Chapter 9
Electrochemical Micromachining of Titanium and Its Alloys

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Abstract Miniaturization has covered every area of modern world. Micromachining is one of the key technologies that can enable the realization of almost all requirements of the microproducts and related domain. However, materials which can micromachined easily and used in present day Microsystems, MEMS and microengineering applications have some limitations such as low strength to weight ratio, corrosion resistance and biocompatibility. Titanium is one of the potential material and arising as alternative to the conventional MEMS materials particularly silicon or silicon based materials or glass. Titanium is known as super metal due to its high strength to weight ratio, excellent corrosion resistance and superior biocompatibility. This chapter highlights the challenges in micromachining of titanium and its alloys as well as potential use of electrochemical micromachining (EMM) technique for micromachining of titanium. Utilization of masked i.e. TMEMM as well as maskless electrochemical micromachining techniques for generation of various microfeatures on titanium has been presented in this chapter. Effect of various EMM process parameters on machining accuracy of microfeatures of titanium as well as most suitable EMM process parameters for fabrication of various complex microfeatures on titanium has also been discussed. This chapter provides comprehensive information on electrochemical micromachining of titanium and its prospective applications in the area of MEMS, Bio-MEMS and microengineering fields.

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9.1 Introduction

Miniaturization of the product and systems is in increasing demand in today's world. The miniaturization has covered every area of modern world. To name a few are micro-electromechanical systems (MEMS), micro-sensors, micro-actuators and also to machine micro size features. For example in electronic devices, e.g. computers, cell phones, CD players, etc. Relays and switches are required to be assembled to produce functional micro sized mechanical parts. In aerospace industries lightness of aircraft or satellite is one of the most vital requirements, which demands to design and manufacture components in smallest possible size on advanced materials with high accuracy. Another example is the fuel injection nozzles for automobiles; several factors of environmental safety have forced manufacturers to improve the nozzle. In addition to that a new potential area requiring microproducts is the field of biotechnology. Since the objects in this field include biological cells and genes, the tool that handles them must have micro effectors. Similarly in medical applications miniaturization of medical tools is one of the effective approaches to arrive at this target of inspection and surgery without pain as well as micro devices for drug delivery system. Micromachining is one of the key technologies that can enable the realization of all of the above requirements for microproducts and fields with such requirements are rapidly expanding. The potential advantages of microproducts are less material requirements, lesser space requirements, compactness, minimum energy consumption etc. Hence, due to this growing demand of society for micro products, scientists and engineers forced to develop stable micro-manufacturing process which can efficiently produce micro components, mechanisms and micro features by machining engineering material precisely in micron scale by utilizing various micromachining methods. However, materials which can micromachined easily and used in present day Microsystems, MEMS and microengineering applications have some limitations such as low strength to weight ratio, corrosion resistance and biocompatibility therefore these materials may not cope up with the demands of next generation microproducts. Hence, there is an urgent need to identify such materials which can have edge over conventional MEMS materials and importantly these materials should successfully micromachined. Titanium is the potential material as alternative to the conventional MEMS materials particularly silicon or silicon based materials or glass. Titanium is known as super metal due to its high strength to weight ratio, excellent corrosion resistance and superior biocompatibility. Therefore, titanium is ideal material for fabrication of microfeatures or microcomponents of new age microstructures. Introduction of advanced metals such as titanium, forces researchers to develop newer efficient and stable micromachining processes which can machine this advanced material efficiently and cost effectively.

9.2 Electrochemical Micromachining (EMM)

The non-conventional machining processes discussed above are thermal oriented machining processes except Chemical machining process e.g. Electro discharge machining (EDM), Laser beam machining (LBM), Electron beam machining (EBM), etc., which may cause thermal distortion of the machined surface [1]. Chemical machining and electrochemical machining are thermal free processes, but chemical machining cannot be controlled properly in this micromachining domain. However, accuracy level of ECM can be highly improved if the inter-electrode gap i.e. gap between microtool and workpiece is reduced in the order of less than fifty microns. Electrochemical machining (ECM) process can be applied in the microscopic domain for manufacturing of ultra precision micro features, is called electrochemical micromachining process (EMM).

Electrochemical micromachining process is based on the principles of electrolysis and governed by Faraday's laws of electrolysis. In this process high frequency DC voltage of pulsed current is applied between the cathode of micron scale size, acts as a microtool and metallic work piece which acts as an anode. Both the electrodes i.e. cathode and anode are immersed in an electrolyte usually stagnant in nature and are separated by small gap of few microns generally termed as inter electrode gap (IEG) as shown in Fig. 9.1. As soon as the pulsed current passed through these electrodes anodic material dissolves into metallic ions by the electrochemical reactions, and hydrogen gas bubbles are generated on the cathode surface. In order to achieve anodic dissolution in desired direction and shape, the microtool moves with constant feed rate towards the workpiece to maintain the predetermined inter-electrode gap (IEG). Ideally, anodic dissolution rate or material removal rate (MRR) must be synchronized with microtool feed rate to obtain controlled dissolution with shape accuracy.

EMM appears to be a very potential technology for micro machining due to its advantages that include high machining rate, better precision and control, rapid machining time, reliable, flexible, environmentally acceptable and it also permits machining of chemically resistant materials like titanium, copper alloys, super

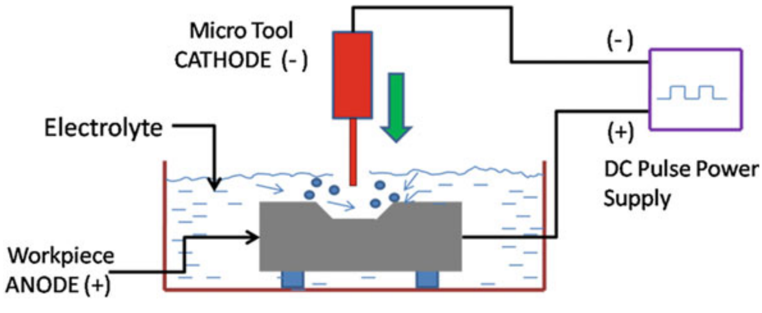


Fig. 9.1 Schematic diagram of electcrochemical micromachining process

alloys and stainless steel, which are widely used in biomedical, electronic and MEMS applications. EMM can be advantageously employed in most applications related to micromachining of metallic parts due to its cost effectiveness and achievable high precision, which are previously fabricated by chemical micromachining.

Neutral solution like aqueous solution of $NaNO_3$, NaCl, NaBr etc. are mostly used as electrolyte in electrochemical micromachining process and hence it does not cause any harmful effect to the operators. Electrochemical micromachining process generates sludge during electrochemical dissolution. Most of the cases the sludge is formed during the process are neutral salts, which are not harmful to the human beings as well as to the environment. But some time these sludge materials may contains small amount of metal ions, acids, nitrates, oils and even traces of heavy metal ions which may be harmful to the environment and finally to the human beings. Electrolyte is filtered during the EMM operation, which reduces the amount and frequency of electrolyte disposal. During electrochemical micromachining material removed only from the specified area, which also reduces the material removal rate as well as the generation of sludge. Furthermore, the harmful sludge is treated before disposal to the atmosphere to make the process environmental friendly. Since miniaturization will continue as long as people require effective space utilization with more efficient and better accuracy products without introducing any harmful material to the environment, electrochemical micromachining process will be more important in the future.

Furthermore, the use of EMM will widen the range of materials application for electronic industries, MEMS etc. The role of convective mass transport and current distribution on the surface finish and shape evolution is very important. Effective EMM process can be achieved by optimal combination of the process parametric conditions. In order to achieve the effective and highly precise material machining in the order of microns, the predominant process variables of the EMM system will have to be optimally controlled.

