact’ condition is achieved, the stepper motor stops and starts moving the required number of steps in the reverse direction to set the initial IEG of $50\text{ }\mu\text{m}$. The system then starts generating pulses of 60 KHz frequency at the micro-electrode and actual machining begins. During machining, the micro-electrode moves down with a pre-set feed rate and the corresponding current is recorded. Whenever a contact occurs, the micro-controller switches off the pulse power supply instantly to avoid damage due to sparking. Then the micro-electrode is retracted to provide an IEG of $12\text{ }\mu\text{m}$ to avoid short circuit after which machining resumes. The total number of steps is defined by adding the IEG and the thickness of the workpiece. Each step is counted

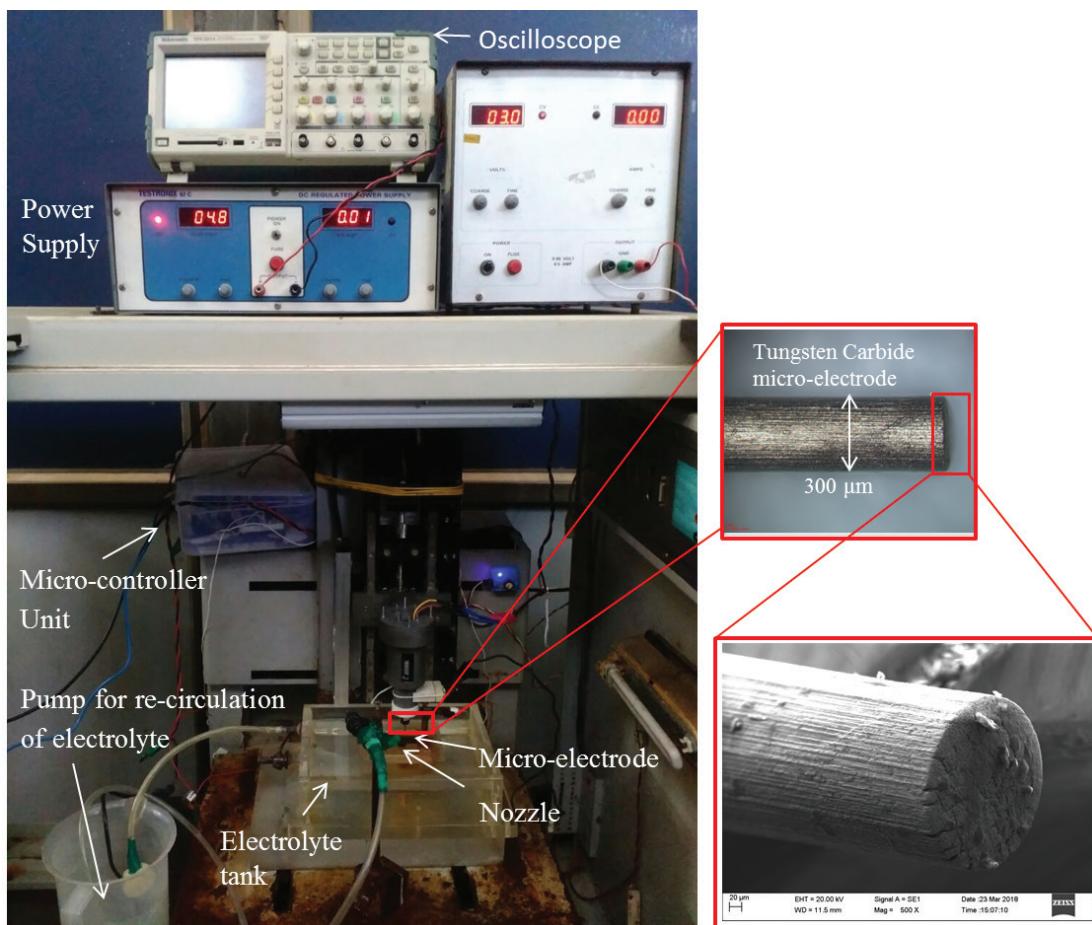


Figure 2. Different system components of ECMM experimental set-up.

and once the micro-electrode has moved to the defined number of steps, machining stops and the micro-electrode is completely retracted so that the workpiece can be inspected or changed. The experimental set-up is shown in Figure 2. The detailed scheme of ECMM operation is shown in the flow diagram shown in Figure 3.

Experimental planning

During experiments, a tungsten carbide (WC) micro-electrode in the form of a straight wire (diameter 300 µm) is used. The wire was reduced to small strips using wire-cut EDM, following which the tip of the wire was polished with a grit paper of grade C-1200. A titanium grade 5 sheet of thickness 400 µm is used as the workpiece.

Trial experiments were conducted to determine the range of process parameters: machining voltage, feed of a micro-electrode, pulse frequency, duty cycle and electrolyte concentration. During the course of the trial experiments, it was observed that no machining occurred for voltages less than 8.5 V. At 9.0 V, only pitting was seen on the surface, but no hole was formed. The pitting is due to a slight increase in the current value breaking the passive layer at certain regions on the workpiece surface. The voltage range 11 V–13 V 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 16.6 µs per cycle, it was set 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 decreasing due to more time available (t_{off}) for flushing of precipitates formed during machining time (t_{on}). For this reason, a duty cycle of 20% at the earlier frequency was selected.

