Int J Adv Manuf Technol (2016) 86:2147–2160
DOI 10.1007/s00170-015-8309-2

ORIGINAL ARTICLE

Experimental investigation on suitability of electrolytes for electrochemical micromachining of titanium

Sandip S. Anasane[1] · **B. Bhattacharyya**[1]

Received: 2 November 2014 / Accepted: 28 December 2015 / Published online: 18 January 2016

Abstract Titanium is a potential material for MEMS and biomedical uses owing to its unique high strength to weight ratio and their excellent corrosion resistance property. Machining of titanium by conventional as well as non-conventional methods is a challenge due to its inherent mechanical and chemical properties. Machining of titanium in micro domain is a topic of great research interest. Electrochemical micromachining (EMM) technique could be possible alternative for machining of titanium especially in micro domain. This paper presents systematic investigation of suitability of electrolyte for anodic dissolution of titanium through electrochemical micromachining. In order to investigate the performance of electrolytes, seven different types of electrolytes have been selected. The nature of dissolution of titanium and influence of electrolyte has been studied by machining a set of through micro holes in pure commercial titanium with all these different types of electrolytes. Five electrolytes out of seven have been demonstrated successful anodic dissolution of titanium using EMM process parameters. Out of these five electrolytes, two non-aqueous electrolytes were further evaluated, based on various criteria, i.e. material removal rate, radial overcut and conicity of micro hole. Amongst the two non-aqueous electrolytes, electrolyte with combination of ethylene glycol and sodium bromide has demonstrated excellent results during titanium micromachining by EMM.

Keywords Electrochemical micromachining · Titanium · Microhole · Electrolyte · Ethylene glycol

1 Introduction

Titanium (Ti) and its alloys possess best strength-to-weight ratio and corrosion resistance among metals. Ti and its alloys have much higher fracture toughness, better electrical conductivity and greater biocompatibility. Therefore, they are very attractive for MEMS and biomedical uses. Machinability of titanium and its alloys is generally considered to be poor because titanium is very chemically reactive and, therefore, has a tendency to weld to the cutting tool during conventional machining, thus leading to chipping and premature tool failure [1]. Non-traditional machining methods such as electric discharge machining (EDM) and laser beam machining (LBM) have been applied to the machining of titanium and its alloys during recent times. With EDM process, one problem is that the debris in machining gap cannot eliminate easily, and the machining status is unstable during the process. LBM can also be applied for machining titanium, but even this process has its own problems in forming pear-shaped holes and tapering of holes with straight profile are difficult to obtain and formation of hot spot due to thermal effect [2]. Ultrasonic machining (USM), with a thinner zone affected by machining, is suitable for hard and brittle materials. However, the disadvantages of USM are lower material removal rate (MRR) compared with other processes and serious tool wear that usually affects machining precision [3].

✉ Sandip S. Anasane
anasane@gmail.com

B. Bhattacharyya
bb13@rediffmail.com

[1] Production Engineering Department, Jadavpur University, Kolkata, India

Electrochemical machining (ECM) is a process in which material removal takes place due to anodic dissolution irrespective of material hardness. When ECM is used for fabricating features or structures in the range from 1 to 999 μm, it is called electrochemical micromachining [4]. Electrochemical micromachining (EMM) offers many advantages, such as no tool wear, stress-free and smooth surfaces, and the ability to machine materials, regardless of their hardness and high strength [5]. EMM appears to be a very promising micromachining technology due to its advantages that include high MRR, better precision and control, rapid machining time and environmentally acceptable, and it also permits machining of chemically resistant materials like titanium, copper alloys, super alloys and stainless steel, [6].

Electrochemical machining could be one of the alternative processes for machining of titanium by anodic dissolution. However, electrochemical dissolution of titanium is a challenge due to the phenomenon of formation of oxide film on surface of titanium during machining. As per the position of titanium in periodic table and its electrochemical behaviour, titanium is known as the metal, whose surface is always covered with a natural oxide film, when exposed to air, water or other oxygen-containing media. Thickness of this natural oxide film of titanium ranges from 5 to 70 A^o [7]. The titanium gains its excellent corrosion resistance due to the existence of this tenacious and passivating surface film of oxide. This corrosion resistance property of stable oxide layer hinders electrochemical dissolution of titanium; therefore, this appears a major task before the researchers to find out suitable electrolyte, which will dissolve the metal at an acceptably low voltage [8]. However, few attempts have been reported to achieve anodic dissolution of titanium in macroscopic as well as in microscopic domain. The attempt have been made to generate regular pattern on pure titanium by electrochemical dissolution through the patterned photoresist up the depth of 13 μm using sodium bromide and methanol solution containing sulfuric acid and the etching performance of these two electrolytes has been tested. [9]. Further, solution of methanol sulfuric acid has been utilized to study the mechanism of electro polishing of titanium by steady-state measurements and by ac-impedance spectroscopy using a rotating disk electrode. It has been reported that the electro polishing of titanium in methanol sulfuric acid electrolytes is mass transport controlled. It was also observed that the limiting current density vary with electrolyte composition. This concluded that the dissolution of titanium tetravalent species from anode surface to the bulk solution is rate limiting due to the presence of compact salt film at the anode surface under limiting current conditions [10]. Crucial role of mass transport phenomenon in anodic dissolution process and presence of thin salt film at the limiting current has confirmed the linear growth of passive film with potential until a critical value reached where the film breakdown occurs and initiates the transpassive dissolution. [11]. The porous anodization of titanium was also carried out to create nano-scale features on titanium surfaces by utilizing sulfuric acid and H_3PO_4 electrolyte with potential sweep [12]. Electrochemical anodization of titanium through patterned photoresist mask using 0.5 M sulfuric acid and phosphoric acid (H_3PO_4) was also performed [13]. Electrolyte system containing sodium chlorate ($NaClO_3$), sodium nitrite ($NaNO_2$) and sodium fluoride (NaF) is found suitable for the generation of etchants of hydrofluoric acid (HF) and nitric acid (HNO_3) for machining of Ti alloy (Ti6Al4V) with the help of confined etchant layer technique (CELT). Its micromachining resolution depends mainly on the rate of the scavenging reaction. Sodium hydroxide (NaOH) was used as an effective scavenger to obtain submicrometre resolution [14].

Use of high concentration of aqueous sodium bromide with working voltage of as high as 200 V through jet electrochemical micromachining (Jet-EMM) technique was also utilized to create deep holes in titanium alloy [15]. Anodic dissolution of titanium has been performed in NaCl containing ethylene glycol solution. The voltammetry techniques with a general electrode or a rotating disk electrode (RDE) were utilized to investigate electropolishing mechanism. Anodic polarization of titanium electrode in NaCl-containing ethylene glycol solutions involves dissolution of titanium as tetravalent species with the gas being evolved initially [16]. The electrochemical micromachining of pure titanium with ethylene glycol and sodium bromide of higher molar concentration up to 5 M delivered satisfactory results by sacrificing machining time due to the slower etch rate [17]. Aqueous solution of sodium bromide has been suitable for carrying out anodic dissolution of titanium with the help of conventional ECM in macroscopic domain [18].

As discussed above, various efforts have been taken by researchers for electrochemical dissolution of titanium utilizing a range of diverse type of electrolytes either by electrochemical etching, electrochemical polishing (EP) or by generating micropatterns with the help of photoresist, by using jet-EMM or with confined etchant layer technique. All these techniques were either utilizing expensive sophisticated processes or toxic and hazardous electrolytes mainly to generate micropatterns for surface structuring. Considering all these efforts and understanding emerging trend of micro machining domain, there is an urgent need to explore the potential use of electrochemical micromachining technique to generate micro features on commercially pure titanium. The most important factor in electrochemical micromachining of titanium is the selection of suitable electrolyte for successful electrochemical dissolution of titanium that too in micro domain. Therefore, attempts have been made in this paper to investigate the performance of seven different types of electrolytes to find out suitability for successful anodic dissolution of titanium in micro domain by generating through micro holes.