9.3 Titanium and Its Alloys: Types and Usage

Titanium was first discovered in 1791 by William Gregor, who was the mineralogist and chemist. William Gregor observed the magnetic sand from the local river, Helford, in the Menachan Valley in Cornwall, England, and isolated "black sand", now known as "ilmenite". By removing the iron with a magnet and treating the sand with hydrochloric acid he produced the impure oxide of a new element, called as "mechanite". Subsequently, Martin Heinrich Klaproth, who is the Berlin chemist, isolated titanium oxide from a mineral, identified as "rutile". Greek mythology provided him a new name the Titanium from the children of Uranos and Gaia, the titans. Matthew Albert Hunter from Rensselaer Polytechnic Institute in Troy, N.Y., was able to isolate the metal in 1910 by heating titanium tetrachloride ($TiCl_4$) with sodium in a steel bomb. Finally, Wilhelm Justin Kroll from Luxembourg is recognized as father of the titanium industry. In 1932 he produced significant quantities of titanium by combining $TiCl_4$ with calcium and then changed reducing agent from calcium to magnesium. Today this is still the most widely used method and is known as the "Kroll process". In 1948 the DuPont Company was the first to produce titanium commercially [2]. Titanium is the ninth element available in the earth's crust, and the fourth metallic element. Titanium is naturally available in the forms of rutile (titanium dioxide, TiO_2) and ilmenite (titanium iron oxide, $FeTiO_3$). These two mineral forms are the most common and commercially exploitable. Titanium is a material known for its superior physical and mechanical properties such as high strength to weight ratio, high compressive and tensile strength, low density, high fatigue resistance in air and seawater, and exceptional corrosion resistance. Therefore, titanium is a perfect material for micro engineering and allied applications. Fabrication of micro features on titanium has great potential in the area of micro electromechanical systems (MEMS) because titanium provides superior properties to traditional semiconductor materials since it has excellent fraction toughness and corrosion resistance. Titanium also possesses exceptional biocompatibility. Today titanium and its alloys are widely used in aerospace chemical processing, medicine, power generation, marine and offshore, sports and leisure, and transportation industries.

Titanium naturally resists corrosion from acids, alkalis, natural salt and polluted waters. This tendency of titanium metal is achieved by formation of hard, protective oxide film when it is exposed to oxygen present in the air or water. This thin tenacious film makes titanium resistant to erosion. Titanium is the only metal, which is completely immune to microbiological induced corrosion (MIC) in seawater. Titanium has a low modulus of elasticity about half that of steel. This gives it excellent flexibility. It is the most biocompatible of all metals. It is non-toxic, it resists attack from bodily fluids, it's strong and light, and its flexibility is close to bone. Commercially pure titanium finds variety of applications from aerospace industry to medical industry. Typical applications of titanium in various fields are discussed in brief:

(a) **Aerospace Applications**

The exceptional properties of titanium alloys include high specific strength and excellent corrosion resistance. Therefore, titanium alloys are found in aerospace applications where the combination of weight, strength, corrosion resistance, and/or high temperature stability of aluminum alloys, high strength steels, or nickel based super alloys are insufficient. The main drivers for use of titanium in aerospace applications are:

i. Weight reduction (substitute for steels and Ni-based super alloys)
ii. Application temperature (substitute for Al alloys, Ni-based super alloys, and steels)
iii. Corrosion resistance (substitute for Al alloys and low-alloyed steels)
iv. Galvanic compatibility with polymer matrix composites (substitute for Al alloys)

v. Space limitation (substitute for Al alloys and steels).

The most common and prime use of titanium is in aircraft fuselage applications, for hydraulic tubing of modern aircraft. Aircraft floors surrounding on-board kitchens and toilets where the corrosive environment is present. Aircraft landing gear are manufactured from forged titanium, it has also find its application in the engine bay of fighter aircraft, where temperatures can quickly exceed. The main area of application for aerospace titanium and its alloys are in the gas turbine engine. Approximately one third the structural weight of modern turbine engines is made up of titanium. Compressor blades were the first engine components to be made from titanium. For helicopters, titanium alloys are used in the most highly stressed component i.e. the rotor head. In the space vehicles titanium and its alloys are also used for fuel and satellite tanks and high-pressure piping in the hydrogen pumping systems of the Space Shuttle.

(b) **Process Industry Applications**

Other than aerospace industry titanium found suitable in the areas where harsh environment is very common such as chemical, process and power generation industry. Preferred applications are in heat exchangers in which the cooling medium is seawater, brackish water, and also polluted water. Titanium is also employed in millions of meters of welded and seamless titanium tubing in steam turbine power plants, refineries, chemical plants, air conditioning systems, multi-stage flash distillation, desalination and vapor compression plants, offshore platforms, surface ships and submarines, as well as for swimming pool heat pumps. Commercially pure titanium grades and alloys are applied in production facilities for acetaldehyde and acetone, acrylic fibers, and urea. Another interesting application of titanium is in architecture, titanium has been increasingly used as exterior and interior cladding material for roofing, curtain walls, column covers, soffits, fascias, canopies, protective cladding for piers, artwork, sculptures, plaques, and monuments.

(c) **Sports and Leisure Applications**

Tennis Racquets, Baseball Bats and Pool Cues, head of the golf club, titanium accessories for racing bikes, Scuba Diving Equipment, for trekking and hiking applications such as High strength climbing gear like snap shackles, hooks, rings and eyes, latches, locking carabineers, pins, clips, eye bolts, cliffhangers, and straps are usually manufactured from forged titanium and its alloys.

(d) **Medical Applications**

Another popular application of titanium is in medical industry due to the excellent compatibility with the human body titanium is generally used as the biocompatible metallic material. Additionally, titanium is extremely resistant to corrosion from body fluids, and is compatible with bone and living tissue, and is elastically deformable as thin foil material. Thus, pure titanium combines many of the attributes desirable for heart pacemaker cases and as the carrier structure for replacement heart valves. Titanium possesses excellent fatigue behavior which is decisive for the choice of material for orthopedic devices such as various implants for hip, knee, as well as it is used to make substitute parts of the shoulder, the spine, the elbow, and the hand. Titanium has a relatively low modulus of elasticity, which reduces the differences in stiffness between the human bone and the implant.

The introduction of a titanium implant into the jawbone favors osseointegration before the superstructure is built onto the implant. Today, titanium is successfully used in prosthetic dentistry for implant screws, crowns, bridges, dental posts, inlays, and removable partial dentures.

9.3.1 Challenges in Titanium Machining

Titanium possesses two electrons in the third shell and two electrons in the fourth shell. Titanium has arrangement of electrons, in which outer shells are filled before the inner shells are completely occupied, which makes titanium transition metal. This arrangement of electrons is responsible for the unique physical properties of titanium. Due to the versatile physical and mechanical properties such as high strength to weight ratio, high compressive and tensile strength, low density, high fatigue resistance in air and seawater, and exceptional corrosion resistance. Titanium, machining is always a concern to the researchers. Owing to poor thermal properties of the titanium as well as low modulus of elasticity with its ability to maintain high strength at elevated temperature made machining of titanium an intricate task.

9.3.2 Machining of Titanium by Conventional and Non conventional Processes

Titanium proved its wider range of applications in different domains due to its excellent properties. However, machining of titanium is difficult either by conventional or non-conventional machining methods. In conventional machining process, where cutting tool removed material by shearing due to deformation through physical contact, in this mode, Titanium and its alloys are considered as difficult to cut materials due to the high cutting temperature and the high stresses at and/or close to the cutting edge during machining. The poor thermal properties of the materials forced the larger portion of heat generated in machining process which will be absorbed by the tool thus causes the rapid wear of tools. Both the high temperature and the high stresses developed at the cutting edge of the tool may create plastic deformation and/or accelerate the wear of the tools [3].

Low modulus of elasticity of titanium can cause chatter, deflection, and rubbing problems [4]. During conventional machining forces perpendicular to the workpiece may increase three to four times as a result of a build up of titanium on the wear land of the tool [5]. Because of this high thrust force and the low elastic modulus of titanium, the deflection of the workpiece can be a serious problem. Cutting tool materials undergo severe thermal and mechanical loads when machining titanium alloys due to the high cutting stresses and temperatures near the cutting edge, which greatly influence the wear rate and hence the tool life. Flank wear, crater wear, notch wear, chipping and catastrophic failure are the prominent failure modes when machining titanium and its alloys. Flank and crater wear may be attributed to dissolution-diffusion, abrasion and plastic deformation, depending on the cutting conditions and the tool material, whilst notch wear is caused mainly by a fracture process and/or chemical reaction.

Non-conventional machining techniques such as Electric Discharge Machining (EDM), Laser Beam Machining (LBM) and Electron Beam Machining (EBM) are thermal oriented machining process which put constraints to machine titanium and its alloys beyond i.e. formation of pear shaped and tapering effects on holes as well as possibilities of hot spot due to lower heat dissipation rate due to low thermal conductivity of titanium [6]. In EDM, formation of thermal stresses in a small heat-affected zone is a serious issue which can lead to micro-cracks, decrease in strength and fatigue life and possibly catastrophic failure of the component [7]. In case of USM, serious tool wear as well as lower material removal rate has been encountered during machining of titanium and its alloys [8]. Electrochemical machining (ECM) technique based on the principle of electrolysis proved to be partial successful in machining of titanium and its alloys. But passive oxide layer present on titanium surface is a concern in ECM and limits the process up to macroscopic level. However, electrochemical micromachining (EMM) has proved its capability to produce metal microstructures based on anodic dissolution principle. In EMM material removal takes place at atomic levels irrespective of their hardness and toughness. EMM of titanium by electrochemical process could be one of the promising alternative technique for machining of titanium.