During machining, for 10 wt% NaCl solution, a large overcut was noted and a reddish brown precipitate was observed in the solution. In order to reduce the overcut, NaNO₃ was added to the NaCl solution. However, the addition of nitrates releases oxygen and enables the formation of a TiO₂ film at the surface of the workpiece. The oxide film thus formed is not conductive and the formation of a small layer reduces the overcut. At the same time, a thick layer severely restricts the formation of holes and evenness of the layer severely distorts the profile of the holes. In order to reduce the formation of TiO₂, 2.5 wt% of EDTA was added to the solution as a complexing agent. EDTA reacts with metals ions and forms a soluble complex. This can reduce the formation of TiO₂ 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 1.

Table I. 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 (V)	11, 12, 13
Pulse frequency (KHz)	60
Duty cycle (%)	20
Inter-electrode gap (µm)	50
Feed rate (µm/s)	2.4

Notes: *All values of electrolyte are in weight percentage (wt%);

[#] Ethylenediaminetetraacetic acid disodium salt.

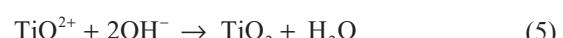
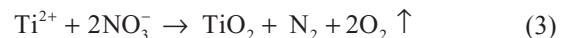
Anodic dissolution of titanium in EDTA

The anodic dissolution of titanium alloys is a very complex task when compared with other metals in ECMM. Titanium and its alloys have excellent corrosive resistance due to the presence of stable TiO₂ layer on its surface. This oxide layer is formed when it comes in contact with oxygen-containing environment. The oxide layer formed is highly passive in nature and hinders the anodic dissolution of titanium alloys. EDTA disodium salt is a kind of complexing agent with a chemical formula of Na₂H₂Y (where Y is C₁₀H₁₂N₂O₈) and has capability to react with most of the metal ions and forms a soluble complex compound.¹⁷ The possible chemical reactions which occur in the mixture of NaCl, NaNO₃ and EDTA of titanium alloy grade 5 (Ti6Al4V) are:

At cathode:



At the interface of anode and electrolyte:



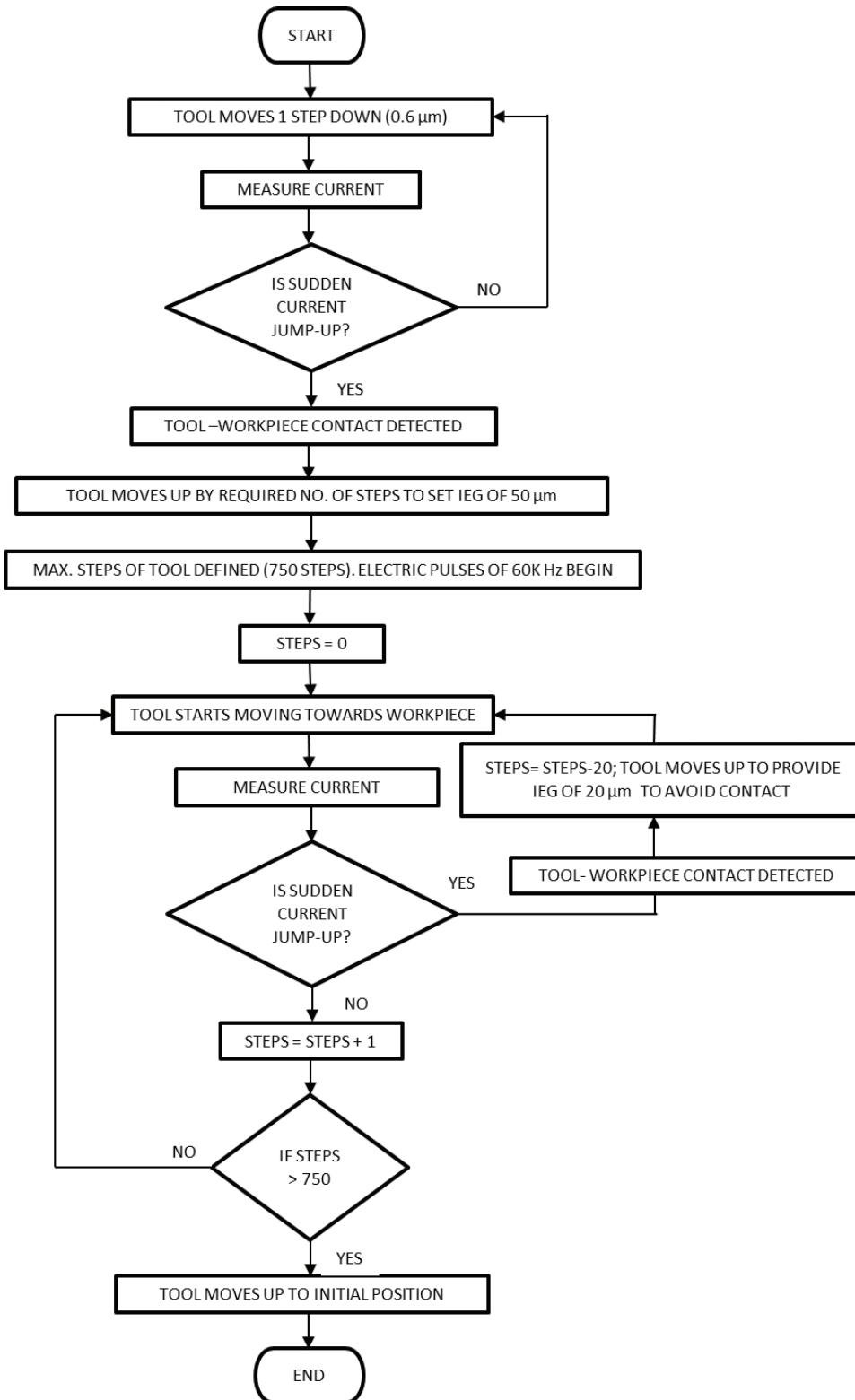


Figure 3. Flowchart of ECMM operation.