2 Experimental setup

EMM experimental setup used for generation of through micro hole in pure commercial titanium consists of different subsystems namely mechanical machining unit, desktop computer, DC pulsed power supply, digital storage oscilloscope (DL 1520 YOKOGAWA, Japan) and measuring microscope (Leica DM-2500, Germany), as shown in Fig. 1. Electrolyte tank fabricated from Perspex material with work holding arrangement was used for the experimentation. Mechanical machining unit consists of three long travel linear stages representing X, Y and Z axes. The stepper motors of each linear stage has a resolution of 0.1 μm/step, controlled by stepper motor controller unit, which is interfaced with desktop computer. Various feeds can possible to all or any of three stepper motors at a time by using position controller software installed on desktop computer. DC pulsed power supply were used for generating required nature of pulse power for micro machining operation. For online monitoring of pulse, digital storage oscilloscope is used, and for measurement of current values, Agilent multimeter has connected in series to the circuit. Stereo type microscope was utilized for observation and Lieca DM 2500 measuring microscope was used for measurement of machined microfeatures, i.e. micro hole.

3 Experimental planning

Tungsten micro rod of 200 μm diameter and 150 mm long is cut into small pieces of 20 mm each and soldered on copper tool holder. The front end of the tungsten micro rod was rubbed against fine grade of emery paper to make it perfectly flat. Pure commercial titanium of grade-1 sheet of 150 μm thickness and 20 mm in length and 10 mm in width were used. Composition and major properties of titanium are given in Table 1. The titanium workpiece was thoroughly cleaned and rinsed with acetone to remove grease and dirt. Electrolytes used in this experimentation are of seven different types. These seven different types of electrolyte were classified into two different categories, viz. aqueous base electrolytes and non-aqueous base electrolytes, i.e. electrolytes with very little or no water contents. Table 2 presents the type and concentration of electrolytes as well as specific conductivity of all seven electrolytes, measured at standard KCL solution with the help of conductivity meter. Values of EMM process parameters were determined based on extensive trial experiments. Selected process parameters such as applied voltage, pulse frequency, electrolyte concentration, duty ratio, etc. were represented in Table 3. Experiments were systematically planned and conducted and repeated thrice to remove the experimental error. All the machined samples were finally examined under scanning electron microscope (Zeiss EVO 40) for obtaining SEM images

3.1 Experimental methodology

All these seven electrolytes were experimented for possibility of anodic dissolution of titanium by attempting to generate micro holes utilizing maskless EMM technique with the help of developed EMM set up shown in Fig. 1. Out of these seven electrolytes, the electrolytes which demonstrated successful fabrication of micro holes by anodic dissolution were further evaluated based on radial overcut and degree of taper, i.e. conicity of micro holes. Thereafter electrolytes, which demonstrated controlled dissolution, were further, evaluated based on MRR, overcut and taper angle.

The entry diameter and exit diameter of micro holes have been measured and volume of micro hole has been calculate

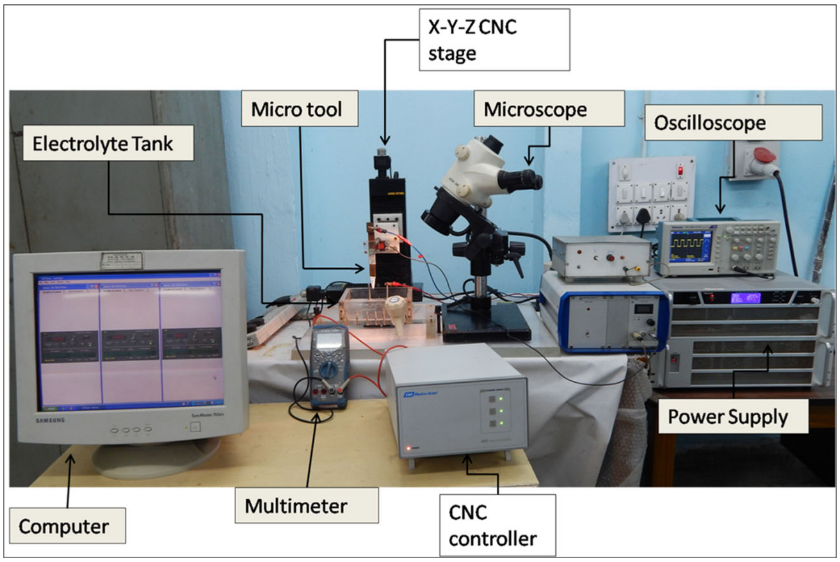


Fig. 1 Experimental set up

Table 1 Composition and major properties of titanium

S.No.	Description	Values
1	Composition of material	Commercially pure Ti grade Ti-99.2 % Fe-0.35 %, O-0.3 %, C-0.1 % N-0.05 %
2	Tensile strength (UTS)	240 MPa
3	Yield strength	170 MPa
4	Elongation	24 %
5	Modulus	102.7 GPa
6	Type of alloy	α

with the help of Eq. 1 assuming shape of micro hole as a frustum of cone. The volume of micro hole was converted into mass volume using density of commercial titanium (4.51 g/cm^3). Machining time of all the holes was recorded, based on recorded time MRR has been derived.

$$V_{\mathrm{m}} = \frac{\pi L}{3}\left(R^2 + R.r + r^2\right) \tag{1}$$

Where V_{m} is the volume of material in mm^3, R is the radius of entry side of micro hole, r is the radius of exit end of micro hole and L is the length of micro hole, i.e. thickness of workpiece as shown in Fig. 2.

The radial overcut (ROC) of micro hole was calculated by Eq. 2

$$ROC = \frac{Dh - Dt}{2} \tag{2}$$

Where D_{h} is the hole diameter at entrance and D_{t} is microtool diameter. Whereas the conicity has been derived from calculating taper angle (θ) of micro hole with the help of Eq. 3

Table 3 EMM process parameters

S.No.	Parameter	Value
1	Applied voltage (V)	12
2	Pulse frequency (kHz)	50
3	Duty ratio (%)	20
4	Tool feed rate (μm/s)	1
5	Inter electrode gap (μm)	15

$$Taper\ \mathrm{angle}(\theta) = \tan^{-1}\frac{Dh - d}{2L} \tag{3}$$

Where d is the diameter at exit of the hole and L is total length of hole, i.e. workpiece thickness.

4 Results and discussion

Formation of surface oxidation is one of the major problems associated with anodic dissolution of titanium due to recurrence of passive oxide film when titanium is exposed to atmosphere containing oxygen. This oxide film, which is passive in nature, prevents direct contact of material with the electrolyte hence normal electrochemical dissolution could not takes place. Formation of passive oxide layer on titanium surface in an electrochemical cell with aqueous medium was initiated by reacting Ti^{2+} with hydroxide ions (OH^-) ionized from water. Following plausible electrochemical interactions represent stable titanium oxide (TiO_2).

At anode and electrolyte interface, the reactions taking place are:

$$Ti \rightarrow Ti^{2+} + 2e^- \tag{4}$$

$$Ti^{2+} + H_2O \rightarrow Ti\,O^{2+} + H_2\uparrow \tag{5}$$

Table 2 Electrolytes and their concentration with specific conductivity

S.No.	Description	Molar concentration	Specific conductivity mS (milli Siemens)
1	Sodium bromide (NaBr)	1 M/L	15.5
2	Sodium chloride (NaCl)	1 M/L	15.4
3	Sodium perchlorate ($NaClO_4 \cdot H_2O$)	1 M/L	14.3
4	Hydrochloric acid (HCl)	1 M/L	14.7
5	Sulfuric acid (H_2SO_4)	1 M/L	14.2
6	Ethylene glycol (EG) and sodium bromide (EG + NaBr)	1 M (NaBr) with 1 L EG	6.5
7	Ethylene glycol (EG), sodium bromide and sodium chloride (EG + NaBr + NaCl)	1 M(NaBr) and 0.5 M (NaCl) with 1 L EG	7.3

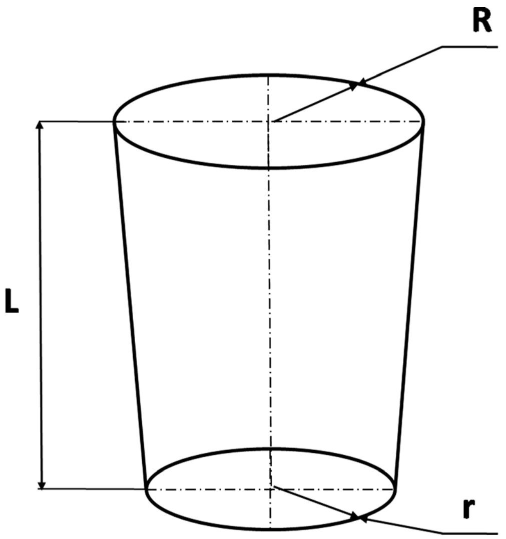


Fig. 2 Micro hole representing as frustum of cone

The oxocation, TiO^{2+} is acidic in nature and subsequently reacts with OH^- to form stable TiO_2 [19] following chemical reaction takes place:

$$\mathrm{Ti\,O^{2+}} + 2\mathrm{OH^-} \rightarrow \mathrm{TiO_2} + \mathrm{H_2O} \tag{6}$$

During the anodic dissolution process, the externally applied electric field accelerates formation of oxide film with the help of titanium and hydroxide ions.