Titanium machining is always a complex task before the researchers and manufacturing engineers because the pace of material research could not be maintained with machining or machinability research of titanium and its alloys.

9.4 Machining of Titanium by Anodic Dissolution

Material removal based on the principle of anodic dissolution was started in early twentieth century. The Russian engineer V.N. Gusev was the first to develop Electrochemical machining set up and patented all basic principles of ECM. The ECM process is conducted in the working chamber (electrochemical cell) of the machine, where a workpiece (Anode) and a tool electrode (Cathode) are positioned. The anode is connected to the positive polarity of a power supply, and the tool electrode to the negative polarity of the power supply. The electrolyte (usually an aqueous solution of an inorganic salt is pumped through the inter-electrode gap (IEG) in order to remove the electrode reaction products (gases, hydroxides) and the heat generated by the current. Electric current is passed through the electrodes by the movement of electrons. Flow of electric current in the electrolyte is takes place by the movement of ions. As the electrons transferred between the electrodes and the electrolyte, physical changes occur at the electrodes and anodic dissolution begins. To continue the process of material removal by anodic dissolution tool electrode is moved in the direction of the intended anodic dissolution (metal loss) in order to maintain a prescribed machining gap. As the anode dissolves, the cathode shape is reproduced on the anode i.e. work piece.

Machining of titanium by anodic dissolution is different than anodic dissolution of other metals such as Stainless steel, copper and mild steel etc. According to the position of titanium in periodic table and its electrochemical behaviour the titanium is metal, which always contain a natural oxide film, when it is exposed to air, water or media containing oxygen. Thickness of this natural oxide film of titanium ranges from 5 to 70 Å [9]. Titanium gains its excellent corrosion resistance due to the existence of this persistent and passivating surface film of oxide. This corrosion resistance property of stable oxide layer obstructs the electrochemical dissolution of titanium. Hence, to achieve controlled anodic dissolution of titanium it is necessary to dissolve protective oxide film of titanium.

9.4.1 Difficulties Encountered with Anodic Dissolution of Titanium in Microscopic Domain

Successful anodic dissolution process occurred when ionic conductivity between the electrode and electrolyte is sufficient. This ionic conductivity is depends on the metal and electrolyte combination. Dissolution of the metal electrode can be influenced by the formation of the oxide film on the anode surface. If the oxide film is passive in nature then its ionic conductivity is weaker. Hence, this passive oxide film acts as a barrier between the surface of the electrode and electrolyte. Development of this passive film depends on the relationship between current density and applied potential, i.e., polarization curve of the used electrolyte. This Passivating nature of oxide film present on the surface of titanium may terminate anodic dissolution process. The strength of this passive oxide film and its transpassive dissolution behaviour is based on how this passive film is formed on the titanium. In the case of macroscopic dissolution i.e. with ECM, the electrolyte is circulated with external pressure which creates high turbulence and thus reduces the effect of concentration polarization, which limits the passivation. In addition to that higher anode potential also causes anodic dissolution at higher valency by breaking down the passive oxide film. However, in microscopic domain i.e. with micro-ECM, the electrolyte flow is much lower or almost stagnant electrolyte is preferred as well as potential difference is also lower compared to ECM, this creates favourable situations for passivation. Selection of appropriate electrolyte combination as well as power parameters may minimize the chances of Passivating effect of oxide film. As discussed, titanium always possesses highly passive oxide film.

The nature of this thin tenacious film of oxide is highly passive in nature, which makes the anodic dissolution of titanium difficult compared to most of the other metals.

9.4.2 *EMM as a Potential Process for Titanium Micro Machining*

Electrochemical micromachining is appears as effective micromachining process due to its several advantages discussed in sect. 9.2. EMM is also capable of micromachining of chemically resistance material due to its ability to generate localized current density. Machining of titanium through EMM is relatively different from EMM of common metals. Titanium gains resistance to corrosion because of its protective surface oxide film. When titanium undergoes electrochemical actions, the role of transfer of Ti^{2+} and O^{2-} is to contribute for the development of anodic film. Formation of passive oxide layer on titanium surface during electrochemical process with aqueous environment was initiated by reaction of Ti^{2+} with hydroxide ions (OH^-) ionized from aqueous solution. Following electrochemical reactions represents stable titanium oxide (TiO_2) [10]. At the interface of anode workpiece and electrolyte, the reactions taking place are:

$$Ti \rightarrow Ti^{2+} + 2e^- \tag{9.1}$$

$$Ti^{2+} + H_2O \rightarrow TiO_2{}^{+} + H_2 \uparrow \tag{9.2}$$

The oxocation, $TiO_2{}^+$ is acidic in nature and subsequently reacts with OH^- to form stable TiO_2 [11].

Following chemical reaction represents the formation of stable TiO_2:

$$TiO_2{}^{+} + 2OH^- \rightarrow TiO_2 + H_2O \tag{9.3}$$

Throughout the anodic dissolution process, development of oxide layer with the help of titanium and hydroxide ions has been accelerated by the application of electric field. This thin oxide film is highly passive in nature, causes anodic dissolution of titanium difficult. The controlled anodic dissolution titanium contains this oxide film is difficult by EMM process parameters generally utilized for micromachining of other metals especially in terms of machining voltage and type of electrolyte. Hence, in order to attain uniform transpassive dissolution of titanium, the oxide film that obstructs the controlled dissolution of pure titanium in the passive potential region must lose its passivation phenomenon. Removal of oxide film is possible when the applied potential is adequately high [12]. The passive oxide film develops linearly with potential until a significant value is attained and the breakdown of the film takes place from random pitting at higher current densities and then shape controlled dissolution begins [13]. An additional factor, which plays vital role in rupturing this passive oxide film, is the electrolyte type. EMM offers both the advantages i.e. to achieve higher localized current density as well as possibility to utilize various non toxic eco-friendly aqueous as well as non aqueous electrolytes. Hence, EMM can be a potential micromachining method to achieve controlled anodic dissolution of pure titanium as well as titanium alloys.

9.5 Effect of Various EMM Process Parameters on Maskless EMM of Titanium

Material removal in electrochemical micromachining is based on anodic dissolution where metals are liberated from anode surface in atomic level. In order to achieve efficient and precise machining in the sub-microns level, the various process parameters of the EMM system play crucial role. The accuracy of the micro machined product in EMM is highly influenced by process parameters e.g. applied machining voltage, duty ratio, pulse frequency, concentration and type of electrolyte and micro tool vibration etc. During electrochemical micromachining of titanium these process parameters should be optimally selected and controlled due to Passivating phenomenon of titanium. Hence, appropriate selection along with controlling of all these EMM parameters play a vital role in attaining the preferred results during titanium micro machining utilizing EMM. Some of the predominant factors, which have major influences on EMM of titanium, are discussed to obtain fundamental information about how to control the EMM process most optimally while micromachining of titanium.

9.5.1 Role of Electrolyte

When potential is applied between the electrodes, electrolyte plays crucial role in flowing the electric current from electrode to electrolyte solution to achieve anodic dissolution through electrochemical reactions by completing the electric circuit. Selection of electrolyte is governed by material properties of workpiece and micromachining criteria such as machining rate, accuracy, surface texture, and surface integrity. Type and concentration of electrolyte proves crucial in anodic dissolution of materials which posses passive oxide film such as titanium.

Electrolytes of different combination and concentrations have been employed by various researchers during masked as well as maskless electrochemical micromachining of titanium. Regular pattern of up the depth of 30 μm on pure titanium by electrochemical dissolution through the patterned photoresist using sodium bromide and methanol solution containing sulfuric acid and the etching performance of these two electrolytes has been tested [14]. With the aqueous solution of bromide irregularly shaped cavities with a rough surface have been appeared. However, Regular shape and smooth surface textures were obtained when titanium was dissolved in the methanol electrolyte. Solution of methanol sulfuric acid has also effective in electro polishing of titanium. It has been reported that the electro polishing of titanium in methanol sulfuric acid electrolytes is mass transport controlled. 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 [15]. 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 [13]. The porous anodization of titanium to create nano-scale features on titanium surfaces has been possible 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) were also performed [16]. Electrolyte combination containing Sodium chlorate ($NaClO_3$), Sodium nitrite ($NaNO_2$) and sodium fluoride (NaF) can be 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) is an effective scavenger to obtain sub-micrometer resolution [17]. Use of high concentration of aqueous sodium bromide with working voltage of as high as 200 V through jet electrochemical micromachining (Jet-EMM) technique were also successful to create deep holes in titanium alloy [18]. Anodic dissolution of titanium has been performed in NaCl containing ethylene glycol solution. Anodic polarization of titanium electrode in NaCl-containing ethylene glycol solutions involves dissolution of titanium as tetravalent species with the gas being evolved initially [19]. The electrochemical micromachining of pure Titanium with Ethylene glycol and Sodium Bromide of higher molar concentration up to 5 M can deliver satisfactory results however, machining time is very high due to the slower etch rate [20]. Aqueous solution of sodium bromide has been suitable for carrying out anodic dissolution of titanium with the help of conventional ECM in macroscopic domain [21].