Results and discussion

The radial overcuts have been observed when holes are machined in the mixtures of NaCl and NaNO₃ with different concentrations. The percentage overcuts of holes observed in each mixture, with and without EDTA, at different voltages have been analysed and their results are discussed as follows.

Effect of sodium nitrate concentration

When the concentration of NaNO₃ is decreased from 5% to 0% by making the overall concentration of the salt mixture

(NaCl + NaNO₃) to be 10%, the oxygen percentage at the inside surface of the holes decrease from 41.3% to 25.3% as seen from the EDS spectrum shown in Figure 4. This means that the TiO₂ film formation at the surface is also reducing. From Figure 5, it is observed that the increase in TiO₂ layer tends to reduce the MRR at a higher voltage and thus the overcut. The addition of NaNO₃ to NaCl solution also leads to a reduction of the overcut. As NaNO₃ is a passive electrolyte, it encourages the growth of a passive layer on the surface of the workpiece and lowers the dissolution process and hence reduces the overcut.

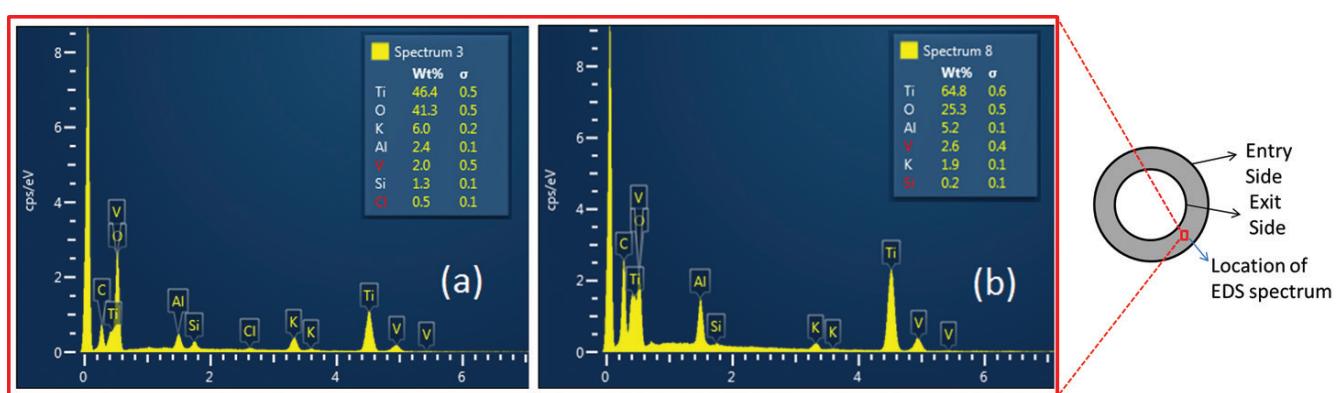


Figure 4. EDS spectrum at machined surface of hole in: (a) 5% NaCl + 5% NaNO₃ and (b) 10% NaCl.

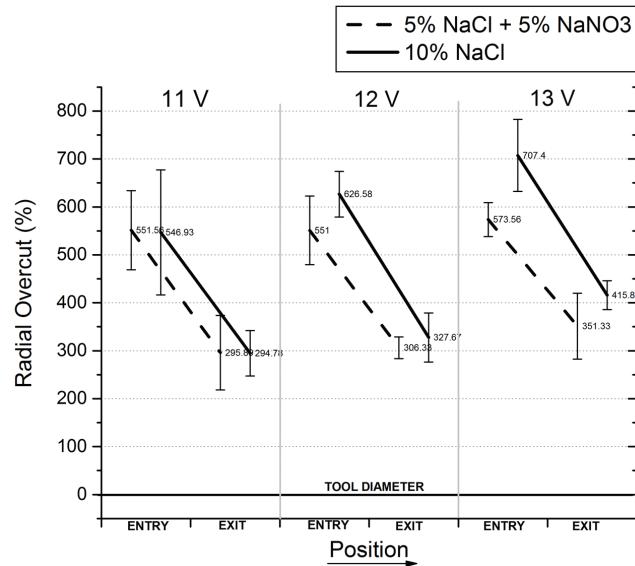


Figure 5. Radial overcut at entry and exit of micro-holes drilled at 11 V, 12 V and 13 V in 5% NaCl + 5% NaNO₃ and 10% NaCl.