4.1 Effect of electrolytes on average current density

In order to make smoother anodic dissolution of titanium, passive oxide film must break. To break this passive oxide layer of titanium, nature of electrolyte and machining voltage is the major influencing EMM process parameters. Machining voltage utilized in this study is comparatively higher machining voltage of 12 V, which is higher than the normal range of machining voltage utilized in maskless EMM of other metals.

Average current density obtained at this machining voltage with each electrolyte has been obtained from measured machining current during micromachining. Figure 3 represents the average current density of each electrolyte. Performance of aqueous and non-aqueous electrolytes during electrochemical micromachining of titanium is discussed hereunder.

4.1.1 Effect of aqueous base electrolytes on anodic dissolution of titanium

Aqueous base electrolytes were prepared with one molar concentration in a litre of double distilled water. Electrolyte containing aqueous hydrochloric acid (HCI) was the first candidate studied for anodic dissolution of titanium by electrochemical micromachining process. The machining voltage were applied between tungsten microtool and titanium workpiece, which is maintained IEG of 15 μm, the other process parameters were fixed as pulse frequency 50 kHz, duty ratio 20 % and microtool federate as 1 μm/s. From Fig. 3, it has been observed that the average current density achieved up to 1.97 A/mm^2. The specific conductivity of aqueous HCI electrolyte is found to be 14.7 mS. Chloride ions present in the aqueous HCI solution reacts with titanium to form titanium tetrachloride. Following electrochemical interaction takes place at the anode in the electrolytic cell:

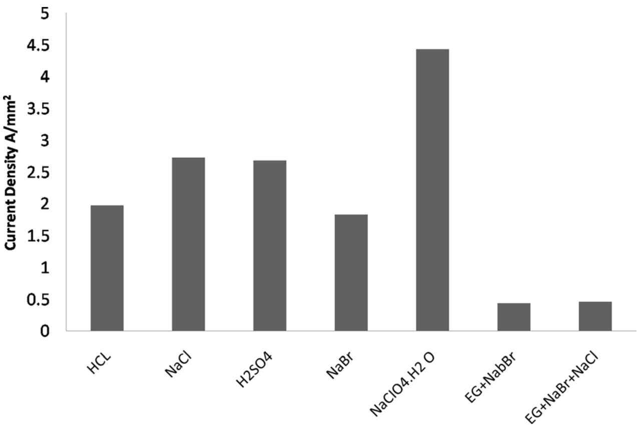


Fig. 3 Average current density achieved in all seven electrolytes

$$\mathrm{Ti} + 4\mathrm{Cl^-} \rightarrow \mathrm{Ti\,Cl_4} + 4\mathrm{e^-} \tag{7}$$

Titanium tetrachloride formed in above reaction is further hydrolyses to form $Ti(OH)_2^{2+}$ cations, which is soluble in water due to lower pH value of HCl solution because of acidic medium [19]. Hence, dissolution of titanium is possible with aqueous HCl electrolyte.

Machining continues up to 3.19 min and through micro hole has been generated. Figure 4 shows the SEM micrograph of machined micro holes. From Fig. 4, it is clear that the anodic dissolution of titanium is uncontrolled with uneven etching leading to high pitting area formed at the entry of the micro hole. Formation of black oxide layer with pitting marks is clearly visible on the entry as well as on the wall surface of the micro hole.

Another acidic electrolyte utilized was aqueous sulfuric acid of 1 M concentration with specific conductivity of 14.2 mS, average current density achieved by applied potential is 2.68 A/mm^2. Aqueous nature of electrolyte enhances passivity of oxide film. Therefore, achieved average current density is not sufficient to initiate dissolution by converting passive oxide film into transpassive nature. The cathode microtool continues to advance towards anode workpiece and finally touches the anode surface leading to short circuit situation results in termination of machining process. Probable interaction of passive oxide film with aqueous solution of H_2SO_4 is represented in Eq. (8).

$$\mathrm{TiO_2} + \mathrm{H_2SO_4} \rightarrow \mathrm{TiO\,(SO_4).H_2O} \tag{8}$$

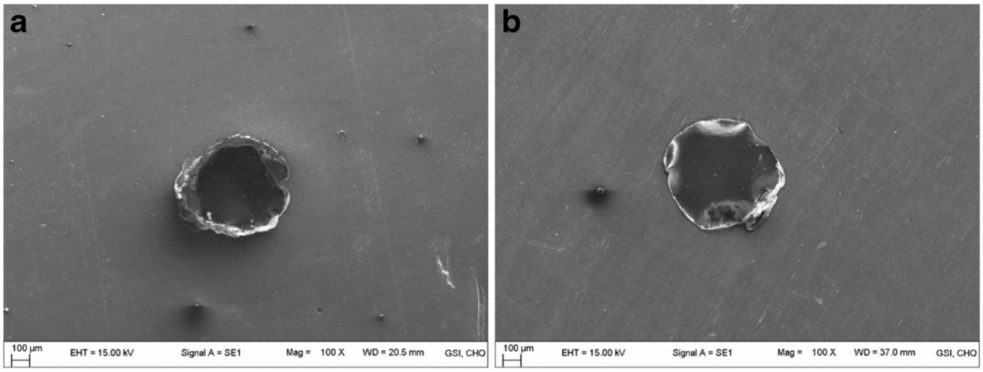


Fig. 4 Micro hole machined with aqueous HCl electrolyte. **a** Entry; **b** exit of micro hole

In this interaction, titanium oxide reacts to form monohydrate titanium oxosulfate [19], which is insoluble in nature and deposit on the surface of anode thus prevents etching of material.

A highly irregular small local pitting mark with passive oxide film has clearly seen in and around the machining zone as shown in Fig. 5.

Further machining was performed with aqueous electrolyte of 1 M/L concentration of sodium chloride (NaCl). One molar per litre concentration of sodium chloride (NaCl) possesses fairly good specific conductivity of 15.4 mS and falls in the category of strong electrolytes. Current density rose to 2.75 A/mm^2 at voltage of 12 V. The experimental observation reveals that it is not capable to break down passive oxide film uniformly to initiate anodic dissolution for micromachining of titanium. This may be due to the aqueous nature of electrolyte, which further enhances the passivity of titanium as well as presence of chloride raise the break down potential of passive film [8]. Also, presence of chloride ions in aqueous NaCl solution reacts with titanium to form titanium tetrachloride, but due to the neutral pH value of NaCl solution, hydrolysis of titanium tetrachloride does not takes place significantly [19] and it may be deposited on the surface of titanium and slow down dissolution process. Hence, dissolution process ceases and microtool did not travel beyond 35 micron. The uncontrolled pitting with poor surface has been formed, which is clearly visible in SEM micrograph as shown in Fig. 6.

Color of the electrolyte changes to yellowish and formation of brown colored layer of sludge has been observed around the microtool in machining zone. The formation of brown sludge is due to the particles which emerge out from local pitting of oxide film which is rapidly formed owing to aqueous nature of electrolyte. Titanium surface changes to brown colour and its crystallization starts with evolution of chlorine gas [16]. To break down this crystallized oxide film and to achieve smooth dissolution, further increase in the potential may be required.