Majority of electrolytes which can dissolve titanium in microscopic domain are Sulphuric acid, Hydrofluoric acid (HF), Nitric acid (HNO_3) and combination of Methanol and Sulphuric acid. All these electrolytes are either hazardous as well as toxic and may create problem to environmental issues. Aqueous solution of Sodium Bromide (NaBr) and sodium perchlorate can 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. However, formation of black oxide film is predominant in all these aqueous base electrolytes. In order to overcome the effect of regeneration of oxide film due to aqueous base electrolytes non-aqueous base electrolytes can be effectively employed. Non-aqueous base electrolytes, which are non-toxic and environment friendly are combination of ethylene glycol and sodium bromide

(EG + NaBr) as well as combination of ethylene glycol, sodium bromide and sodium chloride (EG + NaBr + NaCl) were 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 [10]. Electrolyte solution includes bromide ions can promote anodic dissolution of titanium with valance of 4 i.e. Ti $\rightarrow$ Ti_4 + Electrolytes containing bromide ions have been effective in breakdown of oxide film [22].

9.5.2 Effect of Machining Voltage

In order to dissolve the titanium anodically, passive oxide film must lose its passivity. To overcome this difficulty suitable composition and type of electrolyte plays vital role to attack on the film and to break it through pitting. However, mere pitting or breaking the passive film at random points is not adequate. Phenomenon of pitting should be controlled to achieve uniform dissolution of base metal i.e. titanium. Another factor which is crucial to attain controlled anodic dissolution of titanium is applied voltage i.e. voltage between cathode and anode. To achieve uniform transpassive dissolution of titanium, the anodic oxide film that usually protects the titanium in the passive potential region must lose its protective properties. Rapid removal of oxide film is obtained when the applied potential is sufficiently high. The passive oxide film develops linearly with potential until a critical value is attained and after that the breakdown of the film takes place from local pitting at higher current densities and then shape controlled dissolution begins. Hence, to achieve proper current density with the application of appropriate potential range is crucial to overcome passivity of the oxide film. In order to attain shape controlled dissolution the desired current density in the appropriate potential region should maintain until the controlled dissolution gains stability. To make the process stable so as to attain desired accuracy of the machined product, influence of applied machining voltage, play vital role.

Study based on the breakdown voltage in terms of a change in efficiency of film growth the change in slope of the voltage/time relation at constant current density, are deceptive in the case of Ti in that such changes are not always accompanied by a change in columbic efficiency. This indicates that the higher voltage is necessary to breakdown the oxide film because the film consists of amorphous oxide which gives way to a new anodic behaviour low efficiency oxide growth and gas evolution associated with crystalline oxide in the film [23]. Based on the changes in the slopes of the voltage/time relations at constant current density occurred at $\sim$100% efficiency for growth indicated that there is variable oxide field strength. During through-mask electrochemical machining, regular shape and smooth surface textures were obtained when titanium was dissolved at 8 V with mass transport limiting current density [14]. Micro-dimples with a diameter of 110 μm and depth of 20 μm could be generated with applied voltage of 24 V, pulse duty cycle of 10% and frequency of 100 Hz [24]. In masked EMM of titanium feature aspect ratio is limited as well as toxic and reactive electrolytes can be used hence, applied potential can vary from 5–30 V. However, in maskless EMM machining voltage can be limited to the range of 8–20 V, in few exceptional cases such as jet-electrolyte titanium machining voltage can be elevated to 200 V [18]. Maskless EMM of titanium, machining voltage is the major parameter in breaking down the passive oxide layer. Removal of passive oxide film under the influence of increased machining voltage is governed by the induced current density, as the current density increases passive layer breaks randomly at some weaker points and exposes the base metal. Further, increase in machining current rupture the passive oxide film and turns into transpassive leads to initiation of controlled anodic dissolution of titanium. Increase in machining voltage tends to rise in machining current. According to Faraday's law material removal rate increases with machining current and hence, higher material removed at higher machining voltage. With the increase in machining current in the narrow machining zone Joule heating effect generated which leads to elevation in the temperature in the narrow machining zone. This causes variation in electrolyte conductivity results in non-uniform current distribution in the inter electrode gap. Hence, reduces localization of current flux flow leads to random material removal with higher stray machining. Therefore, higher stray current flows in the micromachining zone causes more material removal from the larger area of workpiece, results in an increase in overcut. Figure 9.2 shows typical behaviour of radial overcut and material removal rate of micro holes machined on pure titanium sheet of 100 μm thickness, machining voltage is varied in the range of 8–14 V, utilizing maskless EMM process.

The micro holes machined with machining voltage of Fig. 9.3 shows the SEM micrographs of micro holes machined at 8 and 14 V machining voltage. From the

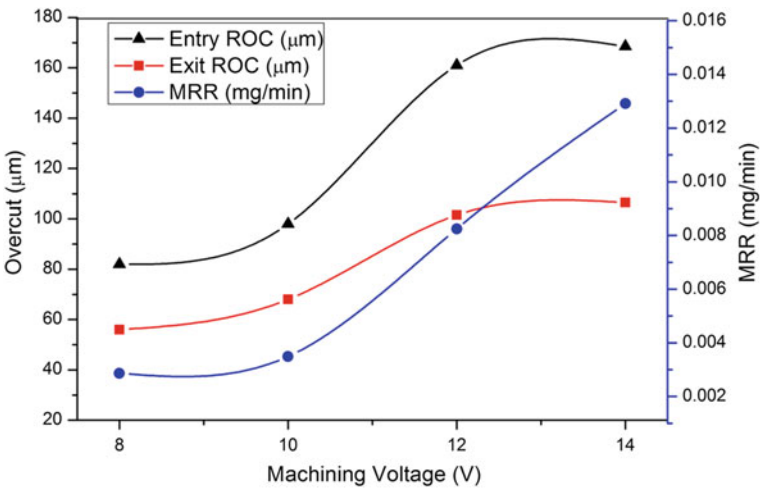


Fig. 9.2 Effect of machining voltage on radial overcut and MRR of micro hole

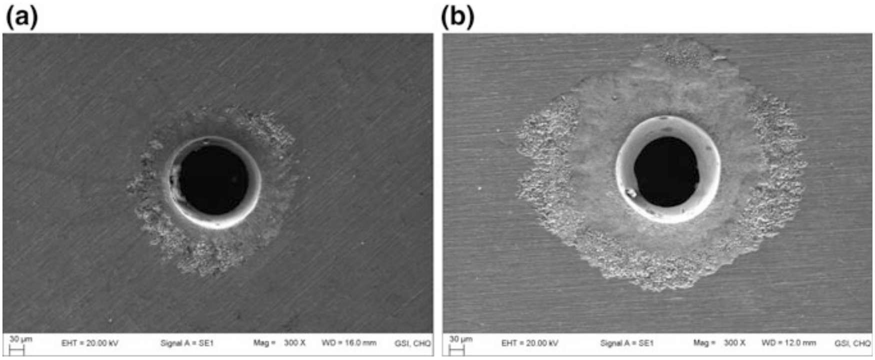


Fig. 9.3 Micro holes machined at **a** 8 V and **b** 14 V machining voltage [32]

SEM micrograph it is also confirmed that the effect of stray machining is predominant in micro hole machined at 14 V.

Stray machining induced by higher machining voltage can also increase conicity or tapering effect during microfeature fabrication on titanium. The effect of stray machining is higher at higher machining voltage, majority of stray machining takes place at the entry of the micro hole. When micro tool further advances into the workpiece machining depth increases, circulation of fresh electrolyte becomes crucial and accumulation of sludge in the narrow machining gap increases which in turn lower down material removal rate result in generation of smaller diameter at exit of micro hole compared to entry. Hence, tapering effect takes place and micro hole becomes taper in shape. However, this tapering effect can be utilized for fabrication of micro nozzles. To reduce the effect of stray machining during micro hole generation lower machining voltage is preferred or suitable microtool insulation has been applied.