Effect of applied voltage

The hole size and hence the radial overcut increases as the voltage increases. The variation in the entry and exit dimensions of micro-holes due to the stray current attack from side-walls of the micro-electrode is seen in Tables 2 and 3. Since a higher voltage corresponds directly to the denser electric field lines which are responsible for higher MRR, this effect is expected. Second, the TiO_2 layer decreases as the voltage increases. As observed in the EDS analysis shown in Figure 6, the oxygen levels reduce from 51.3% to 39.4% at 11 V and 13 V, respectively. The reduction in the oxygen content leads to decrease in the formation of a TiO_2 film and subsequently the reduction in the overcut. In Table 3, especially at 13 V, the effect of voltage dominates, as the overcut is greater when the solution with EDTA is used. The overcut is observed to be smaller at 11 V and 12 V. The solution, which has a greater concentration of salt, will exhibit a higher electrical conductivity of the electrolyte solution. In summary, even though the addition of EDTA reduces TiO_2 layer formation, the higher voltages lead to increase in the overcut. Figure 7 shows the variation in the percentage radial overcut at entry and exit of the micro-hole machined at different voltages and different electrolyte solutions of NaCl and NaNO_3 with and without EDTA. It is observed that the percentage radial overcut is less with

EDTA as compared to without EDTA in the electrolyte solution of 5% NaCl and 5% NaNO_3 . The volatility of radial overcut at entry in 10% NaCl at 11 V as shown in Figure 7(c), is due to the influence of the precipitates of titanium chlorides and weak electric field strength at lower voltage. These precipitate particles divert the field lines leading to the volatility in the overcut.

The diameters of the drilled holes are larger than the tool diameter. This is primarily because of the following factors. First, uninsulated WC micro-electrodes are used in the experimentations due to which electrical field lines from the tool sidewalls spread out over a larger area resulting in unwanted material removal, and thereby larger holes, particularly at the entry side. Second, the electrolyte flow is playing an important role in ECMM. For a low electrolyte flow velocity, the titanium oxide layer formed on the workpiece surface is not removed and hinders the electrolysis process. Hence, the electrolyte flow velocity is maintained high and directed to the IEG. This causes the machined holes size to be larger on the entry side. The oscillatory tool movements occur due to its retraction from the workpiece surface in order to maintain the IEG in case of a short circuit between the electrodes. Such oscillating movements of the tool increase the overall interaction time with the workpiece and leads to an increase in the overcut at the entry side of the hole.

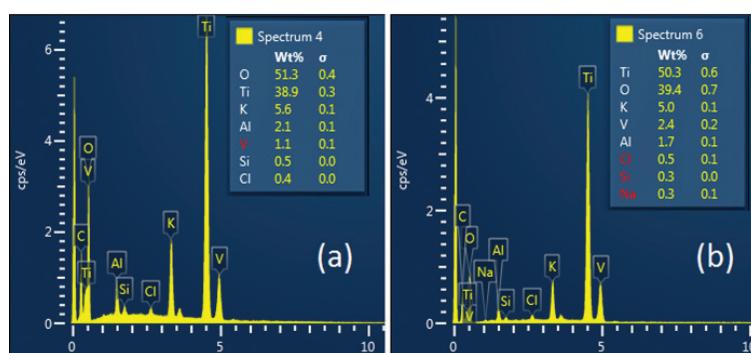


Figure 6. EDS spectrum at machined surface of hole in 5% $\text{NaCl} + 5\% \text{NaNO}_3 + \text{EDTA}$ at (a) 11 V and (b) 13 V.

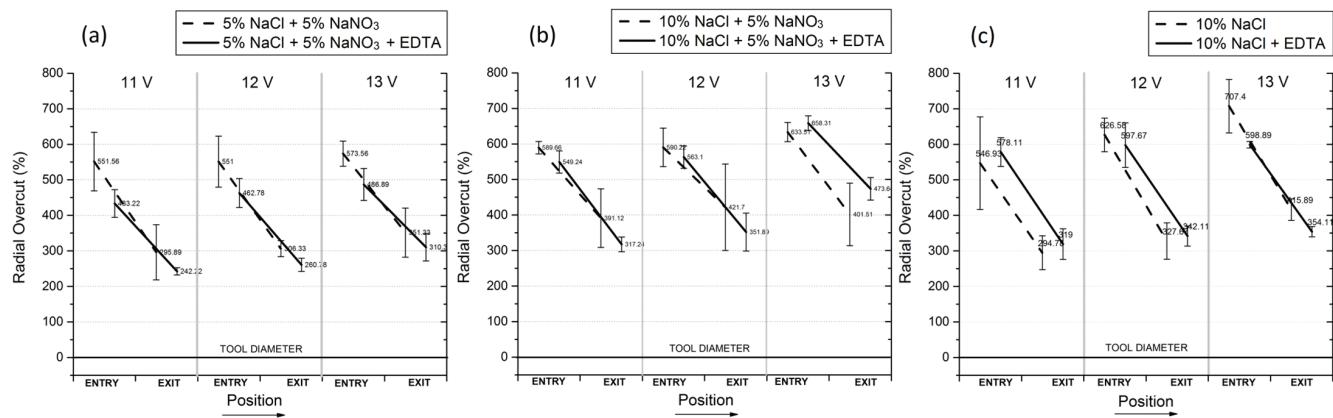


Figure 7. Comparison of mean radial overcut at the entry and exit of micro-holes drilled at 11 V, 12 V and 13 V: (a) 5% $\text{NaCl} + 5\% \text{NaNO}_3$ with and without EDTA; (b) 10% $\text{NaCl} + 5\% \text{NaNO}_3$ with and without EDTA; (c) 10% NaCl with and without EDTA.