Electrolyte of aqueous solution of sodium bromide (NaBr) with the highest specific conductivity of 15.5 mS has shown satisfactory dissolution at an average current density of 1.83 A/mm^2. The efficiency for the dissolution of titanium in bromide electrolytes is based on the 4-valent reaction to form stable crystalline titanium(IV) bromide, as shown in Eq. (9).

$$\mathrm{Ti} + 4\mathrm{Br}^- \rightarrow \mathrm{TiBr}_4 + 4e^- \tag{9}$$

A micro hole generated with aqueous NaBr electrolyte is visible in SEM image represented in Fig. 7. The micro hole machined with aqueous NaBr has shown improved anodic

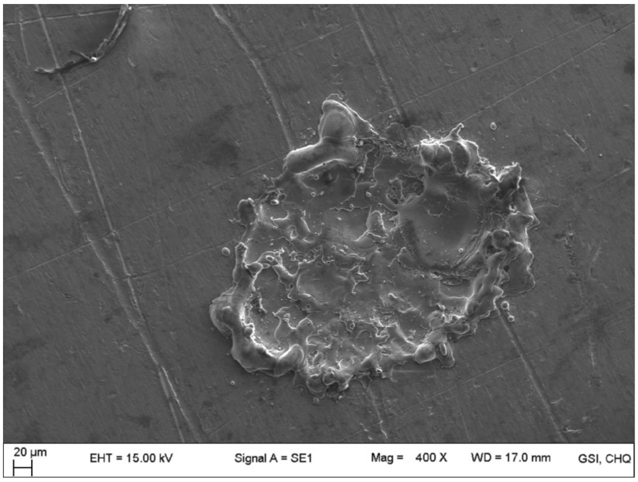


Fig. 5 Un-machined micro hole with aqueous H_2SO_4 electrolyte

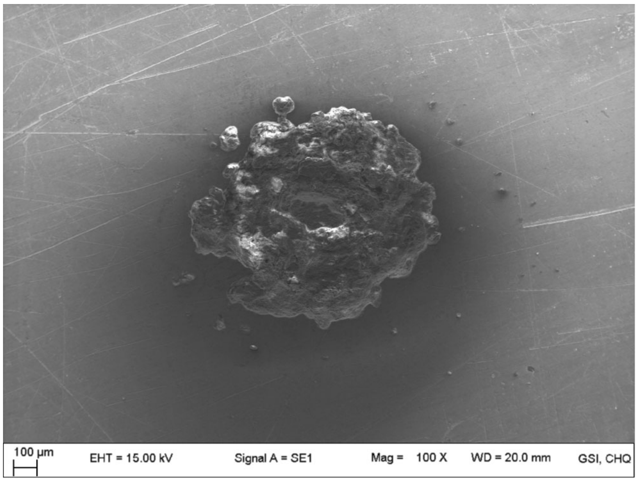


Fig. 6 Un-machined micro hole with aqueous NaCl electrolyte

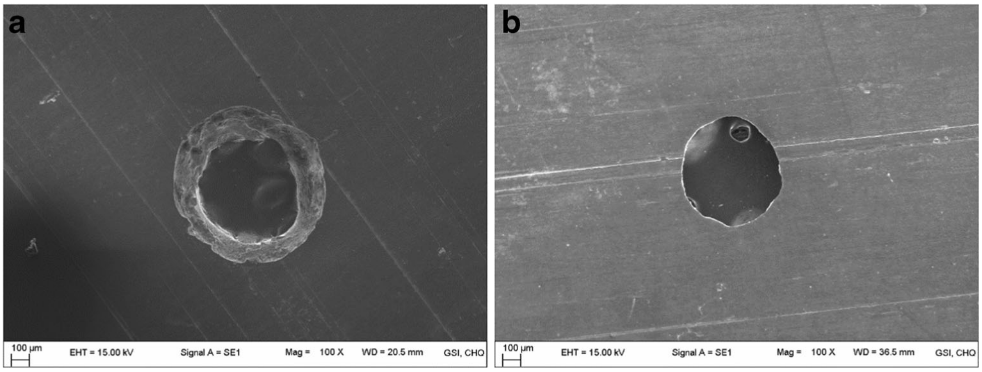


Fig. 7 Micro hole machined with aqueous NaBr electrolyte. **a** Entry; **b** exit of micro hole

dissolution compared to acid base electrolyte as discussed earlier. Surface of the inner wall of micro hole shows less pitting marks and demonstrate uniform dissolution with controlled shape profile at the entry and exit of micro hole. Average machining time taken to generate a through micro hole with aqueous sodium bromide electrolyte is 2.49 min, which is less than the dissolution achieved in dilute HCL electrolyte.

Further, the dissolution of titanium has performed with aqueous solution of sodium perchlorate ($NaClO_4.H_2O$) by converting the passive oxide film into transpassive. Sodium perchlorate ($NaClO_4 \cdot H_2O$) is having ability to lower down oxidizing power and it has reported to produce less oxide during electrochemical interaction with titanium [20]. The ClO_4 ions is known to attack the oxide film, causing pitting which leads to increase in current efficiency and hence dissolution [21]. The average current density of 4.43 A/mm^2 was observed which is highest amongst these seven electrolytes. The specific conductivity of this electrolyte is 14.3 mS which is less than aqueous sodium bromide solution. The rise in current density is due to high dissolution rate, which leads to rapid dissolution of metal result in generation of through microhole, which is shown in SEM micrograph presented by Fig. 8. From the SEM micrograph, it has seen that the micro hole maintained good shape profile compared to micro hole machined with aqueous sodium bromide. High pitting marks with peaks and valleys with poor surface quality appeared at the entrance of hole as well as on the wall of micro hole due to the high current density, as shown in Fig. 9, which is a magnified view of circled area "A" of Fig. 8.

All the above-mentioned electrolytes were aqueous base electrolytes, i.e. they all have presence of water contents. Hence, formation of black oxide layer has been observed in all the micro holes machined with aqueous base electrolytes.

4.1.2 Effect of non-aqueous base electrolytes on anodic dissolution of titanium

To study the behaviour of dissolution of titanium in non-aqueous base electrolytes, titanium has been electrochemically dissolved using electrolyte prepared by combination of 1 M sodium bromide with 1 L of ethylene glycol. The micromachining results show formation of shiny ring like area at the entry of the hole with local pitting marks has been observed, which is clearly visible in SEM image as shown in Fig. 10.

The addition of sodium bromide helps to dissolve titanium with its valence to form $TiBr_4$ which reacts with glycol to yield soluble titanium glycolate [19]. Ethylene glycol also prevents the contact of oxygen during machining. The advantage of using ethylene glycol is formation of less gas bubbles due to very low or no water content, i.e. less than 0.3 % in the ethylene glycol electrolyte as compared to aqueous electrolytes.

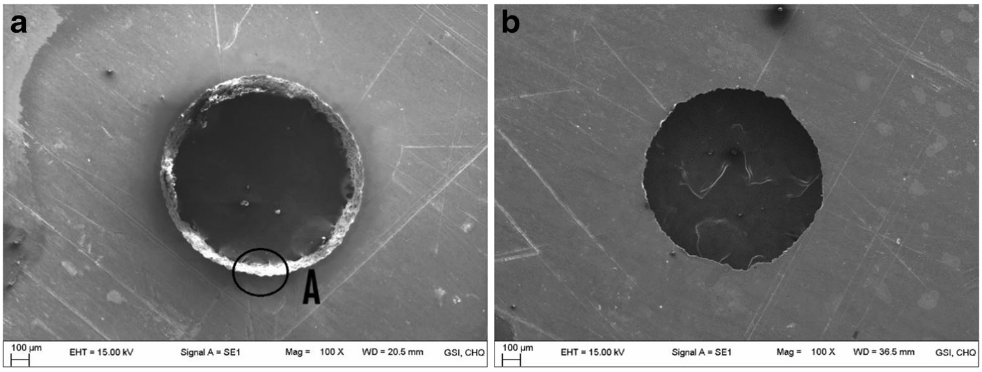


Fig. 8 Micro hole machined with aqueous sodium perchlorate electrolyte. **a** Entry; **b** exit of micro hole