9.5.3 Effect of Pulse Duty Ratio

Duty ratio represents the percentage of time for which pulse remains on i.e. percentage of time available for both faradic and non-faradic current. Increase in duty ratio in turn increases time available for faradic current. Hence, the amount of faradic effect and current density increases results in more material removal and causes increase in overcuts and MRR. Micro holes machined with varied duty ratio keeping other process parameters fixed at machining voltage 8 V, pulse frequency 200 kHz, tool feed rate 0.2 µm/s and keeping electrolyte concentration as 2 M/L. the influence of duty ratio on overcut and MRR during micro holes generation on titanium by EMM has been shown. From Fig. 9.4, it can be observed that radial overcut of micro hole at entry and exit is increases as duty ratio increases. Figure shows the influence of duty ratio on overcut and MRR during micro holes

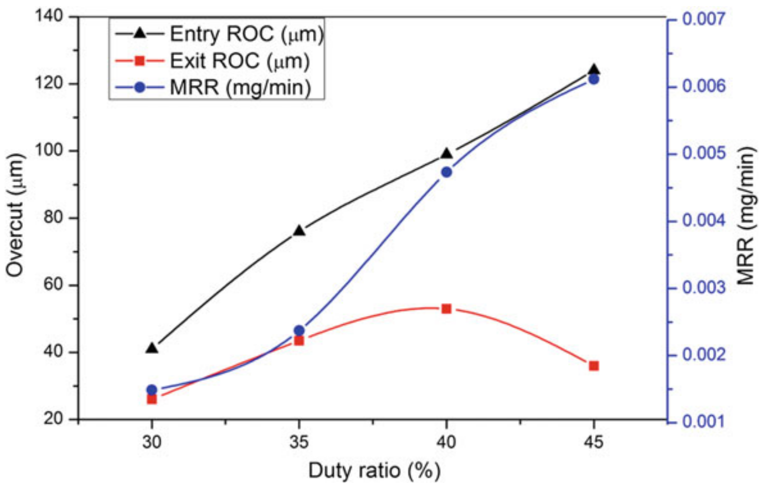


Fig. 9.4 Influence of duty ratio on radial overcut and MRR of micro hole

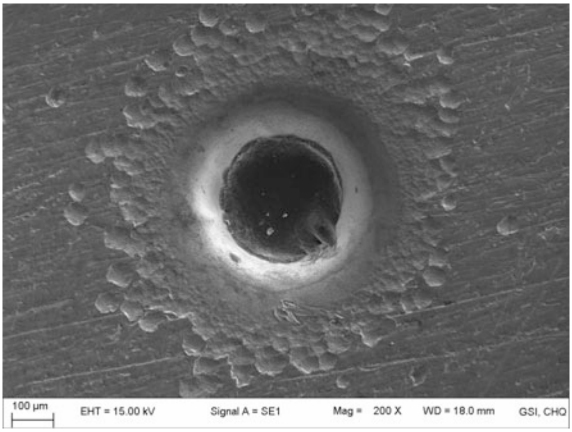
generation by EMM. From Fig. 9.4 it can be observed that radial overcut of micro hole at entry and exit is increases as duty ratio increases.

Increase in radial overcut at entry follows linear trend. The lowest radial overcut at 30% duty ratio at entry and exit is found to be 41 and 26 μm respectively. The highest radial overcut is found to be 124 and 36 μm at entry and exit at 45% duty ratio. As the duty ratio increases pulse ON time increases and machining current flows for higher time, which causes higher material removal as well as stray machining effect is also increases at the entry. Hence, radial overcut at entry is much larger than exit, which in turn increases taper of micro hole. The micro hole with highest taper angle of 41° has been obtained at 45% duty ratio. The SEM micrograph represented in Fig. 9.5 exhibits dominant effect of larger metal removal right from the entry of micro hole, machined at higher duty ratio of 45%.

9.5.4 Effect of Pulse Frequency

In EMM, pulse frequency directly governs pulse period. Total pulse period decreases as the pulse frequency increases, results in proportionate reduction in pulse ON time. Pulse ON time plays crucial role in charging and discharging of double layer capacitance. In the EMM, during pulse ON time of pulse period, the total current available consists of two components i.e. non faradic current and faradic current. Charging and discharging of double layer capacitance has been performed by Non faradic current and faradic current governs material dissolution rate. Thus, material dissolution performed only during faradic time of every cycle. Increase in pulse frequency results in lower faradic time tends to lesser material

Fig. 9.5 Micoholes machined with 45% duty ratio



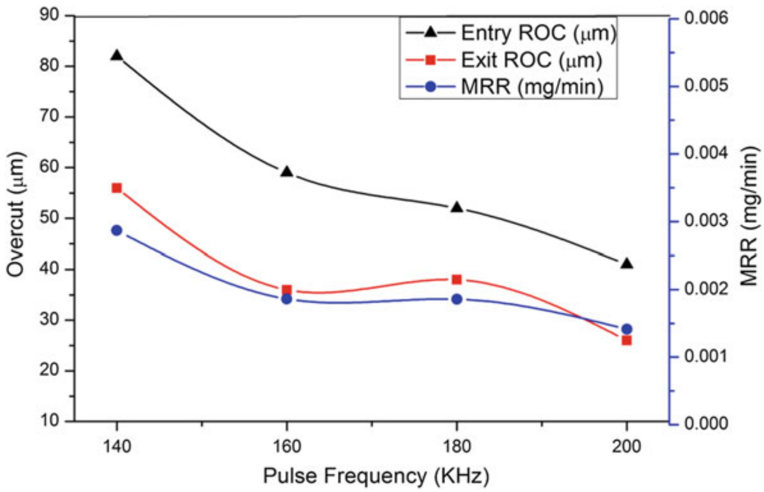


Fig. 9.6 Influence of pulse frequency on radial overcut and MRR of micro hole

removal per cycle as a result amount of sludge and gas bubbles are also lesser which will washed out completely from the narrow machining zone during pulse OFF time. Hence, it facilitates completely clean machining zone to accomplish more controlled dissolution. Therefore, controlled and localized material removal takes place which in turn improves the geometric accuracy of the microfeature. This is clearly observed from the experimental results of MRR as plotted against pulse frequency as shown in Fig. 9.6.

Micro hole machined with lower range of pulse frequency i.e. at 140 kHz has 282 μm entry diameter and 226 μm exit diameter. Whereas, micro hole machined with higher pulse frequency of 200 kHz has entry as well as exit diameter is reduced to 196 and 167 μm respectively. Hence, remarkable improvement will

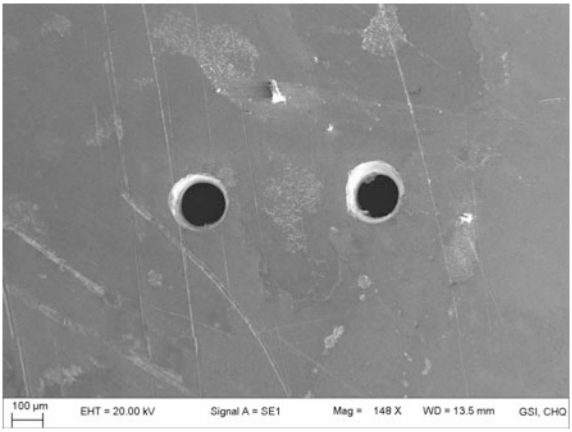


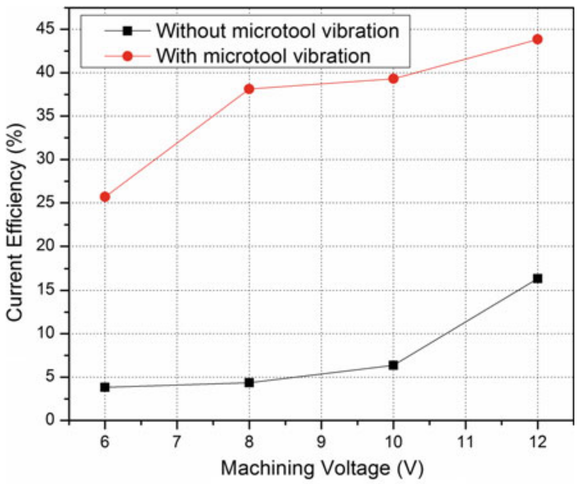
Fig. 9.7 SEM micrograph of micro holes machined at 200 kHz pulse frequency

takes place in machining accuracy of microfeatures machined at higher frequency compare to lower frequency. The micro holes machined at higher frequency is shown in Fig. 9.7. From the SEM micrograph, it is clear that the micro hole exhibits controlled geometrical shape and minimum overcut.