Effect of EDTA addition to the electrolyte

Being a passive electrolyte, NaNO_3 reduces the rate of the electrolysis reactions. However, when NaNO_3 is added in NaCl solution, a layer of TiO_2 is also formed. A thick layer of TiO_2 severely hampers the machining along the axial direction and causes large radial overcuts. It is thus imperative to maintain only a thin layer of TiO_2 while machining so that only stray currents are reduced. The presence of EDTA reduces the formation of TiO_2 as it is a chelating agent, which forms soluble complexes with titanium ions. The EDS results shown in Figure 8 depict that the oxygen content without EDTA is 45.3% and with EDTA it is 29.1%. This suggests that with an EDTA-based solution, only a thin layer of titanium oxide is formed, which leads to machining of micro-holes with lesser overcuts. The micro-holes drilled at a voltage of 11 V in 5% $\text{NaCl} + 5\%$ NaNO_3 solution with and without EDTA are shown in Figures 9(a)–9(d). It is clearly observed that the size of the micro-holes drilled with electrolytes having EDTA

is also lesser than those drilled with the electrolytes without EDTA. Microstructural investigations have been carried out using electron backscattering diffraction (EBSD) in order to assess the microstructural behaviour during electrochemical machining. Figures 9(e) and 9(f) EBSD results depict that no microstructural changes are found near the edge of the micro-holes as we move away from the machining zone, which indicates that there is no heat affected zone (HAZ) and no residual stresses are generated.

Figure 10 depicts the profile of the peak current at every 2 seconds from the real-time recorded current data at each step movement of the micro-electrode while machining the micro-holes in 5% $\text{NaCl} + 5\%$ NaNO_3 solution with and without EDTA. As observed from the plot, solutions with EDTA allow lesser current to be generated compared with solutions without EDTA. This results in a lesser MRR when the EDTA is present in the electrolyte solution, which is further responsible for the reduction in overcut.

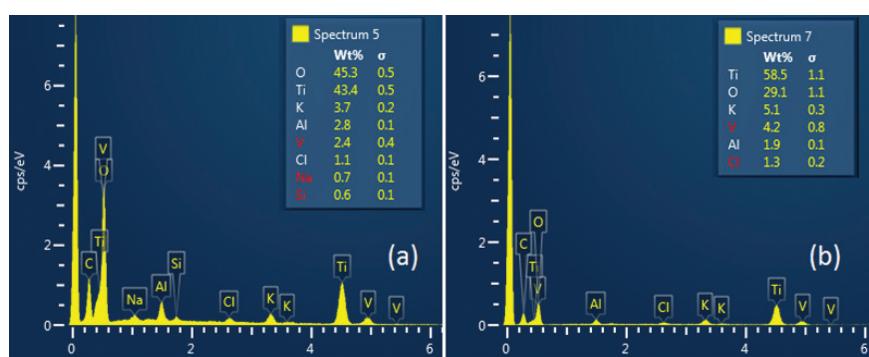


Figure 8. EDS spectrum at machined surface of hole in: (a) 10% $\text{NaCl} + 5\%$ NaNO_3 and (b) 10% $\text{NaCl} + 5\%$ NaNO_3 + EDTA.

Table 2. Mean radial overcut in 5% $\text{NaCl} + 5\%$ NaNO_3 with and without EDTA.

Voltage	5% $\text{NaCl} + 5\%$ NaNO_3		5% $\text{NaCl} + 5\%$ 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 3. Mean radial overcut in 10% $\text{NaCl} + 5\%$ NaNO_3 with and without EDTA.

Voltage	10% $\text{NaCl} + 5\%$ NaNO_3		10% $\text{NaCl} + 5\%$ 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