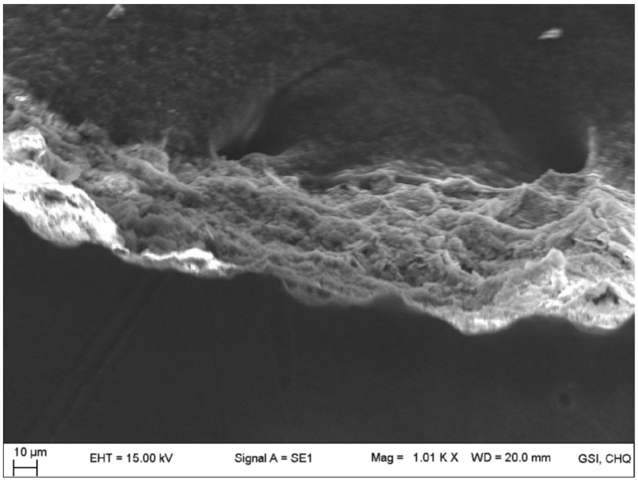


Fig. 9 Magnified image of surface area of micro hole machined with sodium perchlorate

The minimization of gas bubbles is due to the reduction in evolved gas, i.e. hydrogen at cathode and oxygen at the anode surface. A ring of uneven etched surface with pitting marks has been observed at the entrance of the hole due to the effect of lateral current flux flowing through the peripheral surface of bare uncoated cylindrical tungsten micro tool. The average current density has found to be 0.43 A/mm^2, which is far less than aqueous electrolytes. The presence of bromide ions with non-aqueous solution has demonstrated controlled nature of titanium dissolution even though at low specific conductivity of 6.5 mS. Hence, it has proved that water-free bromide electrolyte deliver excellent results compared to aqueous base bromide electrolyte for electrochemical micromachining of titanium.

It has been reported that the smoother surface was obtained if titanium is to be electrochemically dissolved in sodium chloride with low or no water content [22]. Hence, an electrolyte containing combination of NaCl and NaBr in ethylene glycol was employed in the further investigation. The advantage of using sodium bromide along with sodium chloride is valence dissolution of titanium by breaking of its oxide film. The results obtained by utilizing this electrolyte are shown in Fig. 11

Effect of using NaCl with NaBr in ethylene glycol has reduced the effect of pitting at the entry of the hole. The entry side of the hole shows lesser stray current effects compared to hole machined in electrolyte containing NaBr with ethylene glycol. The average current density was observed to be 0.46 A/mm^2, which is slightly larger than the previous electrolyte due to its specific conductivity of 7.5 mS. This clearly indicates that these electrolytes are potential candidates for anodic dissolution of titanium in micro domain.

Anodic dissolution of titanium is possible with five out of seven different electrolytes by generating through micro holes utilizing EMM technique. The electrolyte that consist of sodium perchlorate ($NaClO_4$) has shown highest current density, whereas lowest current density was obtained with non-aqueous electrolyte of ethylene glycol and sodium bromide (EG + NaBr). Only two electrolytes consist of aqueous sulfuric acid and aqueous NaCl do not exhibit satisfactory dissolution of titanium.

4.2 Effect of electrolytes on radial overcut and degree of taper in micro hole

Micro holes machined with five different electrolytes were evaluated based on radial overcut at the entry and exit of micro as well as conicity of micro hole. Figure 12 represents average radial overcut at entry of the micro hole machined in all these five electrolytes.

From Fig. 12, it has been clearly observed that the radial overcut of micro hole machined by utilizing sodium perchlorate electrolyte is highest amongst the holes generated with other electrolytes. This is due to the higher mass transfer dissolution of titanium in sodium perchlorate. The mass transfer dissolution is the mass of the workpiece that dissolves, is transferred away from it, resulting in flow of mass transfer current. Mass transfer occurs due to migration, diffusion and convection. An increase in current density leads to an increase in the rate of metal dissolution at the anode. In the present study, it has been observed that the current density obtained during anodic dissolution of titanium with sodium perchlorate electrolyte is highest amongst all electrolytes; hence, higher

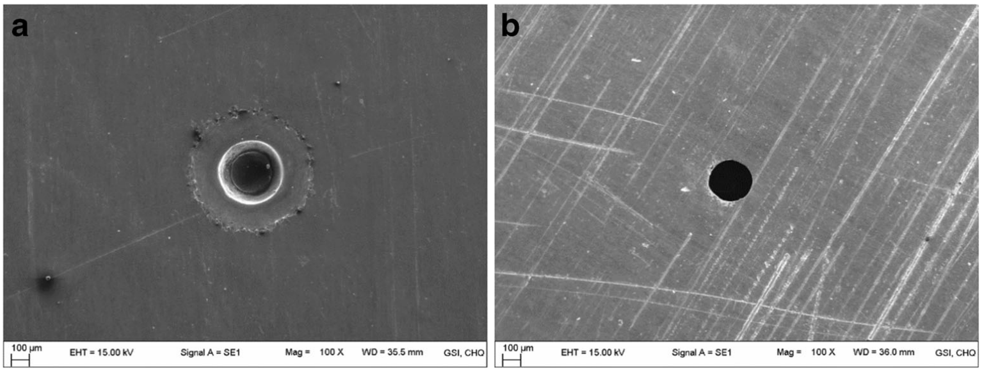
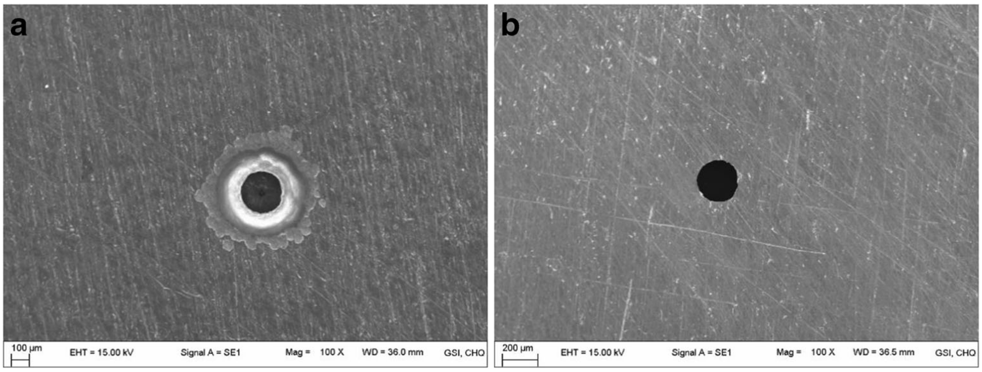


Fig. 10 Micro hole machined with ethylene glycol (EG) and sodium bromide electrolyte. **a** Entry; **b** exit of micro hole

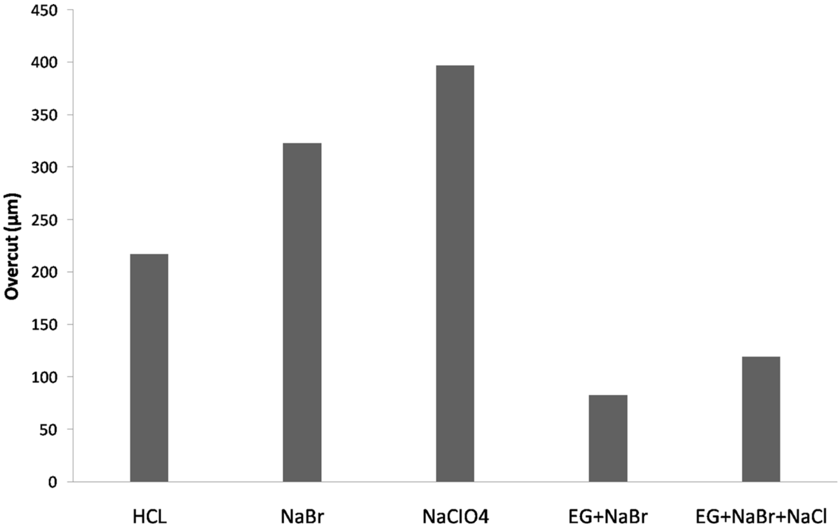
Fig. 11 Micro hole machined with ethylene glycol (EG) with sodium bromide and sodium chloride electrolyte. **a** Entry; **b** exit of micro hole