9.5.5 Effect of Micro Tool Vibration

During micromachining material dissolution takes place in very narrow gap between the cathode and anode electrodes. To maintain smooth anodic dissolution in this constricted machining zone flow of fresh electrolyte is important to flow off sludge and gas bubbles. If, external pressure applied to electrolyte to create the flow in this highly narrow machining zone may displace the microtool. However, vibrations of very small amplitude with fairly high frequency have been applied to microtool, made substantial effect on enhancing the dissolution process by circulating electrolyte in the form of micro-jets produced due to microtool vibration. Microtool vibration creates hydrodynamic effects on the bubble behavior, which has been utilized for the effective removal of sludge, hydrogen bubbles and replenishment of fresh electrolyte [25]. The application of microtool vibrations made significant influence on the diffusion and convection of dissolved metal ions because of hydrodynamic effects on the bubble performance. This phenomenon of enhancing anodic dissolution in EMM has also effectively utilized in maskless electrochemical micromachining of titanium. Machining voltage has been lowered down as well as controlled dissolution of titanium could be achieved by introduction of microtool vibrations. Machining current density induced by applied voltage is important in dissolution of material during electrochemical reaction. Machining current density has been considerably elevated by the effect of microtool vibrations. Microtool vibrations within the narrow machining zone will help to

Fig. 9.8 Effect of microtool vibration on change in current efficiency



circulate the fresh electrolyte and hence increase the convective mass transport which in-turn increase rate of diffusion as well as conductivity results in increase in current density.

The current efficiency, which is the ratio of observed amount of metal dissolved to the theoretical amount predicated from Faraday's law has been influenced by dissolution of titanium with the application of microtool vibration. Figure 9.8 shows the change in current efficiency with respect to voltage during micro hole machining on pure titanium.

The major change in current efficiency proves that the application of microtool vibration facilitates circulation of electrolyte, which causes increase in the utilization of considerable portion of machining current for the metal dissolution and leads to increase in current efficiency which further enhances mass of metal removal results in increase in machining depth. Figure 9.9 shows the comparison of machining depth achieved by two conditions of with microtool vibration and without microtool vibration. It is clear that the microtool vibration significantly improves the controlled anodic dissolution of titanium even at lower machining voltage.

SEM micrograph shown in Fig. 9.10 exhibits the micro holes machined on titanium with and without microtool vibrations with machining voltage of 8 V.

9.6 Through Mask EMM of Titanium

Through-mask EMM (TMEMM) is a typical masked electrochemical micromachining process. This process is commonly employed for fabrication of micropatterns, as well as for shaping and finishing of 2D microfeatures. In TMEMM anode workpiece is covered with photoresist patterned in the form required shape pattern.

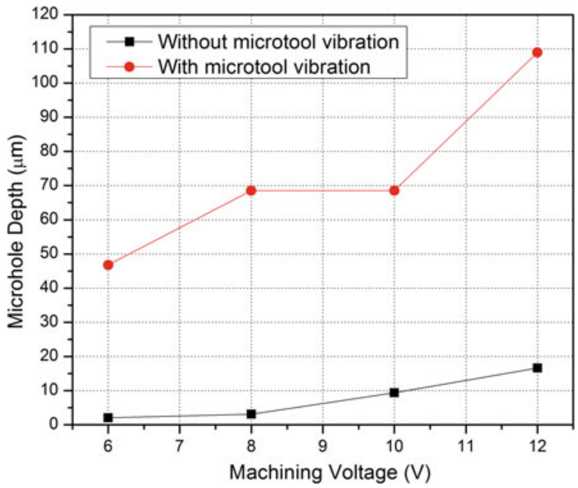


Fig. 9.9 Effect of microtool vibration on change in machining depth

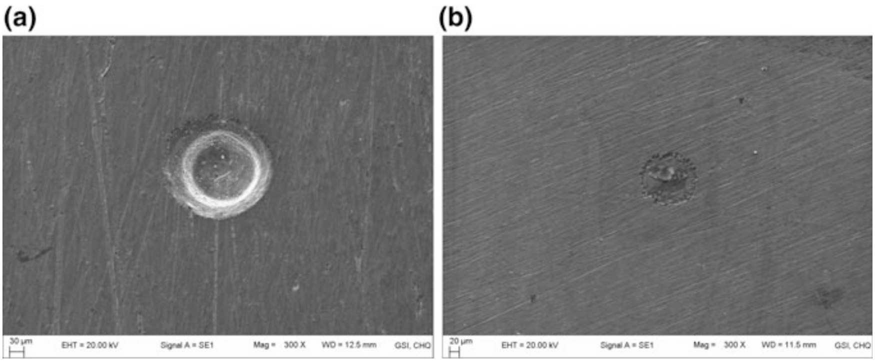


Fig. 9.10 SEM image of microhole machined at **a** with microtool vibration **b** without microtool vibrations [32]

Uncovered or unmasked metal surface is removed by high rate anodic metal dissolution. In through-mask EMM, metal dissolution takes place at the workpiece surface that lies at the bottom of the cavity created by the photoresist mask [26]. The metal removal in TMEMM can be possible by two ways i.e. on one side of masked metal or from two sides of masked anode workpiece which is as shown in Fig. 9.11.

Through mask electrochemical micromachining of titanium has been carried out in solutions containing hydrofluoric acid. Figure 9.3 shows a SEM micrograph of an individual cavity etched for 2 min in a solution containing aqueous hydrofluoric acid. An irregular shape and a rough surface texture result from crystallographic attack by the acid solution. Anodic dissolution of titanium through the patterned photoresist was also accomplished with the NaBr electrolyte at applied potentials

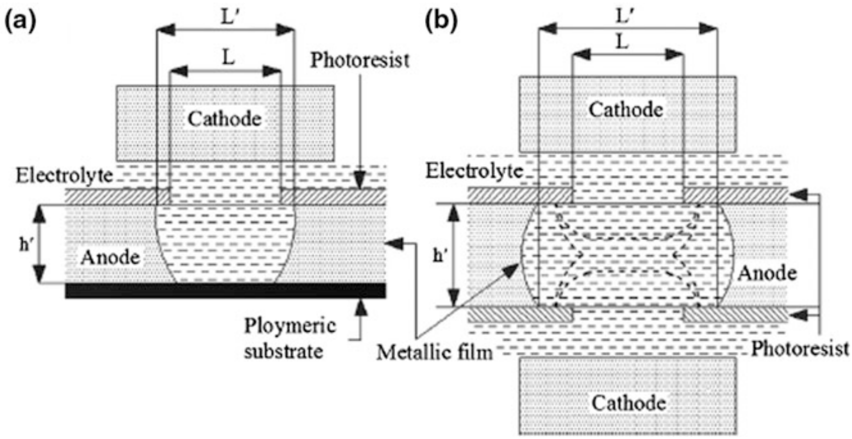


Fig. 9.11 Through-mask EMM: **a** one sided and **b** two sided [29]

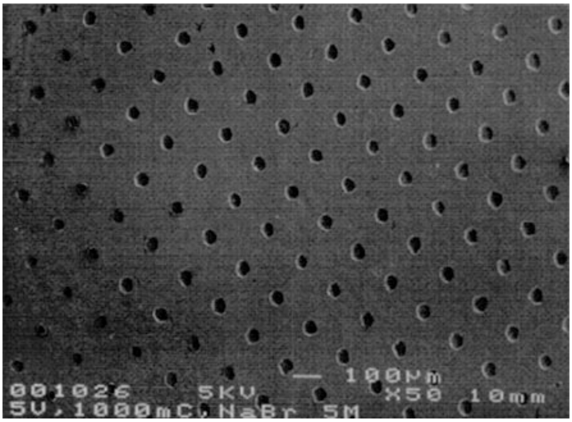


Fig. 9.12 SEM micrograph of a regular pattern etched on a titanium surface at 5 V in the NaBr electrolyte by passing a charge of 4 C. The pattern consists of 50 m diameter cavities, separated by 130 m [14]

ranging between 2 and 8 V. At 2 V only a few cavities dissolved randomly across the pattern while the remaining features of the pattern were not etched; moreover, the etched cavities were large and irregular. The patterns achieved are of pitting nature of titanium dissolution in NaBr electrolytes at the lower potential. However, at 8 V all the cavities dissolved across the pattern. When dissolution was performed at a potential of 5 V all the cavities were etched uniformly across the surface. The etched pattern were enhanced geometric feature with better surface quality when etched with 5 V. Figure 9.12 shows a regular pattern etched on a titanium surface at 5 V in the NaBr electrolyte by passing a charge of 4 C. Dissolution time corresponded to 2 s. The pattern consists of 50 µm diameter cavities, separated by 130 µm.