Note: *All dimensions in μm

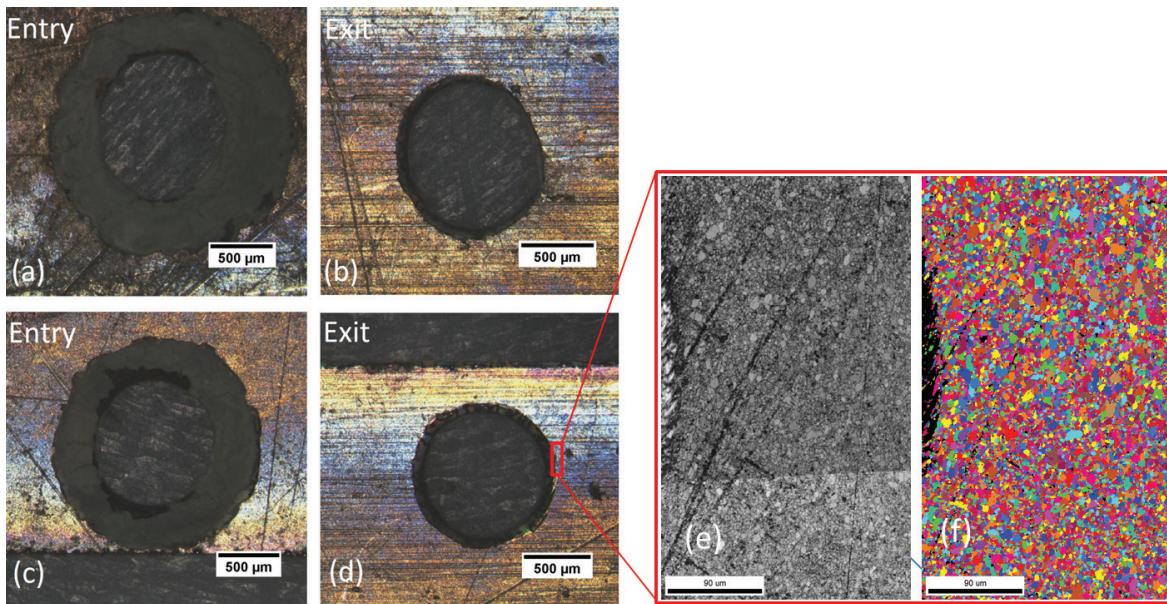


Figure 9. Optical images of micro-holes with 5% NaCl + 5% NaNO₃ at 11 V at (a) entry (b) exit without EDTA; at (c) entry and (d) exit with EDTA; (e)–(f) EBSD profiles at edge surface of the micro-holes.

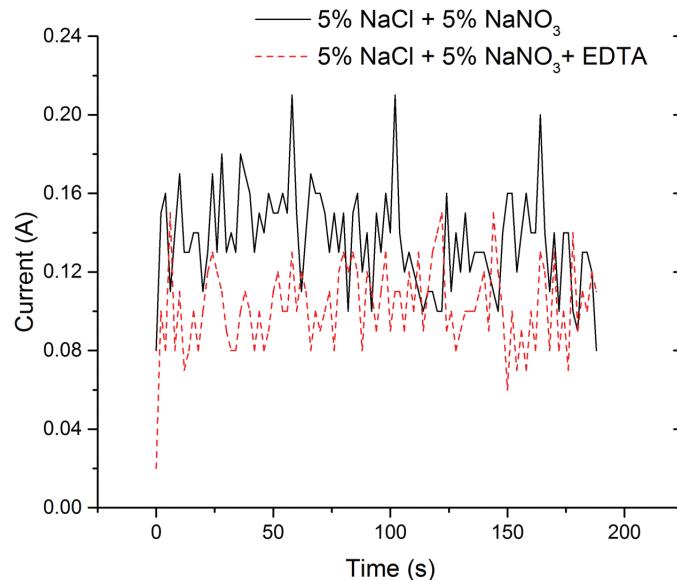


Figure 10. Current profile at 11 V in 5% NaCl + 5% NaNO₃ solution with and without EDTA at a feed rate of 2.4 $\mu\text{m s}^{-1}$.

Effect of feed rate of the micro-electrode

Salt mixture of 5% NaCl and 5% NaNO₃ with added EDTA is taken for further analysis. A series of experiments with different micro-electrode feed rates have been conducted separately to investigate the effect of feed rate on radial overcut with all the other parameters kept constant. It can be seen from Figure 11 that, for the same parameters, as the feed rate increases, the overcut of the micro-hole decreases. The current originating from the micro-electrode is responsible for the machining of the titanium alloy. When the micro-electrode moves at a higher feed rate, the IEG goes

on decreasing as the tip of the micro-electrode comes closer to the machining surface. This causes most of the current to be concentrated in a very small region, and thus the overcut decreases. Moreover, the micro-electrode gets lesser time to interact with the machining area. Thus, at higher feed rate due to the combined effect of the smaller IEG and lesser reaction time per unit area, the MRR along the radial direction decreases while along the linear direction it increases. This means that the radial overcut decreases when machining at the higher feed, while the surface area of machining reduces. However, the overall material removed is less because the machining is completed in shorter period.

In an ideal condition, the feed rate must be equal to the linear MRR. If the feed rate is too slow, more time is available for machining which leads to a larger overcut. At a higher feed rate of the electrode, the IEG reduces and the sludge particles may not flush properly due to small IEG, and these sludge particles give rise to frequent short circuits resulting in larger overcut at the entry side. Therefore, both cases lead to an unstable machining which ultimately affects accuracy and precision of the micro-hole. Hence, optimum feed rate always maintains the constant IEG for localized and stable machining.

Effect on the micro-electrode

In ECMM, the ion transfer and the chemical interactions between the electrodes and the electrolyte solution are dominant mechanisms. The electrolytic products formed

during machining may get deposited over the electrode and can affect the machining characteristics. The experiments are conducted at 11 V, tool feed rate of $6.6 \mu\text{m s}^{-1}$ and the electrolyte solution of 5% NaCl + 5% NaNO₃ with and without the addition of EDTA. The electrodes are analysed using Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS), before (Figure 12(a)) and after the experiments (Figure 12(b–c)). The EDS spectrum of the micro-electrode used without the presence of EDTA (Figure 12(b)) reveals an increase in the oxygen content from 8.4% to 13.3% on the surface of the electrode, indicating the presence of oxide/hydroxide scattered deposits. In contrast, when EDTA is added to the electrolyte (Figure 12(c)), a non-uniform thick layer deposits over the micro-electrode, having an oxygen content of nearly 31%. The layer being non-conductive in nature aids the ECMM by lowering the strength of electric field lines to some