metal dissolution through mass transport takes place with 12 V potential. Whereas, in the case of electrolytes such as aqueous H_2SO_4 and aqueous NaCl, the current density achieved with the same potential is not capable to break down oxide film to initiate smooth dissolution therefore mass transfer dissolution is not predominant for these two electrolytes. However, the rest of all electrolytes demonstrated mass transfer dissolution of titanium under 12 V machining voltage. The hole machined in HCl also shows high value of overcut but generating poor geometry of the hole. Overcut observed in non-aqueous electrolytes, i.e. EG + NaBr and EG + NaBr + NaCl, is much lesser than aqueous base electrolytes keeping all other EMM process parameters same as mentioned in Table 3. The minimum overcut obtained with ethylene glycol and sodium bromide electrolyte is due to its very low current density compared to aqueous-based electrolytes, mainly aqueous sodium bromide and aqueous sodium perchlorate ($NaClO_4$). The microtool feed rate was constant in both the cases; hence, with the same microtool feed rate, the material removal with aqueous base electrolytes is higher than that with non-aqueous base electrolytes which results in higher overcut in the microhole machined with aqueous electrolytes. The effective microtool stay time with respect to current density achieved is more in aqueous base electrolytes than non-aqueous base electrolytes. Hence, material removal and thus overcut is higher in microholes machined with aqueous base electrolytes.

Figure 13 represents average taper angle of the micro holes machined in different electrolytes. All the microholes were machined with bare microtool, i.e. microtool with no insulation applied on its sidewall. Hence, tapering effect is predominant in almost all microholes. However, higher taper angle has been observed in the micro hole machined with aqueous NaBr as an electrolyte. It has also been observed that the taper angle of micro hole machined with sodium perchlorate ($NaClO_4$) is lesser even though it has the highest current density. This effect is due to higher dissolution rate at a constant feed rate and travel of microtool, i.e. the material removal is much higher right from entry point of microhole to the exit point hence, less difference between the entry and exit diameters of microhole machined with sodium perchlorate ($NaClO_4$) electrolyte. However, it generates the highest radial overcut due to higher dissolution rate with less taper angle. In addition to that, the time of stay of tool in the workpiece during travel of tool, which is dependent on feed rate. The effect of taper can be reduced by selecting optimum tool feed

Fig. 12 Radial overcut of each electrolyte



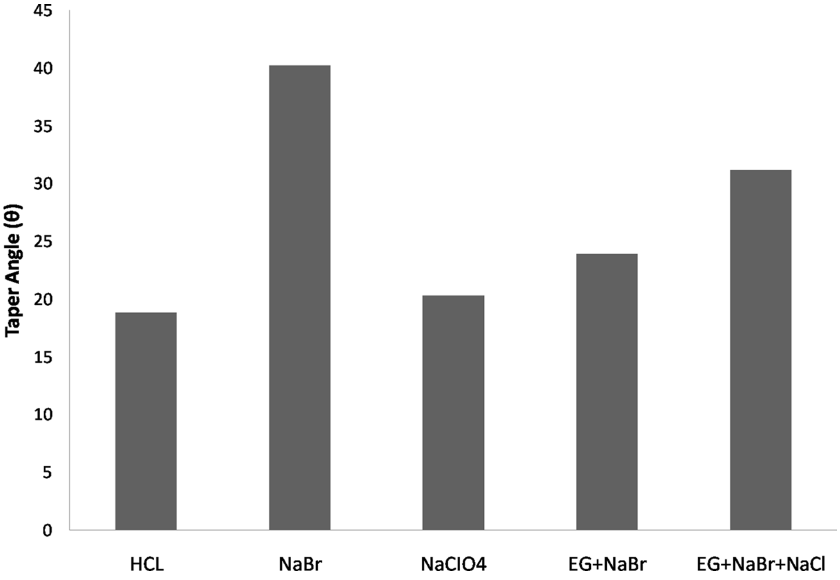


Fig. 13 Variation in degree of taper with each electrolyte

rate and utilizing the cylindrical micro tool with insulated peripheral surface by keeping the front-end surface open for current flux. Minimum taper was observed in aqueous electrolyte of HCL and electrolyte with sodium perchlorate.

The successful machining of through micro holes by anodic dissolution of titanium through EMM is possible with five electrolytes, i.e. aqueous HCl, NaBr, $NaClO_4$, EG + NaBr and EG + NaBr + NaCl. Out of these five different electrolytes, two non-aqueous electrolytes containing ethylene glycol, i.e. EG + NaBr and EG + NaBr + NaCl, exhibit controlled anodic dissolution of titanium with lesser current density and lesser radial overcut but relatively larger taper effect compared to aqueous base electrolytes with same EMM process parameters settings. Hence, these two electrolytes are further evaluated based on MRR, overcut and degree of taper of microholes machined individually utilizing these two non-aqueous base electrolytes and are discussed hereunder.

4.3 Effect of ethylene glycol-based electrolyte on MRR, overcut and degree of taper in micro hole

To study the suitability of non-aqueous electrolytes for electrochemical micromachining of titanium, a set of experiments was further carried out to machine micro holes by varying duty ratio and keeping all other machining parameters unchanged.

4.3.1 Effect of ethylene glycol-based electrolyte on material removal rate

Machining time of each micro hole was recorded and volume of material removed was calculated with the help of Eq. 1, and based on that, the material removal rate was calculated. Variation of MRR has been plotted against the duty ratio as shown in Fig. 14.

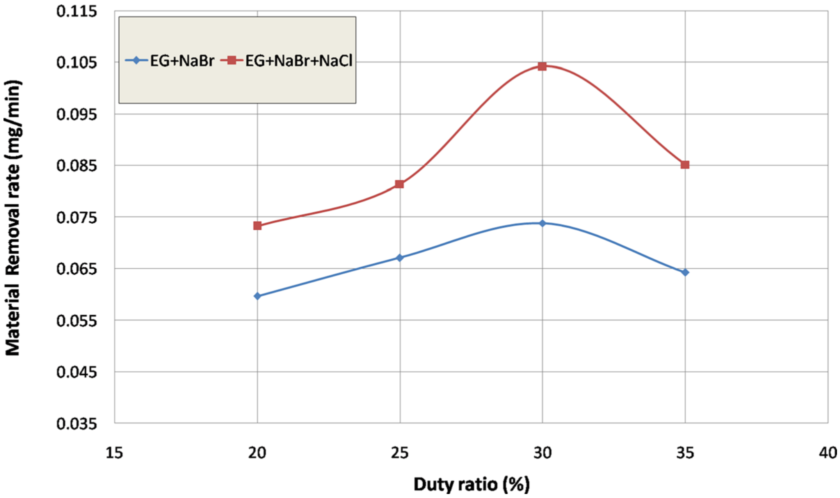
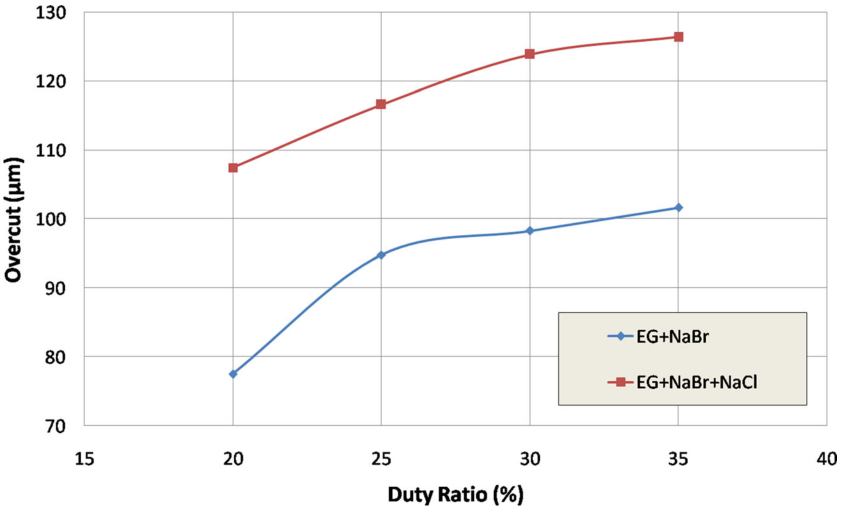