Electrochemical dissolution of titanium through the patterned photoresists was performed with the 3 M sulphuric acid containing electrolyte at 0 °C. Figure 9.13

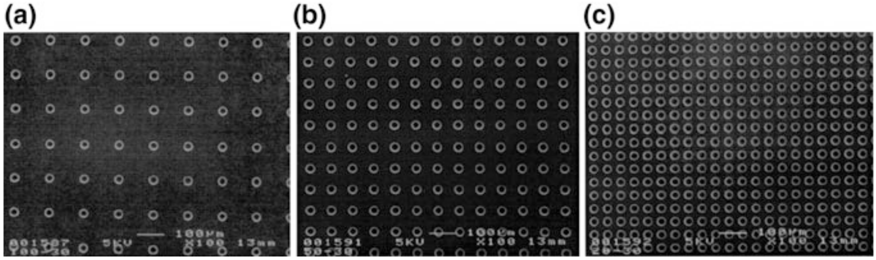


Fig. 9.13 SEM micrograph of a pattern etched on a titanium surface at 8 V in 3 M H2SO4 in methanol. The pattern consists of 30 μm diameter cavities, separated by 130 μm (**a**), 80 μm (**b**), and 50 μm (**c**) [14]

shows regularly shaped and smooth patterns fabricated by electrochemical etching at 8 V. The pattern consists of 30 μm diameter cavities, separated by 130, 80 and 50 μm.

The extended application of through mask electrochemical micromachining (TMEMM) is by combining maskless UV and electron beam lithography in combination with robust SU-8 photoresist technology for increasing the flexibility in pattern shape and potential scale down of feature size on planar substrates [16]. In this technique, features with a gradient in etch depth have been possible in one single micromachining process. Electrolyte of 3 M H_2SO_4 in methanol at −10 °C using a 2-electrode setup in a jacketed and tempered glass cell was utilized. Maskless Ultraviolet and e-beam patterned SU-8 is highly suitable for planar electrochemical surface micromachining from submicron to several hundred microns feature scale, excellent chemical stability of SU-8 together with the flexibility of maskless UV lithography providing great freedom in the pattern design. This technique is suitable for patterning of highly curved surfaces with substrate material choice, good mask patterning speed and freedom in feature shape. Figure 9.14 exhibits Ti surface with well-defined hemispherical cavities by TMEMM via maskless UV patterned SU-8.

Through mask electrochemical micromachining is an effective way to produce regular patterned microfeatures on titanium. However, in TMEMM processes relatively low achievable aspect ratio is the main limitation.

9.7 Micro Features Generation on Titanium

Masked as well as maskless EMM has proved its compatibility in fabrication of various microfeatures on titanium. Masked EMM i.e. TMEMM or oxide film laser lithography (OFLL) are the methods popular for machining regular patterned microfeatures such as micro dimples or microholes on titanium. As discussed, TMEMM can be effective in generation of micro patterns by applying photoresist

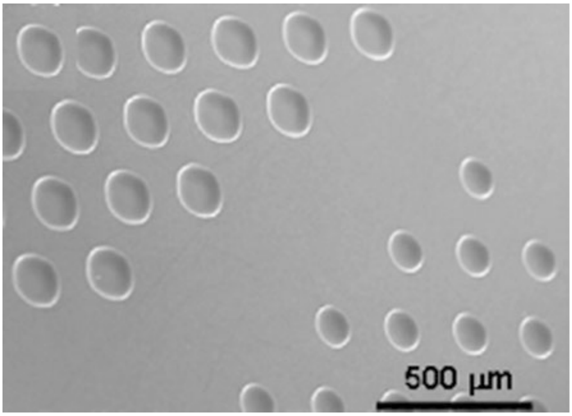


Fig. 9.14 Hemispherical cavities by TMEMM via maskless UV patterned SU-8 [16]

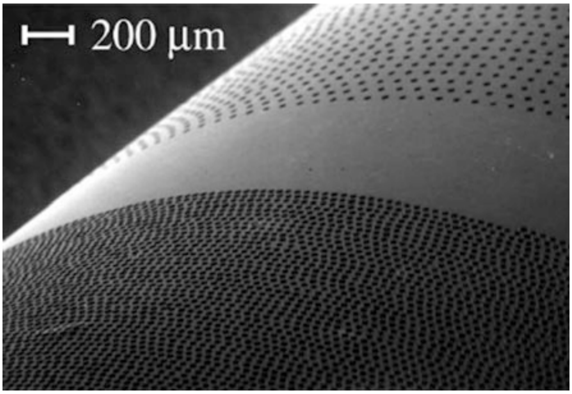


Fig. 9.15 Titanium cylinder surface electrochemically microstructured using OFLL [13]

mask on the anode workpiece. However, in oxide film laser lithography oxide layer on the surface of titanium is developed through anodic oxidation of the titanium in an anodising electrolyte such as sulphuric acid, thereafter patterning of the oxide layer has been carried out by excimer laser irradiation in air to form desired pattern in such a way that the irradiated area of oxide layer is exposed for anodic dissolution. Electrochemical dissolution of the exposed titanium metal from the irradiated areas has been performed with an electropolishing electrolyte such as H_2SO_4 in methanol. After dissolution, protruded oxide film due to under-etching is removed by ultrasonic cleaning [27]. The OFLL technique is better adapted for fabricating multilevel structures since it does not require application of a photoresist. Figure 9.15 shows microstructure fabrication by EMM utilizing OFLL. Various microfeatures which will find potential applications in MEMS can be effectively produced by this method.

Electrochemical bulk micromachining method named the confined etchant layer technique (CELT) for micromachining of titanium and its alloys. In this process the etchant is generated electrochemically on the surface of a machining tool or a mold with desired 3D microstructures [17]. A specific scavenger added to the electrolyte that captures the etchant within a very short duration so as to prevent the etchant from diffusing away from the mold surface. Thus, the etchant layer around the mold is kept so thin that its profile takes approximately the contour of the microstructures of the mold. When moving the mold until the etchant layer contacting the workpiece, the workpiece will be etched. An approximate mirror-image replica of the microstructures of the mold is obtained by continuously approaching the mold to the workpiece with etching process. This process can control precisely the machining depth by controlling the moving distance of mold. It can be used in a batch process with fewer steps than in photolithography. Authors demonstrated the creation of microstructures consists of trapezoidal slots fabricated on Ti6Al4V alloy as shown in Fig. 9.16.

Generation of microfeatures into titanium substrates of various thicknesses, ranging from 0.5-mm sheet to 10 μm free-standing titanium foils has been fabricated by Metal Anisotropic Reactive Ion etching with Oxidation (MARIO) process [28]. This process has capability to fabricate arbitrarily high-aspect-ratio structures with straight sidewalls micromachined structures free of residual stresses. The MARIO process permits the creation of bulk titanium MEMS, which offers potential for the use of a set of material properties beyond those provided by traditional semiconductor-based MEMS.

Maskless electrochemical micromachining can also be effectively utilized for fabrication of microfeatures on titanium. Various microfeatures such as microholes, micrnozzles and microslots can be successfully machined by maskless electrochemical micromachining. Microholes and micronozzles can be fabricated by

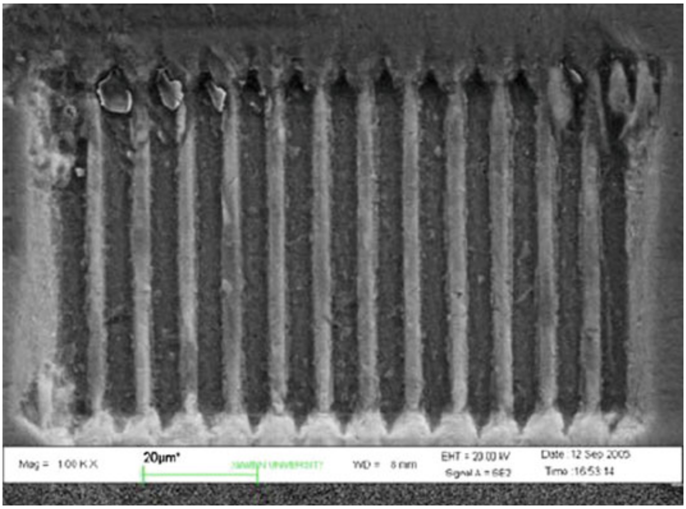


Fig. 9.16 Trapezoidal slot microstructure fabricated on Ti alloy surface in the solution composed of 0.2 M NaF + 0.4 M $NaClO_3$ + 0.6 M $NaClO_4$ + 0.3 M $NaNO_2$ + 0.1 M NaOH [17]