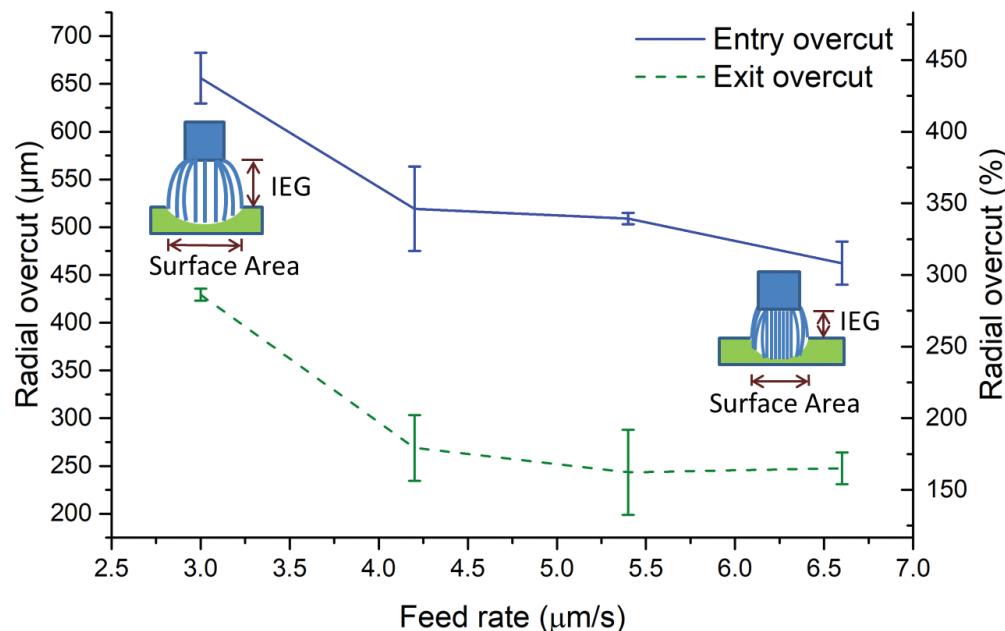


Figure 11. Radial overcut at the entry and the exit of micro-holes machined with different feed rates of micro-electrode in 5% NaCl + 5% NaNO₃ with EDTA.

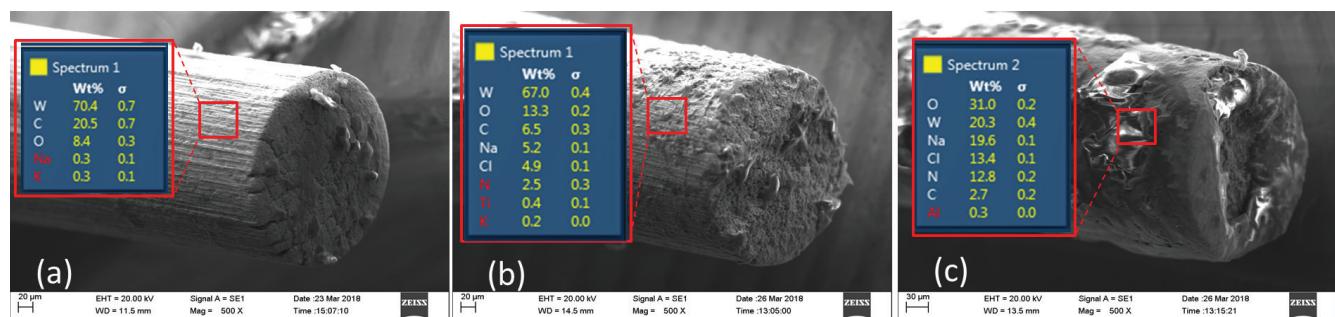


Figure 12. SEM micrograph and EDS spectrum of micro-electrode (a) before ECMM; after ECMM (b) in 5% NaCl + 5% NaNO₃ solution and (c) in 5% NaCl + 5% NaNO₃ + EDTA solution.

extent, particularly towards the sidewalls of the hole. This reduces the radial overcut. From SEM images, it has also been perceived that there is no significant tool wear during the ECMM process.

Conclusions

In this article, electrochemical drilling on titanium alloy with the addition of non-toxic EDTA as a complexing agent to the electrolyte has been studied. The study focuses on how the percentage radial overcut is affected by the applied voltage, the concentration of salt and the addition of EDTA to the electrolyte. The specific findings from the experimental investigation can be summarized in the following.

(a) When a complexing agent, EDTA is added to the 5% NaCl + 5% NaNO₃ solution, the percentage radial overcut of the micro-hole reduces by 21.5%, 16% and 15.1% at entry and 18.1%, 14.8% and 11.7% at exit for applied voltages 11 V, 12 V and 13 V, respectively. It is also observed that the effect of EDTA reduces as the voltage increases.

(b) The radial overcut is less in the electrolyte solution of 10% NaCl + 5% NaNO₃ without EDTA at higher voltage, that is, at 13 V, as compared to the radial overcut obtained with the addition of EDTA to the same solution. Therefore, the effect of EDTA reduces as the voltage increases.