Fig. 14 Effect of duty ratio on material removal rate

Fig. 15 Effect of duty ratio on radial overcut



Both these electrolytes have shown increase in material removal rate with duty ratio. As the duty ratio increases, the pulse ON time increases results in more time available for machining current leading to higher material removal. In the case of electrolyte containing EG + NaBr + NaCl material removal rate has increased rapidly from 0.081 to 0.104 mg/min with increase in duty ratio from 25 to 30 % and then reduces to 0.085 mg/min. The further increase in duty ratio results in increase of dissolution efficiency due to more time is available for flowing of machining current tends to increase in stray current phenomenon leading to less localization of machining and hence reduction in linear material removal rate. Similar trend is also observed in micro holes machined with EG + NaBr electrolyte except the rate of material removal is comparatively lower, i.e. MRR increases from 0.067 to 0.073 mg/min from 25 to 30 % duty ratio and then declined to 0.064 mg/min at 35 % duty ratio. Hence, this indicates that out of these two electrolytes, electrolyte containing EG + NaBr has demonstrated controlled material removal rate up to 30 % duty ratio.

4.3.2 Effect of ethylene glycol-based electrolyte on overcut

Micro holes machined with both non-aqueous electrolytes, i.e. EG + NaBr and EG + NaBr + NaCl, demonstrated the trend of increase in radial overcut with increase in duty ratio; Fig. 15 clearly exhibits the trend.

In the case of electrolyte EG + NaBr + NaCl, the change in overcut is linear from duty ratio 20 to 30 % due to steady increase in dissolution rate. The micro hole machined with electrolyte containing EG + NaBr shows the rapid change in overcut from 77.4 to 94.7 μm is observed with the change in duty ratio from 20 to 25 % and then increases steadily.

From the Fig. 15, it can be observed that the overcut is increasing with duty ratio. In the case of larger duty ratio, the on-time of pulse duration increases and improves the dissolution not only in linear direction but also in radial direction which causes more material removal from the larger surface area of the workpiece especially along the inner wall of micro hole and hence increase in radial overcut of micro hole. In the case of shorter duty ratio, more localized anodic dissolution was achieved which results in less overcut. If pulse ON time is less, more time is available for pulse OFF time within a pulse period, and hence, possibility of achieving lesser overcut is more. Increase in pulse off time helps to dissipate Joule heat from the machining zone, as well as easy removal of sludges and gas bubbles, which results in improved linear dissolution with minimum overcut. As discussed earlier, duty ratio increases, larger material removal takes place leading to higher

Fig. 16 Micro hole machined at 20 % duty ratio. **a** With EG + NaBr; **b** EG + NaBr + NaCl

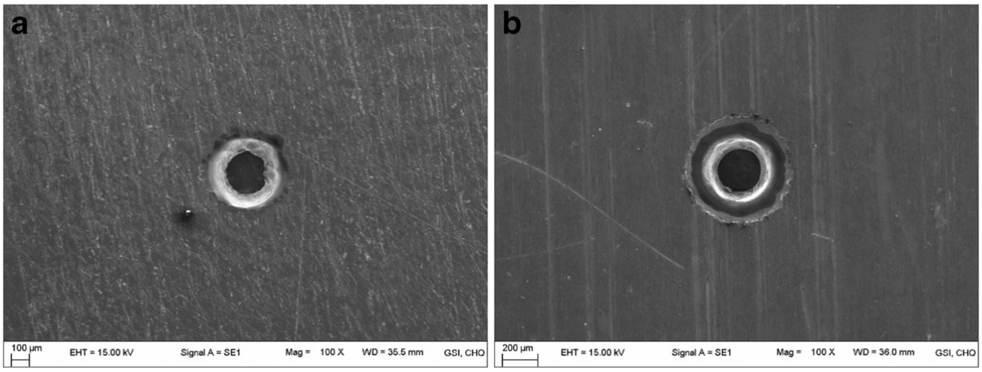
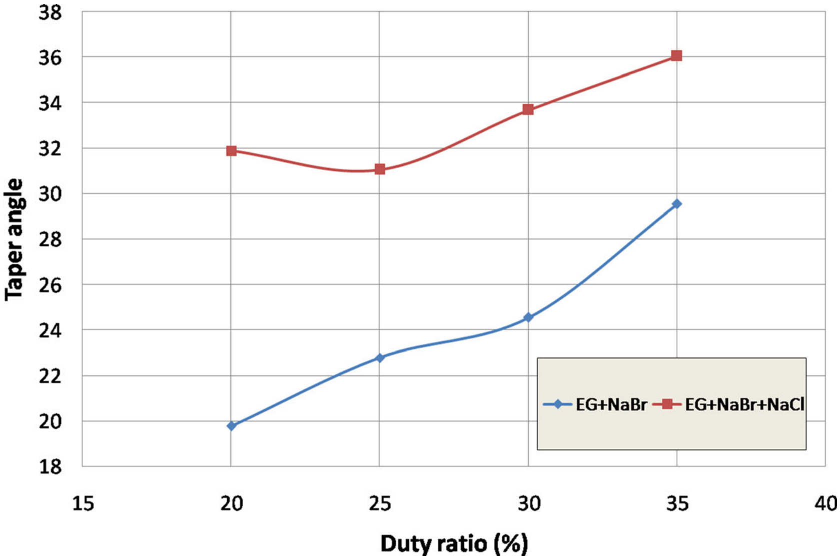


Fig. 17 Effect of duty ratio on taper angle



overcut phenomenon. Overcut can be minimized by selecting proper feed, i.e. the feed of the tool should synchronized with rate of material removal so that constant IEG should be maintain throughout the travel of tool. Use of insulated micro tool minimizes stray current effect, which in turn reduces overcut.

Electrolyte containing EG + NaBr demonstrated lesser overcut compared to electrolyte with EG + NaBr + NaCl. Micro hole machined with 20 % duty ratio in both the non-aqueous electrolytes is shown in Fig. 16.

4.3.3 Effect of ethylene glycol-based electrolyte on conicity or degree of taper in micro hole

Degree of taper or conicity of micro holes is an important quality consideration of micro holes. Machining of micro size holes having straight walls is a major requirement. Conicity is caused by the rate of metal removal varying along the length of the hole [23]. Variation of taper angle of micro hole with duty ratio has been plotted as shown in Fig. 17.

Micro holes machined with electrolyte consisting of EG + NaBr show lower degree of taper at lower duty ratio and increase with duty ratio. As the duty ratio increases, localized machining decreases results in reduction of linear material dissolution, leads to uncontrolled and scattered nature of material removal particularly, while microtool approaching workpiece within initial IEG results in larger overcut at the entry of micro hole. Thereafter, microtool further advances into the anode workpiece machining depth increases, circulation of fresh electrolyte becomes crucial and accumulation of sludge in the narrow machining gap increases, which results in lower down material removal rate leading to generation of smaller diameter at exit of microhole compared to entry. Hence, tapering effect takes place and microhole becomes tapered in shape. Effect of taper in micro hole is clearly observed in SEM micrograph represented in Fig. 18. The micro hole shown in Fig. 18 was machined with EG + NaBr electrolyte keeping all EMM process parameters remain same as presented in Table 3.

This phenomenon of formation of taper can be minimized by achieving more linear dissolution of material by maintaining linear relationship between the microtool feed rate and material removal rate. Employing smaller IEG with reduced stray current effect and utilizing proper insulation on the side walls of micro tool will also help to control the tapering effect of micro hole.