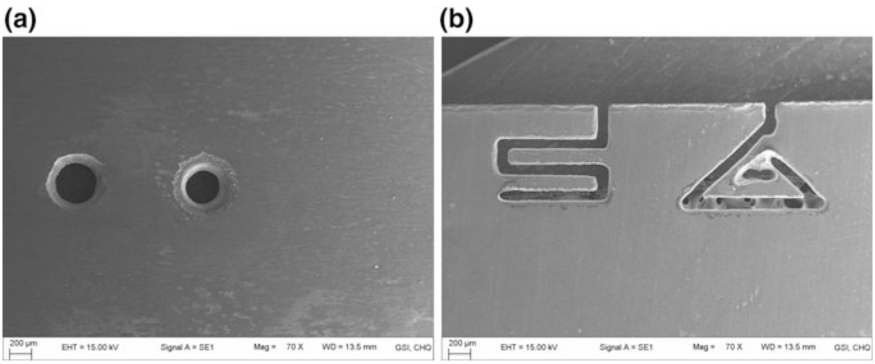


Fig. 9.17 Microfeatures fabricated by maskless EMM **a** microholes **b** microcantilevers

utilizing stagnant electrolyte of mixture of ethylene glycol and sodium bromide by advancing microtool into the titanium workpiece made as anode. Microfeatures other than microholes can fabricate by employing micromilling strategy i.e. cylindrical microtool which acts as cathode removes material in layer by layer travelling mode or by sinking and milling method in the sinking and milling method initially microdrilling is performed up to the required depth of the microfeature, followed by milling along the path of the microprofile [29]. Effect of stray machining and pitting of oxide layer is still an Issue in maskless EMM. However, utilizing various shaped microtools such as disc, cone, conical disc shape and insulated microtools or optimizing various process parameters can minimize these issues to some extent. Figure 9.17 shows microholes and microcantilevers fabricated on titanium by maskless EMM.

Microfeature such as micro slits were also fabricated on titanium alloy using Wire electro chemical machining (WECM) [30]. In this process tungsten wire of diameter in the range of 10–50 µm were utilized. The electrolyte has been introduced between the machining zone by axial electrolyte flushing system to facilitate removal of electrolysis products and renewing electrolyte. Various process parameters such as wire feed rate, machining voltage, electrolyte concentration for cutting microslots or micro slits with various structures were optimized and various micro slits as well as slots can be machined with this process. Instead of using single wire, multi-wire can be used to improve the machining productivity of WECM. Figure 9.18 shows typical microfeature fabricated with WECM.

9.7.1 Suitable Range of EMM Process Parameters for Fabrication of Micro Features on Titanium

Fabrication of microfeatures on titanium by EMM is relatively different than microfeatures fabricated on other metals such as stainless steel, copper etc.

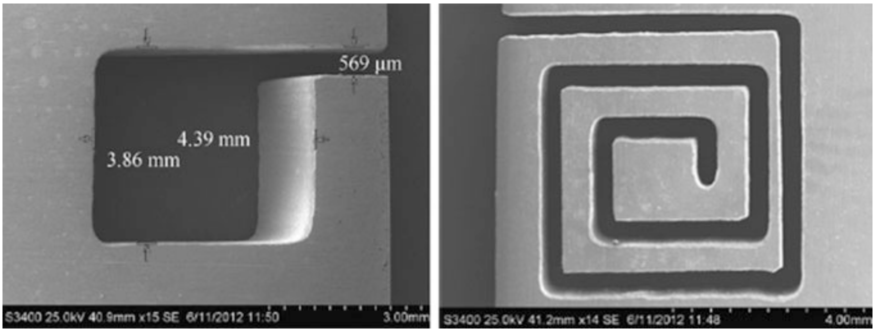


Fig. 9.18 Microfeatures fabricated by WECM on titanium alloy (Ti6Al4V) [30]

especially in terms of machining voltage and electrolyte. However, identification and selection of suitable range of EMM process parameters either in masked or in maskless EMM process parameters play crucial role in achieving machining accuracy of microfeatures generated on titanium. In masked EMM, dissolution of metal is confined to the exposed metal surface among the patterned photoresist therefore, anodic dissolution must occurs within the patterned area. Hence, machining time and machining current induced due to applied potential plays vital role. In addition to that electrolyte combination is also an important factor, mostly toxic acidic base electrolytes are preferred in masked EMM or TMEMM of titanium. Generally, in reported work of the masked EMM of titanium, machining voltage ranges from 8 to 150 V with machining temperature as low as −10 °C with electrolyte combination of sulphuric acid in methanol of higher concentration up to 3 M or hydrofluoric acid were also employed [14, 16, 29]. However, in maskless EMM major challenge during micromachining of titanium lies in controlling the dissolution process by localizing the machining area. Localization of dissolution in maskless EMM is inversely proportional to stray machining effect. Therefore, highly localized controlled dissolution is important to achieve higher machining accuracy of microfeature generated by maskless EMM. Selection of suitable process parameters can directly influence accuracy of microfeature. In order to generate precise microfeature in pure titanium machining voltage in the range of 8–10 V with pulse frequency 160–200 kHz keeping duty ratio 30–35% and optimum microtool feed rate of 0.6–0.8 µm/s has been found suitable process parameters of maskless electrochemical micromachining [31]. Machining accuracy of microfeatures generated by maskless EMM can be further improved by utilizing electrolytes which can break passive layer of titanium in lower current density which will further reduce machining voltage in turn achieving more localized dissolution of titanium.

9.7.2 Potential Applications of Titanium Micro Features

Titanium and titanium alloys gained popularity in aerospace, chemical process and biomedical industry due to their biocompatibility, good mechanical properties and excellent corrosion resistance. Titanium has also possesses plasticity-based failure when subjected to external loading which makes titanium superior device safety capability with increase safety and reliability. These properties qualifies the titanium as potential material to MEMS and BioMEMS applications. Titanium has also a established superior biocompatible metal with a proven applications in dental and orthopaedic implants, which confirms its physiological compatibility for novel biomedical microdevices. To state few examples of such devices are microneedles for transdermal drug delivery [22], thin-foil devices for biomolecule separation and characterization [23], large-area thermal ground planes for electronics cooling [24, 25], and rationally nanopatterned substrates for improved cellular response [26]. Titanium has also proved its compatibility for sophisticated area such as aerospace. In many aerospace applications, array of micro holes, micro-nozzles in titanium alloy plays vital role in critical aerospace applications. EMM can provide better and reliable micromachining solution for titanium micromachining so as to meet these emerging titanium microfeatures requirements.

9.8 Future Scope and Challenges in Titanium Micromachining

Titanium, due to its versatile physical and mechanical properties is a highly demanding material in MEMS and biomedical engineering applications therefore titanium will replace traditional MEMS materials such as Silicon and/or semiconductor material. These new opportunities of this material will pose a new challenge of effective micromachining of titanium and its alloys. EMM has proved its compatibility to micromachine various microfeatures on titanium and its alloys. However, few issues are still to be addressed to make EMM more stable and more precise technique for titanium micromachining. Masked EMM or TMEMM have to be improved in terms of effective photoresist masking technique in order to achieve more confined precise material dissolution so as to minimize undercut material dissolution below the edges of mask. Masking of cathode needs to be done instead of anode workpiece which will enhance the productivity in terms of minimizing the complexity of workpiece masking. Use of non-toxic and environment friendly electrolytes should be promoted during EMM of titanium. During maskless EMM total control of anodic dissolution of titanium can be achieved by lowering down the machining voltage in the range of 2–5 V. This will allow application of higher range of pulse frequency and thus more localized machining. Micromachining of high to very high aspect ratio microfeatures is still a challenge which needs to be addressed.

9.9 Conclusions

Electrochemical micromachining is the only process stress free and clean machining in the microscopic domain irrespective of material hardness. Titanium and its alloys known for its excellent material properties and difficulty in machining either in macro or in microscopic domain can be smoothly micromachined by EMM. To generate precise regular micro patterns on titanium and its alloys by the application of Masked EMM or TMEMM technique is highly suitable, which is proved by generating various micro patterns on titanium surface. Maskless EMM for titanium microfeature generation through stagnant non-aqueous base electrolyte by employing various micromilling strategies is found effective. These techniques established suitable process parameters for EMM of titanium either by masked or maskless techniques. Considering the emerging potential of titanium microfeatures in various MEMS and BioMEMS applications EMM will appear as a most reliable and stable micromachining process for titanium micromachining.

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