(c) Addition of EDTA to the electrolyte solutions results in a reduction of the oxygen content on the inside surface of the micro-holes and therefore a reduction in the TiO₂ layer. The passivation effect of NaNO₃ on Ti6Al4V in the electrolyte solution of NaCl and NaNO₃ is minimized by the addition of EDTA to the solution mixture.

(d) While using the electrolyte solution with EDTA, a thick layer of oxide/hydroxide deposits over the micro-electrode is observed. The thick layer being insulating in nature assists in reducing the radial overcut to a certain extent.

The experimentation has successfully demonstrated that the addition of EDTA to a solution during pulse-ECMM of titanium sheets reduces the formation of titanium oxides on the machined surface of the holes, which in turn tends to reduce the stray currents. The EDS results show the presence of oxygen in decreases while machining in the electrolyte with EDTA. Through EBSD, no change in the microstructure of titanium alloy is observed in the machining zone near the edge of the micro-hole. This indicates that there is no HAZ and no residual stresses are generated due to ECMM. Electrolyte solutions with EDTA bring improvement in machining of titanium alloy and therefore a reduction in the overcut of holes is obtained. In summary, the addition of EDTA to the electrolyte solutions improves the dimensional characteristics of the micro-holes generated in the pulse-electrochemical micro-drilling.

Acknowledgement

The authors are thankful to Professor Sushil Mishra of MMMF lab, IIT Bombay, for facilitating the use of the SEM/EBSD.

Declaration of conflicting interests

The authors declared no potential conflicts of interest with respect to the research, authorship and/or publication of this article.

Funding

This work was financially supported by Portescap India Pvt Ltd, CSR fund.

References

1. Kim BH, Ryu SH, Choi DK and Chu CN. Micro electrochemical milling. *J Micromech Microeng* 2005; 15: 124–129.
2. Jiang LM, Li W, Attia A, et al. A potential method for electrochemical micromachining of titanium alloy Ti6Al4V. *J Appl Electrochem* 2008; 38: 785–791.
3. Dhobe SD, Doloi B and Bhattacharyya B. Surface characteristics of ECMed titanium work samples for biomedical applications. *Int J Adv Manuf Technol* 2011; 55: 177–188.
4. Zeng Y, Fang X, Zhang Y, et al. Electrochemical drilling of deep small holes in titanium alloys with pulsating electrolyte flow. *Adv Mech Eng* 2014; 6. DOI: 10.1155/2014/167070
5. Hackert-Oschätzchen M, Lehnert N, Martin A, et al. Jet electrochemical machining of particle reinforced aluminum matrix composites with different neutral electrolytes. *IOP Conf Ser Mater Sci Eng* 2016; 118. DOI: 10.1088/1757-899X/118/1/012036
6. Jain VK, Kalia S, Sidpara A, et al. Fabrication of micro-features and micro-tools using electrochemical micromachining. *Int J Adv Manuf Technol* 2012; 61: 1175–1183.
7. Jain VK, Lal GK and Kanetkar Y. Stray current attack and stagnation zones in electrochemical drilling. *Int J Adv Manuf Technol* 2005; 26: 527–536.
8. Anasane SS and Bhattacharyya B. Experimental investigation into fabrication of microfeatures on titanium by electrochemical micromachining. *Adv Manuf* 2016; 4: 167–177.
9. Mi D and Natsu W. Proposal of {ECM} method for holes with complex internal features by controlling conductive area ratio along tool electrode. *Precis Eng* 2015; 42: 179–186.
10. Liu W, Ao S, Li Y, et al. Modeling and fabrication of microhole by electrochemical micromachining using retracted tip tool. *Precis Eng* 2017; 50: 77–84.
11. Zhang YJ, Tang YJ, Liu XK, et al. Development of ultra-short pulse power supply applicable to micro-ECM. *Mater Sci Forum* 2009; 626–627: 369–374.
12. Devilliers D, Dinh MT, Mahé E, et al. Behaviour of titanium in sulphuric acid: Application to DSAs. *J New Mater Electrochem Syst* 2006; 9: 221–232.
13. Thanigaivelan R, Arunachalam RM, Karthikeyan B, et al. Electrochemical micromachining of stainless steel with acidified sodium nitrate electrolyte. *Procedia CIRP* 2013; 6: 351–355.
14. Liu W, Zhang H, Luo Z, et al. Electrochemical micromachining on titanium using the NaCl-containing ethylene glycol electrolyte. *J Mater Process Technol* 2018; 255: 784–794.

15. Hui C, Wang YK, Wang ZL, et al. Effects of complexing agent on electrochemical micro machining of stainless steel. *Am J Nanotechnol* 2011; 2: 100–105.
16. Tak M, Mote RG, Reddy VS, et al. Studies in pulsed electrochemical micro-drilling on titanium alloy with an addition of complexing agent to electrolyte. In: Proceedings of the 10th International conference on precision, micro, meso and mano engineering (COPEN 10), Indian Institute of Technology Madras, 7–9 December 2017, http://www.copen.ac.in/proceedings/copen10/copen/46.revised_manuscript_227.pdf (accessed 8 June 2018).
17. Sreekumar NV, Bhat NG, Narayana B, et al. Selective complexometric determination of titanium(IV) using sodium potassium tartrate or ascorbic acid as masking agent. *Mikrochim Acta* 2003; 141: 29–33.