Out of these two non-aqueous electrolytes, electrolyte which consists of EG + NaBr demonstrated excellent results compared to electrolyte of EG + NaBr + NaCl on the basis of radial overcut and degree of taper, whereas material removal rate is larger in the case of EG + NaBr + NaCl electrolyte. Addition of NaCl increases average current density as well as specific conductivity of the electrolyte during micromachining compared to only bromide base ethylene

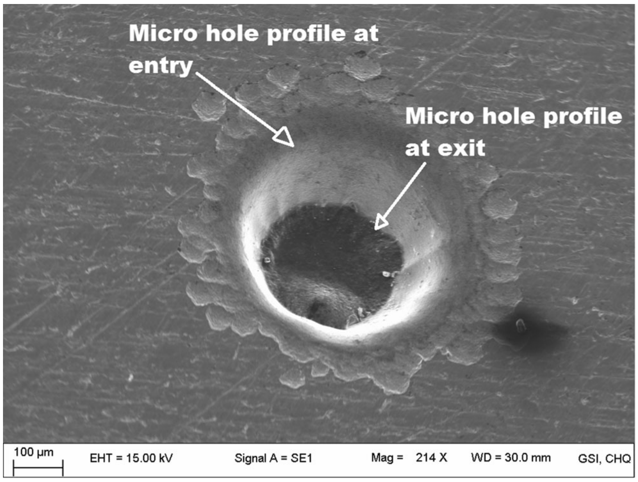


Fig. 18 Micro hole profile

glycol electrolyte. Formation of black oxide layer is not significant on the wall of micro holes machined with non-aqueous electrolytes.

5 Conclusions

Anodic dissolution of titanium through electrochemical micromachining process is relatively different from EMM of commonly used metals due to the tendency of formation of passive oxide layer. To break this passive nature of oxide layer and to make it transpassive in order to carry out the anodic dissolution of titanium successfully in EMM, electrolytes play a major role. The present study has demonstrated successful investigation of suitability of electrolyte for anodic dissolution of titanium through maskless EMM by utilizing seven different types of electrolytes by means of machining through micro holes in pure commercial titanium. The electrolytes are classified into two different categories, i.e. aqueous base electrolytes and non-aqueous base electrolytes. Aqueous base electrolytes contain acid base and salt base electrolytes and non-aqueous base electrolytes comprising of ethylene glycol with sodium bromide and sodium chloride. Based on the various results obtained in this study in terms of current density, radial overcut of micro holes, conicity or degree of taper of micro holes and comparative study of two non-aqueous base electrolytes, the following concluding remarks have been derived.

(i) Based on the criteria of anodic dissolution of titanium, five electrolytes, viz. aqueous solution of hydrochloric acid (HCl), sodium perchlorate ($NaClO_4$), sodium bromide (NaBr), ethylene glycol (EG) with sodium bromide and ethylene glycol (EG), with sodium bromide and sodium chloride (NaCl), has demonstrated successful machining of through micro holes using maskless EMM process parameters.

(ii) Amongst the category of aqueous base electrolytes, sodium perchlorate and sodium bromide are found to be suitable for anodic dissolution of titanium. These two electrolytes can be effectively utilize for controlled electrochemical micro machining of titanium by employing lower range of machining voltage and duty ratio. Formation of black oxide film is predominant in all the aqueous base electrolytes.

(iii) Two non-aqueous base electrolytes, which consist of EG + NaBr and EG + NaBr + NaCl, have demonstrated excellent controlled anodic dissolution of titanium based on the criteria of lesser radial overcut and lower taper angle of the micro holes machined with these electrolytes.

(iv) Higher metal removal rate has been observed in electrolyte solution of EG + NaBr + NaCl compared to electrolyte solution of EG + NaBr. Considering the test results, overall performance in terms of overcut, current density and electrolyte solution of EG + NaBr is preferred amongst the two non-aqueous electrolytes for anodic dissolution of titanium through maskless electrochemical micromachining process.

The prime objective of this study was to investigate suitable electrolyte for successful electrochemical micromachining of titanium. To fulfill the said objective, this study has contributed towards the suitability of electrolytes for electrochemical micromachining of titanium, which is an urgent need for EMM of titanium. Electrolytes with aqueous base of sodium bromide and sodium perchlorate can also be effectively employed for controlled anodic dissolution of titanium by carefully choosing EMM process parameters. Dense black oxide layer was obtained in all aqueous base electrolytes, which has versatile applications in biomedical implants where titanium is a preferable material.

Outcome of this experimentation has explored the effective utility of eco-friendly and cost effective non-aqueous electrolyte solution of ethylene glycol with sodium bromide for EMM of titanium. This can further exploit to machine micro nozzles as well as complex micro features on titanium for MEMS as well as micro engineering and biomedical applications by utilizing the optimum combination of various electrochemical micromachining process parameters.

References

1. Ezugwu EO, Wang ZM (1997) Titanium alloys and their machinability—a review. J Mater Process Technol 68:262–274
2. Kumar Jatinder, Khamba JS, Mohapatra SK (2008) An investigation into the machining characteristics of titanium using ultrasonic machining. Int. J. Mach Mach Mater 3:Nos. 1/2
3. Lin YC, Yan BH, Chang YS (2000) Machining characteristics of titanium alloy (Ti6Al4V) using a combination process of EDM with USM. J Mater Process Technol 104:171–177
4. Jain VK, Kalia S, Sidpara A, Kulkarni VN (2012) Fabrication of micro-features and micro-tools using electrochemical micromachining. Int J Adv Manuf Technol 61:1175–1183
5. Lee ES, Baek SY, Cho CR (2007) A study of the characteristics for electrochemical micromachining with ultrashort voltage pulses. Int J Adv Manuf Technol 31:762–769
6. Bhattacharyya B, Malapati M, Munda J (2005) Experimental study on electrochemical micromachining. J Mater Process Technol 169: 485–492
7. Aladjem A (1973) Anodic oxidation of titanium and its alloys. J Mater Sci 8:688–704
8. Bannard J (1976) On the electrochemical machining of some titanium alloys in bromide electrolytes. J Appl Electrochem 6:477–483
9. Madore C, Landolt D (1997) Electrochemical micromachining of controlled topographies on titanium for biological applications. J Micromech Microeng 7:270–275

10. Piotrowski O, Madore C, Landolt D (1998) The mechanism of electropolishing of titanium in methanol-sulfuric acid electrolytes. J Electrochem Soc 145:7, The Electrochemical Society, Inc
11. Landolt D, Chauvy PF, Zinger O (2003) Electrochemical micromachining, polishing and surface structuring of metals: fundamental aspects and new developments. Electrochim Acta 48: 3185–3201
12. Zinger O, Chauvy PF, Landolt D (2003) Scale-resolved electrochemical surface structuring of titanium for biological applications. J Electrochem Soc 150(11):B495–B503
13. Kern P, Vehand J, Michler J (2007) New developments in through-mask electrochemical micromachining of titanium. J Micromech Microeng 17:1168–1177
14. Jiang LM, Li W, Attia A, Cheng ZY, Tang J, Tian ZQ, Tian ZW (2008) A potential method for electrochemical micromachining of titanium alloy Ti6Al4V. J Appl Electrochem 38:785–791
15. Lu X, Leng Y (2005) Electrochemical micromachining of titanium surfaces for biomedical applications. J Mater Process Technol 169: 173–178
16. Koji F, Hiroki H (2008) Anodic dissolution of titanium in NaCl containing ethylene glycol. Elechtrochim Acta 53:3371–3376
17. Sjöström T, Bo S (2011) Micropatterning of titanium surfaces using electrochemical micromachining with an ethylene glycol electrolyte. Mater Lett 65:3489–3492
18. Dhobe SD, Doloi B, Bhattacharyya B (2011) Surface characteristics of ECMed titanium work samples for biomedical applications. Int J Adv Manuf Technol 55:177–188
19. Cotton FA, Wilkinson G, Murillo CA, Bochmann M (1999) Advanced inorganic chemistry, 6th edn. Wiley, New York
20. Clifton J, Mount AR, Jardine DJ, Roth R (2001) Electrochemical machining of gamma titanium aluminide in intermettallics. J Mater Process Technol 108:338–348
21. McGeough JA (1974) Principles of electrochemical machining. Chapman and Hall
22. Fushimi K, Kondo H, Konno H (2009) Anodic dissolution of titanium in chloride-containing ethylene glycol solution. Electrochim Acta 55:258–264
23. Mohan S, Shan HS (2005) A review of electrochemical macro- to micro-hole drilling processes. Intl J Mach Tools Manuf 45:137–152